October 2018 Vol.17 No.10 ISSN 1582-9596

Environmental Engineering and Management Journal

Green & Circular Economy
ECOMONDO 2017

"Gheorghe Asachi" Technical University of Iasi

October 2018 Vol.17 No. 10 *ISSN 1582 - 9596*

Environmental Engineering and Management Journal

An International Journal

Green and Circular Economy
ECOMONDO 2017

"Gheorghe Asachi" Technical University of Iasi

Environmental Engineering and Management Journal

Environmental Engineering and Management Journal encourages initiatives and actions concerning the improvement of education, research, marketing and management, in order to achieve sustainable development. This journal brings valuable opportunities for those offering products, technologies, services, educational programs or other related activities, creating thus a closer relation with the request of the market in the fields of environmental engineering, management and education. This journal address researchers, designers, academic staff, specialists with responsibilities in the field of environmental protection and management from government organizations (central and local administrations, environmental protection agencies) or from the private or public companies. Also, graduates of specialization courses or of the Environmental Engineering and Management profile, as well as other specialists may find in this journal a direct linkage between the offer and request of the market concerned with the protection of the environment and the administration of natural resources in the national and international context.

The journal was conceived as a means to develop scientific and technical relationships between people who offer and request solutions for environmental protection and conservation of natural resources, creating thus the premises to enhance the transfer of technology and know-how, the confirmation and implementation of ecological products and services.

Taking into consideration these aspects, we gladly welcome any persons or companies which correspond to the above-mentioned purposes and objectives to use our journal to identify potential collaborators.

For subscriptions and orders please contact us at:

OAIMDD (*Academic Organization for Environmental Engineering and Sustainable Development*),

73 Mangeron Blvd., PO 10, Box 2111, 700050 Iasi, Romania, CIF: 10150285

Phone/Fax: 0040-232-271759

E-mail: brindusa.sluser.at.gmail.com, mgav_eemj.at.yahoo.com

In LEI:

ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU
IBAN: RO87BUCU1032235333663RON
Beneficiary: OAIMDD-EEMJ
Address: PO 10, Box 2111, 700050 Iasi, Romania

In EURO:

ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU
IBAN: RO79BUCU1031215940036EUR
Beneficiary: OAIMDD-EEMJ
Address: PO 10, Box 2111, 700050 Iasi, Romania

Department of Environmental Engineering and Management and
EcoZone Publishing House - O.A.I.M.D.D.
73 Prof.Dr.Docent Dimitrie Mangeron Street, 700050-Iasi, Romania
Phone/Fax: 0040-232-271759

Environmental Engineering and Management Journal

Environmental Engineering and Management Journal

Environmental Engineering and Management Journal is included and indexed in:

CABI
Chemical Abstracts Service/SciFinder (ACS) (since 2002)
EBSCO Database (since 2002)
EVISA
ICAAP (International Consortium for Advancement of Academic Publications)
Index Copernicus Journal Master List (**ICV/2015=156.46**)
Journal Citation Reports® 2018 Edition (**IF=1.334**), (*Environmental Sciences*, Ranked **170 out of 241**; 5-Year Impact Factor: 1.021; Article Influence® Score: 0.086; Immediacy Index: 0.054; Normalized eigenfactor: 0.212; **Quartile: Q3**; *Environment/Ecology*, Ranked **158 out of 359, Quartile: Q2**)
MedSci
ProQuest (since 2002)
The National University Research Council (RO)
Science Citation Index Expanded™
SJR (SCImago Journal&Country Rank) (*Environmental Sciences*, **SJR index/2017= 0.41**; **SNIP index/2017 = 1.166; CiteScore/2017=1.26**; Ranked **680 out of 1633**, **H=29,** *Environmental Engineering:* Ranked **64 out of 219***; Management, Monitoring, Policy and Law:* Ranked **142 out of 306***; Pollution***,** Ranked **62 out of 160; Quartile: Q3**)
SCOPUS (since 2002)
ISI Master Journal List
Web of Science® (**H=28**)

Home page: *http://www.eemj.icpm.tuiasi.ro; http://www.eemj.eu*

Full text: *http://www.ecozone.ro, http://www.eemj.eu*

Founding Editor: Matei Macoveanu,Iasi (RO)
Editor-in-Chief: Maria Gavrilescu, Iasi (RO)

Environmental Engineering and Management Journal is edited by
***Gheorghe Asachi* Technical University of Iasi and *EcoZone* Publishing House of the *Academic Organization for Environmental Engineering and Sustainable Development* (O.A.I.M.D.D.)**

Editorial and Production Office:
Department of Environmental Engineering and Management – *Cristofor Simionescu* Faculty of Chemical Engineering and Environmental Protection and EcoZone - O.A.I.M.D.D., 73 *Prof.Dr.Docent Dimitrie Mangeron* Street, 700050 Iasi, Romania
Phone: +40-232-278680, ext. 2259, 2137
Fax: +40-232-271759
e-mail: eemjournal.at.yahoo.com, eem_journal.at.yahoo.com, eemjeditor.at.yahoo.com, eemj_editor.at.yahoo.com, eemjournal.at.gmail.com, eemj.editor.at.gmail.com, eemj.office.at.gmail.com

Editorial production assistants and secretariat:
Laura Bulgariu
Elena-Diana Comăniță
Petronela Cozma
Raluca-Maria Hlihor
Mihaela Roșca
Isabela Maria Simion
Camelia Smaranda
Sebastian Ionuț Vasilică

Administrative and financial management:
O.A.I.M.D.D. President, Brîndușa Mihaela Slușer

Published 12 issues per year, **under the aegis of the *Gheorghe Asachi* Technical University of Iasi, Romania**
by *EcoZone* Publishing House of the *Academic Organization for Environmental Engineering and Sustainable Development* (O.A.I.M.D.D.), **http://www.ecozone.ro**

Annual subscription rate 2018 (12 issues)

	Print:	**Electronic:**	**Print+Electronic:**
EURO	500 per volume	400 per volume	800 per volume

Individual costs

EURO	50 per issue	40 per issue

Order directly to the Editorial Office, 73 *Prof.Dr.Docent Dimitrie Mangeron* Street, 700050 Iasi, Romania
Phone/Fax: Fax: +40-232-271759, e-mail: brindusa.sluser.at.gmail.com, eemj.office.at.gmail.com

Electronic, full text: Order or purchase on-line at: **www.eemj.eu, www.ecozone.ro**

Bank account (EURO):
ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU,
IBAN: RO79BUCU1031215940036EUR
Beneficiary: OAIMDD-EEMJ, Address: PO 10, Box 2111, 700050 Iasi, Romania

Bank account (LEI):
ALPHA BANK ROMANIA (ABR), IBAN: RO87BUCU1032235333663RON,
Beneficiary: OAIMDD-EEMJ

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2285-2514
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

CONTENTS

Abstract Submission

Authors are invited to consult the Themes and topics list and to prepare their extended abstracts (max 2 pages) by using the template available on www.iceem.ro.

The **extended abstract submission** should be done **no later than January 21, 2019.**

After the review process, authors will be notified for participation and the accepted abstracts will be published electronically in a Book of Abstracts (available in the Conference folder).

Decisions on abstract acceptance will be available **after April 10, 2019.**

Participant Registration and Fee Payment - starting from May 15 until July 1st 2019.

Selected papers by the International Scientific Committee will be published in Special issues of the peer-reviewed international journals:

- **Process Safety and Environmental Protection** (ISI ranked, Elsevier);
- **Environmental Engineering and Management Journal** (ISI ranked, TUIASI).
- Relevant submissions are also invited to **Sustainable Production and Consumption** (ISI, Elsevier) to be considered for publication in a regular issue of the journal.
- Selected abstracts will be suggested for a possible Special Issue in **New Biotechnology** (ISI ranked, Elsevier).

ICEEM10 Conference language is English.

Fees

The ICEEM10 Conference fees will include the conference materials (Program, Abstracts book), coffee breaks, lunches, cocktail and conference dinner.

- Full fee: **300 EUR until June 30, 2019**
- Full fee: **350 EUR after July 1st, 2019**
- Reduced PhD Student Fee**: 250 EUR** (for 20 PhD students, by competition)
- Accompanying person **Fee: 150 EUR**

Please visit www.iceem.ro for additional details on fees.

ICEEM10 registration and fee payment details will be available on www.iceem.ro

Contacts

For details please visit the conference site: www.iceem.ro, or contact the Conference Organizing Committee: **conference@iceem.ro**

www.iceem.ro

Gheorghe Asachi Technical University of Iasi
Cristofor Simionescu Faculty of Chemical Engineering and Environmental Protection
Department of Environmental Engineering and Management

10th INTERNATIONAL CONFERENCE ON ENVIRONMENTAL ENGINEERING AND MANAGEMENT

18 - 21 September 2019, Iasi, Romania

ICEEM 10

Call for Papers

Supporting Partners:

- European Federation of Biotechnology, Environmental Biotechnology Section
- Academic Organization for Environmental Engineering and Sustainable Development (OAIMDD), Iaşi, Romania
- InterMEDIU - Information, Consultancy and DL Department, TUIASI, Romania

www.iceem.ro




Foreword

In 2019, the International Conference on Environmental Engineering and Management (ICEEM) will reach its tenth edition. During this time, ICEEM has grown into an important scientific event in the globally relevant sustainability themes. During this rich history, three main features have represented vividly the ICEEM spirit: internationalization, multi-disciplinarity and collaboration.

ICEEM international features refer not only to the three previous editions which were organised abroad (ICEEM06 in Veszprem, Hungary; ICEEM07 in Vienna, Austria and ICEEM09 in Bologna, Italy), but also to the editions organized in Romania in collaboration with foreign universities/associations. To highlight this evolution, ICEEM10 anniversary edition will be back to its initiation place, at the "Gheorghe Asachi" Technical University of Iasi, Romania.

ICEEM10 strongly encourages researchers, members of the academia, industry and society representatives to contribute to the suggested themes and topics with presentations that focus on innovation, multi-disciplinarity and cross-sectorial approaches to tackle environmental and sustainability problems.

ICEEM10 fosters high quality research dissemination and thus participation is based on a peer-review abstract selection. Selected contributions by the International Scientific Committee will be published as full papers in Special Issues of 3 peer-reviewed ISI ranked international journals.

We hope that the plenary sessions, oral and poster presentations, workshops and side-events of ICEEM10 will enhance international cooperation, knowledge transfer and effective communication of scientists, engineers and managers.

We are looking forward to welcome you in Iasi,

Prof.dr.,dr.h.c. Carmen Teodosiu
ICEEM10 President
"Gheorghe Asachi" Technical University of Iasi

Themes, Topics & Events

I. Environmental biotechnology
- Marine biotechnologies
- Biomineralization for remediation and valorisation
- Microbiome applications for sustainable systems (including food, agriculture and health)

II. Water and wastewater cycles: technologies, recycling and valorisation
- Water and wastewater treatment
- Nutrient recovery
- Water and sludge reuse applications

III. Waste management and exploitation for chemicals, materials and energy in the context of circular economy
- Waste treatment and valorisation
- Bioremediation and rehabilitation
- End-of-waste alternatives for new products and fuels (biowaste, bio-refineries)

IV. Sustainability assessments and eco-innovation
- Life cycle assessments
- Footprint indicators (Ecological, Water, Carbon etc.)
- Eco-design, eco-innovation and eco-entrepreneurship

V. Novel materials for environmental and energy applications
- Solar energy materials
- Materials, eco-processes and eco-products
- Nanotechnologies

VI. Monitoring and modelling of environmental pollution
- Process modelling, optimization and simulation
- Investigation and prognosis tools for environmental issues
- Pollution monitoring and control

VII. Environmental education and curriculum development

www.iceem.ro

International Scientific Committee

Prof.dr., dr.h.c. Maria Madalena dos Santos Alves
University of Minho, Portugal
Prof.dr. Cecilia Maria Villas Boas de Almeida
Universidade Paulista, Brazil
Prof.dr., dr.h.c. Adisa Azapagic
The University of Manchester, United Kingdom
Assoc.prof.dr. Amit Bhatnagar
University of Eastern Finland, Finland
Prof.dr. Hans Bressers
University of Twente, The Netherlands
Prof.dr. Dan Cascaval
"Gheorghe Asachi" Technical University of Iasi, Romania
Prof.dr. Francesc Castells
University of Rovira i Virgili Tarragona, Spain
Assoc.prof.dr. Cezar Catrinescu
"Gheorghe Asachi" Technical University of Iasi, Romania
Prof. dr., dr.h.c. Yusuf Chisti
Massey University, New Zealand
Prof. dr., dr.h.c. Philippe Xavier Corvini
University of Applied Sciences and Arts Northwestern, Switzerland
Prof.dr. Igor Cretescu
"Gheorghe Asachi" Technical University of Iasi, Romania
Assoc.prof.dr. Sabino de Gisi
Politecnico di Bari, Italy
Prof.dr. Camelia Draghici
Transilvania University of Brasov, Romania
Dr.ing. Mihail Dorus
SC APAVITAL SA Romania
Prof.dr., dr.h.c. Gheorghe Duca
Academy of Sciences, Republic of Moldova
Prof.dr.Francesco Fatone
Univesity Politecnica delle Marche, Italy
Prof.dr., dr.h.c. Fabio Fava
Alma Mater Studiorum Università di Bologna, Italy
Prof.dr. Silvia Fiore
Politecnico di Torino, Italy
Prof.dr.,dr.h.c. Anton Friedl
Vienna University of Technology, Austria
Prof.dr. Joan Garcia
Universitat Politecnica de Catalunya, Spain
Prof.dr. Maria Gavrilescu
"Gheorghe Asachi" Technical University of Iasi, Romania
Prof.dr. Biagio Fernando Giannetti
Universidade Paulista, Brazil
Prof.dr. Almudena Hospido
University of Santiago de Compostela, Spain
Prof.dr. Nicolae Hurduc
"Gheorghe Asachi" Technical University of Iasi, Romania
Prof.dr. Ovidiu Gabriel Iancu
"Alexandru Ioan Cuza" University Iasi, Romania
Prof.dr. Nikolas Kalogerakis
Technical University of Crete, Greece
Prof.dr. Emmanuel G. Koukios
National Technical University of Athens, Greece
Prof.dr. Florica Manea
Politehnica University of Timisoara, Romania
Prof.dr. Giorgio Mannina
University of Palermo, Italy
Prof.dr. Antonio Marzocchella
Università degli Studi di Napoli Federico II, Italy
Dr. Marcela Mihai
"P.Poni" Institute of Macromolecular Chemistry, Iasi, Romania
Prof.dr. Mircea Nicoara
"Alexandru Ioan Cuza" University, Iasi, Romania
Prof.dr. Cristina Orbeci
Politehnica University of Bucharest, Romania
Prof.dr. Alexandru Ozunu
Babeş Bolyai University, Cluj Napoca, Romania
Prof.dr. Cristian Predescu
Politehnica University, Bucharest, Romania
Prof.dr., dr.h.c. Ákos Rédey
Pannonia University, Veszprem, Hungary
Prof.dr. Maria Reis
FCT, Universidade NOVA de Lisboa, Portugal
Prof.dr. Sebastien Royer
Université de Lille, France
Prof.dr. Maria Angeles Sanroman
University of Vigo, Spain
Prof.dr., dr.h.c. Wilhelm Schabel
Karlsruhe Institute of Technology, Germany
Prof.dr. Peter Schröder
Helmholtz Zentrum München, Germany
Acad.Prof.dr., dr.h.c. Bogdan C. Simionescu
"Gheorghe Asachi" Technical University of Iasi, Romanian Academy, Romania
Assoc.prof.dr. Brindusa Sluser
"Gheorghe Asachi" Technical University of Iasi, Romania
Dr. Magdalena Urbaniak
University of Lodz
Prof.dr., dr.h.c. Angheluta Vadineanu
University of Bucharest, Romania
Dr.ing. Ilie Vlaicu
SC AQUATIM SA Romania
Prof.dr. Irina Volf
"Gheorghe Asachi" Technical University of Iasi, Romania

www.iceem.ro

Organising committee

Dr. Brindusa Sluser
Dr. George Barjoveanu
Dr. Adela Buburuzan
Dr. Daniela Gavrilescu
Dr. Daniela Fighir
Dr. Corina Musteret
Dr. Petru Apopei
Dr. Irina Morosanu
Dr. Camelia Smaranda
Dr. Petronela Cozma
Dr. Diana Gabur
Dr. Diana Comanita

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2285-2286
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

EDITORIAL

Green and Circular Economy ECOMONDO 2017

21th International Trade Fair of Material & Energy Recovery and Sustainable Development

The papers collected in this Special Issue of *Environmental Engineering and Management Journal* were presented as lectures or posters at the scientific and technical conferences hosted by *Ecomondo 2017* held in Rimini, Italy, 8–11 November, 2017 (http://en.ecomondo.com).

Ecomondo is the second largest European exhibition in the field of *Green and Circular Economy*, with over than 115,000 delegates from 50 different nations and 1200 companies exhibiting their products and processes in a 113,000 square meters. It is hosting over than 100 conferences and workshops, ensuring a weighted and rewarding balance between sales dimension and technical-scientific dimension, with extensive room dedicated to research and innovation, education and training and international networking.

As with the previous editions, the aim of Ecomondo 2017 was to explore recent industrial advances and opportunities in industrial technical waste production reduction, recycling and exploitation; sustainable food and wood chains, biowaste collection and exploitation via integrated biorefinery schemes, with the production of biobased chemicals, materials and biofuels, including methane; industrial eco-design; industrial symbiosis, renewable and critical resources; water resources monitoring, protection and sustainable use in the civil and agrifood sectors; wastewater treatment and valorization with nutrients recovery and water reuse; marine resources protection and sustainable exploitation; sustainable remediation of contaminated sites, ports and marine ecosystems; indoor and outdoor air monitoring and clean up; and circular and smart Cities.

Ecomondo 2017 hosted over than 120 conferences, more than 800 oral communications and almost 120 papers. This special issue provides some of the key information presented and discussed in the frame of some of such conferences.

We believe that this collection of papers will be useful to people who could not participate in the Ecomondo 2017 directly. It is primarily towards them but it also aspires to provide permanent records in the promotion, adoption and implementation of the major priorities and opportunities of the circular economy in Europe and in the Mediterranean with the conversion of some of the key local environmental challenges into new opportunities for a green and sustainable growth.

http://www.ecomondo.com
http://ecomondobrasil.com.br/en/
http://en.keyenergy.it/
http://en.cittasostenibile.net/


Guest editors:

***Prof. Fabio Fava**, Alma Mater Studiorum - Università di Bologna, (University of Bologna), Bologna, Italy*
***Dr. Grazia Totaro**, Alma Mater Studiorum - Università di Bologna (University of Bologna), Bologna, Italy*
***Prof. Maria Gavrilescu**, Gheorghe Asachi Technical University of Iasi, Romania*

Fabio Fava, born in 1963, is Full Professor of “Industrial & Environmental Biotechnology” at the School of Engineering of University of Bologna since 2005. He has about 140 papers on medium/high IF peer-reviewed international journals of industrial and environmental biotechnology, sectors in which he coordinated the FP7 projects NAMASTE and BIOCLEAN and participated in other 7 FP7 collaborative projects. He is vice-chairman of the “Environmental Biotechnology” section of the European Federation of Biotechnology (EFB). He is the Italian Representative in the "Working Party on Biotechnology, Nanotechnology and Converging Technologies" at OECD (Organisation for Economic Co-operation and Development), Paris, in the "European Strategy for the Adriatic and Ionian Region" (EUSAIR) and in the "Western Mediterranean Initiative" (WEST MED). He is member of the "Expert Group on Biobased Products" (DG GROW, European Commission, EC) and is the Italian Representative in the a) Horizon2020 Programming Committee “European Bioeconomy Challenges: Food Security, Sustainable Agriculture and Forestry, Marine, Maritime and Inland Water Research" (SC2, DG RTD, EC), b) “States Representatives Group” of the “Public Private Partnership BioBased Industry” (BBI JU)(DG RTD, EC) and c) BLUEMED Strategic Board (DG RTD and DG MARE, EC). Finally, he is the scientific coordinator of the International Exhibition on green and circular economy ECOMONDO held yearly in Rimini (Italy)

Grazia Totaro, born in 1976, has a degree in Chemistry (University of Ferrara), a Master’s Degree in Science, Technology & Management with a specialization in Environmental Chemistry (University of Ferrara) and a PhD in Materials Engineering (University of Bologna).

She worked at the R&D Centre of Basell Polyolefins in Ferrara for 2 years in the frame of a project addressed to the development of a novel methodology for qualitative and quantitative analysis of additives in polymers. She also worked at ARPA, Regional Agency for Environment in Ferrara, division Water Analysis. Then she started working at the school of Engineering of the University of Bologna for a Ph.D. in Materials Engineering (2007-2010). After that, she had a scholarship "Spinner 2013" in cooperation with Reagens spa (San Giorgio di Piano) on novel PVC nanocomposites. Now she is post doc fellow at the same school on new polymer-based nanocomposites from renewable sources and inorganic fillers. She also worked at the laboratoire de Chimie et Biochimie Pharmacologique et Toxicologique (Université Réné Descartes) in Paris in 2001 and was visiting professor at the Ecole Nationale Superieure de Chimie (Université Blaise Pascal, Clermont Ferrand, FR) in 2012 and 2015. Dr. Totaro has about 25 scientific papers and several participations at conferences and scientific schools. She collaborates on Ecomondo from 2013.

Maria Gavrilescu (born in 1956) is Full Professor at the Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection - *Gheorghe Asachi* Technical University of Iasi, Romania. Her research and teaching interests include: chemical and biological process engineering, biotechnology/ environmental biotechnology, environmental risk assessment and management/ industrial safety, integrated pollution prevention and control/ sustainable industrial production/ cleaner production and waste management, eco-innovation/ eco-design/ eco-technologies, environmental and sustainability evaluations. Professor Gavrilescu is PhD Supervisor in *Chemical Engineering* (since 2002) and *Environmental Engineering* (since 2009). She is author/co-author of more than 650 titles, including 46 books/chapters, 181 papers published in ISI ranked journals, ISI Proceedings and book chapters (13), other peer-reviewed journals and conference proceedings (over 160), 12 patents, keynotes, oral presentations, posters etc. Prof. Gavrilescu coordinated or worked as researcher in over 60 national and international research projects. Also, she is a founder of the *National Society of Environmental Science and Engineering*, being also member of: Editorial Advisory Board of *international journals*; *Romanian Society of Chemistry*; *European Federation of Biotechnology* (member of Experts Board of *Environmental Biotechnology* Section) etc. The scientific visibility is illustrated by over 3400 citations (H-index 27) (WOS and Scopus).

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2287-2296
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

MEASURING METABOLIC RATE TO IMPROVE COMFORT MANAGEMENT IN BUILDINGS

Andrea Calvaresi, Marco Arnesano*, Filippo Pietroni, Gian Marco Revel

Università Politecnica delle Marche, Department of Industrial Engineering and Mathematical Science, Ancona, Italy

Abstract

Indoor environment significantly affects occupants' health and productivity. However, in smart buildings and cities, it can be improved thanks to the implementation of innovative ICT systems and services. Thermal comfort is one of the most complex aspects to be considered to enhance occupants' well-being, because of the relevant role played by subjective parameters (physiological, psychological and cultural) in its evaluation. This challenge can be tackled by integrating wearable devices into the monitoring framework. Thus, this paper presents an innovative methodology to measure metabolic rate (M) based on wearable devices, which can be used to apply Fanger's comfort model. This model makes use of both environmental and physiological quantities to calculate the PMV (Predicted Mean Vote) index. The former can be easily acquired through standard sensors, on the contrary, providing a good evaluation of the physiological variables of the model (i.e. metabolic rate and clothing insulation) is more difficult. In the proposed methodology, a wearable multi-parametric device has been adopted to measure data from occupants and calculate the metabolic rate. Different sets of physiological data have been investigated to derive the optimal set providing the most accurate metabolic rate. Results from laboratory tests are presented, considering activities ranging from sedentary (1 met) to more active ones (4 met). Finally, a virtual test bench has been developed to simulate a building where the methodology proposed is used to control the indoor air temperature by means of a PMV-based set-point calculation. The methodology has then been compared to traditional approaches with constant *M*.

Key words: metabolic rate, smart buildings, thermal comfort, wearable sensors

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Considering that people spend about 90% of their time in an indoor environment, in the last decades great attention has been paid to the assessment and optimization of the indoor thermal comfort in office buildings. It is well-known that the indoor environment and microclimatic conditions greatly affect the health, well-being and productivity of occupants. This extensive interest can be linked not only to the aspects mentioned above, but also to the establishment of a series of European Directives and international and European Standards aiming at improving the energy and environmental performance of buildings without decreasing occupants' comfort (Antoniadou and Papadopoulos, 2017). This theme is also interconnected with the necessity of reducing energy consumption in buildings, which should be able to provide the highest indoor comfort with the minimum energy consumption. To this aim, the development of new technologies and services for optimal comfort management are part of the wider context of buildings' efficiency and sustainability. This approach is the basis of the Energy-efficient Buildings Public-Private Partnership (EeB PPP) initiative supported by the EU Commission, where research projects are founded to achieve the EU goals in terms of energy use, decarbonization, sustainability and improved living and well-being, also taking into account particular sectors like the ageing one. In this

* Author to whom all correspondence should be addressed: e-mail: m.arnesano@univpm.it; Phone: +39 0712204508; Fax: +39 071 2204801

context, several projects have been co-founded to support the development of new technologies under 7 technology clusters (from design to ICT). Given the attention to all levels (from building to urban scale), one of the main exploitations of the results of the initiative can be found in the Smart City paradigm, where new services are provided to improve cities in relation to the above-mentioned themes. In this context, thermal comfort is one of the main services that a building should deliver and, today, the need to improve the state-of-the-art methodology used to assure this is particularly strong. For this reason, comfort management should make use not only of environmental parameters but also of parameters related to occupants, which, however, could vary in time and space according to multi-contextual factors (e.g. activity, age, culture, social rules etc.) (Kim et al., 2018). In this context, the use of innovative technologies, most of them coming from ICTs, integrated with existing models and tools can enhance the comfort delivered with reduced environmental impact (Capolongo et al., 2013; Lee et al., 2017; Petri et al., 2015; Revel et al., 2015a; Zampetti et al., 2018). The work presented in this paper wants to address this topic, illustrating an example of how a traditional thermal comfort model can be empowered with the integration of ICT tools, to increase the monitoring and controlling capacity in a building.

As said, thermal comfort is one of the most important factors for the well-being of building occupants. The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) defined thermal comfort as ‘‘the condition of the mind in which satisfaction is expressed with the thermal environment’’(ASHRAE, 2017). Therefore, according to the above definition, comfort is a subjective sensation.

Thermal comfort is generally measured by sensors compliant with mathematical models that express the overall interaction between human body and the environment (body heat production and exchange, influencing factors, etc.). The most used model is based on Fanger’s comfort theory which enumerates six factors to determine heat balance and provides a formula to calculate the PMV (Predictive Mean Vote) index. Four of the six are environmental parameters: relative humidity, air temperature, mean radiant temperature and air velocity. The remaining two are personal factors: metabolic rate and clothing insulation. The PMV measurement thus requires the capability to sense not only the environmental parameters, but also those factors that are related to occupants’ characteristics. With regard to the environmental quantities, the microclimate station is the most used device for short-term monitoring. Recently, innovative solutions have been developed to provide measurements with the same level of accuracy, although for real-time and continuous monitoring purposes (Revel et al., 2014a). With regard to the personal factors, recent studies have been carried out to explore the impact of subjective parameters on thermal comfort monitoring, as presented in (Luo et al., 2016), also offering some solutions for the measurement of the metabolic rate (Luo et al., 2018). However, in practical building controls, subjective parameters (which greatly affect thermal comfort) are not considered (thermostats) or are still treated as constants, adopting values from standards and according to the typical end-use of the building. This assumption usually does not reflect real conditions and, therefore, leads to incorrect evaluations. In the view of improving these estimations, this work presents a new methodology for the dynamic measurement of the metabolic rate, making use of wearable sensors based on the methodology presented in (Revel et al., 2015b).

Going beyond the results obtained in the work of (Hasan et al., 2016), the continuous assessment methodology has been tested for the monitoring but also for the comfort management of a building. Thus, attention has been focused on both the integration and the uncertainty of the measurement technique proposed, in order to determine the impact on the PMV-based comfort management. Finally, a virtual test bench has been developed to show the applicability to the real-time control of the HVAC of buildings. Therefore, a simulation model of a building has been used to test a PMV-based air temperature controller, with and without the dynamic metabolic rate method. This test has showed the advantages achievable from using the real-time measurements of the metabolic rate thanks to the reduced uncertainty of the PMV index estimated to control the environment.

2. Material and methods

2.1. Model used for comfort monitoring

The PMV model aims at predicting the mean thermal sensation of a group of people in the same environment (Fanger, 1970) through a steady-state heat balance model of the human body. The PMV index is a function of air temperature (t_a [°C]), mean radiant temperature (t_r [°C]), water vapour partial pressure p_a [Pa], which, in turn, is a function of the measurement of relative humidity (*RH* [%]), air velocity (v_a [m/s]), clothing insulation (I_{cl} [clo]) and metabolic rate (*M* [met]) and represents the thermal sensation of occupants (Eq. 1):

$$PMV = f\left(t_a, t_r, p_a, v_a, I_{cl}, M\right) \tag{1}$$

The measurement of the environmental parameters can be easily performed through standard instrumentation such as black-globe thermometers, anemometers, thermistors (e.g. microclimate stations). Moreover, with the recent growth in technologies, new low-cost devices have been developed for the real-time monitoring of ambient parameters, as in (Revel et al., 2014a). On the contrary, personal parameters are difficult to measure. The next Section introduces a new methodology for the integration of the "human dimension" so as to allow a more accurate assessment of thermal comfort.

2.2. Calibration curves for the real-time measurement of metabolic rate

This section discusses the real-time measurement of the metabolic rate. The goal is to provide an innovative methodology for the dynamic evaluation of *M* to enhance thermal comfort assessment. The metabolic rate is defined as the amount of daily energy that a person consumes while at rest in an environment that is temperate and neutral and while in a post-absorptive state. The chemical and physical reactions that occur in an organism are reversible and depend on changes in the energy status. Among the parameters affecting indoor thermal comfort, this physiological parameter is one of the most important. In Revel et al. (2014b) a sensitivity analysis of the PMV index was performed to investigate the PMV variation due to the metabolic rate. The authors report that the metabolic rate has a high influence, which increases especially for lower values (<1met). For this reason, having a good estimation of this quantity is important for an accurate estimation of thermal comfort (D'Ambrosio et al., 2011). Small variations of *M* induce large deviations in thermal sensation.

According to the Standard ISO 8996 (2004), there are several methodologies based on the statistical analyses or measurements of indirect parameters that can be used for the assessment of the metabolic rate. Among these, a methodology based on the continuous monitoring of the subject's heart rate (*HR*) should be able to provide an estimation of *M* with an accuracy of ±10%. In (Revel et al., 2015b) a simplified version of the method described above was applied. The results showed that, by applying this method, different activities can be identified, considering the real perception of the subjects in a room.

The new methodology presented in this work is based on continuous multi-parametric measurements to provide a real-time estimation of the metabolic rate. A wearable device (BioHarness 3.0 BH3), as the one described in (Casaccia et al., 2016), was adopted to measure several physical and physiological quantities. Specific information about the validity and reliability of the BH3 device are discussed in (Johnstone et al., 2012a; 2012b), through dedicated laboratory tests.

Referring to Pietroni et al. (2016), different indicators (i.e., *IN5*, *IN4*, *IN3*) which depend on the number of the parameters considered (i.e., the ones measured by the same device) were found. Combinations of 5, 4, and 3 parameters (Eqs. 2-4) were evaluated. The index derives from a combination of different parameters acquired with the BH3. The single indicators can be expressed through the relationships reported below, which represent the area of an irregular polygon:

$$IN5 = \frac{1}{2}\cdot((HR_n \cdot BR_n \cdot \sin(a_1)) + (BR_n \cdot POS_n \cdot \sin(a_1)) +, (POS_n \cdot ACT_n \cdot \sin(a_1)) + (ACT_n \cdot ACC_n \cdot \sin(a_1)), +(ACC_n \cdot HR_n \cdot \sin(a_1))) \tag{2}$$

$$IN4 = \frac{1}{2}\cdot((HR_n \cdot BR_n \cdot \sin(a_2)) + (BR_n \cdot ACT_n \cdot \sin(a_2)), +(ACT_n \cdot ACC_n \cdot \sin(a_2)) + (ACC_n \cdot HR_n \cdot \sin(a_2)) \tag{3}$$

$$IN3 = \frac{1}{2}\cdot((ACT_n \cdot HR_n \cdot \sin(a_3)) + (HR_n \cdot ACC_n \cdot \sin(a_3)), +(ACC_n \cdot ACT_n \cdot \sin(a_3)) \tag{4}$$

where: *HR* is the heart rate [bpm], *BR* is the breathing rate [bpm], *POS* is the posture of the subject [°], *ACT* is the activity level [expressed as VMU – Vector Magnitude Units], *ACC* is the acceleration module [g]. Subscript "n" indicates that values were normalised. The normalisation was calculated for the following range value: 40÷240 bpm for *HR*, 4÷100 bpm for *BR*, -90°÷90° for posture, 0÷4 for activity level and 0÷6 g for acceleration module. The angles a_1, a_2, a_3 are 72°, 90° and 120° respectively.

To verify the feasibility of the approach proposed, a specific test was conducted to identify the most accurate calibration curve for the dynamic evaluation of metabolic rates. As reported in Table **1**, ten young and healthy individuals recruited among university students were involved (5 females and 5 males, age: 21±1 years, weight: 61±13 kg, height: 1.71±0.09 m, BMI: 20.95±2.72 kg/m^2).

Within the tests conducted, the subjects were asked to perform 4 different kinds of activity. Standard ISO 7730 (ISO 7730, 2005) reports that the PMV model returns an estimate of indoor thermal comfort which can be considered reliable for metabolic rate values not exceeding 4 met.

Table 1. Characteristics of the subjects

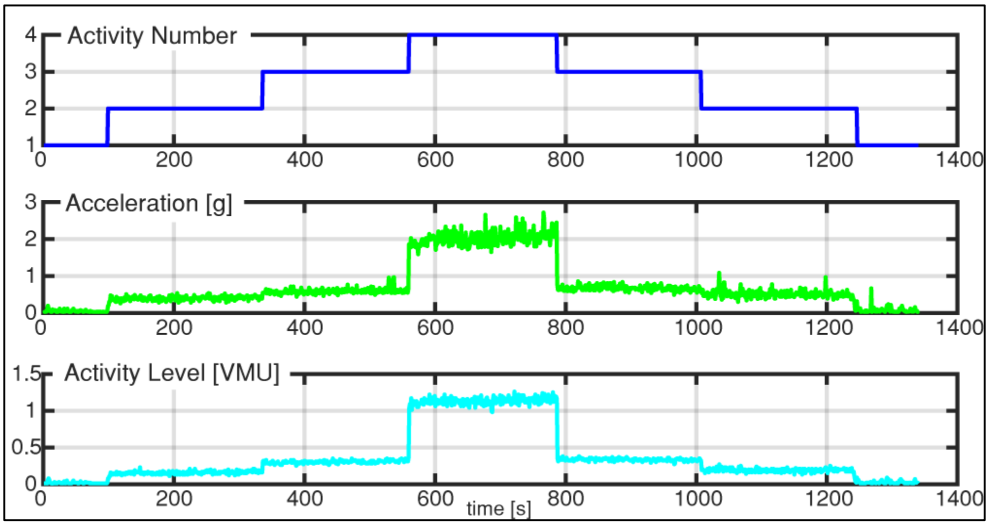
Subject	*Gender*	*Age [years]*	*Weight [kg]*	*Height [m]*	*BMI [kg/m^2]*
1	F	22	44	1.62	16.77
2	F	22	56	1.63	21.08
3	F	21	52	1.60	20.31
4	F	21	55	1.73	18.38
5	F	21	70	1.73	23.39
6	M	19	77	1.80	23.77
7	M	22	70	1.75	22.86
8	M	21	58	1.68	20.55
9	M	21	71	1.88	21.80
10	M	21	58	1.68	20.55

The standard values chosen to perform the tests are reported in Table 2. Each subject completed the activitiy profiles in 20 minutes and tests were carried out following a well-defined order (i.e., ascending profile of metabolic rate per activity, then descending profile of metabolic rate activity). The acquisition of the physiological quantities of interest was performed on-board by the BH3 device and the quantities computed (e.g., heart-rate, breathing rate, acceleration module, etc.) were directly stored inside the device. The data were post-processed and Fig. 1 shows an example of the time-domain variation of each signal acquired during the tests.

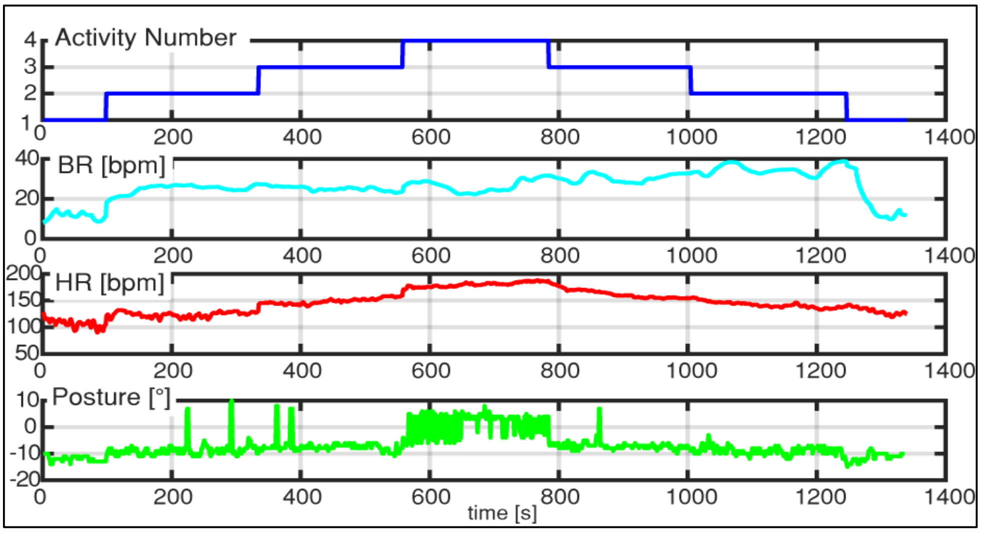
It is possible to observe that both the acceleration and activity signals follow the reference profile (Activity number, as Fig. 1a) with a good approximation. Conversely, the heart rate, breathing rate and posture deviate from the standard (Fig. 1b). This is probably caused by the fact that an increase in metabolic activity is correlated with an increase in these physiological quantities, but these parameters take a longer time to become stable. The same considerations are valid for the descending profile of *M*. A dedicated algorithm for data processing was developed as reported in Fig. 2.

Table 2. Standard value of metabolic rate.

Number of Activity	***Activity***	***Metabolic Rate [met]***
1	sedentary activity	1.2
2	slow walk on the flat	2.5
3	go down the stairs	3.5
4	climbing stairs	4



(a)



(b)

Fig. 1. (a) Trend of standard-based metabolic rate, acceleration and activity level during the tasks; (b) trend of *BH*, *HR*, and posture during the tasks.

Initially, for each activity, a portion of the raw data acquired by the BH3 device was selected. The data average was computed, and a first threshold was determined using the Chauvenet's criterion to remove outliers (Lin and Sherman, 2007) (excluding those that were not within the range ±3 standard deviation). At this point, the average of the remaining data was re-calculated for each single activity performed and a second threshold was applied to remove the outliers through a robust bivariate analysis implemented through a MATLAB toolbox (FSDA - Forward Search for Data Analysis) (Riani et al., 2012). This first step of data processing was applied to all the signals acquired from the respective subjects and for each activity. Fig. 3 reports an example of the data obtained after data processing.

Finally, the indicators expressed by Eqs. (2-4) were correlated with the standard metabolic rate reported in Table 2 and curves for the dynamic evaluation of metabolic activity (Eqs. 5-8) were obtained (Table 3)(Eqs. 5-8).

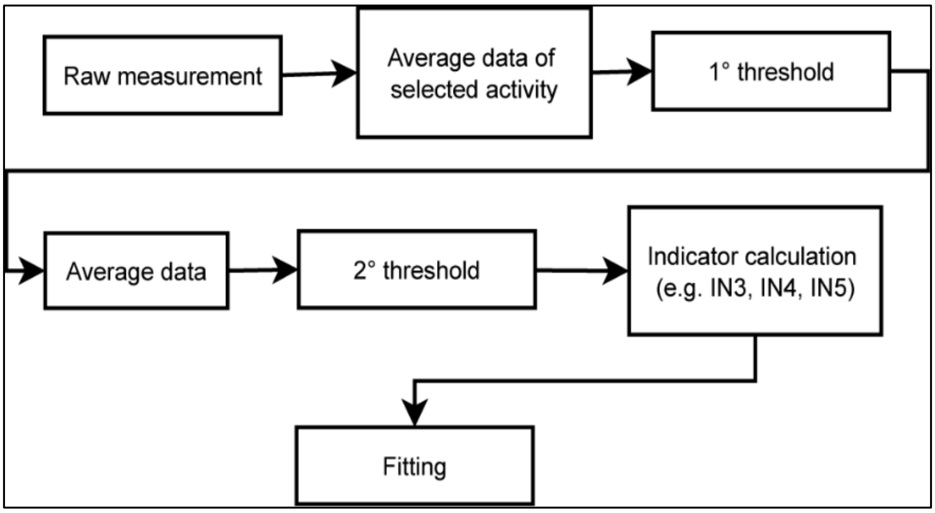


Fig. 2. Scheme of the data processing algorithm.

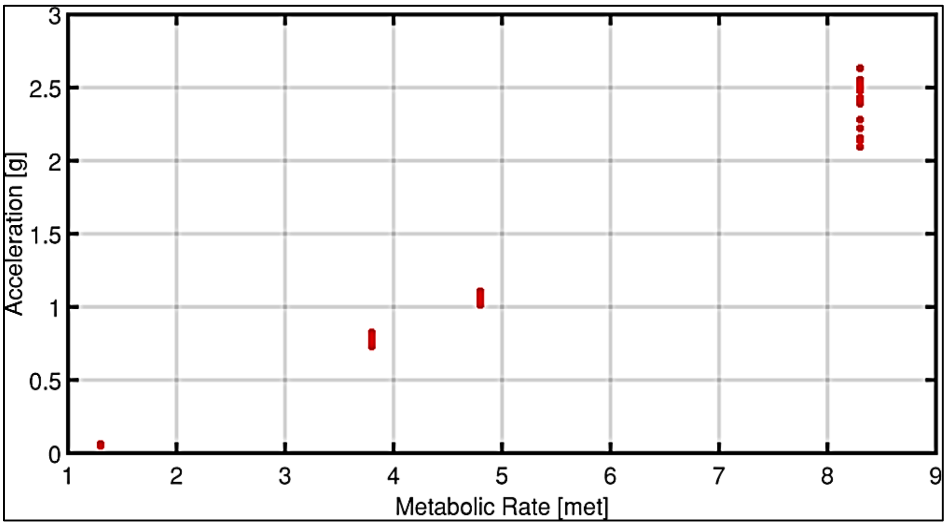


Fig. 3. Example of acceleration data after data processing

Table 3. Relationship for the dynamic evaluation of the metabolic rate based on indicators.

Equations		***R²***	***RMSE (2 σ) [met]***
$M = 8.48 \cdot e^{\left(-\frac{IN5-0.42}{0.27}\right)^2}$	(1)	97 %	0.48
$M = -17.5 + 17.9 \cdot \cos(IN4 \cdot 2.6) + 18.8 \cdot \sin(IN4 \cdot 2.6)$	(2)	96 %	0.50
$M = \left(1.2 + \left(3.4 \cdot \left(1 - e^{-62.0 \cdot IN3}\right)\right) + 15 \cdot \left(1 - e^{-2.22e^{-14} \cdot IN3}\right)\right)$	(3)	96 %	0.20
$M = 1.88 + \left(7.8 \cdot ACC_n\right) + \left(-4.4 \cdot HR_n\right) + \left(-16.6 \cdot \left(HR_n\right)^2\right) + \left(21.4 \cdot HR_n \cdot ACC_n\right) + \left(5.1 \cdot \left(ACC_n\right)^2\right)$	(4)	96 %	0.23

This new methodology provides the curves for the real-time assessment of the metabolic rate expressed as a function of the personal parameters acquired simultaneously. Looking at the results in Table 3, it appears that, to compute an accurate value of *M*, the measurement of the heart rate and physical quantities (i.e., acceleration and *VMU* index) is needed. This suggests that the computing methodology proposed could be applied to wearable devices (e.g., smartwatches, wearable belts), enabling a real-time *M* measurement with an uncertainty of ±0.2 met. This outcome is referred to the sample population involved and to the activities performed. To achieve a wider applicability, the population should be extended to include subjects with different backgrounds.

2.3. Test Bench for the simulation model

The methodology proposed (presented in Section 2.2) was integrated into a virtual environment consisting of a building simulation model with technical systems which allow the control of indoor air temperature by means of a PMV-based approach. In the following, the controller developed is described and the virtual test bench of a house and the integration of the controller are presented.

2.3.1. Development of the controller based on the PMV virtual sensor

Generally, performing the standard control of indoor air temperature means to manually set a predefined indoor temperature. However, there is a lot of interest on how to optimise the selection of such set-point (Dounis and Caraiscos, 2009) also making use of the PMV model, as performed in (Zampetti et al., 2018). To enhance this aspect, in this work an advanced controller (Fig. 4) was developed and tested taking into account the real-time measurements of *M* as well as the other environmental quantities collected to evaluate comfort conditions. The controller is a Proportional-Integral-Derivative (PID) controller which takes as input the air temperature (t_a) and the set-point temperature (T_{set}) calculated with a PMV-based method and provides as output the heat to be supplied to the house.

In this simulation, the winter season was considered. The PID controller regulates the heat required to reach the set-point temperature of the simulated home environment. The set-point temperature used by the PID controller to achieve comfort conditions is determined from a virtual sensor that calculates the PMV. In particular, T_{set} represents the air temperature which allows the highest level of comfort (PMV = 0). A root finding algorithm was used to obtain the value of T_{set}. (Eq. 9):

$$T_{set} \mid pmv\left(T_{set}, t_r, v_a, p_a, I_{cl}, M\right) = 0 \tag{9}$$

A Matlab routine based on the Dekker's algorithm, which uses a combination of bisection, secant, and inverse quadratic interpolation methods to find the roots of nonlinear functions (Brent R.P., 2013), was adopted to compute the set-point temperature.

2.3.2. Integration of the controller into the simulation model

The simulation model was performed in the Simulink environment. Starting from the basic version of the model of a heating system (provided by Simulink libraries), some modifications were applied to implement a PMV virtual sensor and an air temperature controller based on such virtual sensor, as presented in the previous section.

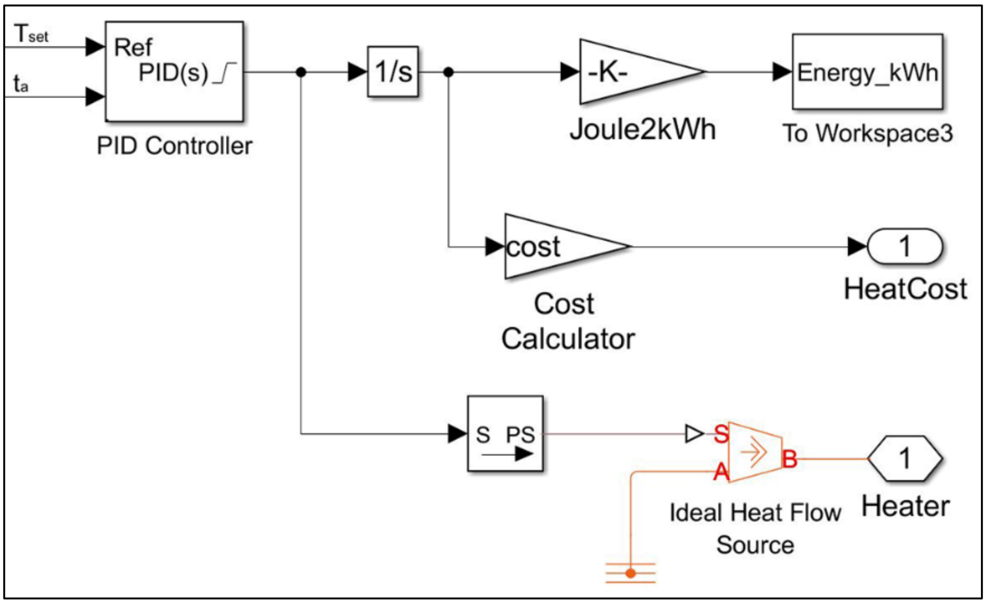


Fig. 4. PID controller applied to the simulation model.

The PMV virtual sensor was modelled with two different working modes: i) as a traditional sensor, without the real-time metabolic rate measurement; ii) as an innovative system with the real-time measurement of the metabolic rate as proposed in this paper. Thus, the virtual test bench was used to evaluate the impact of the PMV uncertainty on the management of the building as a function of the metabolic rate error that can occur when constant values are used instead of continuous monitoring.

The basic version of the model consists of a heater, a thermostat and a lumped parameter model of the house. The heat exchanges between indoor and outdoor environments through walls, windows and roof were modelled with the electrical-analog method for transient heat-flow, as already done in (Revel et al., 2012). Fig. 5 shows the modified simulation model.

To perform the test, the PID element was integrated into the simulation model of the heating house network. First, the initial value of the air temperature inside the house was set at 23 °C. The heater provides, or does not provide, sensible heat according to the set-point temperature. To run the control algorithm, the computation of the PMV was provided by a virtual sensor that gathered environmental variables from the model. In particular, the air temperature (t_a) was assumed to be equal to the room temperature of the modelled house. Since the simulation approach did not include mass balance and moisture, the air velocity (v_a) was set at a fixed value of 0.02 m/s and relative humidity (R_H) at a value varying around 50% with a uniform distribution with a range of ±2.5%.

Given that the simulation was performed for the heating season, the clothing insulation (I_{cl}) was fixed at 0.85 clo. Finally, the evaluation of the mean radiant temperature (t_r) was done with the angle factor methodology in agreement with the ISO 7726 (ISO 7726, 1998). The mean radiant temperature was computed from the indoor surface temperatures of the room and weighted with the view factors calculated for a central position of a subject with respect to the surrounding walls.

During the simulation, the virtual sensor calculated the PMV index continuously and, consequently, the set-point temperature was computed according to Eq. (9).

3. Results and discussion

This Section discusses the results obtained from the two simulated tests adopting the model described in the previous paragraph. In both tests, an indoor temperature control was performed, based on a set-point temperature (i.e., derived from a PMV index). The difference was in the *M* parameter, which is one of the six quantities for the calculation of the PMV value. In the first case, a dynamic profile of *M* was considered (i.e., the time-dependent value obtained with the wearable sensor and the application of the methodology previously discussed). The second case refers to a constant profile of *M* (i.e., a fixed value for the entire duration of the test, as generally done in the state of the art).

In this experiment, a typical 8-hour working day was simulated. The dynamic profile of the metabolic rate was modelled considering the activities which can be performed during the working hours. The metabolic rate profile used for both tests is shown in Fig. 6. The profile simulated an initial activity typical of office work (1.2 met) with a gradual increase in the metabolic rate reaching 1.6 met, which corresponds to standing activities, and, after keeping this rate for 4 hours, the profile returned to the initial value. The values of *M* were derived from the compendium of metabolic activities provided by ISO7730 (2005). Fig. 7 shows the trends of the set-point and air temperatures when performing control strategy with a dynamic *M* (Fig. 7a) and with a constant *M* (Fig. 7b). As said in Section 2.3.1, the set-point temperature depends on the PMV evaluation, which is significantly affected by the metabolic rate.

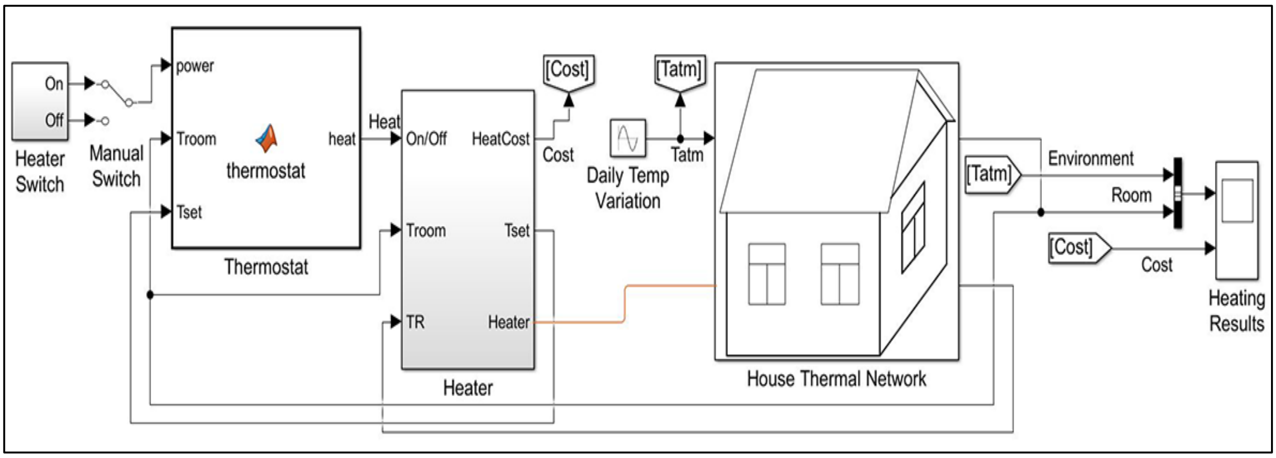


Fig. 5. Simulation model for the Heating house network.

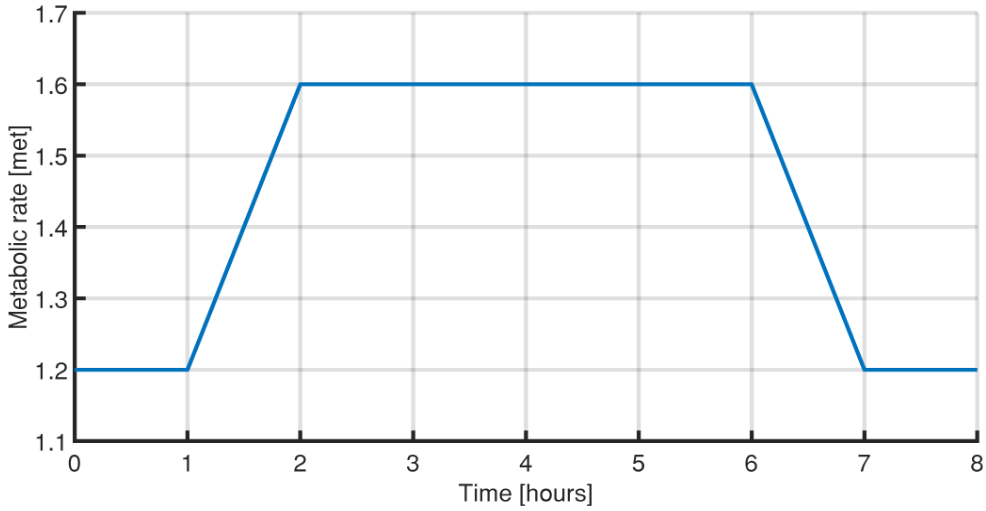


Fig. 6. Dynamic profile for the metabolic rate adopted in the simulation

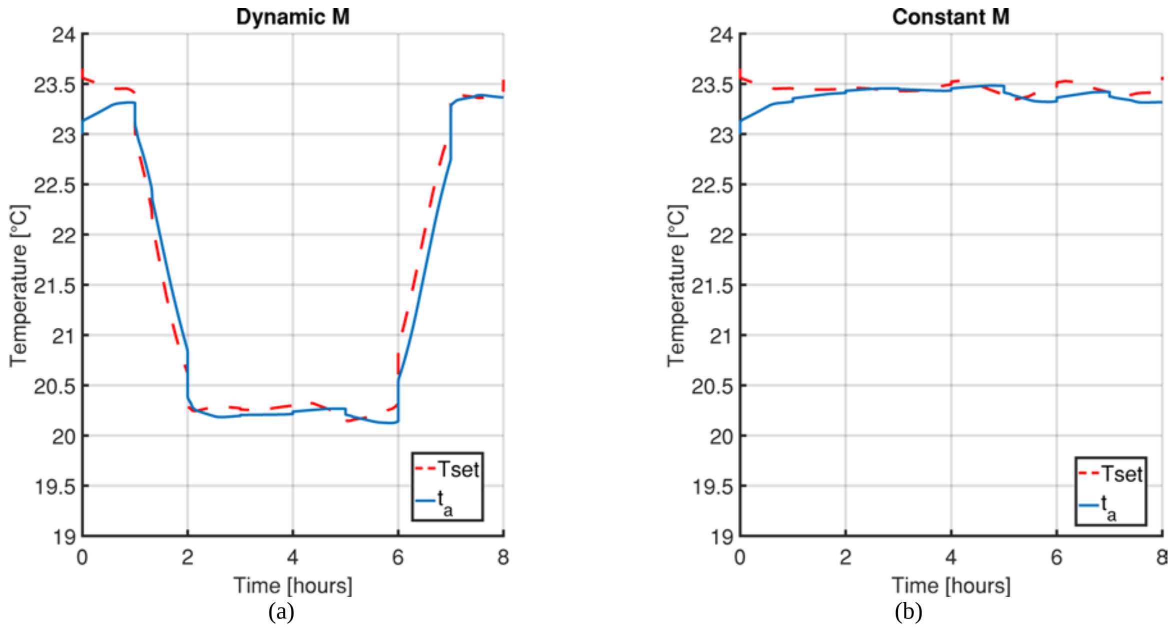


Fig. 7. Trends of the set-point temperatures and the air temperatures obtained by performing the two different controls: (a) with a dynamic profile of the metabolic rate; (b) with a constant value of the metabolic rate

It is possible to observe that, in winter conditions, when implementing a control strategy that uses a constant value of *M* (Fig. 7b), the indoor air temperature is kept almost constant. The heater provides continuous heat to the environment, while the real need of the occupant would be having a lower air temperature, as shown in Fig. 7a, where the use of a dynamic *M* for the set-point calculation provided a variation of T_{set}. In fact, an increase in *M* induces an increase in energy production by the human body that turns out to provide a lower comfort air temperature, therefore a lower T_{set}. The set-point temperature gradually decreased as a function of the metabolic rate increase. Conversely, when the metabolic rate decreased, the system responded correctly by calculating a higher set-point temperature to restore the comfort condition. Comparing the two situations of the case study proposed, the use of a constant metabolic rate instead of real-time monitoring led to an error in the PMV calculation propagated as an error of 3.2°C in the calculation of T_{set}. This error provided an impact in terms of comfort delivered to the occupants and efficiency in the management of the building. Analysing the PMV calculated by the virtual sensor in both tests, the control based on a dynamic *M* provided an average PMV close to zero (mean value of PMV: 0.03±0.09; Fig. 8a - Dynamic *M*). Conversely, the control with a constant value of *M* (Fig. 8a - Constant *M*) turned out to provide an environment near to the slightly warm sensation (mean value of PMV: 0.3±0.3). This happened because the controller was not able to recognize the lower heating needs due to the increased occupants' activity.

As a consequence, overheating occurred, which turned out to provide worse comfort conditions with higher energy consumption, as demonstrated in Fig. 8b, where the energy consumptions recorded with a dynamic *M* (Fig. 8b – Dynamic *M*) and with a constant value of *M* **(**Fig. 8b – Constant *M*) are reported. The first simulation (dynamic *M*) turned out to have an energy consumption of 5.8 kWh against the 8.6 kWh of the second test (constant *M*).

This result leads to the conclusion that the monitoring of occupants' activity optimized the comfort management and produced a gap of energy consumption between the ideal control of the heating system and the traditional one. In the case proposed, a gap of 33% of energy saving was registered.

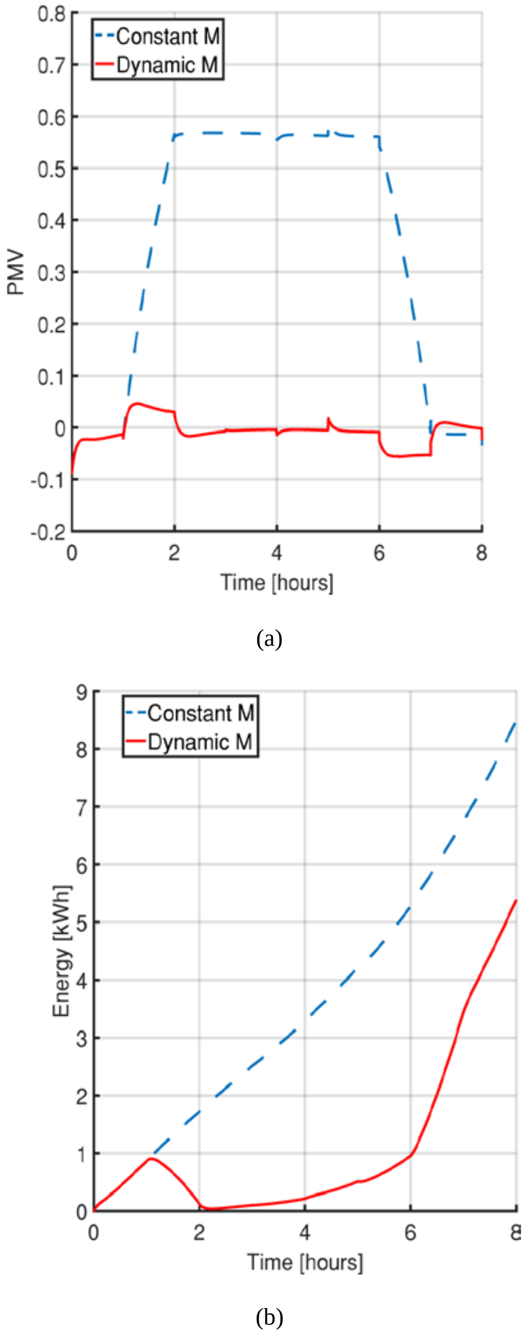


Fig. 8. (a) Trends of the PMV obtained by performing both the simulation cases;(b) energy consumption obtained by performing both control algorithms with a dynamic M and a constant M

4. Conclusions

Providing comfortable environments is a key aspect to enhance well-being and productivity of building occupants. In this perspective, this work investigates how the employment of wearable devices could improve the use of Fangers' model when applied to real-time monitoring and control, when the possibility to measure physiological parameters to estimate occupants' activity is given. To this end, a new methodology that allows the real-time measurement of the metabolic rate *M* has been developed.

A wearable device, which provides simultaneous acquisition of physiological quantities, has been adopted and different indicators have been obtained as a function of the number of physiological parameters taken into consideration. Finally, the curves to estimate the metabolic rate depending on the indicators *IN5*, *IN4*, *IN3* have been obtained. The measurement technique proposed provided an uncertainty of ±0.2 met, referring to the sample population and the tasks conducted in the experiment presented. To test its potential use in building operation (monitoring and control), a test has been performed in a virtual environment to compare the results obtained by adopting a PMV-based approach to control the indoor air temperature in two different cases. Two simulations have been conducted for the heating season: one using a controller based on a dynamic *M* profile and another one based on a static *M*. In both tests, the occupants' activity has been simulated for a profile ranging from 1.2 met to 1.6 met. The results have showed that, under the conditions of the test proposed, the use of a constant *M* provided an error of 3.2°C in the calculation of the PMV-based comfort temperature with respect to the calculation performed with a dynamic *M*, with a consequent condition of overheating and a gap between ideal and actual management in the order of 32%. Thus, the integration of the real-time metabolic rate measurement into PMV-based controllers could reduce the systematic error introduced by the standard and constant activity value assigned to a building. The benefit of the approach proposed has been demonstrated in terms of improved comfort delivered to the occupants and optimised building energy management.

To validate the preliminary results obtained in this work, further research will be carried out taking into account a wider sample population (i.e., in terms of age and contextual factors). Moreover, considering that the wearable device adopted in the tests is accurate but expensive, and generally not used by occupants in daily life, different solutions (e.g., smartwatches) will be tested with the proposed methodology.

References

Antoniadou P., Papadopoulos A.M., (2017), Occupants' thermal comfort: State of the art and the prospects of personalized assessment in office buildings, *Energy and Buildings*, **153**, 136–149.

ASHRAE, (2017), Thermal environmental conditions for human occupancy, Standard 55-2017, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, On line at: https://www.ashrae.org/technical-resources/bookstore/standard-55-thermal-environmental-conditions-for-human-occupancy.

Brent R.P., (2013), An algorithm with guaranteed convergence for finding a zero of a function, On line at: https://maths-people.anu.edu.au/~brent/pd/rpb005.pdf.

Capolongo S., Buffoli M., Oppio A., Nachiero D., Barletta M.G., (2013), Healthy indoor environments: How to assess health performance of construction projects, *Environmental Engineering and Management Journal*, **12**, 209-212.

Casaccia S., Pietroni F., Calvaresi A., Revel G.M., Scalise L., (2016), *Smart Monitoring of User's Health at Home: Performance Evaluation and Signal Processing of a Wearable Sensor for the Measurement of Heart Rate and Breathing Rate*, Proc. 9th Int. Joint Conf. on Biomedical Engineering Systems and Technologies, Rome, vol. 4, 175–182.

D'Ambrosio F.R.A., Palella B.I., Riccio G., (2011), The role of measurement accuracy on the thermal environment assessment by means of PMV index, *Building and Environment*, **46**, 1361–1369.

Dounis A.I., Caraiscos C., (2009), Advanced control systems engineering for energy and comfort management in a building environment-A review, *Renewable and Sustainable Energy Reviews*, **13**, 1246–1261.

Fanger P.O., (1970), *Thermal Comfort. Analysis and Applications in Environmental Engineering*, Danish Technical Press, Copenhagen, Denmark.

Hasan M.H., Alsaleem F., Rafaie M., (2016), Sensitivity study for the PMV thermal comfort model and the use of wearable devices biometric data for metabolic rate estimation, *Building and Environment*, **110**, 173–183.

ISO 7726, (1998), Ergonomics of the thermal environment-Instruments for measuring physical quantities, ISO 7726, International Standard Organization, Geneva, On line at: https://www.sis.se/api/document/preview/615884/.

ISO 7730, (2005), Ergonomics of the enviroment. Analytical determination and interpretation of the thermal comfort using calculation of the PMV and PPD indices and local thermal comfort criteria, ISO 7730, Internation Standard Organization, Geneva, On line at: https://www.sis.se/api/document/preview/907006/.

ISO 8996, (2004), Ergonomics of the thermal environment - determination of metabolic rate, ISO 8996, International Standard Organization, Geneva, On line at: https://www.sis.se/api/document/preview/905211/.

Johnstone J.A., Ford P.A., Huges G., Watson T., Garrett A.T., (2012a), BioHarness^{TM} multivariable monitoring device: part. I: validity, *Journal of Sports Science and Medicine*, **11**, 400.

Johnstone J.A., Ford P.A., Huges G., Watson T., Garrett A.T., (2012b), BioHarness^{TM} Multivariable Monitoring Device: Part. II: Reliability, *Journal of Sports Science and Medicine*, **11**, 409.

Kim J., Schiavon S., Brager G., (2018), Personal comfort models – A new paradigm in thermal comfort for occupant-centric environmental control, *Building and Environment*, **132**, 114-124.

Lee Y.Y., Din M.F.M., Ponraj M., Noor Z.Z., Iwao K., Chelliapan S., (2017), Overview of urban heat island (UHI) phenomenon towards human thermal comfort, *Environmental Engineering and Management Journal*, **16**, 2097-2111.

Lin L., Sherman P.D., (2007), *Cleaning Data the Chauvenet Way*, Proc. SouthEast SAS Users Group, Hilton Head, 1–11.

Luo M., Zhou X., Zhu Y., Sundell J., (2016), Revisiting an overlooked parameter in thermal comfort studies, the metabolic rate, *Energy and Buildings*, **118**, 152–159.

Luo M., Wang Z., Ke K., Cao B., Zhai Y., Zhou X., (2018), Human metabolic rate and thermal comfort in buildings: The problem and challenge, *Building and Environment*, **131**, 44–52.

Petri I., Rezgui Y., Beach T., Li H., Arnesano M., Revel G.M., (2015), A semantic service-oriented platform for energy efficient buildings, *Clean Technologies and Environmental Policy*, **17**, 721–734.

Pietroni F., Casaccia S., Revel G.M., Scalise L., (2016), *Methodologies for Continuous Activity Classification of User Through Wearable Devices: Feasibility and Preliminary Investigation*, IEEE Sensors Applications Symposium (SAS), Catania, Italy, 1–6.

Revel G.M., Sabbatini E., Arnesano M., (2012), Development and experimental evaluation of a thermography measurement system for real-time monitoring of comfort and heat rate exchange in the built environment, *Measurement Science and Technology*, **23**, 035005.

Revel G.M., Arnesano M., Pietroni F., (2014a), Development and validation of a low-cost infrared measurement system for real-time monitoring of indoor thermal comfort, *Measurement Science and Technology*, **25**, 085101.

Revel G.M., Arnesano M., Pietroni F., (2014b), *A Low-Cost Sensor for Real-Time Monitoring of Indoor Thermal Comfort for Ambient Assisted Living*, Proc. Ambient Assisted Living Italian Forum 2013, Ancona, 3–12.

Revel G.M., Arnesano M., Pietroni F., Frick J., Reichert M., Schmitt K., Huber J., Ebermann M., Battista U., Alessi F., (2015a), Cost-effective technologies to control indoor air quality and comfort in energy efficient building retrofitting, *Environmental Engineering and Management Journal*, **14**, 1487–1494.

Revel G.M., Arnesano M., Pietroni F., (2015b), Integration of Real-Time Metabolic Rate Measurement in a Low-Cost Tool for the Thermal Comfort Monitoring in AAL Environments, *Biosystems and Biorobotics*, **11**, 101–110.

Riani M., Perrotta D., Torti F., (2012), FSDA: A MATLAB toolbox for robust analysis and interactive data exploration, *Chemometrics and Intelligent Laboratory Systems*, **116**, 17–32.

Zampetti L., Arnesano M., Revel G.M., (2018), Experimental testing of a system for the energy-efficient sub-zonal heating management in indoor environments based on PMV, *Energy and Buildings*, **166**, 229–238.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2297-2306
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

FIGHT AGAINST PERSISTENT ORGANOCHLORINATED POLLUTANTS: DISAPPEARANCE IN PRESENCE OF MICROORGANISMS

Carla Boga[1*], Erminia Del Vecchio[1], Luciano Forlani[1], Gabriele Micheletti[1], Eros Pancaldi[2], Giuseppe Strazzera[3]

[1]*Alma Mater Studiorum - University of Bologna, Department of Industrial Chemistry "Toso Montanari", Viale Del Risorgimento 4, 40136, Bologna, Italia*
[2]*Environment and Health Bazzanese Committee, Via Circonvallazione sud 11/a, 40053 Valsamoggia, Italy*
[3]*Department of Biotechnology, University of Verona, Strada Le Grazie 15, Verona, Italy*

Abstract

The bioremediation represents an ongoing challenge, especially in the case of organochlorinated compounds, due to the difficulties in their degradation that causes persistence in the environment. Herein we report a study on the ability of a mixture of microorganisms (MOM) to interact with organochlorinated compounds belonging to different chemical classes, i.e. DDT, PCB, tetrachlorobenzene, and lindane. Experiments in vitro showed the disappearance, partially reversible of these compounds in mixtures containing microorganisms, with a trend dependent on the kind of used pollutant. Unexpected 'complexation' by some components of molasses used as growth nutrient for microorganisms was found. Experiments carried out in the presence of soil showed that also in this case the participation of MOM to hide pollutants cannot be excluded. The obtained results may be an interesting starting point for further investigations on the bioremediation of organic pollutants using biological and not expensive method.

Key words: bioremediation, microorganisms, organochlorinated, pollutants

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The degradation of persistent organic pollutants into not-toxic derivatives, both with chemical and/or biochemical methods, is one of the main challenges in the contemporaneous fight against environmental disasters produced by humanity. Among the more persistent pollutants there are organic chlorine-containing substances such as polychlorinated biphenyls (PCBs), polycyclic aromatic carbons (PAHs), and hydrocarbon derivatives (Liu et al., 2017; Liu et al., 2018; Savic et al., 2016). From a lot of scientific reports (Kruger et al., 2008; Ritter et al., 1995), as well as from media information, it is well known that organic chlorine-containing substances, which are largely used as pesticides or in industrial technical devices, are very persistent under natural conditions and they are considered severe dangerous pollutants. This is the case of the DDT (2,4-dichlorodiphenyltrichloroethane, listed in class 2A of IARC (IARC, 2013), as probably carcinogenic to humans) which is banned in several nations by exception of those infested with mosquitos to eliminate malaria epidemics. Polychlorobiphenyl (PCB) class involves a large number (209) of chlorine-containing biphenyl derivatives which mixtures were used in industrial processes and discharged in cities

* Author to whom all correspondence should be addressed: e-mail: carla.boga@unibo.it; Phone: +39 051 2093616; Fax: +39 051 2093654

and countryside by several fortuitous accidents: in Italy, large amount of PCB [generally included in Group 1 of IARC, (IARC, 2015)] are present in the territory of Brescia (Italy). Lindane is also listed in class 1 of IARC. Thus, the bioremediation of soils polluted with many and different organic compounds is of great and growing interest, as documented by many literature reports (*e.g*. Cheng et al., 2016; Megharaj and Naidu, 2017, 2018; Muñiz et al., 2017).

Recently we studied the possibility to carry out experiments to make bioremediation of aldehydes, in particular formic aldehyde, by a mixture of microorganisms (Boga et al., 2014). Our searches indicate that aldehydes are wholly eliminated by simple treatment with microorganism mixture.

Now we are trying to obtain elimination of the chlorine-containing pollutants reported in Fig. 1. In a preliminary way, we checked the possibility to have bioremediation also on a polycyclic aromatic hydrocarbon, fluorene, which is also reported in Fig. 1.

2. Material and methods

2.1. Materials

Gas chromatographic analyses were carried out with a Hewlett-Packard (HP) 5890 gas chromatograph directly interfaced with an Agilent 5970 mass selective detector. Injection temperature was 250 °C (split injection mode split ratio 50/1) (HP-5MS column, 30m, 0.25mm, 0.25μm film thickness). The oven temperature was programmed as follows: 60 °C for 2 min, increased up to 260 °C at the rate of 20°C/min, followed by 260 °C for 20 min. In the case of experiments in soil with PCB 15 the above parameters were as follows: 60 °C for 2 min, increased up to 160 °C at the rate of 20°C/min, 160 °C for 5 min, increased up to 200 °C at the rate of 3°C/min, 200 °C for 5 min, increased up to 260 °C at the rate of 20 °C/min, 260 °C for 2 min. The carrier gas was helium, used at a flow rate of 1 mL/min; the transfer line temperature was 280 °C; the ionization was obtained by electron impact (EI), acquisition range was 50–500 m/z. ^{1}H NMR spectral data were recorded on a Varian Inova 600 spectrometer at 600 MHz in $CDCl_3$. Chemical shifts were measured in parts per million (ppm) and referenced to the solvent (7.26 ppm). EM-1® and sugar cane molasses were supplied by Punto EM S.r.l. (Sanremo, Italy). EM-1 contains five families, ten genera and more than 80 types of aerobic and anaerobic microbes including photosynthetic bacteria, lactic acid bacteria, yeast, actinomycetes, fungi (Ahn et al., 2014; Gaggia et al., 2013). San Benedetto mineral natural water from the spring in Scorzè (Venezia, Italy) was used for the activation of EM-1. The activation procedure was performed as previously reported (Boga, 2014) and the activated mixture will be hereafter indicating as MOM. All other reagents used were purchased by Sigma-Aldrich (Milano, Italy). Solvents were from VWR International PBI Srl (Milano, Italy). The soil sample was collected in the park of the Department of Industrial Chemistry, Viale del Risorgimento, 4, Alma Mater Studiorum - University of Bologna to a depth of about 30 cm. The soil was analyzed by the CSA Group S.p.A. laboratory (Rimini, Italy), and their main parameters are reported in Table 1.

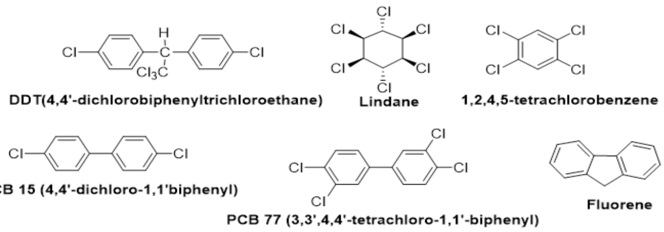


Fig. 1. Selected pollutants tested for bioremediation by microorganism's mixture

Table 1. Physical-chemical properties of the test soil

Parameter	*Measure Unit*	*Value*	*I.M.*
pH (in water)	pH units	7.18	± 1.08
Electric conducibility at 25 °C	μS/cm	772	± 116
Sand	%	59	± 9
Silt	%	31	± 5
Clay	%	10	± 2
Total limestone (calcium carbonate)	%	13.7	± 2.1
Cationic exchange capacity (CSC)	meq/100 g	26	± 4
Organic matter	%	3.97	± 0.60
Total nitrogen (as N)	%	0.23	± 0.03
C/N Ratio	-	10	± 2
Assimilable fosforus (as P)	mg/kg	7	± 1
Exchangeable Potassium	mg/kg	136	± 20
Sulfur	%	0.03	± 0.01
Assimilable iron	mg/kg	6.9	± 1.0
Magnesium	mg/kg	4069	± 610
Sodium	mg/kg	< 300	

2.2. 'In vitro' tests on organic pollutant/MOM mixture. General procedure.

The organic pollutant was dissolved in ethanol (in an ultrasound bath) and brought to volume with ethanol in a volumetric flask (DDT: 0.03170g in 20 mL; PCB 77: 0.00517g in 10 mL; PCB 15: 0.0027g in 10 mL; tetrachlorobenzene: 0.00772g in 10 mL, Lindane: 0.012g in 10 mL; Fluorene: 0.00732g in 10 mL). In some vials 0.5 mL of the above mother solution (DDT, PCB 77, lindane, or fluorene) and 5 mL of MOM were added; other vials with 0.5 mL of the mother solution and 5 mL of water were prepared. After opportune time (Figs. 2 and 4) the mixture was extracted with dichloromethane (4 x 5 mL) and the solvent was removed. The residue was dissolved in 1.0 mL of CH_2Cl_2 and added of 0.1 mL of a solution of hexamethylbenzene (0.008M in dichloromethane); 0.7µL of the solution were injected in the GC-MS spectrometer. In case of PCB 15 and 1,2,4,5-tetrachlorobenzene several vials with 0.5 mL of the mother solution and 9 mL of MOM and other vials with 0.5 mL of the mother solution and 9 mL of water were prepared. After opportune time (Fig. 3) the sample was extracted with dichloromethane (4 x 5 mL), the solvent was removed and the residue dissolved in 1.0 mL of $CHCl_3$ and added of 0.2 mL of a solution of phenanthrene (0.0603 g in 50 mL of $CHCl_3$); 0.7µL were injected in the GC-MS spectrometer.

2.3. 'In vitro' tests on soil samples. General procedure.

Mother solution of analyte in acetone (1.4 mL) was added to 50g of soil sample made homogeneous by sifting and poured in a glass vessel. Acetone was removed by evaporation at 60°C for 5 min. then 25 mL of the activated MOM mixture was added. An equal number of samples was prepared as above except for the substitution of MOM with an equal amount of water (control sample). After the time indicated in the corresponding Figures (Figs. 6 and 7) $CHCl_3$ (50 mL) was added to the mixture, the system was stirred and subjected to vacuum filtration over Celite (Sigma-Aldrich, Milano, Italia). The cake was transferred in vessel, extracted with $CHCl_3$ (20 mL) and filtered as above. The procedure was repeated a third time. The filtrate was introduced in a separatory funnel and the organic layer was dried over anhydrous $MgSO_4$. After filtration and solvent removal under vacuum, the residue was dissolved in 1.0 mL of $CHCl_3$ and after addition of 0.2 mL of standard solution (phenanthrene) the sample was analyzed by GC-MS. In most cases the solution was concentrated and dissolved in $CDCl_3$ to be analyzed by ^1H NMR.

Three series of tests have been carried out on soil samples contaminated with PCB 15 or lindane. The first series of experiments was carried out in summer 2015 with 30°C average room temperature. Three mother solutions were prepared dissolving 0.1257g of lindane in 100 mL of acetone, 0.0508g of PCB 15 in 50 mL of acetone, and 0.1275 g phenanthrene (standard) in 100 mL of $CHCl_3$. After the time indicated in Figs. 6 and 7 the mixture was treated and analyzed as above indicated in general procedure. The second series was carried out in November-December 2015 with 15°C average room temperature and the following mother solutions were prepared: 0.0324g of DDT in 50 mL of acetone, 0.1068g of PCB 15 in 100 mL of acetone, and 0.0613 g of phenanthrene (standard) in 50 mL of $CHCl_3$. All the experiments (including the corresponding control mixture) were monitored through the above general procedure.

The third series of experiments was run between January and March 2016 and the following mother solutions were prepared: 0.0408 g of DDT in 50 mL acetone, 0.0531 g of PCB 15 in 50 mL of acetone, 0.0498 g of lindane in 50 mL acetone, 0.0664 g phenanthrene (standard) in 50 mL of acetone. In these cases, the analyte solution was added to the soil a week prior the addition of MOM. All the vessels were kept in a thermostatic bath (28±2°C) and monitored using the above procedure. Moreover, two samples of every analyte (immediately after the addition of MOM and at the end of the experiment) were subjected to Soxhlet extraction with $CHCl_3$.

3. Results and discussion

This study was carried out in two steps: a preliminary *in vitro* approach focused on the monitoring of the variations with time of the amount of the considered pollutant in the presence of the microorganism mixture (MOM) and a second phase in which the method was applied to a soil sample.

3.1. 'In vitro' experiments on the effect of MOM on analytes

Fig. 2 reports data obtained from a preliminar experiment *in vitro* about the variation of the amount of DDT (reported as DDT/standard ratio) in the presence of the microorganism mixture (MOM). The first part of the plot shows a regular decrease of DDT amount until about 10 days: the DDT is apparently eliminated for more than 50% of the initial amount, but, unexpectedly, after longer times the DDT amount recovered was more than that detected at zero reaction time. This behaviour was observed also by using PCB 77, PCB 15, 1,2,4,5-tetrachlorobenzene, lindane, and fluorene. The relative rapid decrease of the analyte appears to be not its definitive and irreversible transformation in other compounds, but it resembles a reversible (and apparent) concealment by MOM-containing mixture. The fast decrease of chlorine-containing organic compounds was observed by other authors (Derbalah et al., 2013) and it was considered an indication of the ability of some microorganisms to resolve the pollution arising from the presence of chlorine containing compounds.

The behaviour showed in Figs. 2–4 cannot be immediately explained but it is a clear indication of the ability of the mixture containing MOM to hide the chlorine-containing compound monitored and quantified by extraction methods using chloroform or dichloromethane as generally indicated by official protocols. The trend reported in plots of Figs. 1–4 is not the same for all analytes considered: this fact cannot be surprising, owing the different chemical classes of analytes considered.

This trend resulted to be reproducible being it observed in other experiments carried out in our research group (Strazzera, 2015); as a matter of fact, in all cases, about 1 week, the inversion of the decreasing trend of the analyte/standard ratio was observed.

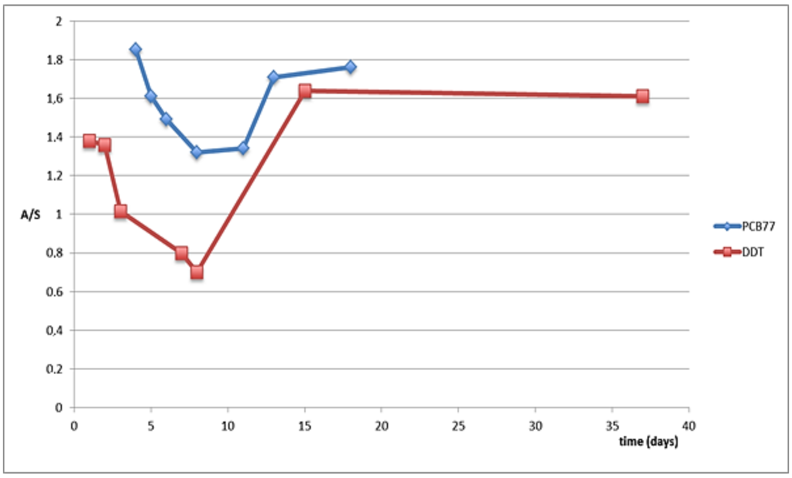


Fig. 2. Variation of amount of the analyte/standard ratio caused by addition of MOM

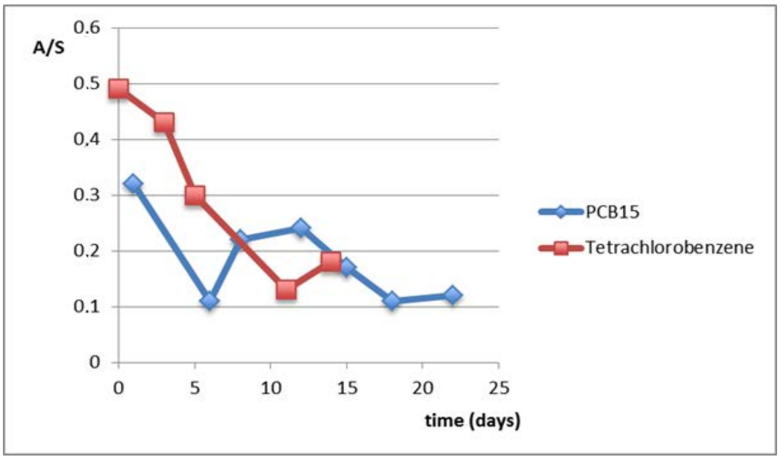


Fig. 3. Variation of amount of the analyte/standard ratio caused by addition of MOM

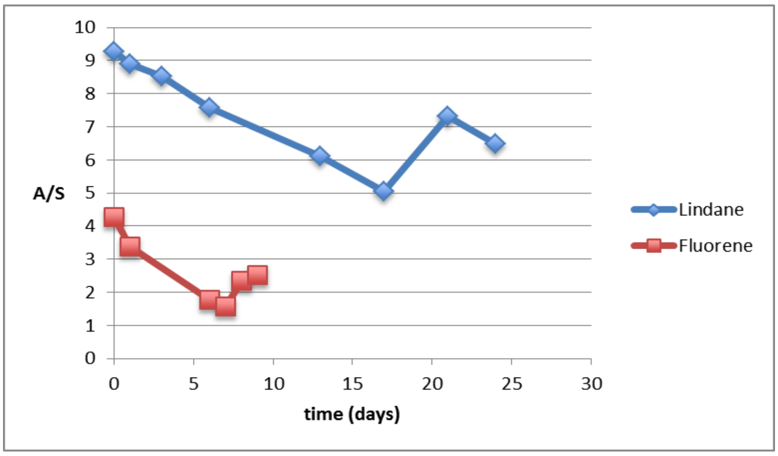


Fig. 4. Variation of amount of analyte/standard ratio caused by addition of MOM. For fluorene, the monitoring was stopped after 10 days

This might be ascribed to the presence, even contemporary, of several phenomena as follows:

1. A fast and partially reversible seizure of the analyte, almost immediate in the case of DDT, by “inert” substances added together with microorganisms, or by microorganisms itself.

2. The second phenomenon concerns the actual transformation of the analyte in unknown metabolites.

3. In the case of a fast interaction between analyte and microorganisms, a third process may be the decrease of the amount of active microorganisms (under the used experimental conditions) due to some nutritional shortages, with the consequence of the release from the microorganisms of the amount of the analyte not yet transformed.

With the purpose to investigate the anomalous behaviour of plots above reported, we performed parallel experiments adding MOM or only water (control) to a solution of analyte and working up in the same manner the mixture immediately after the addition. The values of the analyte/standard ratio obtained in both cases by GC-MS analysis are reported in Table 2.

Table 2 clearly shows that some chlorinated compounds (*i.e.* DDT and lindane) present an instantaneous decrease: for instance, the 75% amount of DDT is quickly (and apparently) depressed with respect to the control test carried out in the presence of only water. It has to be point out that data of Table 2 are obtained after usual extraction of the reaction mixtures (see experimental). On the contrary, after extraction with more drastic methods, *i.e.* by extracting under ultrasound irradiation or by heating the mixture in the presence of sulfuric acid, the analyte/standard ratio of the residue coming from treatment with MOM becomes very near to that obtained in the presence of water only. From these data, it is possible to evince that some chlorinated compounds are strongly complexed after the addition of MOM. This suggested us to check the effect of the addition of sugar cane molasses, the main component of the microorganism’s culture broth added as nutrient for microorganisms, to a solution of DDT, without presence of microorganisms. Plot of Fig. 5 reports the results obtained after addition to the DDT solution of increasing amount of molasses and immediate work-up and analysis. Data of Fig. 5 show a noticeably decrease of the amount of DDT recovered by increasing the amount of molasses until to reach an almost constant DDT/Standard value independent from the amount of molasses thus suggesting the occurrence of a saturation phenomenon.

After this result we tried to investigate which component of molasses might be responsible for the behaviour observed. The composition of molasses depends mainly from the plant used as source, from the climate of the growing area and from the production process (http://www.feedipedia.org/node/561).

In the literature (Browne, 1919; Hashizume et al., 1966;) it has been reported that molasses is a complex mixture containing sucrose as main constituent, followed by D-glucose and D-fructose derived from the hydrolysis of sucrose during the production process, ash, aminoacids, inorganic salts, gums and pectins. The addition of a solution of DDT to an aqueous solution of sucrose did not produce effect on the amount of DDT recovered, as well as the addition of a mixture of D-glucose and D-fructose. On the contrary, pectin, separately added to a solution of DDT, produced remarkable decrease (27%) of the amount of DDT recovered with respect to the control experiment (DDT solution dispersed in water and worked-up as described in experimental section).

Table 2. Analyte/standard ratio in the presence of microorganism’s mixture (MOM) or in the presence of water only (H_2O), immediately after mixing

→ ***Analyte*** ↓ ***Medium***	***DDT***	***Lindane***	***PCB 15***	***Tetrachlorobenzene***	***Fluorene***
H_2O	2.1	3.3	0.4	0.5	2.9
MOM	0.5	2.7	0.15	0.5	3.0

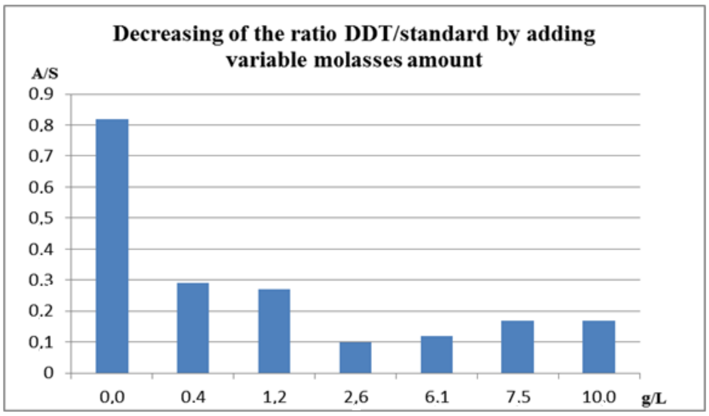


Fig. 5. Decrease of the DDT/Standard ratio after addition of variable amount of molasses

3.2. *'In vitro' experiments on soil contaminated with organochlorinated compounds*

In order to investigate the possibility to use MOM in experimental conditions near to those presumably existing in natural conditions, we performed a series of test, carried out by adding a mixture of analyte (A) and MOM (or analyte and water) to a soil sample and monitoring with time the amount of analyte recovered that was quantified both through ^{1}H NMR and GCMS analyses.

The experiments were carried out by using PCB 15 and lindane as soil contaminants, and the results are summarized in plots of Figs 6 and 7, respectively. A not contaminated soil specimen (see experimental) was collected in the park of the Department of Industrial Chemistry, Viale del Risorgimento, 4, Alma Mater Studiorum–University of Bologna in a not anthropic hilly area. Plots A and B of Fig. 6 are obtained using soil as is stand. Plots C and D are obtained by soil "sterilized" as reported in the experimental part. Plots B and D of Fig.7 are obtained in soil as is stand. Plots A and C are obtained by soil "sterilized" as reported in the experimental part.

Apparently, the soil by us used (see experimental) presents very similar effect on the disappearance of the analyte considered in the presence and in the absence of MOM: in both cases there is a significant decrease of the amount of analyte. It is interesting to note that in the case of PCB 15, the A/S ratio found extracting the mixture immediately after the addition of the soil to MOM (plot A and C at t=0) was minor for about 40% of that found for the case of addition of soil to water (plots B and D, Fig. 6).

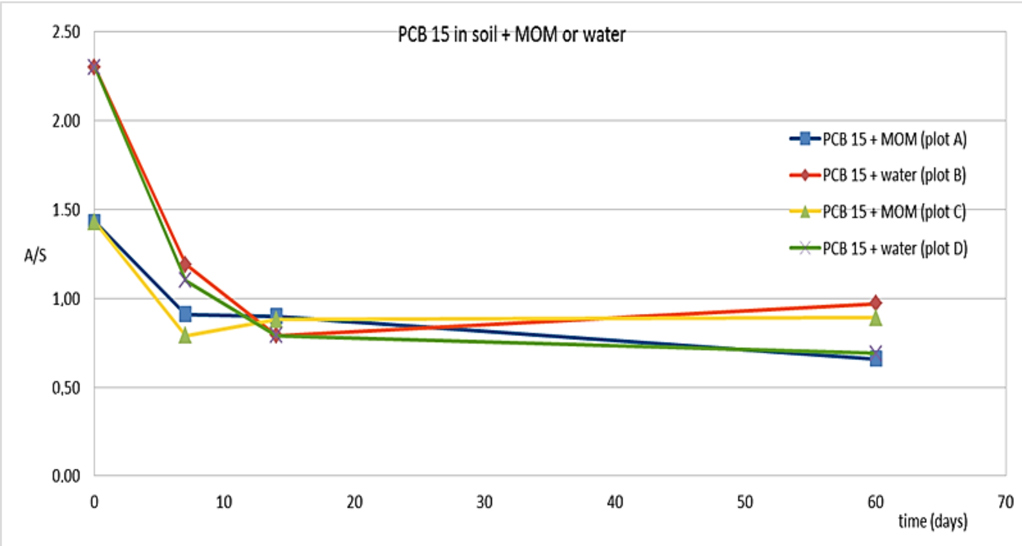


Fig. 6. A is PCB15. plot A: PCB15 + MOM; plot B: PCB15 + water, plot C: PCB15 + MOM in soil pre-treated in autoclave, plot D: PCB15 + water in soil pre-treated in autoclave

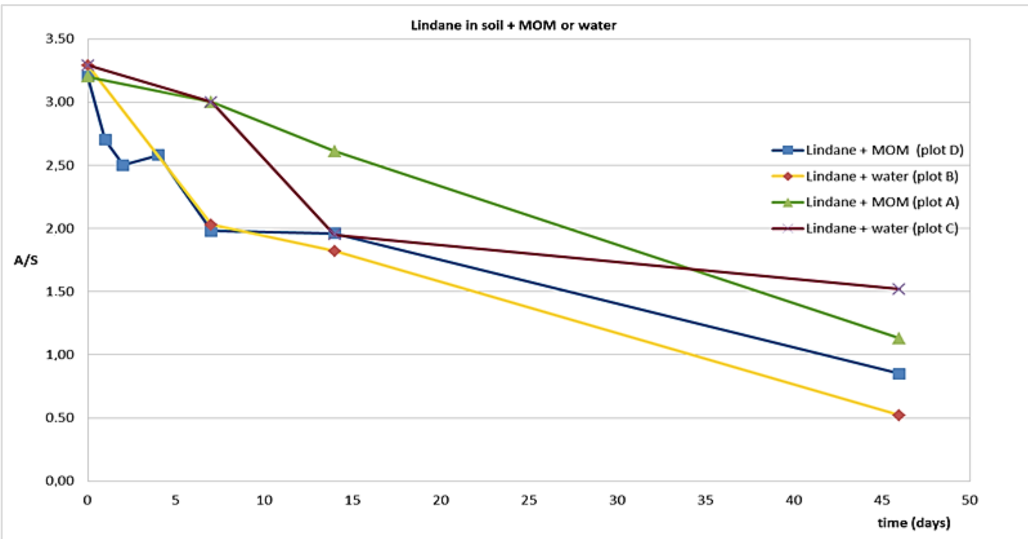


Fig. 7. A is lindane and S is phenanthrene used as standard. plot A: lindane + MOM in soil pre-treated in autoclave; plot B: lindane + water, plot C: lindane + water in soil pre-treated in autoclave, plot D: lindane + MOM

This difference is almost the same of that observed in the case of 'in vitro' experiments reported in Table 2; this finding provides a further confirmation of the occurrence of an immediate complexation phenomenon due to the presence of molasses in the culture broth. Data shown in Fig. 7 are also in line with those reported in Table 2: in this case no significant decrease of the amount of the analyte was observed after addition of MOM both on a solution of lindane (Table 2) and to a soil sample contaminated with lindane (Fig. 7, all plots at t=0) thus supporting the above deduction that lindane is not subjected to complexation phenomenon by molasses.

The general trend observed in Fig. 6 is the decrease with time of the A/S ratio within the first 15 days; the very close values found in the case of sterilized and not-sterilized soil suggest a not significant role by indigenous microorganisms of the soil while almost the same value reached after the following weeks for all plots might indicates the occurrence of a sequestering action by the soil: this might hinder the bioavailability of the analyte to microorganisms. Similar deductions can be applied to the trends observed in Fig. 7 for the case of lindane.

In order to gain support to the above hypothesis of a complexation phenomenon involving the soil components we planned to carry out further experiments using the Soxhlet extraction method. Table 3 reports the results obtained using this drastic extraction method. Both lindane and PCB 15 shows a strong decrease after long time, also in the presence of water only (without MOM): probably, the soil is able to hide, in some way, these chlorine-containing pollutants.

These findings can be considered an indication that the disappearance of the analyte may be hardly ascribed to a simple complexation (obviously, in a reversible process) and suggest the occurrence of another not-reversible process which causes the decrease the analyte (after long reaction time) probably by forming other different compounds which might be metabolites of the starting materials. We tried to have more information of the presence of metabolites (see section 3.3).

A particular behaviour was observed when analyte was DDT in presence of soil, as reported by plot of Fig. 8: the test carried out in the presence of MOM shows an apparent complete disappearance of DDT, while experiments in water show an initially noticeable decrease, but after the amount of DDT remains constant with time. Even if this experiment cannot be conclusive, we consider this behaviour as an indication of the formation of a complex between soil and DDT, while the possibility of a more important complexation or metabolization appears a reasonable explanation of the complete disappearance of DDT in the presence of MOM as indicated by plot B. However, we don't have the possibility to completely discriminate between the complexation or metabolization of analyte.

Table 3. Analyte/standard ratios in soil additioned with MOM or water. Data obtained after extraction with Soxhlet apparatus

Analyte	*Time = 0*	*Time =40 days*
Lindane/water	3.0	0.4
Lindane/MOM	2.1	0.6
PCB15/water	0.4	0.1
PCB15/MOM	0.4	0.2

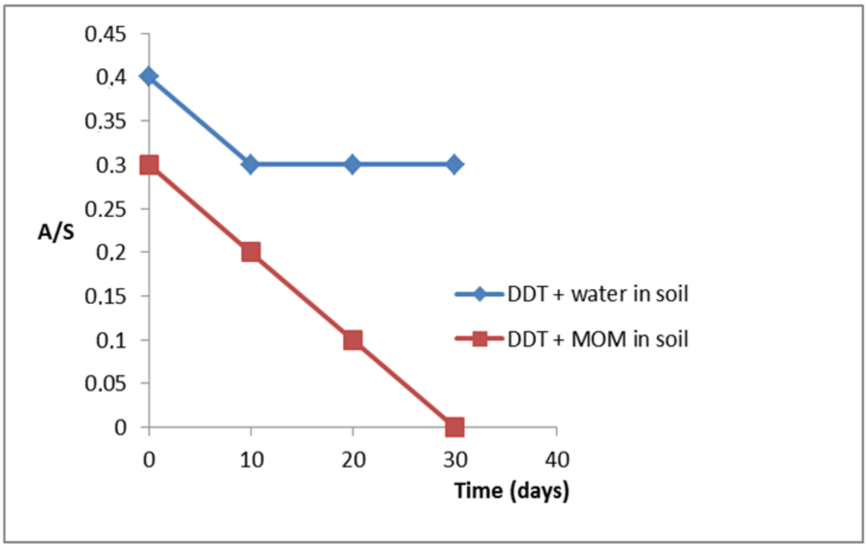
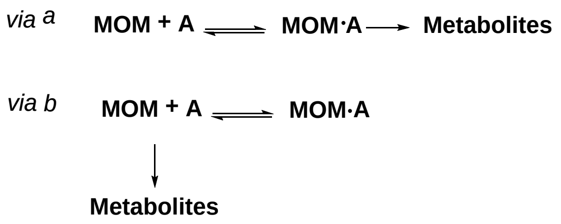


Fig. 8. A is DDT and S is phenanthrene used as standard. Plot A: DDT + water in soil; plot B: DDT + MOM in soil

The following schemes of interaction between chlorine-containing pollutants and MOM may be an explanation about the disappearance of these pollutants and they might be a starting point of further and more detailed investigations since the discrimination between the two schemes is a difficult problem, also from a chemical point of view Eq. (1).



(1)

were: A is the used analyte and MOM is the whole mixture containing microorganisms and culture medium. MOM.A indicates the interaction between MOM and the analyte producing the apparent decrease of the amount of analyte: this interaction may be an essential step in obtaining metabolites, *i.e.* the destruction/transformation of the analyte (Scheme 1, *via* a) or it may be a simple "cul de sac" which is non-producing metabolites (Scheme 1, *via* b).

A further parameter that can play an important role in determining the decrease of the rate of the amount of analyte is the temperature. Table 4 collects some data about this effect applied to mixtures containing DDT or PCB 15: at 30°C the mixture analyte/soil shows a regular decrease with time, while at 15 °C the amount of the analyte presents a trend to increase this amount: probably, at low temperature after an initial formation of a non-covalent interaction between analyte and soil or microorganism mixture (perhaps by the molasses components), complexes are destroyed and the analyte is prone to be revealed by usual analytic procedures.

However, the decrease with time of the analyte amount in soil observed when the mixture was kept at 30 °C cannot be ascribed to the only complexes formation through non-covalent bonds because usually this phenomenon is depressed by temperature increasing due to a dissociation of the complex. The fact that at higher temperature the amount of analyte recovered decreases, even if in slight amount, might indicate a certain activity of the MOM that is favoured at 30 °C.

3.3. Presence of 4-methyl-phenol in experiments carried out with chlorine-containing pollutants in soil by addition of microorganism mixture

During the first series of experiments carried out with PCB 15 in soil, after 60 days from the addition of EM and extraction of mixture with chloroform, we observed the presence, in the ^{1}H NMR spectrum, of two intense doublets at 6.73 e 7.03 ppm, coupled one with the other with J = 8.3 Hz and of one singlet at 2.27 ppm. These signals suggested the presence of an aromatic ring with *para*-substituents and of a methyl group, and we hypothesized the unexpected compound was 4-methyl-phenol. This was confirmed by addition in the NMR tube of an amount of authentic sample of 4-methyl-phenol, which enriched the above signals. These signals were not present in the ^{1}H NMR spectrum of PCB 15 in soil immediately after the addition of EM (zero reaction time) and were absent also in experiments carried out *in vitro* without soil. The presence of *p*-cresol was also confirmed by analysis by GC-MS apparatus. The absence of contamination of soil was ascertained by extraction of a soil sample both with chloroform and n-hexane; ^{1}H NMR analysis of the residue did not showed signals belonging to *p*-cresol.

From the KEGG PATHWAY Database (http://www.genome.jp/kegg/pathway.html) data bank emerged that the first steps of biodegradation pathways of some aromatic chlorine-containing compounds involve the functionalization of the aromatic ring with formation of phenols. 4-Methyl-phenol was also indicated (Natarajan et al., 1999) to arise, as transient intermediate, from the biodegradation of diphenyl derivatives produced in a reductive dichlorination process of PCB derivatives. This suggested, as first hypothesis, that in our case *p*-cresol was produced from the biodegradation of PCB 15 but it was confuted by the finding of 4-methyl-phenol also in mixtures containing the other considered organochlorine analytes in experiments carried out in soil, both after addition of MOM and in some cases also in the presence of only water. In Table 5 are collected the 4-methyl-phenol/standard ratios calculated from ^{1}H NMR spectra of the residues obtained after work-up of the systems mixture MOM/soil/analyte and H_2O/soil/analyte monitored with time. The fact to have found *p*-cresol not only in mixtures containing PCB15 but also DDT and lindane agrees with the hypothesis that *p*-cresol can originate from microorganisms or from their action on some soil constituents (Dawson et al., 2011; Mathus et al., 1995). From data of Table 4 emerges that *p*-cresol is detected after 30 days (20 days in case of DDT-containing mixtures) and in major extent when MOM is present in the mixture. In the literature, *p*-cresol was indicated to be easily destroyed in aerobic situation (Boyd and King, 1984) the decrease (at 40 days reported in Table 5) may be ascribed to a similar phenomenon.

Based on the above, it is reasonable to admit that *p*-cresol is arising from some unknown reactions involving soil and microorganisms, or from the simple endogenous soil microorganisms. Even if this preliminary conclusion deserves more accurate investigation, in our opinion, in here reported experiments, it appears reasonable to state that is very poorly probable to ascribe the presence of p-cresol as metabolite of anyone chloro-containing pollutants, including PCB.

Table 4. Effect of variation of temperature on the apparent decrease of DDT and of PCB 15 amount (measured by the ratio analyte/standard) in the presence of soil and MOM

Days	*15°C DDT + MOM*	*30°C DDT + MOM*	*15°C PCB + MOM*	*30°C PCB + MOM*
0	0.4	0.4	1.8	1.4
7	0.4	0.2	1.9	0.9
14	0.4	0.1	2.9	0.9
60	0.8	0.0	3.2	0.7

Table 5. Presence of 4-methyl-phenol, at different times, of soil samples contaminated with organochlorine-containing pollutants

Time (days)	*Para-cresol / standard ratio from PCB15/MOM mixture*	*Para-cresol / standard ratio from PCB15/H_2O*	*Para-cresol / standard ratio from Lindane/MOM mixture*	*Para-cresol / standard ratio from Lindane/H_2O*	*Para-cresol / standard ratio from DDT/MOM mixture*	*Para-cresol / standard ratiofrom DDT/H_2O*
10	-	-	-	-	-	-
20	-	-	-	-	0.2	< 0.1
30	0.5	-	0.9	0.2	0.8	0.4
40	0.1	-	0.3	N.D.	0.3	0.6

4. Conclusions

The problem herein discussed shows severe complications arising from his natural complexity, however the data obtained and the consequent observations are exciting in biologically solving a pollution situation very diffused in large countries in the world.

The main conclusions from the current study can be summarized as follows:

- Experiments *in vitro* showed the disappearance of organochlorine-containing pollutants in mixtures containing microorganisms. The decrease of amount of pollutants is (in some cases) partially reversible and cannot have immediate explanation.
- In agreement with the fact that herein considered chlorine-containing pollutants belong to different chemical classes, the trend of the observed decreasing amount is dependent on the kind of used pollutants.
- Our experiences (even if they are part of a preliminary study) support the statement that the used microorganism mixture is able to depress the amount of chlorinated compounds.
- Some analytes (in particular DDT) are quickly hidden by mixtures containing microorganisms by some component of molasses, probably pectine.
- Experiences carried out in the presence of soil and in the presence/absence of microorganism mixture, suggest the same conclusion of the above point. The participation of microorganisms to hide pollutants cannot be excluded.
- Owing the fact that, in the natural environment, the chlorine-containing pollutants are very persistent), why the soil is able to hide (complexed or destroyed) some chlorine-containing compounds (such as DDT) is yet an unresolved problem. However, the formation of reversible non-covalent complexes can explain our findings as well as the results of other literature reports.
- Overall, the obtained results may be an interesting starting point for further investigations on the bioremediation of organic pollutants using biological and not expensive methods.

Acknowledgments

Authors thank ALMA MATER STUDIORUM-Università di Bologna and Associazione "*Environment and Health Bazzanese Committee*" for financial support. Many thanks to Dr.s Luciana Malferrari and Fabrizio Odorici of The National Institute for Nuclear Physics (INFN, sezione di Bologna), Punto EM S.r.l. (Sanremo, Italy) for a gift of EM1® and sugar cane molasses, and Prof. Giovanna Cristina Varese of the University of Torino (Italy).

References

Ahn K., Lee K.-B., Kim Y.-J., Koo Y.-Mo., (2014), Quantitative analysis of the three main genera in effective microorganisms using qPCR, *Korean Journal of Chemical Engineering*, **31**, 849-854.

Boga C., Del Vecchio E., Forlani L., Franceschetti M., (2014), Microbes to clean indoor pollutants, *Environmental Microbiology*, **7**, 1329-1338.

Boyd S.A., King R., (1984), Note absorption of labile organic compounds by soil, *Soil Science*, **137**, 115-119.

Browne C.A., (1919), The composition and calorific value of sirups and molasses derived from sugar cane, *Journal of the American Chemical Society*, **41**, 1432–1440.

Cheng M., Zeng G., Huang D., Lai C., Xu P., Zhang C., Liu Y., Wan J., Gong X., Zhu Y., (2016), Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil, *Journal of Hazardous Materials*, **312**, 184–191.

Dawson L.F., Donahue E.H., Cartman S.T., Barton R.H., Bundy J., McNerney R., Minton N.P., Wren B.W., (2011), The analysis of para cresol production and tolerance in clostridium difficile 027 and 012 strains, *BMC Microbiology*, **11**, 1-10.

Derbalah A.S., Ismail A., Hamza A., (2013), Monitoring of organochlorine pesticide residues and bioremediation of the frequently detected compound (lindane) in soil, *Egyptian Journal of Plant Protection Research*, **1**, 133-150.

Gaggia F., Baffoni L., Di Gioia D., Accorsi M., Bosi S., Marotti I., Biavati B., Dinelli G., (2013), Inoculation with microorganisms of *Lolium perenne* L.: evaluation of plant growth parameters and endophytic colonization of roots, *New Biotechnology*, **30**, 695-704.

Hashizume T., Higa S., Sasaki Y., Yamazaki H., Iwamura H., Matsuda,H., (1966), Constituents of Cane Molasses. Part 1. Separation and Identification of the Nucleic Acid Derivatives, *Agricultural and Biological Chemistry*, **30**, 319-329.

IARC, (2013), *Polychlorinated Biphenyls and Polybrominated Biphenyls,* In: *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans,* vol. 107, IARC Press, Lyon, France.

IARC, (2015), *DDT, Lindane, and 2,4-D,* In: *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, vol. 113, IARC Press, Lyon, France.

Kruger T., Spano M., Long M., Eleuteri P., Rescia M., Hjelmborg P.S., Manicardi G.C., Bizzaro D., Giwercman A.L.U., Toft G., Bonefeld-Jorgensen E.C., (2008), Xenobiotic activity in serum and sperm chromatin integrity in European and inuit populations, *Molecular Reproduction and Development*, **75**, 669-680.

Liu Y., Zeng G., Zhong H., Wang Z., Liu Z., Cheng M., Liu G., Yang X., Liu S., (2017), Effect of rhamnolipid solubilization on hexadecane bioavailability: enhancement or reduction?, *Journal of Hazardous Materials*, **322**, 394–401.

Liu Z., Liu Y., Zeng G., Shao B., Chen M., Li Z., Jiang Y., Liu Y., Zhang Y.; Zhong H., (2018), Application of molecular docking for the degradation of organic pollutants in the environmental remediation: A review, *Chemosphere*, **203**, 139-150.

Mathus T.L., Townsend D.E., Miller K.W., (1995), Anaerobic biogenesis of phenol and p-cresol from L-tyrosine, *Fuel*, **74**, 1505-1508.

Megharaj M., Naidu R., (2017), Soil and brownfield bioremediation, *Microbial Biotechnology*, **10**, 1244–1249.

Muñiz S., Gonzalvo P., Valdehita A., Molina-Molina J.M., Navas J.M., Olea N., Fernández-Cascán J., Navarro E., (2017), Ecotoxicological assessment of soils polluted with chemical waste from lindane production: Use of bacterial communities and earthworms as bioremediation tools, *Ecotoxicology and Environmental Safety*, **145**, 539-548.

Natarajan M.R., Wu W.M., Sandford R., Jain M.K., (1999), Degradation of biphenyl by methanogenic microbial consortium, *Biotechnology Letters*, **21**, 741- 745.

Ritter L., Solomon K.R., Forget J., Stemeroff M., O'Leary, C., (1995), A review of selected persistent organic pollutants, On line at: https://www.who.int/ipcs/assessment/en/pcs_95_39_2004_05_13.pdf.

Savic R., Radovic J.R., Ondrasek G., Pantelic S., (2016), Occurrence and sources of polycyclic aromatic hydrocarbons (PAHs) in drainage channel sediments in Vojvodina (Serbia), *Environmental Engineering and Management Journal*, **15**, 287-295.

Strazzera G., (2015), *Preliminary survey on the remediation from organic pollutants by Effective Microorganisms (EM)*, MSc Thesis, Department of Agriculture, Forestry and Food and Department of Life Sciences and Systems Biology, Torino, Italy.

Web sites:

http://www.feedipedia.org/node/561

Environmental Engineering and Management Journal *October 2018, Vol.17, No. 10, 2307-2311*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

ENVIRONMENTAL TAXES TO PROMOTE THE EU CIRCULAR ECONOMY'S STRATEGY: SPAIN *vs.* ITALY

Alfonso Andretta[1], Filippo D'Addato[2], Francisco Serrano-Bernardo[3], Montserrat Zamorano[3], Alessandra Bonoli[2*]

[1]Department of Engineering University of Modena, Via Pietro Vivarelli 10, 41125 Modena, Italy
[2]Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, via Terracini 28, 40131 Bologna Italy
[3]Department of Civil Engineering, ETSI, University of Granada, Campus Fuentenueva, s/n 18071 Granada, Spain

Abstract

As it is widely known, according with European directives, the correct approach for waste management is based on a strict hierarchy of prevention, reuse and recycling, energy recovery and final disposal. In that way, all the countries have to strongly move in urban waste reduction and recycling promotion.
The principles of the Circular Economy have become part of the European and other extra Europe Countries regulations. The European pack on Circular Economy suggests ambitious objectives by 2030 in terms of urban waste reduction and recycling.
Among the different tools, taxation of waste production or dumping, or of other environmental issues can be considered as a stimulus and an interesting support to achieve these goals contributing to implement the environmental knowledge and attention.
In this issue, a research on urban waste management and taxation was carried on to analyse the situation in Europe and specially to compare two similar southern Europe Countries as Italy and Spain. Waste management environmental taxes can be adopted and applied at regional and even local level, with different approaches and a high level of regulatory dispersion. This heterogeneous situation can lead to market fragmentation and economic inefficiencies. In order to have a full picture on waste management strategies, the main questions to which we would response with this research can be related with what the fees for waste disposal or incineration at landfills were and which effects can they produce on the market.

Key words: environmental tax, incineration, landfill, recycling, waste management

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The integrated approach of the European Community with regard to waste management is based on a stringent hierarchy, based on Prevention, Reuse and recycling, Energy recovery and Final disposal, according with the Waste Framework Directive (EC Directive, 2006) and its following revised version, EU EC Directive, 2008), in which they are stressing the idea of reduction in waste production, optimizing recycling rates and aiming at the goal of zero waste. The integrated waste management systems are designed to organize waste streams, methods of collection, treatment and disposal, with the goal of achieving important goals in waste reduction and recycling rate in a general frame of sustainability by environmental benefits, economic optimization and social acceptability (Bamonte et al., 2016; Bonoli, 2014). Because of the variety of these factors, solid waste management is a complex, multidisciplinary problem involving economic and technical aspects, normative constraint about the minimum requirement for the recycling (Ghinea et al., 2014). The so called "4R framework" in waste management, reduce / reuse

* Author to whom all correspondence should be addressed: e-mail: alessandra.bonoli@unibo.it; Phone: +390512090234; Fax: +390512090308

/ recycle / recover, that fit perfectly with the EU hierarchy, represents now the main key words of the concept of Circular Economy that can be defined as: "an economic system based on business models that replace the end-of-life concept with reducing, alternatively reusing, recycling and recovering materials in production / distribution and consumer processes" (Kirchherr et al., 2017) or, considering the most prominent definition provided by Ellen MacArthur Foundation (www.ellenmacarthurfoundation.org/assets/downloads/higher-education/EMF_Priority-Research-Agenda-copy.pdf),), as an industrial system that suggests re-storing, for the elimination of waste.

Economic aspects have a great influence on choose of the end of life destination of urban waste because of the costs related. For instance, from an economic standpoint, in Spain the implementation of "Waste to Energy" (WtE) systems reduces the cost of other waste final destination (Bacenetti et al., 2016; Fernández-González et al., 2017) while in other countries recycling and composting can be better solution both by economic and environmental point.

Many tools are proposed to analyse waste management efficiency or waste production or waste recycling rate. Just to mention one of them the interested tool for waste production forecasting proposed by Ghinea et al. (2016). However, it should be interesting to find an economic and financial incentive to promote a strategic integrated waste management system that is moving towards a "zero waste" goal (Raworth, 2017).

As it is known "zero waste" represents today another concept that fit perfectly with EU directive in waste management and circular economy perspective. Many different market-based instruments, including environmental taxes and charges, can support a circular economy and can be relevant at different stages in the circular economy (EC, 2012). For example, taxes and bans disincentives are used quite frequently in relation to waste management or in some cases are applied (or could be applied) in relation to upstream extraction of resources (Withana et al., 2014). Among the different tools, taxation of waste production or dumping, or of other environmental issues can be considered as a stimulus and an interesting support to achieve these goals contributing to implement the environmental knowledge and attention (European Commission, 2016)

According with European Commission (2016) definition an Environmental tax is *a tax whose tax base is a physical unit (or a proxy of it) of something that has a proven, specific, negative impact on the environment*. Or else, those that meet all of the following principles (Speck and Paleari, 2016): the tax is explicitly linked to the government's environmental objectives and it is structured in relation to environmental objectives and its major goal is to encourage environmentally positive behaviour change. That ***could be*** the main aspect, suggesting a relationship between tax and Circular Economy objectives.

Taxes on energy, carbon and transport (vehicle), urban waste management and disposal, electrical electronic waste, air pollutants (SO_2 and NO_x emissions), charge on packaging (plastic bags and bottles), tax on environmental damage or environmental protection, etc. are largely applied in European Countries, but it's clear that the most important result is to face environmental issues and not to generate some revenues. That is an important subject in terms of circular economy approach and resources saving awareness.

Although the actual number of environmental taxes implemented in EU Member States has increased, in the last decade, the revenues generated as a proportion of Gross Domestic Product (GDP) have in general decreased (Eurostat, 2015) (EEB, 2015). In Table 1 the main environmental taxes distribution in Spain and Italy, according with European Statistics Data in Eurostat 2015, in comparison with %of GDP.

A research on urban waste management and taxation can help to understand the true mechanism in Circular Economy achievement also by tax incentive and disincentive.

Table 1. Spain and Italy environmental taxes: EU statistics (2015)

	Environmental tax revenues % per category			***% of GDP***
	Energy	***Transport***	***Pollution/ Resources***	
Italy	82	1	17	3,6
Spain	84	4	12	1,8

2. Case study

The research was carried on waste management in Europe and was started by the comparison between two similar southern Europe Countries as Italy and Spain and with some other different European Countries. In relation with the definition of a tool to promoting Circular Economy, the main questions to which we would response with this research, in order to have a full picture on waste end of life or final disposal method, and the method we followed, can be related with what the fees for landfills waste disposal or incineration were and which effects can they produce on the market. That could be just a first step to find interesting indicators for Circular Economy.

In the case of Italy and Spain, the study was based on primary data directly collected by the Italian Regional Agencies for environmental services (i.e Atersir in Emilia Romagna Region or ATOs in other Regions) and by Spanish local public environmental services (i.e Ecologia, Urbanisme i Mobilitat office in Catalonia, etc.). All data were integrated with the updated 2015 pro capite data survey performed by Eurostat (2017) (Eurostat, 2017).

Fig. 1 is showing urban waste production per capita during the period from 2000 to 2015, for Spain and Italy, while Table 2 reports a comparison between waste management at the same two different years, in which it is reported the Urban Waste management trend in incineration, recycling and composting, and a landfilling percentage.

In Table 3, urban waste management data are shown, for some European Countries, where percentage of urban waste destined to landfilling, incineration or recycling are present. All data are referred to 2015. In Table 4, they are reported the gate fee and the tax rate related with incineration and landfilling for ten European representative countries.

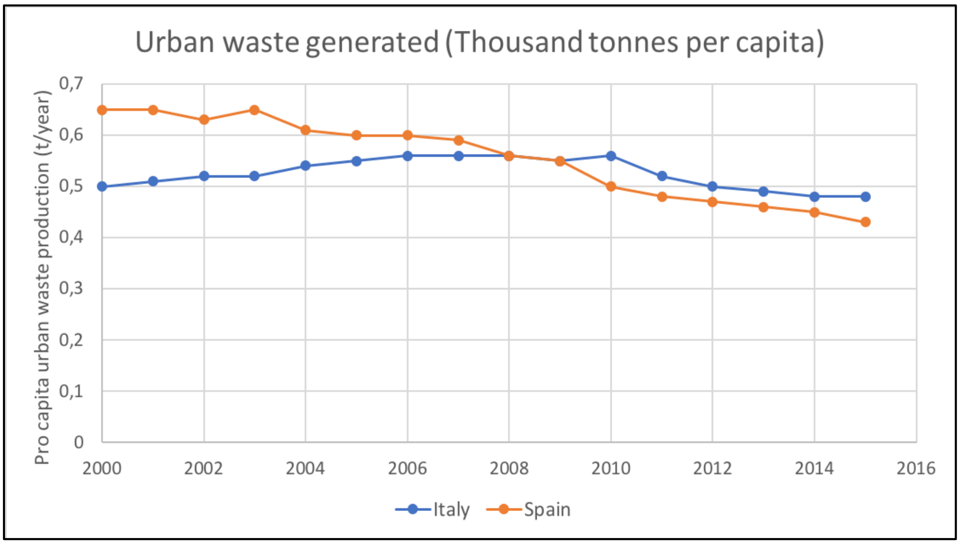


Fig. 1. Waste production in Spain and in Italy (years 2000-2015)

Table 2. Spain and Italy waste management in 2000 and 2015 (by Eurostat Data)

	Urban waste management and disposal (%)							
	Incineration		*Landfilling*		*Recycling*		*Composting or Digestion*	
year	2000	2015	2000	2015	2000	2015	2000	2015
Italy	8	21	78	29	10	29	4	21
Spain	7	12	68	55	9	17	16	16

Table 3. Some European Countries waste management data (%) in 2015

	Urban waste management and disposal (%)		
	Incineration	*Landfilling*	*Recycling and Composting*
Austria	40	1	59
Denmark	52	1	47
France	34	26	40
Germany	32	0	68
Greece	1	84	15
The Nedherlands	48	0	52
Italy	21	29	50
Portugal	20	50	30
Romania	3	82	15
Spain	12	55	33

Table 4. Some EU Countries maximum tax and gate fee (2015) (Eurostat, 2017)

	Incineration		*Landfilling*	
	Tax rate (€/t)	*Gate fee (€/t)*	*Tax rate (€/t)*	*Gate fee (€/t)*
Austria	26	150	26	219
Denmark	44	36	63	95
France	11	120	15	76
Germany	0	250	0	220
Greece	0	/	/	23,5
The Netherlands	0	120	108	30
Italy	0	125	50	90
Portugal	0	/	3,50	10,50
Romania	/	/	/	3,50
Spain	16,50	57	21,60	32,75

3. Results and discussion

In Europe, waste management environmental taxes are adopted and applied, sometimes also at regional and even local level, with a high level of regulatory dispersion and different approaches for the different Countries. This heterogeneous situation can lead to market fragmentation and economic inefficiencies. Data analysis highlights the discrepancy in urban waste production between Italy and Spain: in 2000, a better situation in Italy than in Spain, but in 2015, Italy produces much more waste than Spain. Despite that, Italian waste management policies are much more oriented on a waste valorisation technology devoted to produce secondary raw materials, delivering almost the 50% of the total waste to recycling or composting plants. In the last fifteen years, in fact, a robust reduction of the use of the landfill occurred and a growing recycling and composting percentage were increasing significantly. At the contrary, in Spain, the taxation has been applied late, and not in all the Country but in an inhomogeneous way, just only in few regions. Furthermore, the very low gate fees for landfilling are contributing to the fact that a very high amount of Spanish urban waste (more than 55%) are even today disposed in landfill. The same behavior in Romania or in Greece: in correspondence with a very low landfill gate fee, more than 80% of the total amount of urban waste is landfilled. They were not considered other aspects as economic development or economic crisis in Italy and in Spain because of the similar condition of the two analyzed countries.

In order to understand the role of taxation of urban waste disposals, it's necessary to make a distinction between taxes, that is a levy charged by a public authority for the disposal of waste, and gate fee, that is a charge set by the operators for the service's provision. The sum of tax and gate fee represents the total charge for the waste disposal.

In Italy there are no taxes for incineration, but the gate fee is really high, while in Spain, both taxes and rate are really cheap and they are present only in a couple of regions, the Autonomous Communities of Catalonia and Castile and León. The total charges applied to incineration result higher than in the case of landfilling both for Spain and Italy.

Considering the different analysed Countries, there are really different values in "Tax rates" and "Gate Fee". That could be in relation with each Country technological development but mainly because of differences in local institutional requirements. In Germany, for instance, there are no tax rates but only the gate fee. The management of the charge on the landfilling waste is up to the plant.

Landfilling high taxations in Italy, Austria, Germany and The Netherlands seems to encourage waste recycling and composting. These Countries show the highest gate fee and/or taxation and in general their landfills' costs are over 130 €/t. At the same time, in these Countries, the percentage (over 50%), according with EU objective for 2020, in recycling or composting has been already reached and for some of them, as Austria and Germany, the "zero waste" goal has been already reached (Eurostat, 2017)

4. Conclusions

The environmental taxation could be considered an important instrument to implement waste management and to actually implement circular economy approach. By the comparison between the two similar southern Europe Countries as Italy and Spain and with some other European countries, it can be said that a better behaviour, improving recycling and composting, can be more advantageous by economic point of view just if taxation become too expensive both for landfill and incineration. At the same time, the Countries having the highest landfilling costs have already reached the EU waste percentage recycling goals and they are fastly achieving the "zero waste" goal.

It would be important to harmonize regional taxes in waste management, inside the same country and for all European Countries, and could be important to introduce new environmental taxes on resource use, waste disposal and, in general, environmental damage and pollution. A similar tax reform will be a significant milestone on the way to promote a correct waste management, to improve recycling rates, to reduce landfilling and to have the opportunity to move effectively towards Circular Economy European objectives.

References

Bamonti S., Spinelli R., Bonoli A., (2016), Environmental footprint in the production of recycled wool, *Environmental Engineering and Management Journal*, **15**, 1923-1931.

Bacenetti J., Baboun S.H., Demery F., Aburdeineh I., Fiala M., (2016), Environmental impact assessment of electricity generation from biogas in Palestine, *Environmental Engineering and Management Journal*, **15**, 1915-1922.

Bonoli A., Zanni S., (2014), Air pollution treatment in modern segregated waste treatment facilities, Recent Advances in Urban Planning, Sustainable Development and Green Energy, *WSEAS Transactions on Environment and Development*, **10**, 529-541.

EC Directive, (2006), Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste, On line at: https://publications.europa.eu/en/publication-detail/-/publication/0f484039-4061-4922-9739-76d173d0d919/language-en.

EC Directive, (2008), Directive 2008/98/EC on waste (Waste Framework Directive), On line at: http://ec.europa.eu/environment/waste/framework/.

EC, (2012), DG ENV-Unit G.4 Sustainable Production and Consumption, Use of economic instruments and waste management performances", Final Report, On line at: http://ec.europa.eu/environment/waste/pdf/final_report_10042012.pdf.

EEB, (2015), Country-Specific Recommendations in Support of the European Semester Process), On line at: http://www.foes.de/pdf/2015-02-25_CSR%20Recommendations_FINAL.pdf

European Commission, (2016), Public country-by-country reporting-The EU requires companies in the extractive and logging industries to report on their payments to governments, and is working to promote tax transparency among multinationals, On line at: https://ec.europa.eu/info/business-economy-euro/company-reporting-and-auditing/company-reporting/public-country-country-reporting_en.

Eurostat, (2015), Eurostatistics - Data for short-term economic analysis - Issue number 2/2015, On line at: http://ec.europa.eu/eurostat/product?code=KS-BJ-15-002&language=en.

Eurostat, (2017), Environmental tax revenues, data, On line at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Environmental_tax_statistics

Fernández-González J.M., Grindlay A.L., Serrano-Bernardo F., Rodríguez-Rojas M.I., Zamorano M., (2017), Economic and environmental review of Waste-to-Energy systems for municipal solid waste management in medium and small municipalities, *J.M. Waste Management*, **67**, 360-374.

Ghinea C., Petraru M., Simion I.M., Sobariu D., Bressers H.T.A., Gavrilescu M., (2014), Life cycle assessment of waste management and recycled paper systems, *Environmental Engineering and Management Journal*, **13**, 2073-2085.

Ghinea C., Dragoi E.N., Comaniţă E.D., Curteanu S., Gavrilescu M., (2016), Forecasting municipal solid waste generation using prognostic tools and regression analysis, *Journal of Environmental Management*, **182**, 80-93.

Kirchherr J., Reike D, Hekkert M., (2017), Conceptualizing the circular economy: An analysis of 114 definitions, *Resources, Conservation & Recycling*, **127**, 221-232.

Raworth K., (2017), *The Doughnut Economics: Seven Ways to Think Like a 21st-Century Economist*, Cornerstone Press, Hardback, Hive.co.UK

Speck S., Paleari S., (2016), Environmental taxation and EU environmental policies, EEA Report, Report No 17/2016, Luxembourg: Publications Office of the European Union, On line at: https://www.eea.europa.eu/publications/environmental-taxation-and-eu-environmental-policies.

Withana S., ten Brink P., Illes A., Nanni S., Watkins E., (2014), Environmental tax reform in Europe: Opportunities for the future, A report by the Institute for European Environmental Policy (IEEP) for the Netherlands Ministry of Infrastructure and the Environment, Final Report, Brussels, 2014, On line at: https://ieep.eu/uploads/articles/attachments/84aa183b-9f81-4b00-a4d6-e93a14464252/ETR_in_Europe_-_Final_report_of_IEEP_study_-_30_May_2014.pdf?v=63664509853.

Web sites:

www.ellenmacarthurfoundation.org/assets/downloads/higher-education/EMF_Priority-Research-Agenda-copy.pdf)

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2313-2327
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

CODEVELOP RESEARCH AND INNOVATION FOR BLUE JOBS AND GROWTH IN THE MEDITERRANEAN - THE BLUEMED INITIATIVE

Margherita Cappelletto[1]*, Fabio Fava[2], Luigi Mazari Villanova[1], Fabio Trincardi[1], Andrea Barbanti[3], Angelo Bonanno[4], Bruno Buongiorno Nardelli[4], Elena Ciappi[5], Daniela Palamà[3], Maurizio Ribera d'Alcalà[6], Alessandro Sarretta[3], Mario Sprovieri[4]

[1]*Department of Earth System Science and Environmental Technologies of the National Research Council of Italy, Piazzale Aldo Moro 7, 00185, Roma, Italy*
[2]*Department of Civil, Chemical, Environmental and Materials Engineering, Alma Mater Studiorum, Università di Bologna, Via U. Terracini, 28, I-40131, Bologna, Italy*
[3]*Institute of Marine Science, National Research Council of Italy, Arsenale, Tesa 104 - Castello 2737/F, 30122, Venice, Italy*
[4]*Institute for the study of Anthropic impacts and Sustainability in the marine environment, National Research Council of Italy, Via del Mare, 3 - Capo Granitola 91021, Campobello di Mazara (Trapani), Italy*
[5]*Marine Technology Research Institute, National Research Council of Italy, Via di Vallerano 139, 00128, Rome, Italy*
[6]*Stazione Zoologica Anthon Dorn, Villa Comunale, 80121, Naples, Italy*

Abstract

In the framework of the European Commission Blue Growth Strategy, a joint process among European countries has been put in place since 2014 to promote and implement research and innovation actions to increase the number of jobs in the marine and maritime sectors, commonly named 'blue', and pursue a sustainable growth in the Mediterranean area. The process has then been extended to the non-European (non-EU) Mediterranean countries. The natural and cultural uniqueness of the Mediterranean Sea is recognized worldwide, and the opportunities for social and economic growth in the area are increasing. At the same time, natural and anthropogenic pressures as well as the need for a governance of common space and resources add complexity to the management of such area, whose countries belonging to three different continents have socio-economic differences and express a variety of cultures and political regimes. This paper provides insights on the steps that brought to the development of the BLUEMED Initiative and the progresses made from its launch and the publication of the BLUEMED Strategic Research and Innovation Agenda (SRIA) by European Mediterranean countries to its extension in non-EU ones. It highlights key activities carried out at a policy level and focuses on the tools used for engaging all relevant stakeholders, namely scientists, policy makers, private companies, and civil society, at national and international levels. Moreover, it reports recent activities towards a structured involvement of non-EU countries. Preliminary outcomes of the process indicate that the scientific approach is crucial to manage complexity, not only as a vehicle of diplomacy but also to support knowledge-based decisions.

Key words: blue economy, job creation, Mediterranean Basin, strategic research and innovation agenda, sustainable growth

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The Mediterranean nations strongly depend on marine activities. In a study commissioned by the EC (Eunetmar, 2014), the importance of the maritime activities for the economy of a country is measured in terms of gross value added (GVA) generated. In 2010, Italian GVA in coastal areas was 727 billion €, the

* Author to whom all correspondence should be addressed: e-mail: margherita.cappelletto@cnr.it; Phone: +39 0649933490; Fax: +39 0649933887

53% of national GVA, with maritime economic activities impacting for 23.6 billion €. Opportunities for economic and societal development are represented by established coastal, marine and maritime economy sectors such as according to Johnson et al. (2018) fisheries, offshore oil and gas, shipping and shipbuilding, and tourism, including recreational activities. Also 'blue growth' sectors, i.e. new or more recent maritime activities like aquaculture, marine biotechnology, seabed mining, wave- and current- derived energy, and offshore wind energy offer clear opportunities in the framework of the new maritime economy (Johnson et al., 2018). Consistently, the European Blue Growth Strategy, as defined in the EC Communications (2012) and (2014) identifies the development of sustainable growth and jobs' creation in the marine and maritime economy as important drivers for Europe's welfare and prosperity. All these interlinked activities rely on the same common resource, the sea, potentially threatening the ecosystems' health as widely assessed by Micheli et al. (2013), outlining that in the Mediterranean a vast majority (60-99%) of EU member states' waters within 12 nautical miles off the coastline are subject to medium-high to very high cumulative impact of human activities. Healthy ecosystems actually represent the main prerequisite for maintaining the benefits derived from the environment, ensuring for instance the availability of biological resources in the long term, and the conservation of habitats.

Around 450 ports and terminals show to what extent people and goods circulate in the Mediterranean Basin. In 2015, 20% of the total world's maritime transport and 30% of the oil trades moved through the Mediterranean Basin, two figures that are expected to grow in the next years (OECD, 2016), posing environmental, safety, and security issues.

The European maritime industry has an annual turnover of about 31 billion € and currently counts 300 shipyards and more than 22,000 maritime equipment manufacturers and suppliers (SeaEurope, 2017).

The major environmental hazards related to maritime transport and support infrastructures are linked to the chemical emissions of CO_2, NO_x and SO_x in the air (DNV GL, 2014) and of lubricating oils from the mechanical parts of the ships polluting marine water. Concerning the physical emissions, it is well known that in the last decades the background noise of seas and oceans has increased considerably and that the main cause is the underwater-radiated noise from ships (ITTC, 2014; ITTC, 2017). Moreover, the increase in maritime traffic, if not adequately managed with a high level of safety, can lead to an increase of accidents and therefore, not only to extremely serious consequences for people, but also to ecological disasters (oil spills and leakages from wrecks at the sea floor). Finally, ballast waters of ships passing the Mediterranean have introduced a considerable number of alien species in the basin, beside those entered since the cut of the Suez Canal. A comprehensive discussion about the environmental intensity of maritime transport can be found in Niavis et al. (2017).

The Mediterranean Basin is also characterized by a tourism-centred economy, which strongly contributes to the percentage of employed people, 13% only in Italy, according to the report by Becheri et al., (2016). Due to tourism and recreational travelling, the 150 million coastal population of the Mediterranean area almost doubles in the tourist season. Rapid growth of inhabitants in peak periods add anthropogenic pressures to the coasts resulting in negative impacts on the environment due to increased fresh water consumption, waste production, and need for infrastructural access and accommodation (ECORYS, 2013). This requires solutions to, at least partly, de-seasonalize and differentiate the offer. Coastal tourism is a clear example of impacts caused by inland human activities on the marine environment. According to the briefing from the EPA (2017), waste generation in the southern Mediterranean region has grown approximately 15% over the last decade, demanding effective waste management measures.

Fisheries and aquaculture products guarantee one of the most important sources of proteins, increasingly demanded worldwide to meet the need of feeding a population of more than 8.5 billion people by 2030, (EC, 2016; EC Conference report, 2017), as key components of the Mediterranean healthy diet. On average, a European citizen consumes 24.9 kg of fish or seafood per year. In the last two decades, a clear negative trend in total fish landings was observed in the whole Mediterranean Sea (GFCM Resolution, 2016), likely due to catch levels not balanced by the renewal capability of fished stocks. Therefore, Mediterranean fisheries are facing serious challenges, with roughly 85% of the scientifically assessed stocks considered to be fished outside biologically sustainable limits (GFCM Resolution, 2016).

Great expectations derive worldwide from recent advances in marine and maritime biotechnologies (so-called 'blue'), a promising sector where major developments are associated with research in the pharmaceutical and cosmetic industries, and with the utilization of macro and micro algae in the biofuel production. The availability of marine and maritime observations and big data in combination with advanced Information and Communication Technology tools is also opening chances for new business. This trend can be enhanced pursuing a policy of open data, data preservation and reuse in informed decision making on any issue potentially impacting the marine environment.

Blue careers are increasingly offering new employment opportunities in various sectors, e.g. the marine renewable energies with a potential of 680,000 direct jobs to be created internationally by 2050 (Johnson et al., 2018), gradually overcoming the skill gaps to match the requirements of present and future jobs at (or close to the) sea. In the promising areas identified by the European Union: aquaculture, renewable energies, seabed mining, and blue biotechnology, the work is mature enough to raise the investments and the level of technological readiness in order to favour a sustained growth. On the other hand, accurately assessing the value of natural resources is a long-term process, with controversial measurability limits and high levels of uncertainty (MEA Assessment, 2005). These elements pose several regulatory concerns, for example on the sustainability of seabed mining, which impinges on essentially non-renewable materials. Therefore, knowledge-based approaches to policy-making are recognized as a fundamental component for pursuing the sustainable blue growth. Given the diversity of social, economic, and political environments and beside the general unstable political situation of the Mediterranean area, formulating adequate regulatory frameworks for sea-related activities is often complicated and requires a balance between the policies and laws intervening on the rights of exploitation and the use of resources and their conservation at different spatial scales, from local coastlines of few tenth kilometres to the whole basin. This applies for example in the case of offshore platforms in Europe, mostly used for natural gas extraction in shallow water areas, which are reaching the end of their production lifetime and are entering their decommissioning phase by 2030 and beyond. These platforms, located in waters and/or continental shelves under the jurisdiction of coastal states, could be either totally or partially dismantled, re-located, re-adapted, and re-used for different purposes, with highly diverse and potentially relevant economic and environmental impacts (Caliri et al., 2017). A deeper understanding and new knowledge needs to be achieved in order to find proper solutions or to design a new regulatory framework, where lacking.

More in general, it is recognized that the major threats to the realization of the European Blue Growth Strategy are due to the interdisciplinary knowledge gaps and fragmentation, the conflicting interests among sectors and nations, the lack of information on potential synergies and insufficient exchange of information among scientists, industries, and policy makers (Andrusaitis et al., 2016). Facilitating the cooperation between maritime business and public authorities across borders and sectors is thus fundamental to create new economic value, disclosing emerging features and ensuring the sustainability of the marine environment exploitation in the long-term.

As explained in the EC Report (2017), in order to address marine and maritime challenges, find joint solutions, and maximise common assets for the entire area, the European Commission has identified sea-basin strategies as the proper policy framework for cooperation between the European Union, the Member States and their Regions, including Third countries that are not Member States of the European Union and share the same basin. The main EU research and innovation initiatives of reference presently active in different seas are the Baltic Organisations Network for Funding Science European Economic Interest Grouping (BONUS EEIG), and the Atlantic Ocean Research Alliance, targeting the Blue Growth at basin scale through different instruments and implementation mechanisms.

Recently, the Burgas Vision Paper - A Blue Growth Initiative for Research and Innovation in the Black Sea has been launched in the framework of the European Maritime Day 2018, an event organized yearly by the European Commission, paving the way for the development of a Black Sea Initiative on Blue Growth (https://ec.europa.eu/maritimeaffairs/maritimeday/sites/mare-emd/files/burgas-vision-paper_en.pdf).

The *BLUEMED Initiative* was born as a direct emanation of the European Blue Growth Strategy and adopted to promote research and innovation in the Mediterranean Basin. This paper presents extensively the process implemented since the origin in 2014 to build the BLUEMED Initiative, reporting in section 2 main activities and tools that have been developed. These led, from one side, to the political endorsement of the Initiative and, from the other side, to structure the engagement of relevant stakeholders, including those from non-EU countries, in order to raise awareness and gather additional contributes to the process. Preliminary results are then analysed in section 3, trying to answer to the following overarching question: could the integrated approaches of the BLUEMED Initiative be a means to reduce the fragmentation and better govern the complexity of the Mediterranean system?

2. Developing the *BLUEMED Initiative*: the process

The *BLUEMED Initiative* seeks to foster integration of knowledge and efforts of EU and non-EU Mediterranean countries to create new blue jobs and a sustainable growth in the area. Pulling together top-down and bottom-up approaches, a major engaging process is driving stakeholders in the Basin to share a common vision and commit for joint efforts. This requires an articulated structure for functioning (Fig.1) as well as long and continuous work, which is still ongoing but has already led to some significant results.

2.1. The policy initiative

The *BLUEMED initiative* seeks to promote the social well-being and prosperity of citizens now and for future generations, and to boost economic growth and jobs in marine and maritime sectors. The possible success of the *BLUEMED Initiative* relies on a strong coordination between research, industry and policy at the national, regional, European, and international levels.

Alignment is a long-term process based on mutual trust, effective collaboration as well as a sense of altruism (Amanatidou and Cox, 2015), the value of which affects in the long-term a common good. As addressed in the BLUEMED Vision Document (http://www.bluemed-initiative.eu/wp-content/uploads/2017/10/BLUEMED_Vision.pdf), it is the key to plan and work with both public and private players as well as with decision makers.

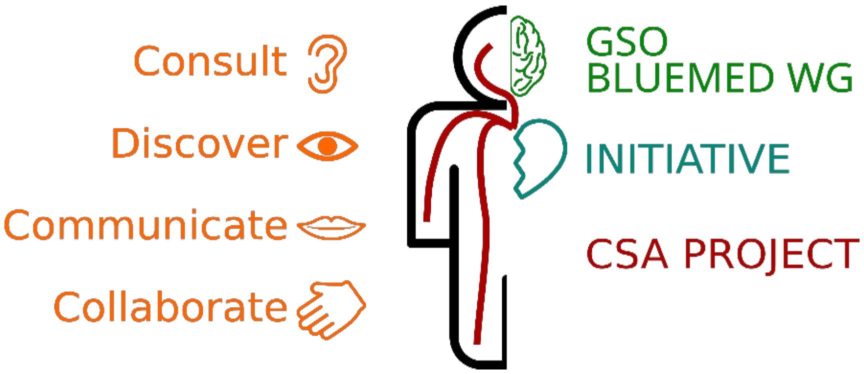


Fig. 1. General articulation and aspects of the BLUEMED Initiative (sub-section 2.1), headed by the Group of Senior Officials BLUEMED Working Group (GSO BLUEMED WG), and of the project that supports its functioning, the Coordination and Support Action (CSA, sub-section 2.2). Key targets include consultation, discovery, communication, and collaboration

The objective is to define relevant research and innovation actions that can concretely tackle social and economic challenges and ultimately boost the creation of new jobs. Raising awareness among citizens through public engagement on the importance of a sustainable prosperous Mediterranean Sea for all surrounding countries is equally important. Education and training are considered fundamental activities to improve and develop new skills to enable sea-based activities oriented towards blue growth careers, including life-long learning and vocational training.

The onset of the *BLUEMED Initiative* dates back to 2014 when, building on the outputs of the EurOCEAN Declaration, (2014), Cyprus, Croatia, France, Greece, Italy, Malta, Portugal, Slovenia, and Spain, with the support of the European Commission, decided to jointly develop a strategic framework for promoting the Blue Growth Strategy in the Mediterranean area through research and innovation. Following the official presentation at the European Competitiveness Council on December 2014 under the Italian Presidency of the Council of the European Union, these countries agreed to work towards the advancement of a shared vision for a healthier, productive, resilient, as well as a better-known and valued Mediterranean Sea.

The top-down process occurred in successive steps, including numerous meetings and the delivery of official declarations. Technically, the starting point has been the mapping and analysis, performed by the European countries involved since the beginning, of more than 900 existing and ongoing national and European projects as well as those implemented by the Regions (e.g. funded through European structural and investment funds). At the same time, a consultation with policy makers and with major public and private stakeholders, including consortia of public and private entities promoting the development of the maritime and coastal economy, the maritime clusters, was carried out to pinpoint needs and gaps. Knowledge, technology, and innovation gaps were identified together with the boundary conditions that enable these gaps to be addressed (e.g. human resources, programmes and tools, and infrastructure and observation capacity). The following high level objectives and benefits put forward by the European project SEAS-ERANET (Nittis, 2012), a pioneering one in addressing the need for a common Mediterranean research agenda, fed the process: improve our understanding of Mediterranean Sea functioning and evolution, support sustainable economic growth in the region, support knowledge-based policy making and management, develop new capacities and promote convergence between Mediterranean countries. Inputs gathered from constant dialogue with the Joint Programming Initiative "Healthy and productive seas and oceans" (JPI-Oceans) were taken as well into due account. Relevant European technology platforms and private associations, e.g. the European Aquaculture Technology Platform (EATiP) (http://eatip.eu), the former Waterborne Technology Platform now Sea Europe (www.seaeurope.eu), and the French technology cluster Pôle Mer Méditerranée (PMM) (https://www.polemermediterranee.com) provided other valuable contributions.

The BLUEMED Vision Document (http://www.bluemed-initiative.eu/wp-content/uploads/2017/10/BLUEMED_Vision.pdf) was finally drafted and became the basis for developing a related Strategic Research and Innovation Agenda, which was then shared with major European marine and maritime public and private stakeholders as well as policy makers for further feedback.

The nine European countries involved in the Initiative since the beginning decided to advance the strategic marine and maritime research and innovation agenda for the blue growth, aiming in particular at:

- promoting cooperation in research and innovation among all Mediterranean countries;
- engaging with both public and private stakeholders, including small and medium enterprises;
- supporting knowledge-based policy making;
- prioritising the implementation of cross-cutting actions with high societal impact;
- ensuring the effective and efficient use of resources and infrastructures;

- developing innovative sea-related competences.

The process, steered by a group of countries' representatives and experts named Strategic Board, gradually led to a cohesion and alignment at the European level, culminating in October 2015 with the endorsement of the *Venice Declaration* (RG, 2015) undersigned by the representatives of the nine European promoters and Romania, which has a long tradition of cross-basin collaboration on marine and maritime research and innovation with the Mediterranean countries. This step marked the official launch of the BLUEMED Strategic Research and Innovation Agenda (BLUEMED, 2015).

The BLUEMED SRIA, whose cover is reported in Fig. 2, officially became the document of reference of the Initiative and the "mantra" of the BLUEMED community. It builds on three major pillars (Table 1) and addresses twelve key challenges on knowledge, economy, and technology to be tackled, reaching the targeted goals through a set of actions, which are to be continuously updated, based on the feedbacks and interactions among all involved stakeholders.

By using a building block approach, other countries were progressively engaged in the process. Eventually, on 4th May 2017 the *Valletta Declaration* (Malta Presidency of the Council of the European Union, 2017) was signed and adopted by all Member States of the European Union and the Union for the Mediterranean (UfM); with this signature the process formally became a Mediterranean Initiative. Table 2 summarizes all the key steps from 2014 to the beginning of 2018. At governance level, the Group of Senior Officials BLUEMED Working Group (GSO BLUEMED-WG) replaced the original steering group (named Strategic Board), chaired by Italy. The GSO was set-up in the framework of the Euro-Mediterranean Research and Innovation Group of Senior Officials. The governance structure comprised of the Directorate General Research and Innovation of the European Commission/ UfM EU Co-Presidency, UfM non-EU Co-Presidency (Jordan at present), and the UfM Secretariat on a standing basis, plus one representative of the GSO BLUEMED WG member countries on a twelve-months rotation basis. The Group has been initially focused at promoting the extension of the BLUEMED SRIA and related activities to the non-EU countries that are member states of the UfM. It also continues the mandate of the Strategic Board in facilitating the adoption of the BLUEMED SRIA as a reference document for the implementation of joint actions. The same participatory process is now extended to non-EU countries that appointed official delegates to the GSO BLUEMED WG. The GSO endorses the updated version of the SRIA including the contribution from non-EU countries.

Fig. 2. Cover of the BLUEMED Strategic Research and Innovation Agenda (BLUEMED SRIA)

Table 1. The three pillars of key challenges on knowledge (left), economy (middle), and technology (right) of the BLUEMED Strategic Research and Innovation Agenda (as from the version dated April 2017)

Key enabling knowledge for the Mediterranean	***Key sectorial enablers in the Mediterranean***	***Enabling technology and capacity creation for the Mediterranean***
A. Mediterranean Sea ecosystems: services, resources, vulnerability, and resilience to natural and anthropogenic pressures B. Mediterranean Sea dynamics: developing services in the field of sustainable adaptation to climate change and plans for mitigation C. Hazards and protection of coastal areas in the Mediterranean	A. Innovative business based on marine bio-resources in the Mediterranean B. Ecosystem-based management of Mediterranean aquaculture and fisheries C. Sustainable tourism in the Mediterranean D. Maritime clusters in the Mediterranean E. Maritime Spatial Planning & Integrated Coastal Zone Management in the Mediterranean	A. Smart, greener maritime transport and facilities in the Mediterranean B. Observing systems and operational oceanography capacities in the Mediterranean C. Multi-purpose off-shore platforms in the Mediterranean D. Marine and coastal cultural heritage in the Mediterranean: discovering, protecting and valuing

Table 2. Key steps of the *BLUEMED Initiative* process

Time frame	***Activity***	***Key steps***
October-December 2014	Defining needs and gaps	Set-up of the working roadmap by nine European countries, eight of which border the Mediterranean Sea plus Portugal, and the European Commission. Mapping of relevant research and innovation projects and initiatives carried out at national level. Merging of information and identification of gaps and needs, opportunities, and boundary conditions. Sharing of findings with relevant scientific communities, public authorities, and industrial associations at national and European levels.
December 2014	Vision document	The BLUEMED Vision Document is endorsed by the Italian Presidency of the European Council and presented at the Competitiveness Council on 4-5 December 2014.
January-October 2015	*Venice Declaration* and Strategic Research and Innovation Agenda	Identification of key challenges, goals, and actions according to the following drivers: boosting blue jobs and growth, knowledge transfer, and SMEs participation. Preliminary draft of the BLUEMED SRIA shared with national, European, and international public and private stakeholders as well as with the Regions that represent the concrete needs of local communities. Signature of the *Venice Declaration* on 16 October 2015 (RG, 2015). Launch of the BLUEMED SRIA.
November 2015	Declaration "Towards a roadmap for Blue Investment and Jobs in the Mediterranean"	Member States of the Union for Mediterranean adopt the *UfM Declaration*, (MHD, 2015), during the Ministerial Meeting on the Blue Economy held in Brussels on 15 November 2015. The Declaration acknowledges among other things the work done by partners to develop the *BLUEMED Initiative* and to identify common key challenges for marine research and innovation in the region. It welcomes the proposal to include the Member States of the UfM in the implementation of the *BLUEMED Initiative* on a voluntary basis and to support the networking amongst maritime clusters in the Mediterranean. It calls Ministers of UfM Member States to consider the possible inclusion of UfM Southern and Eastern partners in the implementation of the *BLUEMED Initiative*.
April 2017	BLUEMED high-level conference and first update of the SRIA	With the BLUEMED conference "A basin of Research and Innovation for sustainable growth" organized in Sliema, Malta, on 18-19 April 2017 under the auspices of the Maltese Presidency of the Council of the European Union, the *BLUEMED Initiative* officially opens to non-European countries stimulating the connection with Mediterranean key players and organisations. The first update of the SRIA is released (BLUEMED, 2017).
May 2017	*BLUEMED Initiative* endorsed by EU and UfM Member States	Signature of the *Valletta Declaration* (Malta Presidency of the European Council, 2017) welcoming the *BLUEMED Initiative* as a means to promote a healthy, productive, and resilient Mediterranean Sea and stressing the importance of structuring Euro-Mediterranean cooperation in marine and maritime sectors to encompass a broad range of objectives comprising the creation of new, blue jobs and social well-being.
February 2018	Group of Senior Officials BLUEMED Working Group	The governing body of the *BLUEMED Initiative* is set up, joined by official delegates appointed by EU and non-EU countries. It is agreed to carry out consultations in non-EU countries towards the publication of a co-owned update of the BLUEMED SRIA.

Finally, the Group promotes cooperation and alignment with the two key sub-regional Mediterranean initiatives in place, the EU macro-regional strategy EUSAIR: "European Strategy for the Adriatic Ionian Region" (European Council, 2014, https://www.adriatic-ionian.eu/) and the WESTMED: "Western Mediterranean Initiative" (EC Communication, 2017) implemented by the UfM (http://www.westmed-initiative.eu/).

The BLUEMED governing body liaises with relevant public and private organisations and with management authorities of relevant programmes for research and innovation, and disseminates the BLUEMED achievements in high-level policy events and towards major framework programmes. To cooperate for the joint adaptive implementation of agendas is crucial (Gauci Borda and Bujeia, 2017) and requires interacting with key organisations of the area. These include the Mediterranean Science Commission (CIESM), the International Centre for Advanced Mediterranean Agronomic Studies (CIHEAM), the Inter-Mediterranean Commission of the Conference of Peripheral Maritime Regions (CPMR-IMC), the General Fisheries Commission for the Mediterranean (GFCM), the Mediterranean Action Plan of the United Nation Environment Programme (UNEP-MAP), and the managing authority of the Interreg-MED Programme. Many of them have been engaged in the preparatory phase and in the key steps of the process (see Table 2). Nevertheless, other relevant organizations will be engaged and consulted on *ad hoc* basis.

2.2. Connecting transnational communities for a shared R&I agenda

Research and innovation strategies shall be designed to drive effectively sustainable and socially inclusive economic growth. Efficient and fair transfer of information among all stakeholders and across different sectors must accompany the generation of new knowledge.

As pointed out by Amanatidou and Cox (2015), developing a research and innovation agenda is not a trivial task. This needs to pursue an inclusive and transparent process as a basic feature for producing consensus. In line with this principle, the *BLUEMED Coordination and Support Action (CSA),* a 3 million € EC funded project coordinated by the National Research Council of Italy leading a partnership of 9 EU countries started in 2016 to build the "legs" of the political Initiative, setting-up a flexible mechanism to favour a virtuous relationship among the research, industry, policy, and society. A constant dialogue with national stakeholders is essential for implementing the objectives of the *BLUEMED Initiative* and in particular for monitoring and updating the SRIA.

Four interconnected thematic working platforms have been created as a tool to ensure constant and broad consultation at the Mediterranean level. Joined at first by representatives of the EU partner countries and then by non-EU experts, the platforms on knowledge, economy, technology, and policy are conceived as *fora* where representatives of nations, the "national pivots," interact and convey the general messages from their own countries' communities, addressing needs and priorities. The BLUEMED platforms allow a cross-national communication flow and interplay among the research organizations, private companies, public administrations, and civil society. In the long term, by a gradual broadening of the participation of experts from the non-EU Mediterranean countries, they are expected to act as a transnational operative network that will continuously monitor, prioritize, update, and make tangible the SRIA in the whole Mediterranean.

The BLUEMED national pivots animate the process. Appointed at the highest possible level, they represent the CSA partner countries in the four platforms. They can be members of national public administrations, research institutions or other stakeholders' bodies, and are competent on their subject, experienced in participating to networks, and/or international organizations and/or projects, and belonging to public and/or private entities. Acting as a main interface between the Consortium and the national communities, the BLUEMED pivots contribute to increasingly mobilize other relevant national stakeholders by collecting and transmitting their messages and bringing the feedbacks to their own countries. The platforms' scheme (Fig. 3) mirrors the three pillars of the SRIA with the addition of a transversal platform dedicated to policy, which has been conceived to take into account the transversal (across pillars) policy dimension of the SRIA actions, and to support the operative engagement of relevant players and organisations acting on the area.

This is also useful to establish a connection with the dense and evolving environment of the legislation and programmes dealing with the Sea. Indications of ongoing and emerging policy measures and regulatory frameworks, such as EU and international Regulations, Directives, Protocols, Conventions, Agreements, and legal constraints to businesses and market operators, have to be constantly updated. Besides the Blue Growth Strategy, the main frameworks of reference for the *BLUEMED Initiative* are the Barcelona Convention (BC, 2004); the Marine Strategy Framework Directive (EC Directive, 2008); the Integrated Maritime Policy (CPCEEU, 2012); the Common Fisheries Policy (EU Regulation, 2013) and the Maritime Spatial Planning Directive (EC Directive, 2014). Any initiative in place at macro-regional and sea-basin scale has indeed to take into due account programmes, strategies, binding Regulations, and policy documents, also in order to support the implementation of relevant regional seas, European, national, and international policies.

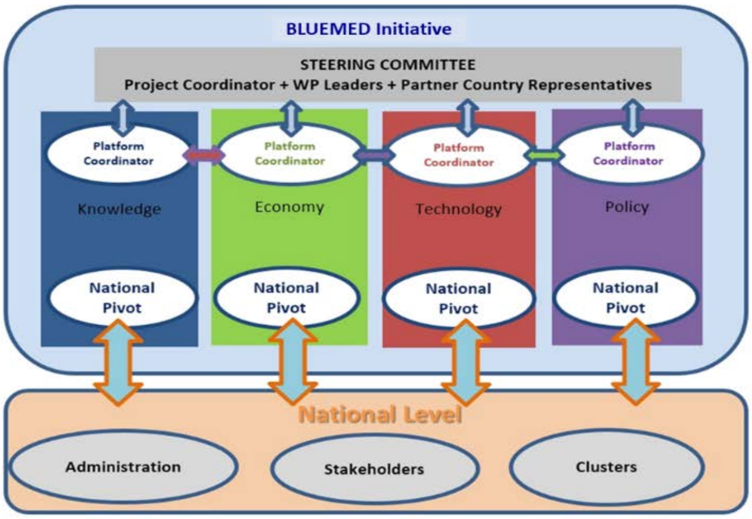


Fig. 3. The BLUEMED platforms, their connections, and their relations to the national communities

For instance, the Maritime Spatial Planning is one of the key sectorial enablers of the BLUEMED SRIA and represents a practice to inject science-based information into decision-making on the uses of marine environments, trying to reconcile existing conflicting interests and avoid new conflicts that may arise among stakeholders that use the same marine space, and between different administrations.

Considering the international dimension of the Initiative, it is important to recall and enhance links with the European International Ocean Governance policy (EC Communication, 2016), addressing some actions in line with the BLUEMED vision at a global level. Equally important is the United Nation Sustainable Development Agenda (UN Resolution, 2015), addressing 17 Sustainable Development Goals (SDGs) to be reached by 2030. The SDG number 11 on sustainable cities and communities, number 12 on responsible consumption and production, 13 on Climate Action, 14 on life below water, and 16 on peace justice and strong institutions are all of direct relevance for the *BLUEMED Initiative*.

When recognizing the differences among the Mediterranean sub-basins and among the stakeholders, alignment is the key to overcome the complexity. The first activities undertaken by the BLUEMED platforms have been devoted to the consolidation of national communities through bottom-up consultations for updating the SRIA.

2.2.1 Consultation tool, the BLUEMED Survey "Share your view on the Research and Innovation agenda for the Med!"

The *BLUEMED CSA* launched a dedicated on-line survey with the purpose of gathering inputs for updating the BLUEMED SRIA. It consisted of a first section with general information on the persons answering, including their affiliation, the sector of expertise, and the level of knowledge of the BLUEMED SRIA. Then, for each key challenge of the SRIA, a set of four open questions asked: (i) if the user felt the need to modify the challenge itself and/or its related goals; (ii) to propose possible new challenges/goals; (iii) to describe possible barriers and bottlenecks for achieving them; (iv) to motivate the reason why investigating a specific theme would be of particular relevance for the Mediterranean Basin. Finally, at a deeper level of detail, the user could also examine the actions related to each goal, proposing possible additional inputs and/or revisions. For each challenge, each responder also had the chance to suggest related policy actions and/or recommendations.

The survey was disseminated in the nine European countries that are partners of the *BLUEMED CSA* project and via the website of the *BLUEMED Initiative*.

The online survey overall counts 161 answers. Graphics of Figs. 4a-c provide a visual description of some features of the survey audience: 76% of responders where already familiar with the *BLUEMED Initiative*; 34% of them were female, and the prevalent age of responders was between 41 and 60 years old.

Given the vast variety of aspects involved in the *BLUEMED Initiative*, and considered that survey as a tool has become increasingly over-utilised, we designed the survey so that users could answer all or parts of it, providing inputs only where they deemed necessary, according to their interest and/or competence, thus minimizing the effort required.

In order to measure how much of the survey was filled by each user and understand how the users perceived the survey, we gave each pillar an overall score of 33% if the related questions were completed entirely. For each pillar, we allocated a half score to the answers to the four initial open questions, and the other half to the detailed inputs possibly provided for each goal (at the level of action). Therefore, we gave a score of 4% for each answer to one of the four questions on top of each pillar, and a score of 2% for each input on one of the goals (Table 3). We filtered out some spurious answers and few compilation errors and then computed for each survey the completion ratio, and finally arranged them in a Spider Graph with a 5% bin width. The Spider Graph (Fig. 5) shows the number of answers against the completion percentage. As we expected, none of the answers had more than 55% of completion (purple line). The section related to the pillar on knowledge, which appeared first, has the higher ratio of completion, while the economy pillar, which appeared last in the survey, has the most 0% of completion. From this consideration, we infer that users probably perceived the survey as too long and "left" it before the end.

Table 3. Survey evaluation score to measure the filling progress

Pillar	*Overall weight*	*∀question*	*∀goal*
KNOWLEDGE	33%	4%	2%
TECHNOLOGY	33%	4%	2%
ECONOMY	33%	4%	2%

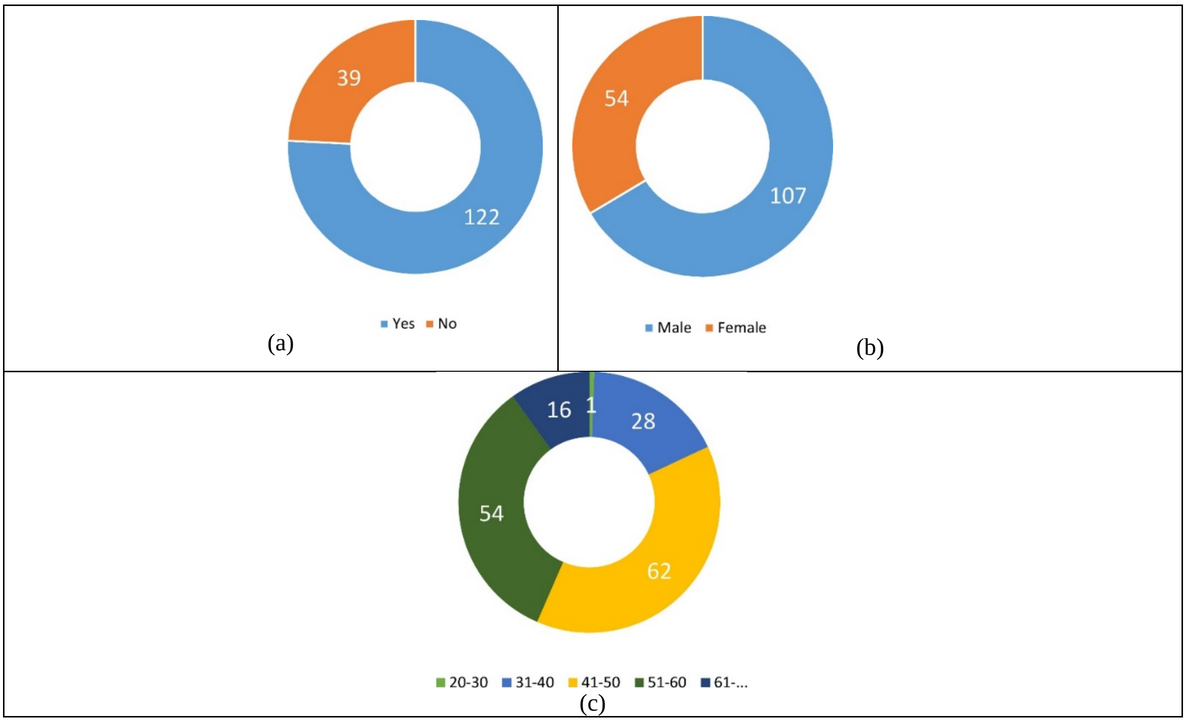


Fig. 4. Features of survey audience: (a) Familiarity with the *BLUEMED Initiative*; (b) Gender of responders; (c) Age range of responders

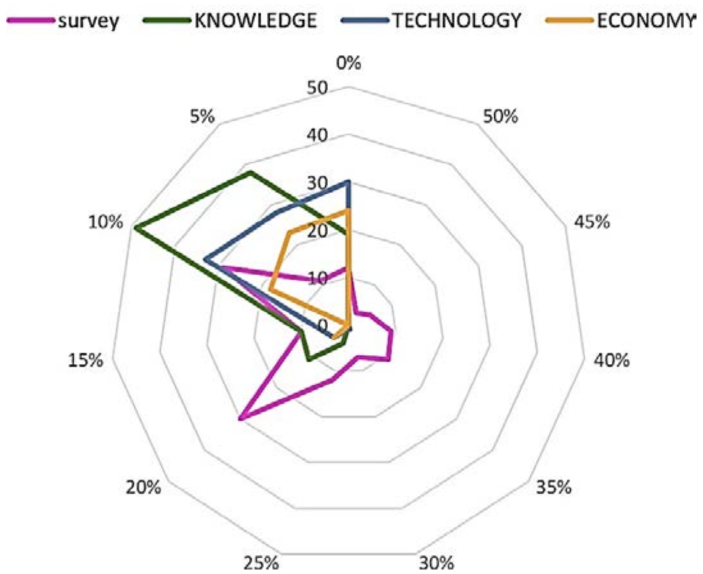


Fig. 5. Rate of completion of the overall survey in percent

Each *BLUEMED CSA* partner also had the opportunity to further engage national actors in the process with different approaches (e.g. through dedicated meetings as reported in the following paragraph 2.2.2), in order to ensure the most effective involvement of national stakeholders and collect meaningful information, as explained in the next paragraph. In addition, partners managed the results of the survey independently and included them in their proposal for updating the SRIA. For example, in most partner countries a translation of the survey in national languages was circulated in order to increase the number of answers, while Slovenia gathered inputs for updating the SRIA through two different surveys and channelled the resulting collective analysis. All contributions have been compared and merged to feed the next updated version of the agenda that is shared at the Mediterranean level. While the graphics of Fig. 4a-c, and Fig. 5 are based only on comparable data collected through the on-line survey; outputs of independent contributions are not included.

2.2.2 Complementing the inputs

Dedicated events and consultations with experts were carried out at the national level, engaging the public at large, targeted Ministries, and Regions. A more complete collection of inputs was gained, complementing the information collected through survey as described above. The coordinators of relevant projects and initiatives active on the Mediterranean Basin were also invited to convene to share relevant inputs, not only from a thematic point of view but also with regard to the supporting instruments they are using for developing actions that are of interest for the Mediterranean blue growth.

The operative perspective of ongoing projects allowed to gather some suggestions on recent achievements that could possibly imply the fulfilment of a goal of the BLUEMED SRIA and/or point out one or more gaps not filled yet. Identification of missing topics included:

- for the knowledge pillar: micro-biodiversity; dynamics of rivers' deltas (mostly anthropogenic); the application of bioremediation measures for sustainable aquaculture;
- for the economy pillar: marine protein; ocean literacy and citizen science; actions dedicated to innovative approaches to solution of different marine hazards (ecosystem recovery, mitigation of anthropogenic impacts, coastal eutrophication and human health, reduction of pollutant inputs at sea, decommissioning of oil and gas platforms, etc.); aquaponics;
- for the technology pillar: measuring impact of pollution in ports on human health and ecosystems; integration of offshore renewable energy; improvement and impacts of desalination processes; enabling the internet of things, i.e. the interconnection of devices embedded in physical objects capable to transmit and receive data, as a solution for marine observation and monitoring;
- for the policy pillar: regulatory framework lacking on unmanned vehicles.

2.3. Engaging non-EU countries

The engagement with non-EU countries is a key aspect of the *BLUEMED Initiative*, i.e. the extension. Non-EU members of the GSO BLUEMED Working Group (paragraph 2.1) are mandated to promote the implementation of the BLUEMED SRIA and its continuous upgrade at national levels in order to develop a cohesive agenda for the Mediterranean Sea at the national, macro regional, European, and Mediterranean levels by nurturing a robust partnership, social inclusion, and access to research infrastructures. The *BLUEMED CSA*, in collaboration with the UfM Secretariat, is supporting the gradual engagement of non-EU stakeholders in the discussion and work of the BLUEMED platforms, to deliver joint recommendations for the consolidation of the SRIA and its implementation plan. A preliminary opportunity to share the strategic agenda with non-EU Mediterranean countries has been given by the workshop "Building a shared research and innovation agenda for blue jobs and growth across the Mediterranean", organized in the framework of the first UfM Regional Stakeholders' Conference on Blue Economy, held in Naples on 29-30 November 2017. On this occasion, Tunisia, Turkey, Egypt, and Lebanon provided a first view of the actual strategies in the field of marine and maritime research and innovation. The following common points were highlighted among others: the importance of fisheries activities, including the tendency to fish in increasingly deep water; the need to design new offshore aquaculture plants; the partial understand of factors that facilitate the entrance and the spreading of alien species in Mediterranean waters; the impact of the plastic debris and garbage patches on marine ecosystems; the necessity to develop plans of maritime space in connection with coastal zone management, considering the Barcelona Convention, the WESTMED Initiative and the joint EC-DG MARE (Directorate General Maritime Affairs and Fisheries of the EC) and IOC-UNESCO (Intergovernmental Oceanographic Commission of the UNESCO) roadmap on Maritime/Marine Spatial Planning for sustainable use of seas and exploitation of resources (EC DG MARE, IOC UNESCO, 2017). A more structured consultation process with non-EU stakeholders carried out in different countries contributing with specific inputs to the SRIA led to the release of a new update version co-owned by all Mediterranean countries (Barbanti et al., 2018).

Non-EU countries were also asked to appoint national pivots to the BLUEMED Platforms (see paragraph 2.2). A continuum from critically processing inputs to producing relevant outputs guarantees the equilibrium and feedback process between the BLUEMED and the external environment (Fig. 6).

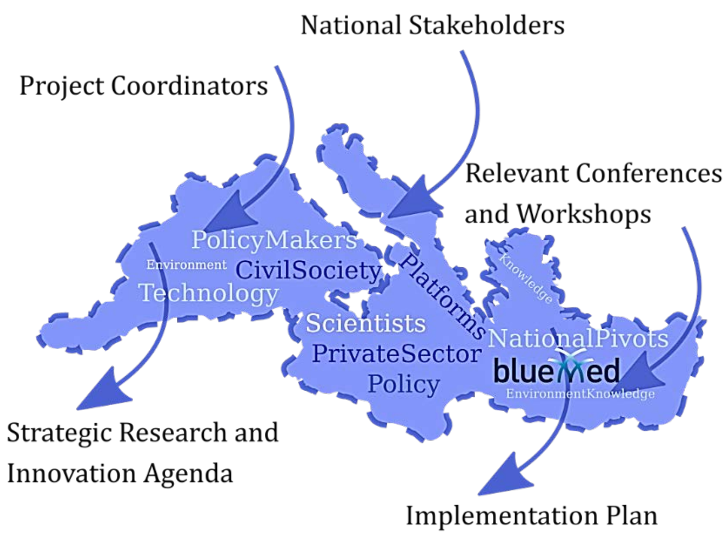


Fig. 6. The pan-Mediterranean BLUEMED input-output mechanism: the key deliverables of the project in support to the process, the updated SRIA and the Implementation Plan, are reached through continuous consultation The system relies on a structure open to feedbacks

The coming phase will lead to prioritisation of actions based on agreed criteria and to their implementation, in order to reach targeted goals.

3. Results and discussion

3.1. Preliminary impact at the European and national levels

As first tangible consequence of the initial joint work described in sub-section 2.1 that brought to the endorsement of the BLUEMED SRIA in 2015, the European Commission Directorate General Research and Innovation (EC – DG R&I) and Directorate General Maritime Affairs and Fisheries (EC - DG MARE), adopted some BLUEMED SRIA key priorities in major research and innovation programmes. In particular, six calls for proposals of research and innovation projects were included in the Work Programme 2016-2017 of the European Commission Research and Innovation Framework Programme Horizon 2020, Societal Challenge 2 on "Food Security, Sustainable Agriculture and Forestry, Marine, Maritime and Inland Water Research, and the Bioeconomy" for a total budget of about 43 M€. The call for proposals entitled "Blue Labs - innovative solutions for maritime challenges & Blue Careers in Europe" launched by the EC DG-MARE in May 2016 and the one entitled "Blue Technology - transfer of innovative solutions to sea basin economies" in September 2016 added to this, allocating overall 8 M€ to the blue growth in the area.

The following year, two additional calls on "Blue networks in the Mediterranean" and on "Restoring marine ecosystem in the Mediterranean" were launched by the EC-DG MARE in November 2017, with a budget of 3 M€ and 1.5 M€ respectively. Almost all projects granted are presently active. Only an analysis of the achievements will make it possible to establish if these projects had an impact on the blue growth and to what extent.

In parallel, the work carried out since 2014 and structured more recently within the platforms designed by the *BLUEMED CSA* (sub-section 2.2) have started to produce some impact, leading to an increased cohesion of national blue growth communities, often experienced for the first time. This allowed the alignment of entities such as Ministries, Regions, and maritime research and innovation clusters. In some cases, it brought to the inclusion of the *BLUEMED Initiative* within national research plans and strategies. For example, in Italy the BLUEMED is targeted as a key initiative of the "National Research Programme 2015-2020" adopted by the Ministry of Education, University, and Research (MIUR, 2015). While the "National Bioeconomy Strategy" (Italian Council, 2017) identifies the *BLUEMED Initiative* as the framework of reference for promoting the blue bioeconomy in the Mediterranean. The National Board on Coastal Erosion established by the Ministry of Environment in 2016 (MATTM, 2016) aims at: promoting cooperation in research and innovation among all Mediterranean countries; supporting knowledge-based policy making; and ensuring the effective and efficient use of resources and infrastructures through Member States cooperation and implementation of joint actions. All these objectives are in line with the BLUEMED vision. At more practical level, the Italian Inter-ministerial group on the Blue Growth has been set-up in 2017 to coordinate under the BLUEMED umbrella the work of different Ministries that have decision-making power on Sea activities. The expectation is that the *BLUEMED Initiative* contributes also to the update of the Smart Specialization Strategies (S3, EC Communication, 2017), thus realizing the objective of aligning the Mediterranean Blue Growth Strategy with the one of Regions. S3 are the research and innovation policies outlined and implemented by the Regions under national coordination in the framework of the EU cohesion policy (EU Treaty, 2007) aimed at creating jobs and boosting competitiveness. The alignment can be facilitated by reinforcing collaborations with relevant authorities. In Italy, despite the 8000 km of coastline, Regions are differently sensitive to marine and maritime themes, one of the more active being the Campania Region. Since 2017, it hosts the National Technology Cluster on Italian Blue Growth (CTN-B.I.G.). As it happened for other sectors, the Cluster become the platform of reference of the national marine and maritime public and private stakeholders' working together to attract investments and funds. To favour alignment and possibly leverage new opportunities, the person responsible for the Internationalization activities of the Campania Region has been directly engaged in the BLUEMED Initiative and participated to a technical workshop organized with the perspective of building an operational network of funders. Indeed, the *BLUEMED CSA* started to support the creation of a network of research and innovation funders from public and private sectors that is expected to provide the operational counterpart of the engagement process, addressing and possibly committing relevant Organizations to jointly implement the selected actions. In addition, given the National Smart Specialization Strategy as overarching policy put in place to create value chains combining interests and funds of regions and nations, a contribution has been asked to the Italian Agency for the Cohesion of Territories to the national position on the SRIA update (see the paragraph 2.2). Besides technical aspects, the Agency affirmed the necessity to further involve Regions and the variety of productive knowledge expressed by the territories. A good premise is represented by the work carried out by the Emilia-Romagna Region. At the European level, its active role led to the publication in 2013 of the European regions Charter for the promotion of a common framework for strategic actions aimed at the protection and sustainable development of the Mediterranean coastal area, the Bologna Charter (www.bolognacharter.eu). At national level, a study (Barbanti, 2018) was implemented with the National Research Council of Italy proposing possible measures for planning the marine space use in front of the Region's coasts, based on the assessment and the analysis of the sea and coastal uses.

3.2. How BLUEMED could reduce the fragmentation to reduce the complexity

The *BLUEMED Initiative* was initially promoted with the aim of increasing the attention of the European and national governing Institutions and funding agencies on the relevance of the policy agenda for the marine and maritime research and innovation in the Mediterranean Sea. Sub-sections 2.2 and 2.3 detail the BLUEMED's great effort in raising awareness and promoting dialogue and cooperation. This might lead to overcome some critical factors underlying this type of initiative, such as: multiple stakeholders often addressing contrasting priorities; the strong need of interactions counterbalanced by the competition for the use of the same resource and/or of a common space; the gap of knowledge and adequate skill leading inevitably to decisions undertaken under conditions of unawareness on the consequences and implications. To give an example, while some countries started to define zones of ecological protection to ensure the sustainability of fisheries resources, part of the basin is legally open to free use and exploitation by all states (art. 87 of UNCLOS, 1982). The added value of BLUEMED can be sought in its support to defragment this complexity, providing knowledge-based solutions, possibly trans-national, to optimize management processes.

Persisting in favouring alignment is fundamental considering not only the cultural diversity, social and economic developments, and geopolitical complexity of the Mediterranean area, but also the sophisticated interaction between research, stakeholders and policy makers. Effective participatory mechanisms and analysis of the interactions among all actors involved can enable the transformation of desirable goals into feasible and measurable actions. This process will be accompanied by the identification of suitable framework conditions that enable the activation of these actions, represented by technology capacity, observation and data, and skills development. A metrics providing quantitative and qualitative indicators of their impacts is also necessary.

Establishing common research and innovation trajectories for implementing actions pursuing a sustainable marine and maritime growth within dedicated policy frameworks does not mean solely to apply and exploit newly achieved knowledge, it implies instead multiple connections and continuous adaptation to create new value, extend knowledge frontiers, and support innovative solutions (Roux et al., 2006). To share objectives is the precondition: the four BLUEMED platforms are conceived to work towards this goal.

4. Conclusions

Research and innovation can contribute significantly to sustainable blue growth in the Mediterranean Region, a unique asset of natural and cultural value. A multidisciplinary approach linking economy, environment, and humans is required. This implies the continuous engagement of diverse communities often with markedly different interests, objectives, and even languages, in a delicate equilibrium between the inputs that are brought into a broad participatory process and the outputs produced, raising awareness and moving forward to the implementation of joint actions. Research and innovation activities on key economic drivers such as food, transportation, tourism, chemicals and materials, energy, security, and ecosystem health, have to be carried out by tackling relevant thematic objectives once they are jointly identified by the scientific community, policy makers, stakeholders from the private sector, and civil society, looking at the potential impact also in terms of societal and environmental benefits.

A clear indication of common priorities, narrowing the list of actions of the BLUEMED SRIA, needs to be addressed to implement durable actions in support to sustainable development, from their realization to the monitoring of possible impacts. The opportunity of witnessing a paradigmatic change envisioning the Mediterranean Basin as a hub for innovation is not far away. In practice, once the policy framework has been set-up, the integration of efforts by managing authorities of relevant research and innovation programmes, at least at the European and EU national levels, to jointly cooperate in this direction has already started. The Mediterranean area is variously exploited by several countries that belong to three different continents taking advantage of its resources including culture, food, and tourism. A broader intervention in designing research and innovation actions to provide knowledge-based solutions to the policy makers for managing the variety of human activities affecting the Mediterranean Sea is the key to guarantee the future well-being of citizens.

The *BLUEMED Initiative* is aiming to structure a suitable science-to-policy feedback mechanism, relying on the scientific environment also as vehicle of diplomacy. In order to face the complexity of such an Initiative, a mechanism has been built as precondition to enable the research community to offer its support to the decision-making process, influencing future policies and the adoption of knowledge-informed strategies at different levels: European, national, regional, international, and, in particular, trans-Mediterranean. Sustainable growth in the Mediterranean Sea is a grand challenge requiring a solid governing capability.

Acknowledgements

Authors wish to thank all members of the *BLUEMED Initiative* Strategic Board for their invaluable contribution to the development of the process as well as to partners of the *BLUEMED CSA*. Thanks, in particular to the Work Package leaders: Estrella Fernandez (Spanish Ministry of Economy, Industry, and Competitiveness), Nicolas Arnaud (French National Center for Scientific Research) and Jean-Francois Cadiou (French Research Institute for Exploitation of the Sea), Irene Mangion (Malta Council for Science and Technology), and Kalliopi Pagou (Hellenic Centre for Marine Research). Vangelis Papathanassiou (Hellenic Centre for Marine Research) has been crucial in designing the *BLUEMED CSA* project. A deep thank goes also to Kathrine Angel-Hansen (JPI-Oceans) and Alessandra Sensi (UfM) for their precious advice.

The Authors are grateful to the BLUEMED Italian pivots, Mara Manente (Centro Internazionale di Studi sull'Economia Turistica), Federica Mastracci (Telespazio), and Silvia Grandi (Italian Ministry of Economic Development). They also express gratitude to the coordinators of the BLUEMED Italian mirror platforms on economy and policy: Monica Cariola and Gemma Andreone (National Research Council of Italy) for their great work.

A final thanks to David Fenton (National Research Council of Italy) for supporting the proofreading.

The *BLUEMED Initiative* is supported by the *BLUEMED CSA* (Grant Agreement nr.727453) funded by the European Commission (www.bluemed-initiative.eu/).

References

Amanatidou E., Cox D., (2015), SWOT analysis of alignment modalities, ERA-LEARN 2020 project Deliverable D4.5, On line at: https://www.era-learn.eu/alignment/comparative-swot-analysis-of-alignment-modalities/copy_of_ERALEARNDel4.4_SWOTalignment_FINAL.pdf.

Andrusaitis A., Cox D., Dosdat A.,Emeis K., Harms J., Heral M., Herrmann P., ten Hoopen F., Jennings S., Johannesson K., Kononen K., Köster F., Laamanen M., Niilonen T., Ollikainen M., Raaska L., Riemann B., Sirola M., Stuefer J., Svensson M., Wolf U., (2016), Towards sustainable blue growth: Outline of the joint Baltic Sea and the North Sea research and innovation programme 2018-2023, *BONUS Series*, **15**, On line at: https://www.bonusportal.org/files/4699/BONUS_Publication_No_15.pdf.

Barbanti A., (2018), Between the Earth and the Sea: analysis and proposals for the Maritime Spatial Planning of Emilia-Romagna (in Italian), On line at: http://doi.org/10.5281/zenodo.1184364.

Barbanti A., Cappelletto M., Ciappi E., de Lara Rey J., Herrouin G., Papandroulakis N., Trincardi F., (2018), Strategic Research and Innovation Agenda (SRIA) Updated version 2018, On-line at: www.bluemed-initiative.eu/wp-content/uploads/2018/12/BLUEMED-SRIA_Update_2018.pdf.

BC, (2004), Conference of Plenipotentiaries on the Convention for the Protection of the Mediterranean Sea against Pollution and its Protocols, (2004), Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean, Barcelona Convention, 9 July 2004, On line at: https://wedocs.unep.org/bitstream/handle/20.500.11822/7096/Consolidated_BC95_Eng.pdf.

Becheri E., Micera G., Morvillo A., (2016), *Report on Italian Tourism* (in Italian), vol. XXI Rogiosi Press, Naples.

Caliri A., Carbone S., Cianell R., Grandi, S., (2017), The Italian experience and state of the art, 14th EUOAG Meeting - Workshop on Decommissioning of offshore installations: Challenges, options and lessons learned, Brussels, On line at: https://euoag.jrc.ec.europa.eu/files/attachments/02._silvia_grandi.pdf.

European Council, (2014), Council conclusions on the European Union Strategy for the Adriatic and Ionian Region (EUSAIR), Brussels, 29 September 20104, On line at: http://ec.europa.eu/regional_policy/sources/cooperate/adriat_ionian/pdf/council_29092014_en.pdf.

CPCEEU, (2012), Cyprus Presidency of the Council of the European Union Declaration of the European Ministers responsible for the Integrated Maritime Policy and the European Commission, on a Marine and Maritime Agenda for growth and jobs, the Limassol Declaration, 7 October 2012, On line at:

https://ec.europa.eu/maritimeaffairs/sites/maritimeaffairs/files/docs/body/limassol_en.pdf
DNV GL, (2014), The Future of Shipping, Onn line at: https://issuu.com/dnvgl/docs/dnv_gl_the_future_of_shipping.
EC, (2016), Facts and Figures on the Common Fisheries Policy, Basic statistical data, European Commission Publications Office of the European Union, 2016, On line at: https://ec.europa.eu/fisheries/sites/fisheries/files/docs/body/pcp_en.pdf.
BLUEMED, (2015), EC ad hoc advisory group of the BLUEMED Initiative, BLUEMED Research and innovation initiative for blue jobs and growth in the Mediterranean area. Strategic Research and Innovation Agenda, October 2015, On line at: http://www.bluemed-initiative.eu/wp-content/uploads/2016/12/Bluemed-SRIA_A4.pdf.
BLUEMED, (2017), EC ad hoc advisory group of the BLUEMED Initiative, BLUEMED Research and innovation initiative for blue jobs and growth in the Mediterranean area. Strategic Research and Innovation Agenda, First update, April 2017, On line at: http://www.bluemed-initiative.eu/wp-content/uploads/2017/09/BLUEMED-SRIA_Update_final.pdf.
EC Communication, (2012), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Blue Growth, opportunities for marine and maritime sustainable growth, 494 final, 13 September 2012, On line at: https://ec.europa.eu/maritimeaffairs/sites/maritimeaffairs/files/docs/body/com_2012_494_en.pdf.
EC Communication, (2014), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Innovation in the Blue Economy: realising the potential of our seas and oceans for jobs and growth, 254/2, 13 May 2014, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0254R(01)&from=EN.
EC Communication, (2016), Joint Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, International ocean governance: an agenda for the future of our oceans, 49 final, 10 November 2016, On line at: https://ec.europa.eu/maritimeaffairs/sites/maritimeaffairs/files/join-2016-49_en.pdf.
EC Communication, (2017), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Initiative for the sustainable development of the blue economy in the western Mediterranean, 183 final, 19 April 2017, On line at: http://www.westmed-initiative.eu/wp-content/uploads/2017/07/westMed-communication.pdf.
EC Communication, (2017), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Strengthening Innovation in Europe's Regions: Strategies for resilient, inclusive and sustainable growth, 376 final, 18 July 2017, On line at: http://ec.europa.eu/regional_policy/sources/docoffic/2014/com_2017_376_2_en.pdf.
EC Conference report, (2017), Harnessing Research and Innovation for FOOD 2030: A science policy dialogue, Conference outcome report, 16 October 2017, On line at: https://ec.europa.eu/info/sites/info/files/conferences/food2030_2017/food2030_report_conferene_2017.pdf.
EC Directive, (2008), Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive), *Official Journal of the European Union*, L 164/19, 25.06.2008, Brussels.
EC Directive, (2014), Directive 2014/89/EU of the European Parliament and of the Council of 23 July 2014 establishing a framework for maritime spatial planning, *Official Journal of the European Union*, L 257/135, 28.08.2014, Brussels.
EC Report, (2017), EC Staff Working Document, Report on the Blue Growth Strategy: Towards more sustainable growth and jobs in the blue economy, 128 final, 31 March 2017, On line at: https://ec.europa.eu/maritimeaffairs/sites/maritimeaffairs/files/swd-2017-128_en.pdf.
EC DG MARE, IOC UNESCO, (2017), Joint Roadmap to accelerate Maritime/Marine Spatial Planning processes worldwide (MSP), On line at: http://www.unesco.org/new/fileadmin/MULTIMEDIA/HQ/SC/pdf/Joint_Roadmap_MSP_v5.pdf
ECORYS, (2013), Study in support of policy measures for maritime and coastal tourism at EU level, Final Report, 15 September 2013, On line at: http://ec.europa.eu/maritimeaffairs/documentation/studies/documents/study-maritime-and-coastal-tourism_en.pdf.
EU Regulation, 2013, Official Journal of the European Union, Regulation (EU) no 1380/2013 of the European Parliament and of the Council of 11 December 2013 on the Common Fisheries Policy, amending Council Regulations (EC) No 1954/2003 and (EC) No 1224/2009 and repealing Council Regulations (EC) No 2371/2002 and (EC) No 639/2004 and Council Decision 2004/585/EC, Official Journal of the European Union, L 354/22, 28.12.2013, Brussels, On line at: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:354:0022:0061:EN:PDF
EU Treaty, 2007, Treaty of Lisbon amending the Treaty on European Union and the Treaty stablishing the Europeam Community, signed at Lisbon, 13 December 2007, Official Journal of the European Union, C 306, 17.12.2007, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:C:2007:306:FULL&from=EN
Eunetmar, (2014), Support to the development of sea basin cooperation in the Mediterranean, the Adriatic and Ionian, and the Black Sea - Report 4, September 2014, On line at: https://webgate.ec.europa.eu/maritimeforum/en/file/7834/download?token=snSXy7pk.
EurOCEAN Declaration, (2014), Rome Declaration, Setting a vision for seas and ocean science: Delivering impact, global leadership and sustainable blue growth for Europe, 8 October 2014, On line at: http://www.marineboard.eu/sites/marineboard.eu/files/public/publication/Rome%20Declaration-249_0.pdf.
EPA, (2017), European Environment Agency, Mediterranean Sea region briefing - The European environment - state and outlook 2015, On line at:

https://www.eea.europa.eu/soer-2015/countries/mediterranean.
Gauci Borda I., Bugeja G., (2017), Report of the BLUEMED Conference: A basin of research and innovation for sustainable growth, Sliema, Malta, 18-19 April 2017, On line at: http://www.bluemed-project.eu/wp-content/uploads/2017/09/BLUEMED-Conference-Malta-18-19-April-2017-Report_final.pdf.
GFCM Resolution, (2016), Resolution GFCM/40/2016/2 for a mid-term strategy (2017-2020) towards the sustainability of Mediterranean and Black Sea fisheries, On line at: http://extwprlegs1.fao.org/docs/pdf/mul166888.pdf.
Italian Council, (2017), Italian Presidency of the Council of Ministers, BIT. Bioeconomy in Italy. A unique opportunity to reconnect the Economy, Society and the Environment, On line at: http://www.agenziacoesione.gov.it/opencms/export/sites/dps/it/documentazione/S3/Bioeconomy/BIT_v4_EN.PDF.
ITTC, (2014), Report of the Specialist Committee on Hydrodynamic Noise of the 27th Towing Tank Conference, Copenhagen, Denmark On line at: https://ittc.info/media/6091/sc-noise.pdf
ITTC, (2017), Report of the Specialist Committee on Hydrodynamic Noise of the 28th Towing Tank Conference, Wuxi, China, On line at: https://www.ittc.info/media/7823/18-sc-hydrodynamic-testing-marine-renewables.pdf
Johnson K., Dalton G., Masters I., (2018), *Building Industries at Sea: 'Blue Growth' and the New Maritime Economy*, In: *River Publishers Series in Renewable Energy* Johnson K., Dalton G., Masters I. (Eds.), Denmark/The Netherlands.
JPI-Oceans, (2015), Joint Programming Initiative Healthy and Productive Seas and Oceans Strategic Research and Innovation Agenda 2015-2020, On line at: http://www.jpi-oceans.eu/library?refid=246303.
Malta Presidency of the Council of the European Union, (2017), Valletta Declaration on Strengthening Euro-Mediterranean Cooperation through Research and Innovation, 4 May 2017, On line at: http://www.bluemed-initiative.eu/wp-content/uploads/2017/05/Declaration_EuroMed-Cooperation-in-RI_1772.pdf.
MATTM, (2016), Ministry of the Environment and Protection of the Land of the Sea, National Guidelines for the defense of the coast from erosion and the effects of climate change, November 2016, On line at: http://www.minambiente.it/sites/default/files/archivio_immagini/Silvia%20Velo/tnec-llgg_nazionali_difesa_della_costa_dallerosione_9nov2016.pdf.
MEA Assessment, (2005), Ecosystems and human well-being: Synthesis, *Millennium Ecosystem Assessment*, , On line at: https://www.millenniumassessment.org/documents/document.356.aspx.pdf.
MHD, (2015), Ministers and Heads of Delegation, Union for the Mediterranean Ministerial Conference on Blue Economy Declaration, Brussels, On line at: http://ufmsecretariat.org/wp content/uploads/2015/11/2015-11-17-declaration-on-blue-economy_en.pdf.
Micheli F., Halpern B. S., Walbridge S., Ciriaco S., Ferretti F., Fraschetti S., Rosenberg A.A., (2013), Cumulative human impacts on Mediterranean and Black Sea marine ecosystems: assessing current pressures and opportunities, *PloS one*, **8**, 1-10.
MIUR, (2015), National Programme for Research 2015-2020 (in Italian), On line at: http://www.istruzione.it/allegati/2016/PNR_2015-2020.pdf.
Niavis S., Papatheochari T., Kyratsoulis T., Coccossis H., (2017), Revealing the potential of maritime transport for Blue Economy in the Adriatic-Ionian region, *Case Studies on Transport Policy*, **5**, 380-388.
Nittis K., (2012), Strategic Research Agenda for the Mediterranean Sea Basin, SEAS-ERA ERANET project Deliverable 7.1.1, On line at: http://www.seas-era.eu/np4/%7B$clientServletPath%7D/?newsId=149&fileName=SEAS_ERA_D.7.1.1_Med_SRA.pdf.
OECD, (2016), The Ocean Economy in 2030, OECD Publishing, Paris, On line at: http://dx.doi.org/10.1787/9789264251724-en.
RG, (2015), Representatives of the Governments of Greece, Spain, France, Croatia, Italy, Cyprus, Malta, Portugal, Romania, and Slovenia, Venice Declaration on Mediterranean Sea Cooperation, Launching a Strategic Marine and Maritime Research and Innovation Agenda for Blue Growth, 16.10.2015, Venice, On line at: http://www.bluemed-initiative.eu/wp-content/uploads/2017/02/Venice-Declaration-final.pdf.
Roux D.J., Rogers K.H., Biggs H.C., Ashton P.J., Sergeant A., (2006), Bridging the science-management divide: moving from unidirectional knowledge transfer to knowledge interfacing and sharing, *Ecology and Society*, **11**, 4.
SeaEurope, (2017), The Voice of Civil and Naval Industries in Europe, Annual Report, On line at: http://www.seaeurope.eu/ClientData/138/660/293101/3660/4/Original%20spreadsheet. pdf.
UN Resolution, (2015), Transforming our world: the 2030 Agenda for Sustainable Development, United Nations Resolution, 25 September 2015, On line at: http://www.un.org/ga/search/view_doc.asp?symbol=A/RES/70/1&Lang=E.
UNCLOS, (1982), United Nations Convention on the Law of the Sea, Montego Bay, USA, On line at: http://www.un.org/depts/los/convention_agreements/texts/unclos/unclos_e.pdf.

Web sites:

https://ec.europa.eu/maritimeaffairs/maritimeday/sites/mare-emd/files/burgas-vision-paper_en.pdf
http://www.bluemed-initiative.eu/wp-content/uploads/2017/10/BLUEMED_Vision.pdf
http://eatip.eu
https://www.polemermediterranee.com
www.bolognacharter.eu
https://www.adriatic-ionian.eu/
http://www.westmed-initiative.eu/
www.seaeurope.eu

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2329-2335
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

MEASUREMENTS TO EVALUATE THE POSSIBILITY TO PRODUCE BRICKS FROM WASTE CUBILOT SLAGS

Domenico Luca Carni[1]*, Francesco Lamonaca[2], Alessandro Vitale[3], Alfonso Nastro[4]

[1]*Departament of Computer Science, Modelling, Electronic and System Science, University of Calabria, Rende (CS), Italy*
[2]*Departament of Engineering, University of Sannio, Benevento, Italy*
[3]*Departament of Civil Engineering, University of Calabria, Rende (CS), Italy*
[4]*Departament of Chemistry and Chemical Technology, University of Calabria, Rende (CS), Italy*

Abstract

In this paper, the typical measurement techniques and production procedures defined in the UNI-EN guidelines for ceramic manufacture are taken into consideration to evaluate the properties and the characteristics of the bricks produced by using a mixture containing cubilot slag. The results of the experimental tests demonstrate that these measurement techniques are not enough to define the safety of the waste bricks. Up to now, UNI-EN guidelines for ceramics do not define crystallinity measurement for the products and then do not foreseen to determine the interaction between slag and clay. In this paper, a solution for this lack is proposed. In particular, the Thermal Analysis, X-Ray Diffraction, and the measurement of dangerous ions releasing are considered. The experimental results suggest that these techniques should be included UNI-EN guidelines because allow the definition of specific properties to the waste materials.

Key words: biomass, biorefinery, systems design, zero emissions

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Social needs to preserve the natural environment and the growing economic pressure have renewed interest in the use of products employing waste as raw materials. Such materials are also called secondary raw materials (Andreola et al., 2005; Dino et al., 2017; Wiemes et al., 2015).

The researches on utilization of waste materials to produce bricks can be divided into three general categories based on the production methods: firing, cementing and geo-polymerization (Zhang, 2013). In this regards, the firing ceramic process can be considered an ideal method to accomplish the inerting of hazardous waste materials (Bingham and Hand, 2006; Coronado et al., 2015). Therefore, many researchers have studied the production of bricks from waste materials based on firing, in the following simply called waste bricks (Zhang, 2013). Although many researches have been conducted on this topic, the commercial production of bricks from waste materials is still very limited. The possible reasons of this limited production are related to: (i) the difficulties to add the waste materials in the production line of traditional bricks, (ii) the scary to have a contamination of the environment from the bricks including waste, and (iii) the slow acceptance of waste bricks by industry and public, and mainly (iv) the absence of relevant standards or guidelines for the use/recycle of waste in bricks. On the other hand, the replacing of natural raw materials by wastes to produce bricks can configure an opportunity to ameliorate waste management of today (Rawlings et al., 2006). The valorisation of industrial wastes and their reuse as alternative raw materials, especially in ceramics technology, can presents several advantages

* Author to whom all correspondence should be addressed: e-mail: dlcarni@dimes.unical.it

when compared with the use of primary natural resources, namely reduction in the extraction volume of clay (Junkes et al., 2012). In addition, encapsulating the waste slags in a ceramics matrix is the best solution for achieving the inertizing and neutralization of the waste (Couto et al., 2001; Ribeiro et al., 2002). Moreover, sometimes a collateral benefit can be derived from the energy properties associated with the content of organic matter in the wastes (Zhang, 2013).

Based on the results showed in previous papers (Acchar et al., 2009), at the typical measurement techniques used to characterize the building materials, and described in the UNI EN guidelines (UNI EN 14411, 2016), further measurement methods of the produced materials must be added to evaluate the safety for humans. In particular, in this research measurement methods based on thermal analysis, x-ray powder diffraction, and dangerous ions releasing are proposed to be included in the UNI EN guidelines. These measurement methods are devoted to define the acceptance properties of the clay with respect to the slag (Lamonaca et al., 2017). As a consequence, experimental results are performed to validate the effectiveness of such method, by considering the use of different amount of cubilot slag added to a Calabrian clay and two different preparation methods of the bricks: extrusion and pressing.

2. Experimental setup

The measurements to qualitatively evaluate the major crystalline phases were performed utilizing the X-ray diffractometry (XRD) techniques. The XRD measurements were carried out by CuKα radiation using a Philips X-Ray Powder Diffractometer PW 1730/10 with a vertical goniometer (30 mA and 40 kV), with 2θ degree from 5° to 70° at 0.02°/s. The chemical compositions were carried out with an Energy Dispersive X-ray Analysis (EDAX) by Link installed on SEM Cambridge 360 microscopy. The thermal behavior of the materials was evaluated by utilizing a NETZSCH STA 409. The STA 409 allows the simultaneous evaluation of the: thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC) curves. The simultaneous acquisition of TG and DSC data allows to easily compare the curves by assuming same experimental condition in the analysis of the sample. A computer controls all the measurement instruments, the calibration, the optimization of the experimental conditions and the hardware description are reported elsewhere (Carni et al., 2013; Lamonaca et al., 2015). The Particle Size Distribution (PSD) was determined by using a series of sieve as defined in the UNI-EN guidelines. Two series of bricks were prepared: the first extruded utilizing an extrusion laboratory brick moulding machine MVP/O series G. The amount of water was automatically defined by the machine. The volume of the hopper is about 5 l and were utilized about 5 kg of charge for each mixture. The size of the samples was 135x22x11 ± 2 mm. A second series of bricks were performed utilizing 75 g of dry mixture with about 10% of water. The mixture was pressed at 300 bars with a laboratory press by Gabrielli. The pressure was maintained for 15 minutes. The size of the stainless steel moulds is 110.0x55.0x5.0 ± 0.1mm. The amount of powder pressed was constant and the size of the pressed bricks is about 0.2% different by the size of the mould after the shakeout. After the preparation the green body, bricks and tablets, were dried into an oven at 100 ± 5 °C for about one day.

The method of preparation is in agreement with procedures utilized by others (Andreola et al., 2005; Coronado et al., 2015; Vasile et al., 2016; Zhang, 2013). Then the samples were normalized and burned into a furnace by Nabertherm mod lh/15-12 for 180 min at 1000 °C for a first series and at 1100 °C for a second series. The heating and cooling cycles were controlled by computer. After any treatment, each sample, normalized for 24 hours at room temperature, was weighed and measured to evaluate the shrinkage and the weight loss. The linear shrinkage was derived from the length of ten samples before and after firing using a calibre with a resolution of ±0.01 mm, the results are reported as mean of the measurements. The bulk density was calculated as the ratio of the dry mass of the brick and its normalized volume.

The clay utilized in this research was mining from the area called Perrotta in the Rosarno town (RC, Italy), located at about 80 m on sea level. The cubilot slag was extracted from the storage platform of Pertusola farm in Crotone (Vasile et al., 2016)

Different amounts of slag were added to the raw clay body. About 5 kg of clay and of cubilot slag were collected and homogenized into a blender. The samples were dried at 60 °C and desegregated into a ball-mill for about 20 min and then sieved before being utilized. In Table 1 the composition of clay and slag used is reported. In Fig. 1 the particle size distribution of the dry slag and of the dry clay after the desegregation are reported considering the amount passing and the amount retained on each sieve in agreement with UNI-EN 933-1 procedures (Eliche-Quesada et al., 2011).

Table 1. EDAX chemical analysis of the slag and clay. % in weight

	SiO_2	Al2O3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	ZnO	SiO_2/ Al_2O_3	CuO	MnO	PbO	Others	Ignition loss	SO_x
Slag	6.72	1.05	40.24	1.39	1.39	0.18	15.48	20.21	6.40	1.33	1.12	6.14	0.66	---	4.09
Clay	55.50	18.20	6.62	4.22	2.15	2.94	1.55	---	3.05	---	0.96	---	1.09	6.99	---

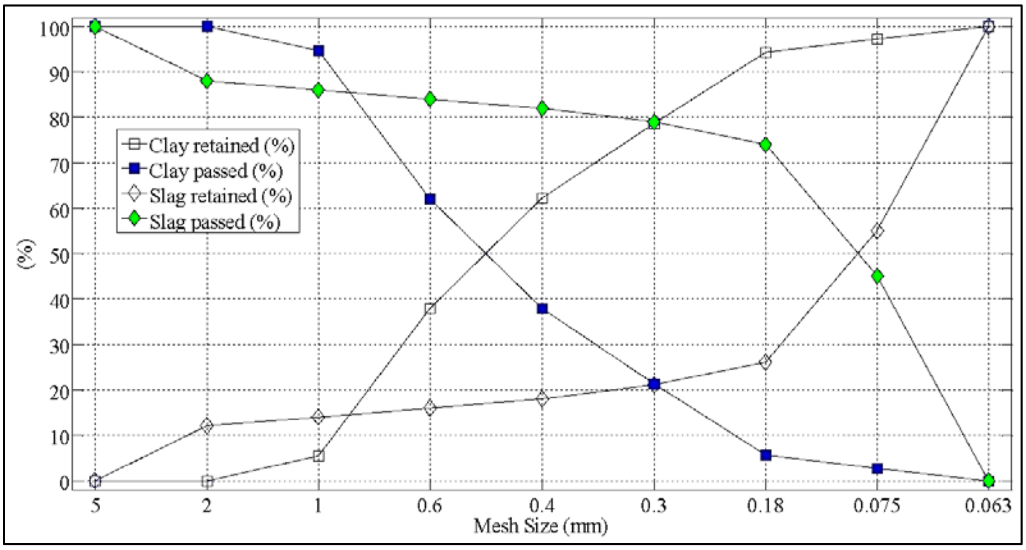


Fig. 1. Size distribution of clay and slag after 20 minutes of desegregation. Mesh size (mm) as reported on the used sieve

Five samples of extruded bricks and five samples of pressed bricks, after the mechanical characterization, are immersed into a beaker containing 800 ml of water to evaluate the ability of the bricks to release metals. In particular, after ten days of immersion at room temperature the water was filtered and analysed with atomic absorption analysis utilizing a Shimadzu AA 660 spectrophotometer.

3. Results and discussions

The chemical analyses of the clay and of the slag (Table 1) confirm the compatibility of the powders. In fact, the addition of slag to the mixture does not modify substantially the SiO_2/Al_2O_3, Na_2O + K_2O/SiO_2 and Na_2O + K_2O/Al_2O_3 ratios. In this regards, the addition of slag does not modify, in particular, the firing temperature of the bricks and the technical properties of the ceramics products obtained after the firing. Also, the mixture slag and clay can be proposed because the curves reported in Fig. 1 show that the clay and the slag are able to be desegregated and homogenized together in a blender having a compatible behaviour. This kind of measure is proposed because it is fundamental in a way to establish the compatibility between the slag and the clay.

Fig. 2 reports the X-ray patterns:

- A, B, C mixtures of clay and slag,
- D curves of the clay fired at 1100°C,
- E, F clay and cubilot slag as made,
- G, H curves of slag after firing at 1000°C and 1100°C.

The patterns clearly show that during the firing the slag does not modify the crystalline product of the bricks and this is the proof that the slag is just incorporated into the clay body. Moreover, the X-ray pattern of the *as made slag* (curve F) does not show the presence of Quartz (there is no peak at about 26° 2θ degree) additionally, there are not peaks detectable with appreciable intensity, related to heavy metal silicates. It is due to the possibility that part of heavy metals can be linked with silicon but the amount of their silicates is very low and the sensibility of the diffractometer is not enough to detect this very low concentration. The peaks attributed to the carbonates or sulfates have not an intensity sufficient to define the type of gypsum or carbonates. In the diffractograms A, B and C, peaks at low intensities attributed to the typical products normally detected in bricks fired at 1000°C and 1100°C are detected as reported in (Carter et al., 2007).

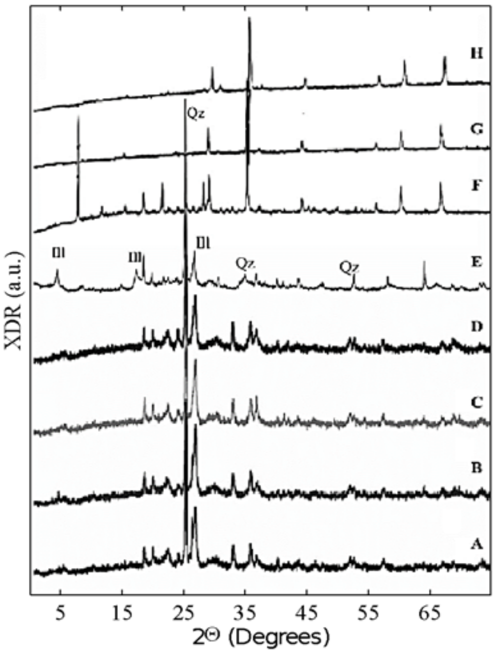


Fig. 2. XRD patterns of materials used to produce bricks and product after firing at 1000°C and 1100 °C. Curves E and F clay and cubilot slag as made; curves G, H slag after firing at 1000°C and 1100 °C respectively; curves A, Clay fired at 1100°C; curves B, C and D, mixtures clay slag after firing at 1100°C containing 2, 4, 8 % of slag respectively. Qz indicates the quartz peaks and III indicates the Sulphates and/or Carbonates

The salts of heavy metals, as sulfates and carbonates, with peak at about 12° 2θ degree, detected before the thermal treatment, are destroyed and transformed into oxides during the heating at 1000°C in air. It is an indication that the SiO_2 present in the slag is not involved, or at least marginally involved, in the formation of the bricks. In this regard the addition of slag to the clay does not produce a variation of the SiO_2/Al_2O_3 ratio in the bricks and it does not produce a variation of the fired ceramics products. The formation of some spinel cannot be excluded. These measurements confirm that the slag is practically inerting and merging into the ceramic matrix of the bricks. This behavior is observed with other type of industrials residues by others (Coronado et al., 2015; Zhang, 2013). Utilizing a firing temperature higher than 1100°C the X- ray patterns are very similar, just a variation of some peak intensities is observed due to the formation of a vitreous phase. The bricks produced after 120 min of firing at 1100°C are slightly deformed and then the use of a temperature higher than 1100°C is not possible with this type of clay. This preliminary conclusion is also supported by DSC curve of clay (Fig. 4) where is evident that at temperature of 1000°C start a fusion of the clay.

The amount of the weight losses evaluated for the slag and for the clay corresponding at the DSC curves of Figs. 3-4 are reported in Table 2.

The thermograms of Figs. 3-4 confirm the hypothesis formulated with the measurements with X-ray. Indeed, the DSC of cubilot slag (Fig. 3) does not show peaks that can be attributed to the formation of silicates of heavy metals. Moreover, the TG and the DTG curves show only weight losses confirming the degradation of the salts and their dehydration. In Fig. 3 the peaks of DTG and of DSC between 100°C and 150°C are linked and can attributed to the loss of the humidity of the slag (water no strongly linked with slag), in fact the DSC peak is endo. The peak of the DTG associated to a small peak of the DSC at about 350°C is attributed to the loss of water strongly linked to the salts and other micro components of slag. The peak at about 800°C is attributed to the thermal degradation of heavy metals salts, as sulphates and carbonates, detected by X-ray analysis. This degradation transforms the salts to metal oxides. The very small effects detected in DSC curves correlated with the small amount of the weight loss, confirm the entity of the effect and the small quantity of these salts. This is in agreement with analysis showed in Table 1. It is the explanation of the disappearance of the peak at about 12° 2θ degree in the X-ray slag pattern after firing (Fig. 2).

As concerning the clay, the thermograms in Fig. 4 show just 3 peaks: the first (about 100°C) attributed to the humidity, the second (about 500°C) is linked to the degradation of the hydrated silicates of the clay, and the third peak (very small at about 800°C) related to the decomposition of traces of carbonates and at the combustion of some organics normally presents in the mines.

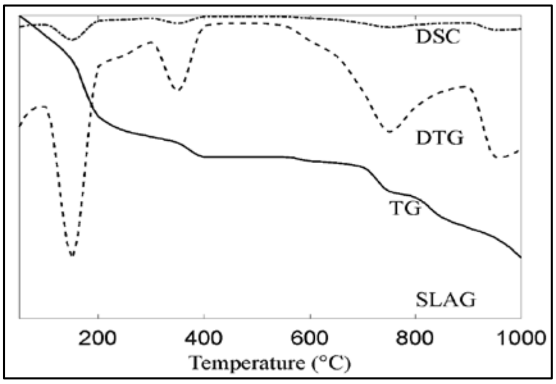


Fig. 3. Thermograms of cubilot slag

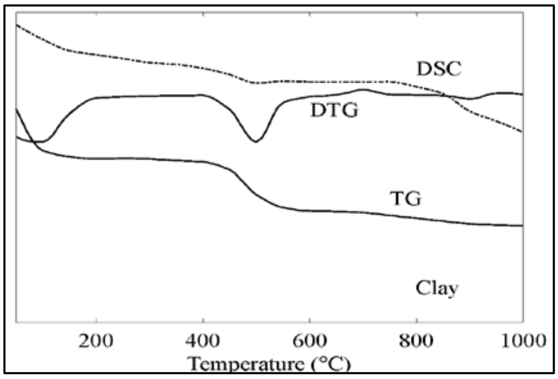


Fig. 4. Thermograms of clay

Also, the modification of the slope of DSC curve, at high temperature, indicates that the fusion of the silicates of the clay starts. In this regards the maximum temperature at which it is possible fire the bricks are 1100°C. In fact, the samples obtained at higher temperature result deformed as above desumed with the XRD patterns.

The intensities of the thermograms peaks is not indicative of the intensity of the phenomena at which are associated, because their intensities are automatically defined by programs to better visualize the effects. It is the reason that ordinates are without a scale. This technique is well known at the users of simultaneous thermal analyzer. The results reported in Table 3 confirm the good effect of the addition of slag to the clay mixture because the weight losses of the formed bricks are reduced as function of the percentage of the added cubilot slag.

Table 2. Weight losses of clay and cubilot slag

	1° DSC peak 129°C	*2° DSC peak 362°C*	*3° DSC peak 686°C*	*Total loss*
Clay	3.13 ± 0.2%	3.58 ± 0.2%	0.85 ± 0.2 %	7.79 ± 0.3 %
Slag	0.54 ± 0.2%	0.23 ± 0.2%	0.58 ± 0.3 %	1.14 ± 0.3 %

Table 3. Weight losses after drying at 110°C and after firing at 1000 and 1100 °C

	Extruded				*Pressed at 300 Barr*			
% Slag	*0*	*2*	*4*	*8*	*0*	*2*	*4*	*8*
Green body weight as made (g)	83.72 ± 1.55	79.20 ± 1.45	80.66 ± 1.49	77.75 ± 1.54	74.30 ± 0.13	74.51 ± 0.12	74.69 ± 0.13	74.02 ±0 .14
Weight losses after drying								
Weight loss %	23.30 ± 1.05	22.85 ± 1.15	21.52 ± 1.13	20.13 ± 1.09	11.01 ± 0.99	11.01 ± 0.89	9.77 ± 0.90	7.95 ± 0.79
Weight losses after firing								
Loss after firing at 1000°C, %	10.10 ± 0.10	10.10 ± 0.06	10.10 ± 0.08	10.10 ± 0.10	10.10 ± 0.12	10.35 ± 0.11	8.78 ± 0.09	7.50 ± 0.09
Loss after firing at 1100°C, %	10.10 ± 0.08	10.10 ± 0.10	10.10 ± 0.05	10.10 ± 0.07	10.15 ± 0.12	10.40 ± 0.14	8.90 ± 0.10	7.61 ± 0.88
The pressed bricks, after the forming shown a sizes variation of about 0.2 %.								

It is evident that the extrusion process needs about the same amount of water (automatically defined by the machine) independently by the amount of slag added. In other hand, in the pressed bricks process the amount of slag modify and reduce the amount of water that is necessary to form the pressed brick. These results are in agreement with the results reported in the following (Figs. 5-7).

The amount of slag in the mixture is not higher than 8%. In fact, during the drying and the firing, the added slag does not lose weight as supported by the results of TG and DSC (Fig. 3 and Table 2). This is because the slag is obtained by a thermal process. These reduction of weight losses are supported by a small shrinkage after the drying and after the firing of the formed bricks. These effects are observed on bricks extruded or pressed. The results are showed in Fig. 5. It is evident that the shrinkage of the pressed bricks is very low. This is due to the small amount of water added to the mixture prior to the molding process. The density of the extruded bricks is not influenced by the addition of slag. In fact, the density is about 1.59 ± 0.15 kg/ml for bricks without slag and 1.70 ± 0.15 kg/ml for bricks with 8% of slag, then there is a low variation. In the same manner, the density of pressed bricks is 2.66 ± 0.55 kg/ml without slag and 2.86 ± 0.56 kg/ml for bricks with 8% of slag, confirming the low influence of the slag addition in both cases.

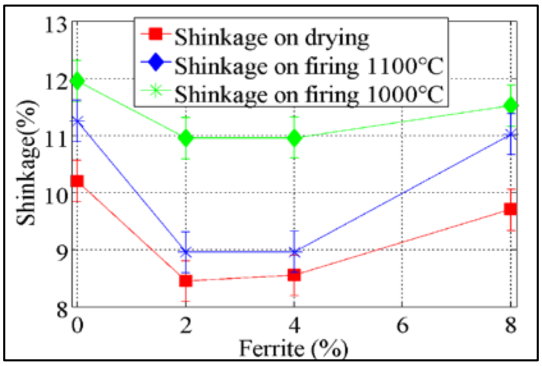


Fig. 5. Shrinkage of the slag-bricks extruded after drying and after firing

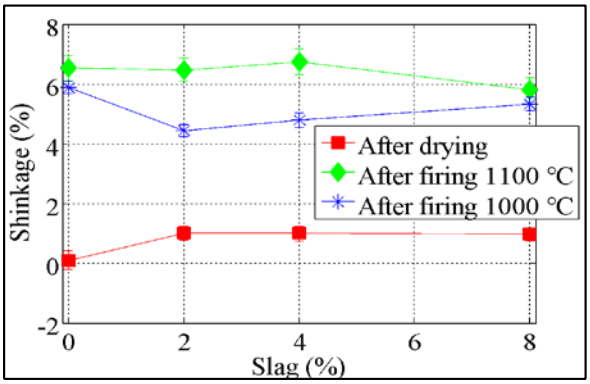


Fig. 6. Shrinkage of slag bricks pressed at 300 Bar after drying and after firing.

The addition of the slag to the clay modifies the shrinkage of the brick. In particular, for bricks extruded, a high reduction is observed when 2% of slag is added to the clay. By increasing the amount of slag the shrinkage increases because of the amount of water that the extrusion machine automatically adds to the mixture in order to have a better plasticity and a good extrusion.

This explanation is supported by the weight loss of the bricks after the drying process. In fact, the increasing of the added slag (more than 2%) produces an increasing of the water loss as confirmed by the results of the porosity reported in Fig. 7.

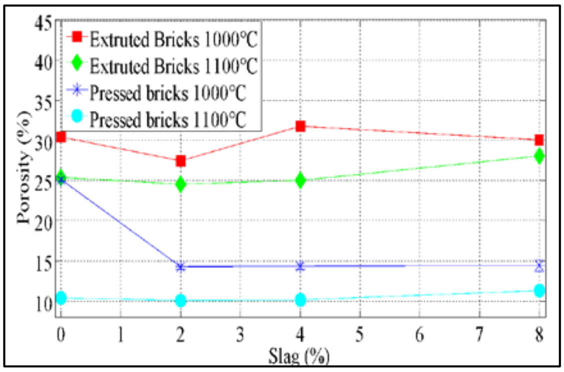


Fig. 7. Porosity of extruted and pressed bricks after firing at 1000 and 1100°C for 120 min. (UNI-EN 8942)

Different trend is observed for pressed bricks. It is due to: (i) the constant small amount of water added to the mixture, (ii) the effect of the pressure, and (iii) because the process is carried out with a constant amount of mixture's powder and forming pressure.

In any case the high variation of the properties above reported, due to the addition of the 2% of slag to the mixture, are quite in agreement with the results observed with other waste materials added to the clays reported in literature (Eliche-Quesada et al., 2011).

The results reported in Table 4 are in agreement with the results of porosity (Fig. 7). Indeed, the porosity of the pressed bricks is at least 50% of the porosity of the extruded bricks. Considering wasted bricks as traditional bricks following the UNI-EN guidelines, the results for pressed define these bricks as ceramics of type B11b (UNI-EN 178), because the water absorption is between 6 and 10% (Table 4). Than at least these materials can be proposed as not antifreeze tile flooring. The extruded presents a low absorption property with respect to the extruded traditional bricks and then can be proposed as bricks for wall because the gelivity is in agreement with properties required by UNI-EN guideline as reported in Table 4. In addition, the results reported in Tables 3-4 and in Figs. 5-7 suggest that the firing temperature equal to 1100°C can be considered a better cooking temperature with respect to 1000°C, and that the 2% of added slag can be considered the best adding percentage to have mechanical properties in agreement with EN-UNI guidelines, used for the traditional bricks.

The mechanical properties of the extruded and pressed bricks are carried out with different procedures due to the different size of the samples and the different producing procedures. In Table 5 are reported the mechanical properties of the extruded bricks. All reported results are measured and calculated following the procedure of the guideline UNI 8942 about completely transposed in the UNI-EN guidelines. From these results, it is evident that the inclusion of slag does not produce a variation of the mechanical properties. Moreover, it is evident that cannot be added, to this kind of clay, an amount of slag higher than 4% because the mechanical properties are not able to satisfy the properties suggested by UNI-EN guidelines for traditional bricks.

The inclusion of the slag in the mixture does not produce bricks releasing heavy metal. Just a concentration of iron and zinc are detect as reported in Table 6. These concentrations are lower than the concentration established by Italian laws and by the European suggestions. For the slag, the concentration of heavy metals as Cd, Hg, and Sn is reported. For each heavy metal is reported the mean value evaluated on 10 samples of the same stock. After the drying of the samples immersed in water, no efflorescence is observed. After the immersion in the distilled water, the pressed bricks have shown a concentration of heavy metals that is at least the 30% lower than the extruded bricks. This result is justified by the lower porosity and then the lower capability to adsorb water. In other hand the firing of bricks carried out in oxidizing environment produce heavy metal completely oxides and/or linked with silicon than are practically insoluble in distilled water. In fact, the ceramization is commonly used to fix the heavy metal, reducing the environmental risk.

Table 4. Absorption and imbibition properties of waste bricks extruded and pressed fired at 1100°C for 120 min (UNI-EN 99; 176-177-178)

	Extruded Bricks			*Pressed Bricks*		
% of slag	*Absorption of water %*	*Saturation %*	*Imbibition of water %*	*Absorption of water %*	*Saturation %*	*Imbibition of water %*
0	12.67 ± 0.31	0.86 ± 0.22	6.80 ± 0.41	4.94 ± 0.51	0.88 ± 0.41	2.80 ± 0.42
2	11.40 ± 0.32	0.88 ± 0.31	5.48 ± 0.61	9.02 ± 0.62	0.87 ± 0.40	4.28 ± 0.61
4	10.72 ± 0.51	0.74 ± 0.52	9.07 ± 0.60	6.03 ± 0.43	0.87 ± 0.31	3.07 ± 0.60
8	6.66 ± 0.32	0.93 ± 0.31	12.36 ± 0.52	6.60 ± 0.51	0.88 ± 0.51	3.36 ± 0.52

Reducing the firing temperature at 1000 °C, these values are increased of about 20 %. It is due to the increasing of the open porosity

Table 5. Mechanical properties: values obtained from the correlation formulas reported in UNI-EN guidelines

Slag %	*Average Decline (kg_f/cm^2)*	*Average Tensile (kg_f/cm^2)*	*Avarege Compress (kg/cm^2)*	*Cylindrical resistance (kg_f/cm^2)*	*Young modulus E compress (kg_f/cm^2)*	*Young modulus E tensile (kg_f/cm^2)*
0	125.23±0.15	62.61±0.12	336.07±0.22	1513.01±0.13	69926.87±0.15	63933.13±0.16
2	148.53±0.13	74.27±0.18	387.20±0.25	1871.16±0.18	77730.86±0.14	71068.21±0.15
4	144.17±0.18	72.09±0.14	377.74±0.28	1803.03±0.15	76308.29±0.17	69767.58±0.13
8	114.55±0.17	57.28±0.15	312.11±0.23	1354.17±0.14	66169.26±0.13	60497.60±0.19

Table 6. Concentration of heavy metals in distilled water after 10 days of immersion of extruded bricks

Slag %	*Fe, ppm*	*Ni, ppm*	*Pb, ppm*	*Zn, ppm*	*Mn, ppm*	*Cd, Hg, Sn, ppm**
0	0.090 ± 0.003	absent	absent	absent	absent	absents
2	0.097± 0.002	-------	------	0.011 ± 0.001	-------	-------
4	0.325 ± 0.002	-----	-----	0.015 ± 0.003	------	------
8	0.362 ± 0.003	------	------	0.044 ± 0.002	-----	------
Slag	0.121 ± 0.002	0.372 ± 0.003	1.084 ± 0.001	5.163 ± 0.002	0.120 ± 0.003	0.051 ± 0.004

4. Conclusions

The measurement techniques typically applied in the paper to characterize traditional materials are used for the characterization of building materials that include waste. These procedures for the evaluation of some characteristics and parameters of the material are standardized for every material in the UNI EN guidelines.

For the building material including waste the guideline must enriched with further measurement methods to evaluate material acceptability as concerning the safety for the human. In fact, if on one side the addition of cubilot slag to the clay can produce some benefit to the environment because reduces the amount of raw material (clay) to take from mine and produce a ceramic in capsulation of this dangerous slag, on the other side, a not proper inclusion of waste in bricks can provokes the generation of dangerous materials, not well intertied in the clay, with hazard for humans.

The combination of the: (i) measurements for material characterization defined by guideline, and (ii) the physical-chemistry measurements presented in this paper can also be effectively used to characterize the properties of traditional bricks. Therefore, it is suggested to add in the UNI-EN guideline for ceramics building materials, in order to extend them also for waste-materials, the (i) thermal analysis, (ii) X-ray powder diffraction and (iii) dangerous ions releasing.

In this paper the effectiveness of the proposed measurements is evaluated by considering several cooking temperatures, production procedure, percentage of included slag. From the experiments and the performed measurements it is possible to asses that bricks including the 2% of cubilot slag, and fired at 1100°C have mechanical properties in agreement with the present UNI-EN guidelines (can be used instead of traditional materials) and by using the proposed adjunctive measurements it is also possible to assess that these materials are not dangerous for human.

References

Acchar W., Rulff B.M., Segadães A.M., (2009), Effect of the incorporation of a spent catalyst reject from the petroleum industry in clay products, *Applied Clay Science*, **42**, 657-660.

Andreola F., Barbieri L., Lancellotti I., Pozzi P., (2005), Recycling industrial waste in brick manufacture. Part 1 (Spanish), *Materiales de Construccion*, **55**, 5-16.

Bingham P.A., Hand R.J., (2006), Vitrification of toxic wastes: A brief review, *Advances in Applied Ceramics* **105**, 21-31.

Carni D.L., Lamonaca F., Nastro F., Nastro A., Vasile M., (2013), *Diagnostic Methodology for the Primary Coxarthrosis Based on Objective Measures*, Proc. of the 2013 IEEE 7th Int. Conf. on Intelligent Data Acquisition and Advanced Computing Systems, 52–56.

Carter M.G., Barry M.G., Norton C.B., (2007), *Ceramic Materials: Science and Engineering*, Springer-Verlag New York, SUA.

Coronado M., Segadães A.M., Andrés A., (2015), Using mixture design of experiments to assess the environmental impact of clay-based structural ceramics containing foundry wastes, *Journal of Hazardous Materials*, **299**, 529-539.

Couto D.M.S., Silva R.F., Castro F., Lanbrincha J.A., (2001), Attempts of incorporation of metal plating sludges in ceramic products, *Industrial Ceramics*, **21**, 163-168.

Dino G.A., Rossetti P., Biglia G., Sapino M.L., Di Mauro F., Sarkka H., Coulon F., Gomes D., Parejo-Bravo L., Aranda P.Z., Lopez A.L., Lopez J., Garamvolgyi E., Stojanovic S., Pizza A., de la Feld M., (2017), Smart ground project: a new approach to data accessibility and collection for raw materials and secondary raw materials in Europe, *Environmental Engineering and Management Journal*, **16**, 1673-1684.

Eliche-Quesada D., Martínez-García C., Martínez-Cartas M.L., Cotes-Palomino M.T., Pérez-Villarejo L., Cruz-Pérez N., Corpas-Iglesias F.A., (2011), The use of different forms of waste in the manufacture of ceramic bricks, *Applied Clay Science*, **52**, 270-276.

Junkes J.A., Prates P.B., Hotza D., Segadaes A.M., (2012), Combining mineral and clay-based wastes to produce porcelain-like ceramics: An exploratory study, *Applied Clay Science*, **69**, 50-57.

Lamonaca F., Carni D.L. Grimaldi D., (2015), Time coordination of standalone measurement instruments by synchronized triggering, *Acta IMEKO*, **4**, 23–29.

Lamonaca F., Carni D.L., Vasile M., Vitale A., Nastro A., (2017), *Measurement Methods to be Included in UNI-EN Guidelines to Characterize Waste Bricks*, IEEE Int. Conf. on Instrumentation and Measurement Technology, Torino, Italy, 1-5.

Rawlings R.D., Wu J.P., Boccaccini A.R., (2006), Glass-ceramics: Their production from wastes-A Review, *Journal of Materials Science*, **41**, 733-761.

Ribeiro M.J., Tulyaganov D.U., Ferreira J.M., Labrincha J.A., (2002), Recycling of Al-rich industrial sludge in refractory ceramic pressed bodies, *Ceramics International*, **28**, 319-326.

Vasile M., Lamonaca F., Carnì D.L., Nastro A., Sciammarella P., Grimaldi D., Vitale A., (2016), *Measurements to Evaluate the Utilization of Industrial Residue as Part of Mixture to Produce Bricks. 1 Measurements to Optimize the Base Mixture*, Int. Conf. on Thermal Equipment, Renewable Energy and Rural Development, Varna, Bulgaria, 1-6.

Wiemes L., Pawlowsky U., Mymrin V., (2017), Incorporation of industrial wastes as raw materials in brick's formulation, *Journal of Cleaner Production*, **142**, 69-77.

Zhang L., (2013), Production of bricks from waste materials - A review, *Construction and Building Materials*, **47**, 643-655.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2337-2348
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

REAL TIME MONITORING OF HYDROLOGICAL VARIABLES FOR OPERATIVE LANDFILL STABILITY AND PERCOLATION FLUX CONTROL

Marco Mancini[1], Alessandro Ceppi[1*], Diego Curti[2], Giovanni Ravazzani[1], Mouna Feki[1], Luca Cerri[1], Luca Galletti[2], Stefania Meucci[2], Mario Bianchi[3], Carlo Senesi[3], Paolo Cinquetti[3]

[1]*Politecnico di Milano, Piazza L. da Vinci 32, Milano, Italy*
[2]*Modellistica Monitoraggio Idrologico, Via Ariberto 1, Milano, Italy*
[3]*AMIU, Via Dannunzio 27, Genova, Italy*

Abstract

Leachate production and management are recognized as one of the greatest problems associated with environmentally operations for landfills. Variations in leachate quality and quantity are related to rainfall depth and its infiltration processes into landfill.
This work examines important hydrological problems of the Scarpino site (Genoa, northern Italy), a garbage dump which covers the valley of a first order flash creek with a surface of 100 hectares, located in one of the rainiest area of Italy. The landfill is one of the largest in Europe and it operates since the Sixties collecting waste at a rate of about 1000 tons per day. Its present structure shows several horizontal layers of waste deposit separated by covers of compacted soil for a depth ranging from 40 to 70 meters. The landfill surface is subdivided in zones delimited by artificial slopes.
The hydrology of the landfill is analyzed with a real time monitoring system which has been set up in order to manage and control leachate fluxes and landfill slope stability acquiring: (i) meteorological variables, (ii) soil moisture profiles, (iii) leachate levels inside the landfill body, (iv) discharge measurements of surface runoff basin and drained leachate at the landfill outlet, and (v) leachate levels inside the storage tanks. Although it was a preliminary development state, this monitoring system was able to provide the necessary information in order to evaluate the overall landfill hydrological response, particularly focused on the leachate volume production.

Key words: landfill hydrology, leachate, real-time monitoring

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

In most European countries, municipal solid wastes (MSW) are commonly eliminated in landfill disposals (EEA, 2013). In spite of many advantages (e.g. waste-derived power production), the generation of heavily polluted leachates, which present significant variations in both volume and chemical composition, constitutes a major drawback. Variation in leachate composition and quantity is often attributed to water volume, which infiltrates through the waste, and directly related to the natural processes occurring inside the landfill (Kulikowska and Klimiuk, 2008; Rusu et al., 2017).

Landfill leachate is a high polluting liquid with great concentration of organic and inorganic compounds (Vaverková and Adamcová, 2015; Yao, 2017), and its uncontrolled outflow is considered as an environmental crime punishable by the Italian law. Unless returned to the environment in a carefully

* Author to whom all correspondence should be addressed: e-mail: alessandro.ceppi@polimi.it; Phone: +390223996231

controlled manner, this leachate may cause harmful effects on groundwater and surface water surrounding a landfill site, due to its significant concentrations of ammoniacal nitrogen which is toxic to many organisms (Salem et al., 2008). Therefore, a proper understanding of leachate generation is highly recommended for a better management and risk mitigation (Aharoni et al., 2017).

For these reasons leachate dynamic is a key problem in the management of urban wastes in landfills, and in the triggering role of hydrologic processes that can enhance leachate volume production and, mainly, its temporal distribution, have to be carefully considered (Di Bella et al., 2011; Fellner and Brunner, 2010; Reddy et al., 2013). For instance, as rainwater infiltrates and flows through the waste, it is expected to extract, dissolve, and finally wash out a wide range of organic and inorganic constituents (Tatsi and Zouboulis, 2002). In addition to the environmental problem, excess level of percolation fluid in the landfill body may affect landfill slopes stability. Monitoring activities allow to understand this complex system and design the right hydraulic works able to reduce the interaction with meteorological conditions. Usually, landfill monitoring deals with problems related to chemical hazards (Clark and Piskin, 1977) that is still a key issue in scientific literature (Vaverkova and Adamcova, 2015), but in some cases, as the one of the Scarpino landfill, monitoring hydro-meteorological processes is also related to percolation production as well as landfill slope stability (Coduto and Huitric, 1990). In this analysis, monitoring activities are carried out in order to provide assurance that landfill operations do not cause harm to human health neither to the surrounding environment. The study case is the Scarpino landfill, built on the main creek of the upper part of a mountain basin (the Cassinelle River, which flows into the Ligurian Sea), that merges leachate production from municipal solid wastes and hydrological processes typically of a river basin. Hence, this high interaction between leachate production with rainfall infiltration and hill slope drainage leads to design a real-time monitoring system of main hydrological fluxes and leachate level control in the landfill.

In this paper, we describe the structure of the landfill monitoring system, which was settled up between September 2013 and July 2014 as a smart network of a wider operative system (later developed) with the objective to test and verify instrument operations in a such complex area as the Genoa garbage dump.

The first section of the paper deals with the system layout, also discussing the underlying assumptions of the monitoring system, variables to be measured, their spatial representativeness, measurement methods and the installed sensors. The second part presents an early application of the monitoring system at its initial development status, evaluating the hydrological water balance for the Scarpino landfill (distinguishing Scarpino 1 and Scarpino 2 landfill areas), based on the available dataset, discussing the general landfill behaviour and the considered hypothesis too.

2. Study area

Established in 1968, the landfill for municipal solid waste of Scarpino (province of Genoa) is one of the largest landfills in Europe. Currently, the disposed waste in landfill feeds a biogas extraction system, through probes and channel network, which transforms the gas naturally produced by waste into electricity (an average of 54 million kWh per year). In 2006, the landfill has obtained the ISO (International Organization for Standardization) 14001 environmental certification, which highlights the AMIU (an Italian acronym that stands for Multiservice Company and Urban Hygiene) commitment for the implementation of a management system aimed at protecting the environment through the use of best available technologies and the use of transparent business processes.

The landfill covers the bottom valley of the Cassinelle creek with a surface of 0.52 km^2, while the entire catchment area is 1.21 km^2 (Fig. 1). The landfill is located in the mountains upstream of Genoa (Italy). It spans from a height of 350 to 600 meters above the sea level with an average slope of about 30%. This site is considered as one of the rainiest areas of Italy with an annual rainfall of about 1400 mm; A few kilometres from this place, the maximum 24-hour precipitation of about 950 mm was recorded in year 1970: this is still the heaviest storm in Italy of any time.

This location was chosen in the Sixties mainly due to its distance from Genoa city centre, presenting the advantage to be far away from urban settlements. On the other hand, the location on the upper stream of the Casinelle creek enhances the strong interaction with hydrological processes and its connection with slope stability problems. Slope stability, in fact, is mainly affected by the level of leachate inside the landfill that, in this case, it is also strongly correlated with the hydrology of the catchment and, in particular, with rainfall infiltration fluxes. The leachate is drained through a drainage system installed inside the landfill body into two reinforced concrete reservoirs of 14000 m^3 as total volume situated at the landfill outlet. These reservoirs are used to regulate the leachate outflow toward the treatment plant, located at the bottom of valley in the western area of Genoa city, that cannot exceed a given threshold value of about 125 $m^3\ h^{-1}$. During January 2014 the leachate reservoirs were completely filled due to the extended severe rainfall occurred on December 2013. After the analysed period 2013-2014, here described, the landfill is now under enlarging works with new caps both in the upper and bottom areas. The landfill is nowadays divided in two zones (Fig. 2): the oldest part, called Scarpino 1 (0.26 km^2), located in the upper area of the catchment, and the recent part, called Scarpino 2 (0.26 km^2, divided into Lot I and Lot II), and composed by a central part (0.20 km^2) and a bottom one (0.06 km^2).

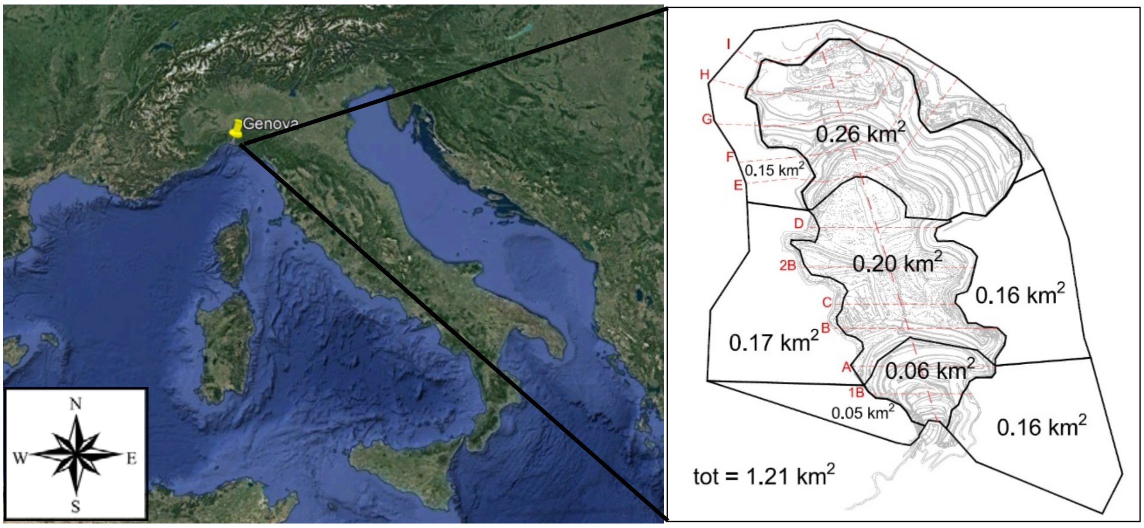


Fig. 1. Geographical area of Scarpino landfill, near Genoa city, North-West of Italy (left). The catchment area of the upper stream of the Cassinelle basin (right) closed at the landfill outlet with the calculation cross sections. The figure shows also the entire hydrological catchment (1.21 km^2), the occupied area by the landfill (0.26 + 0.20 + 0.06 = 0.52 km^2) and the external hill slope areas (0.15 + 0.17 + 0.16 + 0.05 + 0.16 = 0.69 km^2) that partially drains into the landfill

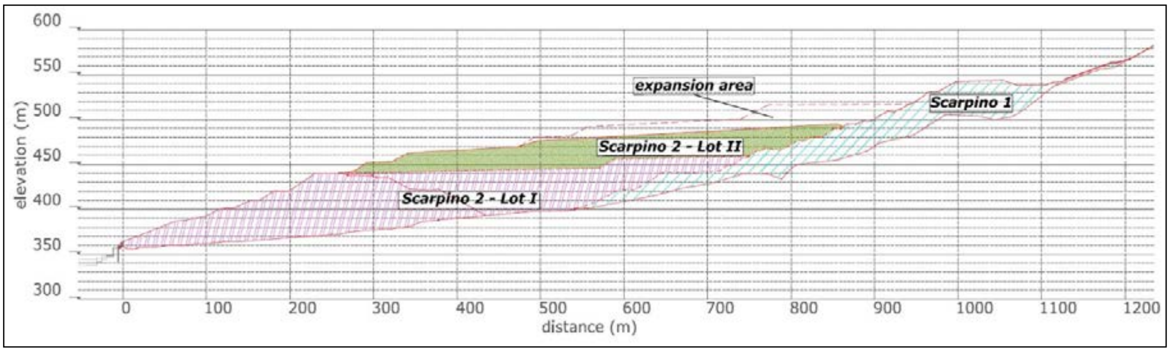


Fig. 2: Longitudinal section of the Scarpino valley with the main layers of the landfill

The Scarpino 1 and the Scarpino 2 bottom sectors present a definitive surface cap to avoid rainfall infiltration according to Italian regulations. The central area of Scarpino 2 shows a surface temporary cap made by silty compacted soil liner with mean saturated hydraulic conductivity of 10^{-7} m s^{-1}. The definitive cap of this part is now under construction, in order to dispose the area for the realization of a planned expansion of the landfill (Scarpino 3).

3. Hydrological monitoring system setup

The current hydrological monitoring system of Scarpino landfill has been designed in 2012, as an update of the previous one, following the recommendations given by the Province of Genoa after the approval of the expansion project of Scarpino 2 in August 2011.

Acquired data instruments are sent to a main server via a specific communication wireless network. This new monitoring system has been planned as a real time system characterized by a continuous and automatically data reading and recording to the monitoring mother stations located at central offices in the upper part of Scarpino landfill. This is the most important difference and upgrade in comparison with the previous monitoring system, which was only constituted by manual and periodical data reading. In fact, from the central station is now possible to: (i) do a remote check of all installed measuring instruments showing any possible instruments failure, (ii) plot all data in real time (Fig. 3), (iii) and display alarms due to threshold value exceeding.

The instrument installation of the current monitoring system took place at different steps. In 2013, an experimental monitoring system (called MO.SE.M.V., an Italian acronym which stands for Experimental Module of Monitoring and Visualization) has been realized to verify the operating working of instruments and their reliability. At the beginning, it was composed by 7 piezometers, 2 soil moisture probes, 1 flowmeter and 1 level sensor. Later in March 2014, following a very intense rainy period, an extension of the MO.SE.M.V. project has been carried out. During this second installation step, 6 piezometers, 2 level sensors and 1 soil moisture probe have been added.

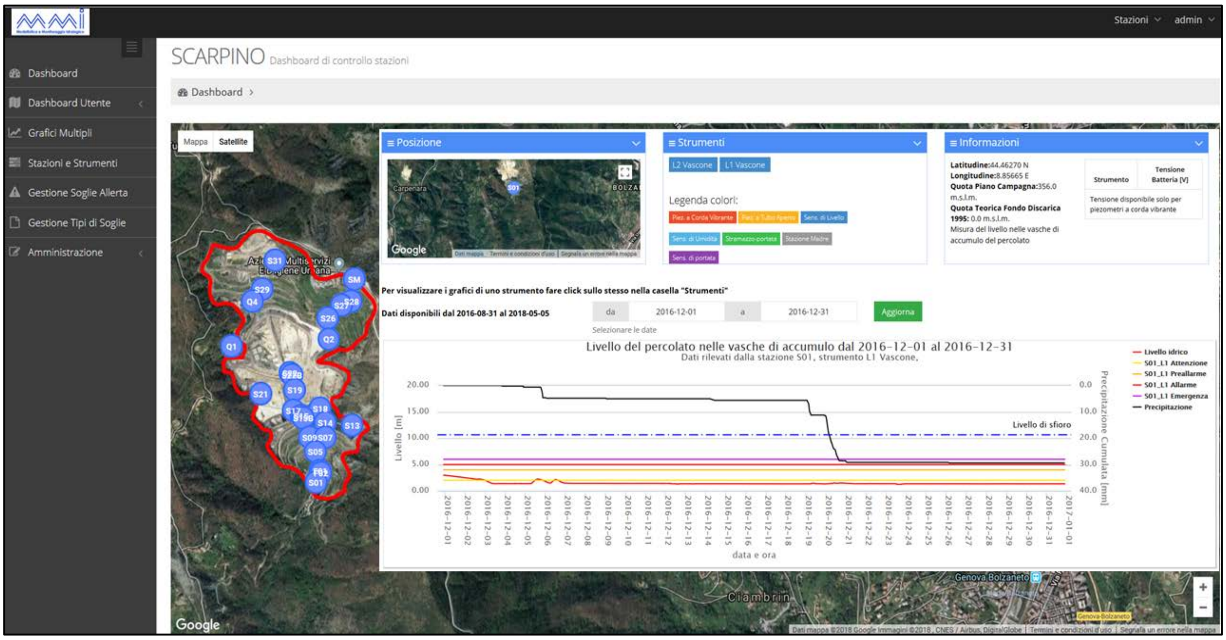


Fig. 3. Dashboard visualization of the monitoring system (left). A zoom, when you click on a station (in this example, S01), of the leachate level data (right) measured by a water level sensor

In total, the hydrological monitoring system, here reported, is composed by nineteen measuring points and two control rooms where data are acquired, as shown in Fig. 4. In particular:

- two weather stations (by Davis in purple rhombus, and by Lastem in pink circle) at the top of the landfill;
- four soil moisture monitoring units by Sentek (U03, U07, U16, U20, respectively located from the bottom part of the landfill to the upper one), equipped with probes for soil water content profile;
- sixteen open pipe piezo-resistive cell (by Adcon Telemetry) for leachate level and pressure measures;
- four vibrating wire piezometers (by Sisgeo) at different depths from the surface (from 25 to 60 m) for leachate pressure measures;
- one flow meter station, the 2150 Area Velocity Flow Module by ISCO (azure dot);
- two piezometers placed in the central area of the landfill along the its perimeter;

two level sensors placed in one of the leachate reservoirs for measuring the storage volume.

A detailed description of the characteristics for each sensor of the MO.SE.M.V. monitoring network of Scarpino landfill is presented in Appendix A at the end of the paper.

4. Landfill hydrological water balance

Leachate flow rate is closely linked to precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through the landfill. The climate has also a great influence on leachate production because it affects the input of precipitation and losses through evaporation. In addition, leachates production depends on the nature of the waste itself, namely its water content and its degree of compaction into the tip. The production is generally greater whenever the waste is less compacted since compaction reduces the filtration rate.

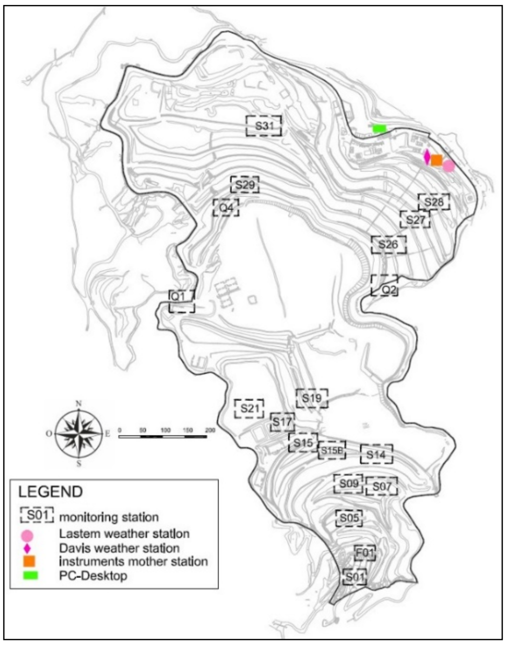


Fig. 4. Map of the installed instruments in the Scarpino landfill

In this section, we show the hydrological water balance of Scarpino 1 and 2 areas, comparing the leachate volume variation obtained by the balance equation and the section discretizing method. The monitoring system plays an important role in the leachate volume evaluation, providing measurements for the estimation of each balance equation terms and for the section discretizing method. In particular, the balance is assessed on a monthly scale in order to take into consideration the complex effects of this peculiar basin on its hydrological response. The reference period considers the time window between September 2013 and June 2014, which is a first test bed period to analyze the landfill monitoring system data and its possible applications even at its early stages of development. A first balance is determined considering the landfill of Scarpino 1 and the surrounding area (hereafter referred to as the "Scarpino 1 hydrological balance"), while a second balance is calculated considering the Scarpino 2 sector (named as "Scarpino 2 hydrological balance").

4.1. The Scarpino 1 area

The oldest area of the Scarpino landfill (called Scarpino 1), which started out as an uncontrolled accumulation zone since the 1960s, does not appear to be hydrologically separated from the external catchment area that surrounds it, and where it forms part of its river basin. Otherwise, Scarpino 1 is separated by a clayey impermeable layer of about 1 m thickness from the more recent area of the landfill (Scarpino 2). These observations, together with the available piezometric measurements, support the hypothesis of the presence of a separate leachate layer in Scarpino 1 as regards Scarpino 2.

4.1.1. The Scarpino 1 hydrological balance

Scarpino 1 is not hydrologically disconnected from its external catchment area; hence, this peculiarity has been evaluated in the balance considering the total contributing area composed by the landfill area and its external part. The hydrological balance is calculated on monthly basis, from September 2013 to June 2014, in order to consider the overall effect of the basin on the hydrological response. Finally, the leachate volume variation, obtained by equations, is compared with the leachate volume variation calculated by the available piezometric measurements.

The Scarpino 1 hydrological balance is modelled according to the Eq. (1):

$$P_T - D - ET - Q_f = \frac{dW_{S_1}}{dt} \qquad (1)$$

where: P_T is the total precipitation; D is the surface runoff; ET is the evapotranspiration; Q_f is the outlet filtration flow; $\frac{dW_{S_1}}{dt}$ is the liquid volume variation in Scarpino 1.

These input to calculate the hydrological balance take into account the entire contributing area, (i.e. inside and outside the boundaries of Scarpino 1, since they have different infiltration characteristics), both for the total precipitation (P_T), the surface runoff (D), the evapotranspiration (ET), and the filtration flow (Q_f) overall collected by the drainage cross line at Scarpino 1 downstream, that conveys the leachate in the covered channel located over the landfill bottom. This culvert runs downstream under the Scarpino 2 accumulation area and it delivers the intercepted leachate towards the two accumulation reservoirs situated at the landfill outlet. The evapotranspiration is calculated based on the Hargreaves equation. The contribution of Scarpino 1 area to the evapotranspiration fluxes is separated from the external catchment area, in order to consider the different land use which characterizes these two zones (discontinuous turf in Scarpino 1, broad-leaved woods and pine forests in the external area of Scarpino 1 catchment); hence an overall weighted parameter of evapotranspiration was estimated.

The filtration flow (Q_f) is evaluated with the Darcy equation, considering an appropriate filtration section into Scarpino 1, deduced from the reconstruction of cross-sections of the landfill volume and piezometric measurements. The interaction between input and output produces a liquid volume variation $\frac{dW_{S_1}}{dt}$ within the domain obtained as a result from the balance equation.

Expliciting each terms, the equation balance (Eq. 1) becomes Eq. (2):

$$\begin{aligned} &P \cdot A_C - (P \cdot A_{S_1} \cdot \varphi_{S_1} + P \cdot A_{S_{1E}} \cdot \varphi_{S_{1E}}) + \\ &-ET \cdot A_C - k \cdot A_f \cdot i = \frac{dW_{S_1}}{dt} \end{aligned} \qquad (2)$$

where: P is the total precipitation per month; A_C is the catchment area given by the surface of Scarpino 1 (A_{S_1}) equal to 0.28 km^2, and the external landfill area ($A_{S_{1E}}$) equal to 0.16 km^2; ϕ_{S_1} is the Scarpino 1 surface runoff coefficient assumed equal to 0.6; $\phi_{S_{1E}}$ is the surface runoff coefficient of its external area, assumed equal to 0.3; k is the saturated permeability of Scarpino 1, estimated equal to $1 \cdot 10^{-5}$ m s^{-1}; A_f is the filtration section area, obtained as an average of the wet areas of sections G and H (Fig. 5) where the calculation domain is subdivided; i is the hydraulic grade line, evaluated as the slope of the reconstructed piezometric surface based on the available measurements.

Particularly in this equation, the term of surface runoff is explicited considering the two contributions of Scarpino 1 area and the external part.

The liquid volume variation, evaluated on a monthly basis, is then compared with the one obtained from the leachate levels observed in Scarpino 1 with a total liquid volume (Eq. 3) valued as:

$$\overline{W_{S_1}} = n \cdot W_{sat} \qquad (3)$$

where: n is the waste porosity, assumed equal to 0.3 (Min et al., 2010), and W_{sat} is the total saturated waste volume.

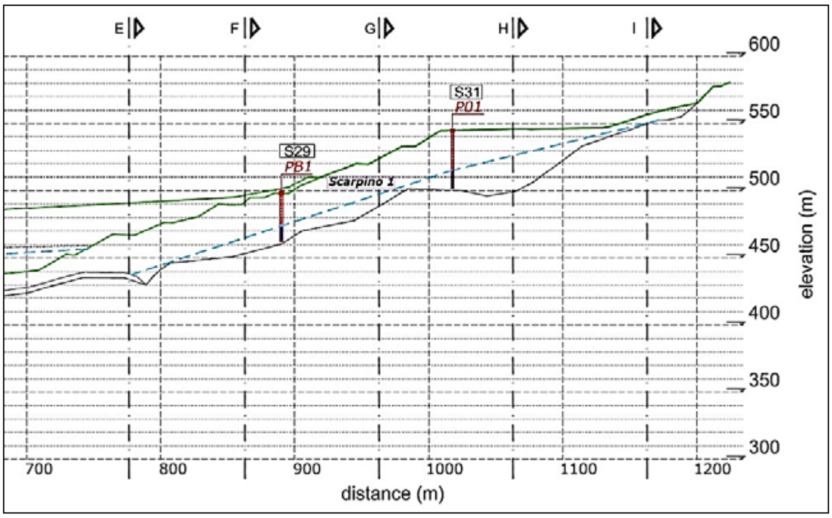


Fig. 5. Longitudinal section with the calculation scheme adopted to evaluate the liquid volume W_{S1} inside Scarpino 1. The landfill surface is shown in green line, the piezometric surface in dashed light blue, while the landfill bottom in black

The saturated waste volume within Scarpino 1 is calculated using the section discretizing method, i.e. dividing the domain into 5 sections (E, F, G, H, I) with around 100 m distance and considering the volume portions across each section. The piezometric surface is reconstructed using the piezometers measurements, in particular the leachate levels measured by the piezometers installed in P01 well of S31 station and in PB1 well of S29 station, assuming that, along the longitudinal development of the landfill, the piezometric line is equal to the one which joins the levels of the two considered piezometers. Therefore, by extending this line upstream and downstream it is possible to obtain the leachate level in the sub-sections.

For each considered day in the hydrological balance analysis, the piezometric level line equation (Eq. 4) is evaluated as:

$$h(x) = ax + b \tag{4}$$

with $a = \frac{h_{P01} - h_{PB1}}{\Delta x}$, where h_{P01} and h_{PB1} are the leachate levels measured, respectively, in P01 and PB1 wells, Δx is equal to the distance between the two wells; b is determined imposing the line crossing P01 or PB1 level.

According to this equation, leachate levels are obtained in sections E, F, G, H and I where the calculation domain is discretized. Finally, in order to calculate the wet area A for each section, relations as $A=f(h)$, which best fit the data, are obtained (Table 1).

The term $\frac{d\overline{W_{S_1}}}{dt}$ is monthly calculated as an algebraic sum of individual daily terms (Eq. 5), which are assumed to be equal to:

$$\frac{d\overline{W_{S_1}}}{dt} = \frac{\overline{W_{S_{1(t+1)}}} - \overline{W_{S_{1t}}}}{\Delta t} \tag{5}$$

Table 1. Relation between leachate level and wet area obtained for the Scarpino 1 discretization sections

SECTION	*A(h) = a*h²+b*h*
E	set to 0 as hypothesis
F	$2.75*h^2 - 0.021*h$
G	$4.51*h^2 - 0.009*h$
H	$5.55*h^2 - 0.017*h$
I	set to 0 as hypothesis

for the generic t day. The monthly overall values obtained by the hydrological balance equation and by the section discretizing method are reported in Table 2.

In order to compare monthly variations in leachate volume within Scarpino 1 obtained by the hydrological balance equation and by the section discretizing method, the Nash index E_{S_1} is calculated according to the Eq. (6):

$$E_{S_1} = 1 - \frac{\sum_i \left(\left(\frac{dW_{S_1}}{dt}\right)_i - \left(\frac{d\overline{W_{S_1}}}{dt}\right)_i \right)^2}{\sum_i \left(\left(\frac{d\overline{W_{S_1}}}{dt}\right)_i - M\left(\frac{d\overline{W_{S_1}}}{dt}\right) \right)^2} \tag{6}$$

where: each term considers the i-month; $M\left(\frac{d\overline{W_{S_1}}}{dt}\right)$ is the average monthly variation in leachate volume obtained by the section discretizing method.

The Nash index, E_{S_1} equal to 0.67 in Scarpino 1 shows a good correlation between the two methods applied to determine monthly variations in leachate volume.

Results in Fig. 6 also show a good match between rainfall and leachate volume variation trends of the two methods; this means a reasonable direct response of Scarpino 1 to precipitation. Indeed, this area, from its origins as an uncontrolled waste accumulation zone, is not hydrologically separated from the one outside the landfill which form part of the water basin it belongs to; moreover, on the landfill surface affected by Scarpino 1, the definitive coverage provided by future development projects has not been realized yet.

In order to better evaluate this relation, the correlation coefficient ρ is calculated for the two methods according to the Eqs. (7-8):

$$\rho_{P\frac{dW_{S_1}}{dt}} = \frac{\sigma_{P\frac{dW_{S_1}}{dt}}}{\sigma_P \sigma_{\frac{dW_{S_1}}{dt}}} \quad (7)$$

$$\rho_{P\frac{d\overline{W_{S_1}}}{dt}} = \frac{\sigma_{P\frac{d\overline{W_{S_1}}}{dt}}}{\sigma_P \sigma_{\frac{d\overline{W_{S_1}}}{dt}}} \quad (8)$$

where: $\sigma_{P\frac{dW_{S_1}}{dt}}$ is the covariance between P and $\frac{dW_{S_1}}{dt}$

σ_P is the standard deviation of P;

$\sigma_{\frac{dW_{S_1}}{dt}}$ is the standard deviation of $\frac{dW_{S_1}}{dt}$

$\sigma_{P\frac{d\overline{W_{S_1}}}{dt}}$ is the covariance between P and $\frac{d\overline{W_{S_1}}}{dt}$

$\sigma_{\frac{d\overline{W_{S_1}}}{dt}}$ is the standard deviation of $\frac{d\overline{W_{S_1}}}{dt}$.

Results show a correlation coefficient equal to 0.88 and 0.73 for the hydrological balance method and for the section discretizing method, respectively, demonstrating the direct correlation between precipitation and leachate volume variation.

Table 2. Monthly values of the Scarpino 1 hydrological balance in cubic meters, and of the liquid volume variation obtained from the hydrological balance and the section discretizing method.

	P_T	$P \cdot A_{S_1} \cdot \phi_{S_1}$	$P \cdot A_{S_{1E}} \cdot \phi_{S_{1E}}$	ET	Q_f	$\frac{dW_{S_1}}{dt}$	$\frac{d\overline{W_{S_1}}}{dt}$
	(m³/month)						
Sep 2013	60626	6463	11725	414	22409	7891	375
Oct 2013	62162	6627	12022	537	25243	5712	19457
Nov 2013	44076	4699	8524	0	26345	-4016	1939
Dec 2013	94341	10057	18245	433	25527	21834	-6389
Jan 2014	148470	15828	28713	1383	30086	43746	53386
Feb 2014	127969	13642	24748	2291	31774	30765	18640
Mar 2014	37622	4011	7276	2079	33955	-16975	-29239
Apr 2014	31476	3356	6087	1488	26864	-12406	-32374
May 2014	26472	2822	5119	1395	24763	-12748	-14233
June 2014	15848	1689	3065	892	22652	-15515	-10014

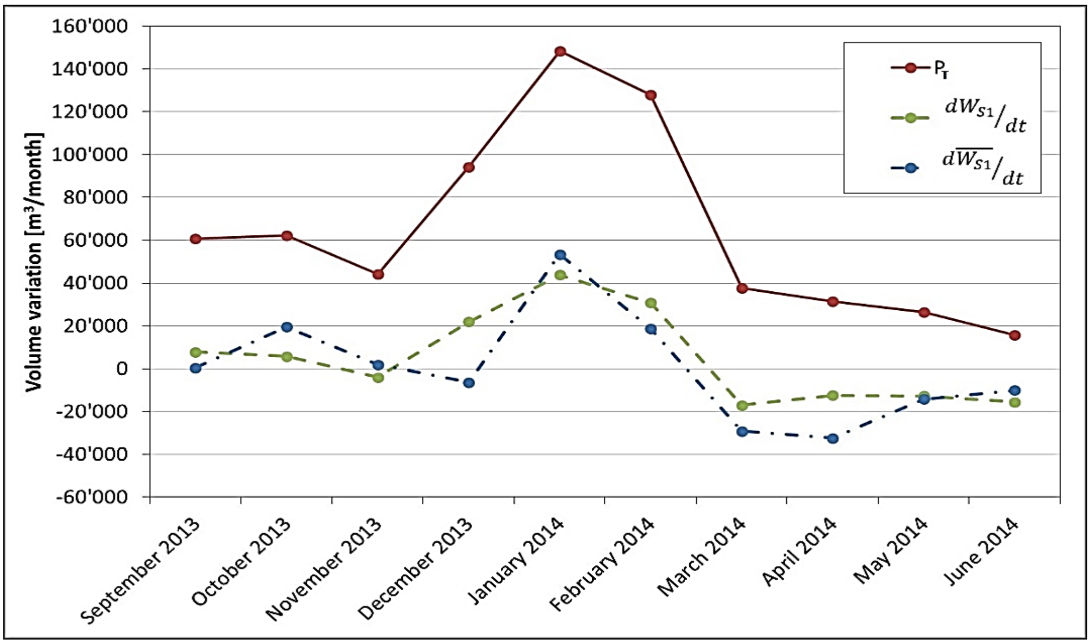


Fig. 6. Trends of the monthly variations in leachate volume within Scarpino 1 obtained by the hydrological balance Equation (green line) and by the section discretizing method (blue line) in comparison with the total precipitation volume (red line)

4.2. The Scarpino 2 area

The most recent area of Scarpino 2 lies above a waterproofing clay layer of about 1 m thickness and impermeable sheets; moreover, it is hydraulically separated from Scarpino 1 through a clay layer of about 1 m thick. Inside Scarpino 2, a further separation, is constituted by a clay layer placed between the Lot I and Lot II. Differently from Scarpino 1, the external catchment of Scarpino 2 does not contribute as input into the control volume. However, a portion of the surface runoff generated in Scarpino 1 and in its external catchment area which is able to infiltrate at the boundary area from Scarpino 1 to Scarpino 2, is considered and calculated in the Scarpino 2 hydrological balance. The drainage system inside the landfill produces an output flow whose flux directly goes into the two leachate accumulation tanks at the downstream end of the landfill.

4.2.1. Scarpino 2 hydrological balance

The Scarpino 2 hydrological balance is evaluated on Lot I, a site of leachate stratum controlled by the piezometric measurements scattered over this area. According to this, in order to estimate the incoming flow, the effect of the Lot II zone reservoir can be considered negligible on the monthly scale balance calculation; therefore, the input into the control volume are represented by the rainfall on the total surface of Lot II (waste accumulation area) of Scarpino 2, the surface runoff portion coming from Scarpino 1, and related external catchment area which infiltrates at the boundary area between Scarpino 1 and Scarpino 2. Considering the different infiltration characteristics between the waste accumulation area (Lot II) compared with the landfill downstream slope (Lot I), the surface runoff is assessed with a different flow coefficient for each of these areas. The two runoff coefficients values are evaluated considering the different compaction grade of the oldest waste stored in the landfill downstream slope (more impermeable) compared to the more recent ones in the accumulation operative area (more permeable). A further input is represented by the surface runoff portion coming from the upstream area of landfill, in particular from Scarpino 1 and its external catchment, which overall infiltrates near the slope discontinuity between Scarpino 1 and Scarpino 2. The infiltration of the surface runoff is separately computed in order to take into account the different contributions of corresponding areas, considering 20% of the surface runoff from Scarpino 1 and a 10% of the surface runoff of the external catchment area obtained by calibration.

As regards the output from the system, evapotranspiration and drained flow inside Scarpino 2 landfill are considered. The evapotranspiration is evaluated taking into account the different land use for the accumulation operative area (bare soil), and the downstream slope (mainly grassy). The output flow from the system is represented by the measurements carried out with an area-velocity sensor installed on the drainage pipe, which discharges into the leachate accumulation tanks. The interaction between input and output generates a liquid volume variation obtained as a result from the balance equation.

The Scarpino 2 hydrological balance is modelled according to the Eq. (9):

$$P_T + Q_D - D - ET - Q_{out} = \frac{dW_{S_2}}{dt} \tag{9}$$

where: Q_D is the contribution deriving from the infiltration of the Scarpino 1 and its external catchment area surface runoff; D is the surface runoff; Q_{out} is the Scarpino 2 drained flow; $\frac{dW_{S_2}}{dt}$ is the Scarpino 2 liquid volume variation.

Expliciting each term, the Eq. (9) becomes Eq. (10):

$$\begin{aligned} & P \cdot A_{S_2} + (\alpha_{S_1} \cdot P \cdot A_{S_1} \cdot \Phi_{S_1} + \alpha_{S_{1E}} \cdot P \cdot A_{S_{1E}} \cdot \Phi_{S_{1E}}) + \\ & -(P \cdot A_{S_{2M}} \cdot \Phi_{S_{2M}} + P \cdot A_{S_{2V}} \cdot \Phi_{S_{2V}}) - ET \cdot A_{S_2} - Q_{out} = \frac{dW_{S_2}}{dt} \end{aligned} \tag{10}$$

where: A_{S_2} is the Scarpino 2 surface equal to 0.30 km^2, α_{S_1} is the contribution coefficient of the Scarpino 1 surface runoff assumed equal to 0.2, $\alpha_{S_{1E}}$ is the contribution coefficient of the Scarpino 1 external catchment area of surface runoff assumed equal to 0.1, $A_{S_{2M}}$ is the Scarpino 2 accumulation area surface equal to 0.21 km^2, $\Phi_{S_{2M}}$ is the surface runoff coefficient of Scarpino 2 accumulation area assumed equal to 0.8, $A_{S_{2V}}$ is the Scarpino 2 downstream slope surface, equal to 0.09 km^2, $\Phi_{S_{2V}}$ is the surface runoff coefficient of Scarpino 2 downstream slope, assumed equal to 0.6, Q_{out} is the output flow measured by the area-velocity sensor installed at the end of the Scarpino 2 drainage system.

Similarly, to the previous Scarpino 1 balance evaluation, from the balance equation it is possible to evaluate the liquid volume variation by discretizing the time on a monthly basis. This variation is compared with the one calculated on the leachate levels measurements available in Scarpino 2.

In particular, the leachate volume $\overline{W_{S_2}}$ of Scarpino 2 is calculated using the same procedure, previously described for Scarpino 1, considering a porosity equal to 0.5. For each section where the domain is discretized (Fig. 7), the leachate level is obtained as a function of the measured levels by the piezometers installed in P13E well of S15 station and in P24A well of S05 station. The reference piezometric surface along the landfill longitudinal section is obtained with two linked lines: the first one joining the piezometers levels in P24A and P13E wells, while the second one joining measured levels in P13E well with the first line of drainage located at the border between Scarpino 1 and Scarpino 2. This piezometric surface is also verified according to the first experimental measurements in P10A-bis, P08C and P06A-bis wells. The leachate levels in the sub-sections are obtained from the intersection of the reconstructed piezometric line with each cross-section.

The equations of the two lines (Eq. 11-12) which the piezometric surface is divided to, are below reported:

$$h_1(x) = a_1 x + b_1 \tag{11}$$

between P24A and P13E

$$h_2(x) = a_2 x + b_2 \tag{12}$$

between P13E and drainage line located at the borders of Scarpino 1 and Scarpino 2

with: $a_1 = \frac{h_{P13E} - h_{P24A}}{\Delta x_1}$, where h_{P13E} and h_{P24A} are the measured leachate levels in P13E and P24A wells respectively, Δx_1 is equal to the distance between the two wells; $a_2 = \frac{h_D - h_{P13E}}{\Delta x_2}$ where h_D is the height of the drainage line located at the border between Scarpino 1 and Scarpino 2, Δx_2 is equal to the distance between P13E well and the drainage line; b_1 and b_2 are obtained imposing the passage of lines in P13E measured levels.

According to these equations, the leachate levels in 1B, A, B, C, 2B, D sections are obtained. Finally, relations as *A=f(h)* that best fit the data are evaluated in order to determine the wet area for each discretizing section (Table 3).

Similarly, to Scarpino 1 domain, the $\frac{d\overline{W_{S_2}}}{dt}$ term is monthly calculated as the algebraic sum of the daily terms (Table 4). The monthly overall values obtained by the hydrological balance equation and by the section discretizing method are reported in Table 4.

The comparison shows good results between the trend of leachate volume variations determined by the hydrological balance compared to those calculated through the section discretizing method (Fig. 8). In order to evaluate this, the Nash index E_{S_2} is calculated according to the Eq. (13):

$$E_{S_2} = 1 - \frac{\sum_i \left(\frac{dW_{S_2}}{dt}_i - \frac{d\overline{W_{S_2}}}{dt}_i \right)^2}{\sum_i \left(\frac{d\overline{W_{S_2}}}{dt}_i - M\left(\frac{d\overline{W_{S_2}}}{dt} \right) \right)^2} \tag{13}$$

where: each term considers the i-month; $M\left(\frac{d\overline{W_{S_2}}}{dt}\right)$ is the average monthly variation in leachate volume obtained by the section discretizing method.

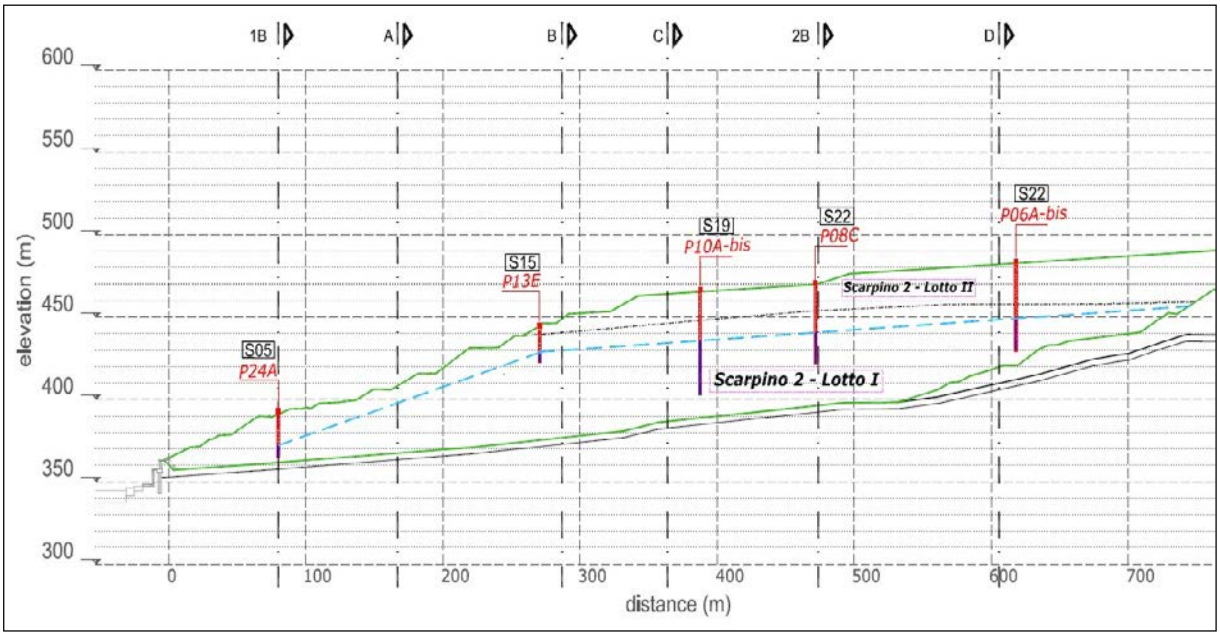


Fig. 7. Longitudinal section with the calculation scheme adopted to evaluate the liquid volume W_{S2} inside Scarpino 2. The landfill surface is shown in green line, the piezometric surface in dashed light blue, while the landfill bottom in black.

Table 3. Relation between leachate level and wet area obtained for the Scarpino 2 discretization sections

SECTION	***A(h) = a*h+b***
1B	set to 0 as hypothesis
A	210*h-2985.0
B	235.53*h-5826.2
C	268.41*h-4467.5
2B	243.27*h-3868.7
D	219.32*h-2284.0

Table 4. Monthly values of the Scarpino 2 hydrological balance terms and of the liquid volume variation obtained from the hydrological balance and from the section discretizing method

	P_T	$P \times A_{S_{2M}} \times \Phi_{S_{2M}}$	$P \cdot A_{S_{2V}} \cdot \Phi_{S_{2V}}$	***ET***	Q_{out}	$\alpha_{S_1} \cdot P \cdot A_{S_1} \cdot \Phi_{S_1}$	$\alpha_{S_{1E}} \cdot P \cdot A_{S_{1E}} \cdot \Phi_{S_{1E}}$	$\frac{dW_{S_2}}{dt}$	$\frac{d\overline{W_{S_2}}}{dt}$
	(m³/month)								
Sep 2013	41154	23422	7126	9	5361	4690	2171	12097	10320
Oct 2013	42197	24015	7307	7	7001	4809	2226	10901	30372
Nov 2013	29919	17028	5181	0	5148	3410	1578	7551	-7724
Dec 2013	64040	36447	11089	0	10094	7298	3378	17086	10490
Jan 2014	100784	57359	17451	0	19551	11485	5317	23225	23368
Feb 2014	86867	49438	15041	60	29128	9899	4582	7680	4063
Mar 2014	25539	14535	4422	183	34281	2910	1347	-23624	-51399
Apr 2014	21367	12160	3700	93	12909	2435	1127	-3933	9313
May 2014	17969	10227	3111	111	60000*	2048	948	-52485	-75136
June 2014	10758	6123	1863	69	4091	1226	567	406	-40400

** Due to an obstruction problem that compromised the area-velocity sensor measures, the May 2014 Q_{out} value is obtained from calibration.*

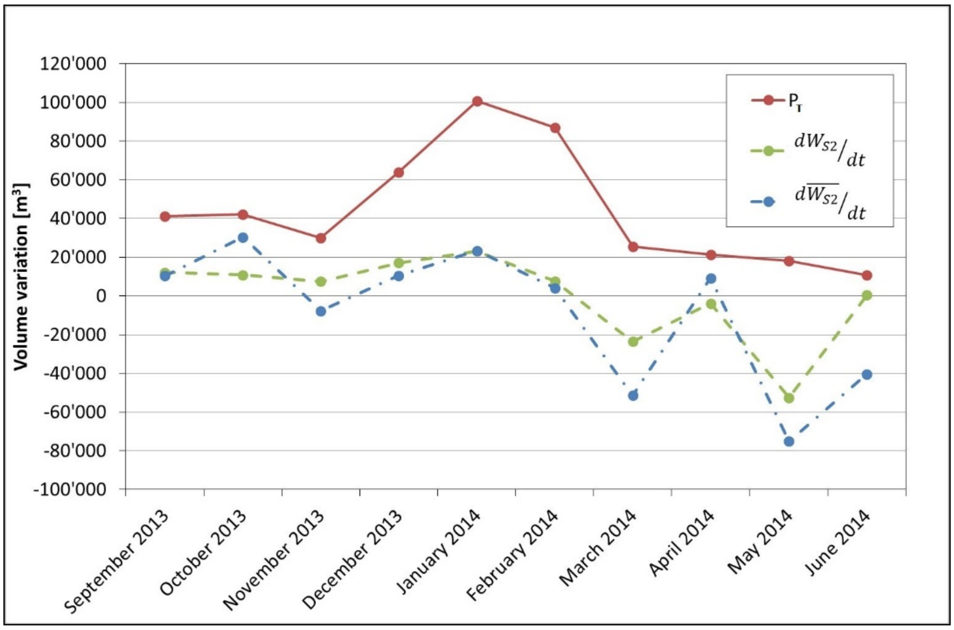


Fig. 8. Trends of the monthly variations in leachate volume within Scarpino 2 obtained by the hydrological balance equation (green line) and by the sections discretizing method (blue line) in comparison with the total rainfall volume (red line)

Also in Scaprino 2, the Nash index E_{S_2} equal to 0.66, shows a good match between the two methods applied to determine monthly variations in leachate volume.

Comparing with Scarpino 1, the Scarpino 2 landfill does not show a significant direct rainy response and it is more affected by the drainage system. The different influence of the precipitation in the leachate production of Scarpino 1 in comparison with Scarpino 2 is also observable in the different level excursion measured in the piezometers of the two landfill areas: more significant in the Scarpino 1 piezometers than in the Scarpino 2 ones.

In order to support this observation, the correlation coefficient ρ is calculated for the two methods according to the Eqs. (14-15):

$$\rho_{P\frac{dW_{S_2}}{dt}} = \frac{\sigma_{P\frac{dW_{S_2}}{dt}}}{\sigma_P \sigma_{\frac{dW_{S_2}}{dt}}} \tag{14}$$

$$\rho_{P\frac{d\overline{W_{S_2}}}{dt}} = \frac{\sigma_{P\frac{d\overline{W_{S_2}}}{dt}}}{\sigma_P \sigma_{\frac{d\overline{W_{S_2}}}{dt}}} \tag{15}$$

where: $\sigma_{P\frac{dW_{S_2}}{dt}}$ is the covariance between P and $\frac{dW_{S_2}}{dt}$

σ_P is the standard deviation of P

$\sigma_{\frac{dW_{S_2}}{dt}}$ is the standard deviation of $\frac{dW_{S_2}}{dt}$

$\sigma_{P\frac{d\overline{W_{S_2}}}{dt}}$ is the covariance between P and $\frac{d\overline{W_{S_2}}}{dt}$

$\sigma_{\frac{d\overline{W_{S_2}}}{dt}}$ is the standard deviation of $\frac{d\overline{W_{S_2}}}{dt}$.

Results show a correlation coefficient equal to 0.54 both for the hydrological balance method and for the section discretizing method, indicating a minor correlation between precipitation and leachate volume variation in comparison with Scarpino 1.

5. Conclusions

Rainfall infiltration processes significantly affect the leachate production with relevant problems on landfill slopes stability, due to the accumulation of leachate into landfill body, and on storage and depuration treatment.

The paper describes the experimental module of a real-time monitoring system for a complex and peculiar landfill in the Italian Apennine mountains near Genoa city. Data series, acquired from the beginning of September 2013 to end of June 2014, a period characterized by many rainfall episodes which also affected the leachate production with a high increase of its level in the landfill body and the saturation of reservoirs system, are reported and discussed in this paper.

The monitoring system is able to provide useful information for the overall hydrological response assessment of the landfill, characterized by complex dynamics, due to the morphological characteristics of the site, the dump heterogeneity, and the plant specificities (subdivision into different accumulation areas, waterproofing system, drainage system, etc.). These preliminary information, available during this first phase of the monitoring system development, are useful to reconstruct a qualitative-quantitative trend of the landfill hydrological balance on a monthly scale. It is possible to evaluate the hydrological response of the landfill, subjected to rainfall events of different intensities with the production of leachate volumes. The Scarpino 1 shows an almost direct response to precipitation, since it is not hydrologically separated from the areas surrounding the landfill which forms part of the catchment basin and it does not have a definitive dump cap yet. On the other hand, the Scarpino 2, in particular the area affected by Lot I, shows a much less significant response to precipitation, relying on a disconnection of the external catchment area, and on a partial waterproofing between the two lots.

Although in its initial development state, this monitoring system shows which measures are necessary in order to evaluate the hydrological water balance of landfill overall, and to assess the main conclusions on landfill hydrological behaviour. Last but not least, the monitoring of hydrological fluxes is an important issue to define the forecasting and control of leachate production.

Appendix

The monitoring system consists of the following components: meteorological measures, soil moisture profiles, groundwater levels, leachate and surface water flow monitor. In particular, three subnets are installed in parallel and in a continuous and remote-controlled way:

- Adcon network, composed by measures of open pipe piezometers and Sentek humidity probes at different depths: the wireless communication with the main board is at 400 MHz of frequency with data recorded every 5 or 30 minutes (according to the instrument);
- Campbell network which conveys the wireless signal of the vibrating wire piezometers at 2.4 GHz of frequency with data recorded every 30 minutes;
- Isco network sends the signal of the flow meter Area-Velocity with data recorded every 5 minutes and transmitted via GSM modem module.

Soil moisture probes provide ground humidity measures of the covering surface of landfill. Each probe is equipped with 3 or 4 sensors, in order to control the moisture level of different layers of the capping.

This groundwater level monitoring system is composed by two kinds of instruments (Adcon and Campbell):

• Adcon: open pipe piezometers equipped with piezo resistive sensor: the precision of the sensor is equal to 0.1% of maximum measured value. Range of measure: 0-3 bar, temperature range: -40°C/+80°C

• Campbell: vibrating wire piezometers with a range of measure of 0-10 bar and a precision of 0.5% and temperature range between 0/+80°C

The leachate flow station is equipped with a pressure-velocity ultrasonic sensor, while the surface water flow stations are equipped with level sensors located upstream of a triangular thin-plate weir.

Each measuring station is equipped with a datalogger and modem which receives the collected data from instruments and sends them to the monitoring central station using radio signals.

Acknowledgements

The authors thank Mr. Giuseppe Milleo from the Politecnico di Milano for his incommensurable support in the preparation and installation phase of this monitoring network.

References

Aharoni I., Siebner H., Dahan O., (2017), Application of vadose-zone monitoring system for real-time characterization of leachate percolation in and under a municipal landfill, *Waste Management*, **67**, 203-213.

Clark T.P., Piskin R., (1977), Chemical Quality and Indicator Parameters for Monitoring Landfill Leachate in lllinois, *Environmental Geology*, **1**, 329-339.

Coduto D., Huitric R., (1990), *Monitoring Landfill Movements Using Precise Instruments*, In: *Geotechnics of Waste Fills - Theory and Practice*, Landva A., Knowles G., (Eds.), ASTM International, West Conshohocken, PA, 1990, 358-370.

Di Bella G., Di Trapani D., Mannina G., Viviani G., (2012), Modelling of perched leachate zone formation in municipal solid waste landfills, *Waste Manageme*nt, **32**, 456–462.

EEA, (2013), Managing Municipal Solid Waste - A Review of Achievements in 32 European Counties, Publications Office of the European Union, On line at: https://www.eea.europa.eu/publications/managing-municipal-solid-waste.

Fellner J., Brunner P.H., (2010), Modelling leachate generation from MSW landfills by a 2-dimensional 2-domain approach, *Waste Management*, **30**, 2084–2095.

Kulikowska D., Klimiuk E., (2008), The effect of landfill age on municipal leachate composition, *Bioresource Technology*, **99**, 5981-5985.

Min J.E., Kim M., Kim J.Y., Park I.S., Park J.W., (2010), Leachate modeling for a municipal solid waste landfill for upper expansion, *KSCE Journal of Civil Engineering*, **14**, 473-480.

Reddy K., Kulkarni H., Srivastava A., Sivakumar Babu, G., (2013), Influence of Spatial Variation of Hydraulic Conductivity of Municipal Solid Waste on Performance of Bioreactor Landfill, *Journal of Geotechnical and Geoenvironmental Engineering*, **139**, 1968-1972.

Rusu L., Suceveanu M., Suteu D., Favier L., Harja M., (2017), Assessment of groundwater and surface water contamination by landfill leachate: a case study in Neamt County, Romania, *Environmental Engineering and Management Journal*, **16**, 633-641.

Salem Y., Hamouri K., Djemaa R., Alois K., (2008), Evaluation of landfill leachate pollution and treatment, *Desalination*, **220**, 108–114.

Tatsi A.A., Zouboulis A.I., (2002), A field investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece), *Advances in Environmental Research*, **6**, 207- 219.

Vaverková M.D., Adamcová D., (2015), Evaluation of landfill leachate pollution: findings from a monitoring study at municipal waste landfill, *Journal of Ecological Engineering*, **16**, 19–32.

Yao P., (2017), Perspectives on technology for landfill leachate treatment, *Arabian Journal of Chemistry*, **10**, 2567-2574

Environmental Engineering and Management Journal October 2018, Vol. 17, No. 10, 2349-2360
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

SYSTEMS FOR RAINWATER HARVESTING AND GREYWATER REUSE AT THE BUILDING SCALE: A MODELLING APPROACH

Sara Simona Cipolla[1*], Margherita Altobelli[1], Marco Maglionico[2]

[1]*CIRI EC- Interdepartmental Centre for Industrial Research in Building and Construction, University of Bologna, Viale del Risorgimento 2, Bologna, 40136, Italy*
[2]*Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Viale del Risorgimento 2, Bologna, 40136, Italy*

Abstract

In the light of water shortages, frequently affecting many regions worldwide, domestic rainwater harvesting, and greywater reuse systems represent an alternative source of water. This study fits this framework providing a hydraulic/hydrological model developed by means of the EPA's Storm Water Management Model. The model has been applied to a case study, which consists of an apartment building located in the city of Bologna and equipped with a hybrid rainwater-greywater recycling system. Cold, hot and recycled water consumptions were monitored for four flats located in the same building. Data analysis shows that the recycled water consumption accounts for a third of the total one, when considering only the supply for toilet flushing, while in garden flats, where recycled water is used also for watering, non-potable water consumption accounts for about 56% of the total. Continuous simulations were performed with 13 years daily rainfall data, and the long-term performance of different system combinations were evaluated. The case study shows a non-potable water saving efficiency of 75.86%, which accounts by 26.71% of the mains water withdrawal. Simulations performed by changing system type demonstrated that, due to the high number of inhabitants and of the great extension of the areas to be irrigated, the contribution of rainwater harvesting is moderate. In fact, non-potable water saving efficiency curves tend to flatten as the values of the tank volume increase. Furthermore, the system demonstrates a good ability in lowering both stomwater runoff and greywater volumes.

Key words: grey water recycling, rain water harvesting, SWMM, water saving

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

1.1. Context of the study

Water scarcity already affects every continent. Provide safe water and sanitation to people, ensuring at the same time a sound management of freshwater ecosystems, the environmental sustainability of solutions, and the economic prosperity of people, is widely recognized as one of the most demanding challenge of the millennium (http://sustainabledevelopment.un.org).

To face this challenge researchers, policy and decision makers cannot neglect that global water consumption rate is double the rate of population increase, which is growing by 83 million people annually (Bitterman et al., 2016). In addition, climate change is nowadays an unquestionable phenomenon that will likely increase precipitation in some places, while reducing it in others, increasing the frequency of both drought and flooding periods. However, population growth and climate change are only two of many factors that influence drinking water availability and then human health, ecosystems and social well-being. Both short-term and long-term water shortages can be addressed only by implementing wise policies that encourages water savings at the agricultural, industrial, and urban levels and through the

* Author to whom all correspondence should be addressed: e-mail: sara.cipolla@unibo.it; Phone: +39 0512093354

simultaneous development and diffusion of technologies that facilitate this transition (WWAP, 2015).

To the maximum extent feasible, building sector should drive this transition by reducing the needs for water and increasing efficiency. At the building scale, several solutions to reduce and reuse water could be promoted, such as for example: the use of high efficiency plumbing fixtures (Maglionico and Stojkov, 2015), the eliminations of leaks (Franchini and Brunone, 2016); the use of rainwater or greywater for on-site activities such as flushing toilets and garden irrigation (Al-Zouby et al., 2017; Campisano and Modica, 2012; De Gisi et al., 2015; Ferraris et al., 2016; Ghisi and Mengotti de Oliveira, 2007; Santos and de Farias, 2017); the capture and use of condensate from HVAC (Heating, Ventilation and Air Conditioning) systems (Dyballa and Hoffman, 2015; Stephan and Stephan, 2017, Zanni et al., 2019).

Although water saving potential differs among buildings type and user habits, several studies agree that water conservation devices such as aerators, high efficiency showerheads, and low flush toilets offer an immediate reduction in water consumption and short payback periods (Ferraris et al., 2016; Mostafavi et al., 2018). Water efficiency efforts can be linked with solutions that, at least, partly replace mains water supply with on-site alternate water sources such as rainwater and grey water.

Rainwater harvesting systems (RHS) are far from being considered new technologies, in fact, the first installations date back to thousands of years ago in many parts of the world (Mays, 2014). RHSs are an alternative to public mains water supply for a variety of non-potable water uses at the home, workplace and garden. Moreover, acting as a source control technology, they reduce the volumes of stormwater discharged into the sewer system (Cipolla et al., 2016; Gambi et al., 2011; Palla et al., 2017). A traditional RHS comprises four basic elements: a collection surface, a collection system, a storage tank (cistern), and a pump system. RHSs are based on a relatively clean natural resource, which can be stored safely for long periods. However, the amount of water harvested depends on rainfall pattern and intensity, consecutive dry weather days, number of inhabitants, roof properties and design return period. Consequently, the water saving efficiency can range from less than 1% to 100% (Domínguez et al., 2017; Ghisi and Mengotti de Oliveira, 2007; Silva et al., 2015). Such a large variation range depends on the fact that this data includes studies carried out in both developing and developed countries, and while for the first ones RHSs efficiency is a matter of economics, for the last ones it is often a human health problem (Imteaz et al., 2012). However, as this study is related to the Italian context, only the possibility to use rainwater to meet non-potable water supply (toilet flushing, garden watering, and car washing) will be investigated.

As the RHS sector expands, there is a need for standardization to protect citizens and to ensure that reliable RHSs are designed, installed and maintained. There are many countries that have technical standards to provide recommendations on the design, installation, testing and maintenance of rainwater harvesting systems supplying non-potable water; e.g. the DIN 1989-1:2002 in Germany, the BS 8515:2009+A1:2013 in UK, the Manual on rainwater Harvesting in Texas (TWDB, 2005), the Rainwater Harvesting and Use Research Report (ABCB, 2016) in Australia, and the UNI/TS 11445 (2012) "Installations for use and collection of rainwater not intended for human consumption - Design, installation and maintenance" in Italy. All of them point up that the reduction of the payback period of the entire system is strongly related to the optimization of the tank volume. This is confirmed by the fact that tank volume optimization is a problem frequently faced by the international scientific community both by authors who aim to satisfy 100% of the non-potable supply (Farreny et al., 2011; Lee et al., 2016; Okoye et al., 2015; Palla et al., 2011; Pelak and Porporato, 2016), and from those who aim to minimize stormwater outflows into the sewers (Campisano and Modica, 2015; Palla et al., 2017). Many authors argue that rainwater harvesting systems are unlikely to pay for themselves during their lifetime (Amos et al., 2018), and this has led some others to investigate others on-site source of water such as for example greywater (De Gisi et al., 2015; Leong et al., 2017b; Oh et al., 2018).

Greywater is the once-used household water, discharged from washing machines, showers, tubs, and bathroom sinks. Greywater makes up the largest proportion of the total wastewater flow from homes and it has a very low nutrient content; it guarantees a daily supply proportional to the inhabitant's consumptions, and it is generated regardless of climate conditions.

Greywater is not recommended for storage because, without treatment, it becomes black-water in less than one day. In terms of daily production, the literature indicates that the greywater volumes can represent from the 50% to the 80% of the total in-house water demand (Failla et al., 2001; Ghisi and Mengotti de Oliveira, 2007; Leong et al., 2017a; Oh et al., 2018). As greywater quality and volume depend significantly on the behaviour of the people using the collection appliances, reliable data providing information on user habits are needed. In Italy, the only data available are those recorded during the monitoring activities carried out within the AQUASAVE project (LIFE 97 ENV/IT/000106). This study measured and analysed the water supply of each plumbing fixture (low consumption) for eight apartments located in the same building in the city of Bologna. Results show that the average consumption of potable water is about 106.35 l/p/d of which 23% is used for toilet flushing; 12% for dishwashers and washing machines, 4% for food preparation, and 28% for other uses. It results in a greywater production of 44.67 l/p/d equal to the 42% of the total drinking water consumption (Failla et al., 2001).

In addition, in this case, as the greywater sector expands, there is a need for standardization to protect public and to ensure that reliable GWSs are designed, installed and maintained. Currently, a very few standards exist that regulate greywater system design, installation and maintenance (e.g. BS 8525-1:2010, BS 8525-2:2011 in UK), and this lack of clear criteria may cause many problems. In fact, from one hand, public authorities provide incentives for the installation of GWSs, from the other the engineers may not have the tools to design the system in the proper way. Moreover, usually grey water systems do not have to be registered or checked on their completion, and this may represent a potential danger for the inhabitants.

Since the systems for the recovery of greywater (GRSs) are often combined with RHSs, giving rise to the so-called "hybrid rainwater-greywater systems" (Leong et al., 2017a), the regulatory gap of the former influences the latter. Hybrid greywater-rainwater systems (HGRSs) are spreading rapidly, and there is a need of tools to support engineers during their design.

The success of HGRSs is determined by the fact that they can achieve a higher water saving potential, with a payback period shorter than those of greywater or rainwater systems (Leong et al., 2017a). Hybrid systems furthermore, offer the combined benefits of rainwater and greywater respectively: managing rainwater locally (Leong et al., 2017b), mitigating urban flooding (Palla et al., 2017), reducing the volume of wastewater, and concentrating the pollution load (Penn et al., 2013). Moreover, HGRSs are generally less sensitive than greywater systems to the variation in the number of inhabitants, and less sensitive than rainwater systems to precipitation changes because the continuous supply of greywater makes it possible to compensate for the seasonal variation in rainfall. Considering all this, it is evident that the achievement of all these benefits is intrinsically connected to a correct design of the overall system.

Based on that, this paper presents a simplified hydrological/hydraulic numerical model, developed by means of EPA's SWMM software (Rossman and Huber, 2016). The model can be used by designers and local authorities to optimise the storage tank volume of a hybrid rainwater-greywater decentralised system, by considering both the water saving efficiency and the stormwater runoff reduction they want achieve (Zanni et al., 2019). To support the investigation the model has been used to simulate the long-term behaviour of a hybrid rainwater-greywater systems installed in 2014 in a building located in the city of Bologna (Italy). Thus this paper aims to: (i) present a simplified model able to simulate the long term hydrological/hydraulic behaviour of a hybrid rainwater-greywater systems; (ii) analyse the overall water consumption (drinking and non-potable water) of 4 flats located in the building proposed as case study; (iii) use the previously presented model to simulate the long term behaviour of a HGRS really present in the building; and finally iv) to provide evidences of the benefits that could be obtained by using a numerical model during the design of the hybrid rainwater-greywater system.

1.2. Hybrid rainwater-greywater systems: design parameters

Hybrid systems contain both a greywater recycling and a rainwater harvesting systems. They can either be operated as separate independent systems or be combined into a single supply source (Fig. 1). Greywater and rainwater may be mixed within cistern or within the distribution network.

As previously said, the cistern is the most difficult element to size in an RHS or in a HGRS. To find its optimum storage capacity the following factors should be taken into consideration: i) the amount and the distribution of rainfall; ii) the type (impervious, green roofs, gravel roof, etc.) and the size of the collection surface; iii) the type and number of intended applications; iv) the volume and usage pattern of these applications.

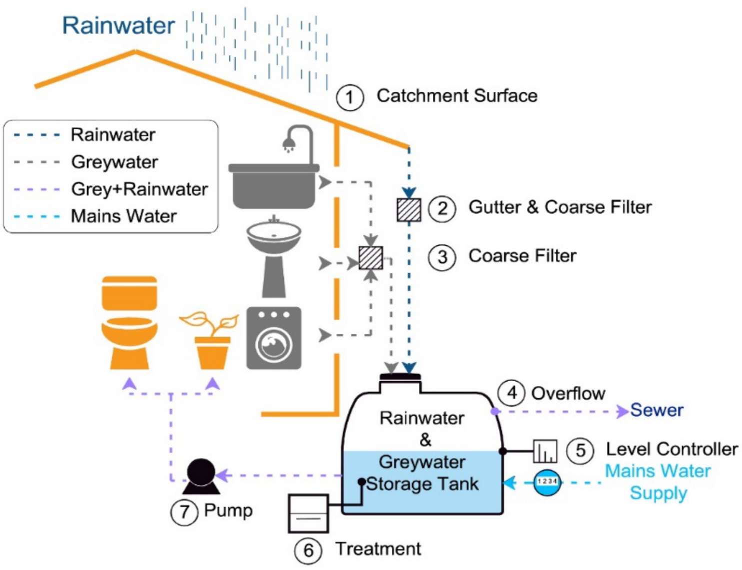


Fig. 1. Scheme of a hybrid system in which the rainwater and the greywater are combined into a single supply source

When considering a hybrid system, several further factors should be considered, including: iv) discharged pattern for all the applications (showers, baths, wash and hand basins and washing machines) connected for reuse; and v) peak capacity treatment rate. As this study is focused on a single supply source configuration, with greywater and rainwater integrated within the cistern, the combined behaviour and the compatibility of the two systems will be investigated and considered. In addition, as the study focuses mostly on the analysis of quantitative aspects rather than qualitative, all the aspects connected with water quality will be neglected.

2. Material and methods

2.1. Case study analysis

The case study is an apartment building built in 2014 and located in the western suburbs of the city of Bologna (Italy). It consists of 7 floors, and it includes 22 apartments of different sizes, ranging from studios (50 m^2) to 4 bedrooms flats (170 m^2). The building has a garden of 892 m^2 of which the 87% (781 m^2) is owned by 3 ground floor flats, while the remaining is a shared garden (Fig. 2).

The building is equipped with water-saving plumbing fixtures and a hybrid system for collecting and recovering rainwater and greywater. Treated rainwater and greywater are integrated in the same cistern that has a capacity of 16 m^3. Systems overflows are discharged into the public combined sewer system (Cipolla and Maglionico, 2014). Cold, hot and recycled water consumptions were measured from 01/12/2014 to 01/04/2016 only for 4 of the total 22 apartments because the others were still uninhabited. Table 1 reports the main characteristics of the building.

2.2. Monitoring activity

The monitoring activity was carried out from 18/12/2014 to 19/02/2016 for 4 flats. Two of them were empty, but the facilty manager irrigated their gardens with non-potable water when were for sale. The others two were inhabited by a family (4 AE), and a single person (1 AE). Cold and hot drinking water, and non-potable water consumptions were measured for each flat. All appartments are equipped with low-consumption plumbing fixture. Table 2 shows the characteristics of the four flats monitored.

Fig. 2. Aerial view of the city of Bologna (left) and of the case study building (right)

Table 1. Characteristics of the building

Variable	***Value***	***System Unit***
City	Bologna (Italy)	[-]
System Type	Hybrid rainwater-greywater	[-]
Area of the roof - impervious	400	[m^2]
Area of the garden	892	[m^2]
Non-potable water cistern	16	[m^3]
Irrigation months	Apr.-Sept.	[-]

Table 2. Characteristics of the four flats monitored

Flat	A1	A2	A3	A4
Size [m^2]	51	103	85	92
Garden size [m^2]	-	243	257	281
Floor	3rd	ground	ground	ground
Inhabitants	1 adult	2 adults and 3 children	-	-

2.3. Hydrologic hydraulic modelling

The hydraulic/hydrological model has been undertaken by means of EPA's SWMM (Storm Water Management Model) software, version 5.1.012 (Rossman and Huber, 2016), as done by other authors (see (Palla et al., 2011) for an overview). Fig. 3 shows each element of the model, which consist of: a subcathment (A), a rain gauge (B), a pipe (C), two storage units (D and E), two pumps (F and G), a weir (I), and two outfalls (L and H).

Greywater has been modelled as a positive constant daily inflow to the tank (D), while the non-potable water demand to meet toilet flushing and garden irrigation supply has been modelled as a negative inflow to the tank (D), and a pump system respectively (G). Water can continue to enter into the tank, raising the water level until it reached the overflow pipe, at that level the water will be discharged into the sewer system though the overflow (I and L). A SWMM rule controls the water level within the tank (A), it allows water to enter from the main water supply (E and F) when the water level drops below the minimum required level.

This model uses the "subcatchment" element (A) to model the roof (rainfall catchments area). A subcatchment is a hydrologic unit whose parameters influence the runoff and thus the storage tank inflow (Rossman, 2015). Subcatchment has modelled as impervious catchments in which the total surface area is the footprint of the roof. Its main parameters (depression depth, N Manning, and% Zero-Imperv) have been assigned in agreement with those proposed by Cipolla et al. (2016b) and are summarized in Table 3. A predesigned Low Impact Development (LID) module can be applied to the roof catchment to model green technologies such as green roofs, pervious pavements, biofilters etc. (Cipolla et al., 2016b; Gambi et al., 2011). Subcatchment runoff is the inflow of the storage unit (D), which represents the cistern of the system. This model considers the indoor water demand (toilette flushing) constant for each time step. This assumption has been considered adequate by other studies (Palla et al., 2011). Regarding outdoor non-potable water demand (i.e. garden irrigation), it usually exhibits a seasonal variation that needs to be parameterised. Irrigation timing and volumes have been determined based on rules depending on the month of the year and the size of the garden. The outputs from this model are the predicted yield and overflow over the period simulated for the specified roof area, rainwater demand, and tank storage volume. Finally, continuous simulations are performed over 13-years at 1-day time interval; as for the initial condition the tank is assumed empty as generally recommended (Palla et al., 2017).

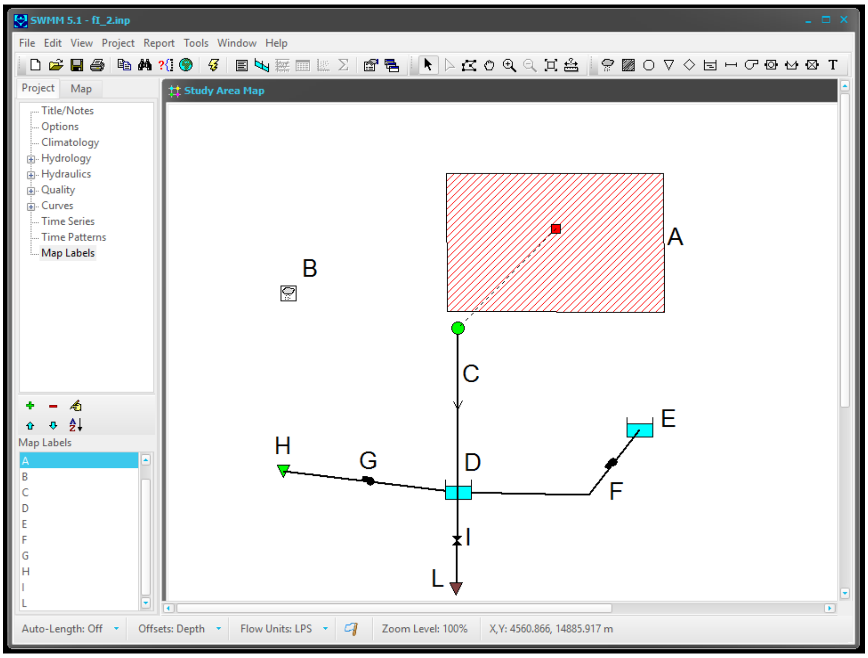


Fig. 3. Graphical representation of the SWMM model. The elements shown in the figure are: a subcathment (A), a rain gauge (B), a pipe (C), two storage units (D and E), two pumps (F and G), a weir (I), and two outfalls (L and H)

Table 3. Parameters assigned to the subcatchment in the SWMM model

SWMM Parameter	*Values*	*System Unit*
Depression depth	1	[mm]
N-Manning	0.011	[s/m$^{1/3}$]
% Zero-Imperv	5	[%]

2.4. Performance analysis

Two indexes, evaluated with respect of the entire simulation period, provide the performances of different system configurations. The first is the non-potable water-saving efficiency, *E* (Eq. 1), in which the non-potable water (rainwater + greywater) supply Y_t [m^3] is compared with the non-potable water demand D_t [m^3] both in each time step *t*, and *T* is the total number of time steps in the period of simulation (Andrade et al., 2017).

$$E = \frac{\sum_{t=1}^{T} Y_t}{\sum_{t=1}^{T} D_t} \quad (1)$$

The second index is the wastewater (rainwater + greywater) overflow ratio, *O* (Eq. 2), in which the wastewater exceeding the tank capacity O_t [m^3] is compared with system inflow Q_t [m^3] both in each time step *t*, and *T* is the total number of time steps in the period of simulation.

$$O = \frac{\sum_{t=1}^{T} O_t}{\sum_{t=1}^{T} Q_t} \quad (2)$$

2.5. Model set-up

Despite the model can be used to simulate any system configuration, rainfall pattern, and water-end use, it has been used to simulate the long-term behaviour of the hybrid system located in the case study.

2.5.1. Weather data

Simulations were performed using daily rainfall and air temperature data for a 13-year period, i.e., 1st January 2004 – 31st December 2016. Data were sourced from the historical daily climate records provided by the ARPAE - Regional Agency for Prevention, Environment and Energy (http://www.arpae.it/dettaglio_generale.asp?id=3284 &idlivello=1625). Rainfall data was used as input into the rain gauge (Fig. 4).

The average rainfall depth, obtained for the whole period of 13 years, is 804.5 mm/year, while the minimum and maximum rainfall depth recorded were 464.2 mm in 2011 and 1083.2 mm in 2004 respectively. It can be observed that rainfall is mainly concentrated in fall and winter (October- March), while summers (June - September) are quite dry.

2.5.2. Water end-uses

The total water consumption was assumed equal to 106.35 l/p/d as indicate by Failla et al. (2001). By considering a maximum capacity of 66 inhabitants (one inhabitant for each bedroom with a surface of less than 14.0 m^2, and two for those with upper surfaces), and a garden area 892 m^2, the water consumption of non-potable water for WC flushing ($Cons_{WC}$) and irrigation ($Cons_{Garden}$) were estimated by using Eq. (3) and Eq. (4). Others non-potable water end-uses were not considered.

$$Cons_{WC} = Cons_{Tot} \times Perc_{WC} \times I\,[\, l/d\,] \quad (3)$$

where: $Cons_{Tot}$ is the total water consumption, assumed equal to 106.35 l/p/d as indicate by Failla et al. (2001) and $Perc_{WC}$ is the percentage of the potable water demand consumed for toilet flushing, 23% as suggested by Failla et al. (2001).

$$Cons_{Garden} = Vol_G \times A_G \times m\,[\, l/d\,] \quad (4)$$

where: Vol_G is the average irrigation demand (4 l/m^2/day), A_G is the size of the garden (m^2), and *m* is equal to 1 from April to September and 0 in the other months.

$Cons_{WC}$ has been simulated as negative inflow to the cistern (element D in Fig. 5) while $Cons_{Garden}$ represents the flow rate attributed to the irrigation pump (element G in Fig. 5).

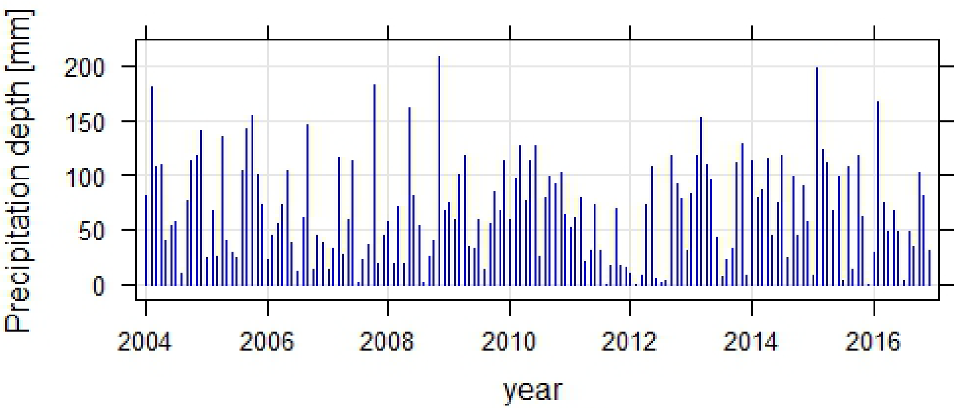


Fig. 4. Precipitation depth from 01/01/2004 to 31/12/2016, rainfall depth is shown on a month base

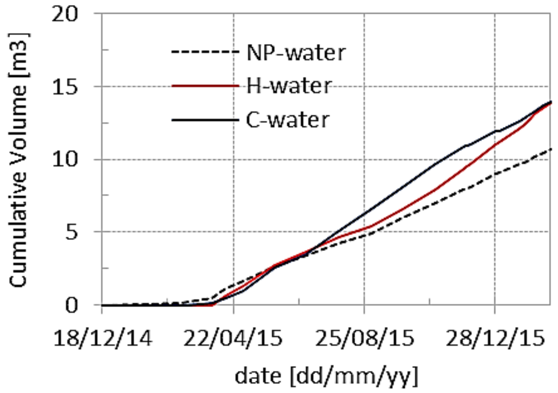


Fig. 5. Hot, cold and non-potable water consumption for flat A1

2.5.3. Greywater production

The volume of greywater produced day by day in the building was determined according with the plumbing fixtures really connected to the existing hybrid plant (showers, lavatories, and washing machines) and with the values proposed by Failla et al. (2001). Thus, the greywater inflow ($Inflow_{GW}$) to the cistern was estimated by using Eq. (5).

$$Inflow_{GW} = Cons_{Tot} \times Perc_{GW} \times I\,[\,{}^{l}\!/_{d}\,] \quad (5)$$

$Perc_{GW}$ is the percentage of the potable water demand consumed by plumbing fixtures that however generate greywater, equal to 42% as suggested by Failla et al. (2001). $Cons_{WC}$ has been simulated as a positive inflow to the cistern (element D in Fig. 2).

3. Results and discussion

3.1. Data analysis

Flat A1 is a one bedroom flat of 51 m^2 located on the third floor of the building, with no garden. It has been inhabited by a female person (40 years old) since April 1st 2015. Recycled water is used only for toilet flushing. Fig. 6 shows the water consumptions during the monitoring activity (354 days). The average total daily consumption is of 108.76 l/p/d, of which 72.26% is potable water subdivided in hot (36.0% or 39.43 l/p/d) and cold (36.26% or 39.1 l/p/d) water. The remaining 27.2% (30.17 l/p/d) is non potable water used for toilet flushing. Non-potable water consumption remains almost constant throughout the year, while in summer there is a reduction in the consumption of hot water in favour of the cold one, and vice-versa in winter.

Flat A2 is a 103 m^2 flat located at the ground floor. It consists of a living room, a kitchen, a double bedroom, two single bedrooms and two bathrooms, one with the shower and the other with a bathtub. This appartment has a private garden of 243 m^2. It has been inhabited since December 18, 2014 by a family of 5 people including a new-born and two childrens. Non-potable water is used for both toilet flushing and garden watering (Apr. - Sept). Fig. 6 shows the cold, hot and non-potable water consumptions during the monitoring activity (428 days). By considering 4 equivalent inhabitants, the average hot and cold water consumption results in 31.15 l/p/d and 28.06 l/p/d respectively. The consumption of hot water is higher than the cold one during the entire monitoring period, both consumptions show a constant trend. The consumption of non-drinking water shows a trend which is completely different from those observed in flat the warmest months (April-September) summer.

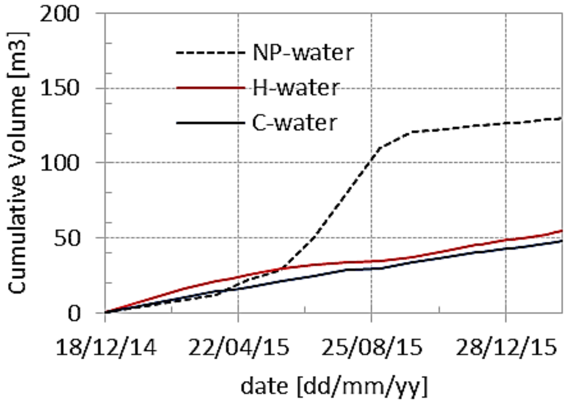


Fig. 6. Hot, cold and non-potable water consumption for flat A2

Table 4 shows the measured recycled water comsuntion (toilet flushing + irrigation) of apartment (A2), and the main weather parameters sourced from ARPAE database. As non-potable water has been measured on a aggregate basis (toilet flushing + irrigation), it was necessary to identify a procedure that would make it possible to split such volumes. The average non-potable water consumption recorded in cold months (Oct.- March) was 21.44 l/p/d (standard deviation 6.24). In order to estimate the volumes of non-potable water used for garden watering, this value have been subtracted from the measured data. Values estimated with this procedure have been highlighted in bold in Table 3.

Irrigation volume ranges between 0.94 (May) and 4.06 l/m^2/d (August). Moreover, it seems that there is no direct correlation between the monthly precipitation depth and volumes of water used for irrigation.

Flat A3 and flat A4 are an 85 and a 92 m^2 ground floor flats with 257 m^2 and 281 m^2 garden surfaces respectively. During the monitoring period, the apartments were for sale, but the building's owner irrigated the lawn. This allows measuring the volumes of non-potable water, used exclusively for irrigation purposes (Fig. 7 and Fig. 8).

Table 5 shows the average monthly consumption of non-drinking water for garden watering, it ranges from a minimum value of 0.5 l/m^2/d (A4, March 2015) to a maximum of 8.0 l/m^2/d (A4, August 2015), with an average value of 4.0 and 3.5 l/m^2/d for flats A3 and A4 respectively.

Table 4. Non-potable water consumption for the flat A2, total monthly rainfall, maximum and minimum average monthly air temperature

Date	***WC flushing***	***Irrigation***	***Rainfall***	***Temperature max***	***Temperature min***
	l/p/d	***[l/m²/d]***	***[mm]***	***[°C]***	***[°C]***
Jan-15	30.74	-	7.8	17.2	1.3
Feb-15	30.74	-	197.2	14	1.8
Mar-15	21.50	-	122.4	23.4	7
Apr-15*	**21.44**	**1.39**	110.0	26.6	7.8
May-15*	**21.44**	**0.94**	67.6	29.1	12.8
Jun-15*	**21.44**	**2.86**	98.2	32.8	19.3
Jul-15*	**21.44**	**3.96**	2.6	37.5	22
Aug-15*	**21.44**	**4.06**	107.0	35.9	20.9
Sep-15*	**21.44**	**1.42**	13.6	34.1	14.7
Oct-15	19.60	-	117.2	25.2	10.9
Nov-15	17.08	-	62.8	21.9	3.8
Dic-15	13.71	-	0.0	13.5	3
Jan-16	17.28	-	28.4	18.4	0.6
Feb-16	20.83	-	166.6	16.2	5.7

** is used to indicate the months in which the garden has been watered*

Table 5. Non-potable water consumption for the flat A3 and A4

Date	**A3** *[l/m²/d]*	**A4** *[l/m²/d]*
Jan-15	-	-
Feb-15	-	-
Mar-15	-	2.4
Apr-15	2.6	0.5
May-15	1.8	2.0
Jun-15	3.5	3.8
Jul-15	4.7	3.2
Aug-15	5.2	4.5
Sep-15	6.0	8.0
Oct-15	-	-
Nov-15	-	-
Dic-15	-	-
Jan-16	-	-
Feb-16	-	-

The values measured in these apartments are slightly higher than those that have measured in the apartment inhabited by the family, this is certainly due to the greater sensitivity of private citizens towards their consumption.

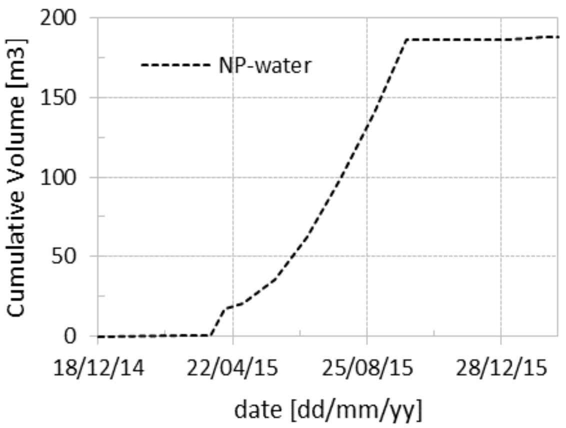


Fig. 7. Non-potable water consumption for flat A3

To sum up, the monitoring campaign allowed to measure the hot, cold and recycled water consumption for 2 flats (A1 and A2), and the recycled water used for garden watering for the others two flats (A3 and A4).

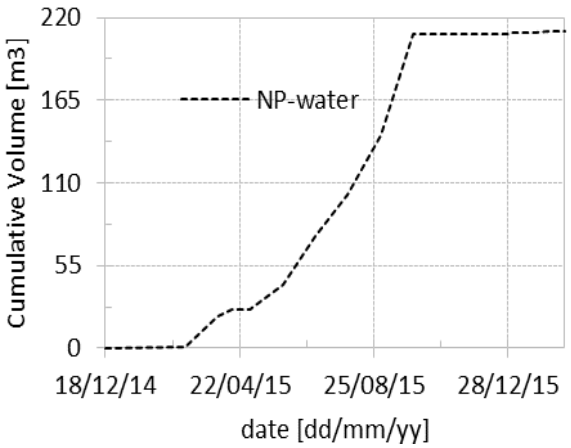


Fig. 8. Non-potable water consumption for flat A4

The results obtained are comparable with those published by Failla et al. (2001) and related to the Italian context, but also with others (Antonopoulou et al., 2013; Ghisi and Mengotti de Oliveira, 2007; Marinoski et al., 2018).

Due to the reduced number of measured data (low number of families, short monitoring period, etc), they were not used for modelling, but to support the choice of using results already published by other authors.

3.2. Simulation results

Thirteen years of daily rainfall data were used to perform the simulations. During that time, there were 1393 rainfall days, of which 341, 59 and 5 with a daily precipitation above 10, 30 and 60 mm respectively. September 09, 2005 was the rainiest day of the dataset (109.4 mm).

Table 6 reports the total number of wet days for each year and the number of consecutive dry weather days. The longest dry weather period was recorded in 2012 (60 days), while the average number of consecutive days without precipitation ranges between 2.57 (2010) and 4.18 (2017). By considering the whole data set, the number of consecutive days without precipitation longer than 10, 20 and 30 days was 97, 28 and 9 respectively.

As demonstrated by some studies (Silva et al., 2015), consecutive dry weather days strongly influences the behaviour of rainwater harvesting systems. The longer the dry weather periods, the bigger the volume of the storage tank. Since the modelled system is hybrid, the daily supply of graywater should be able to compensate for the high number of consecutive dry weather days.

Simulation results show that the HRGS, with a cistern of 16 m^3, assures an average non-potable water saving efficiency (*E*) of 75.86%. It means that only the 24.14% of non-potable demand should be supplied from the mains. Considering the building as a whole, HRGS reduces the drinking water withdrawal by around 16%.

The other performance indicator, *O*, assumes an average value of 26.71%, demonstrating the effectiveness of the system in reducing the volume of wastewater discharged by the building into the sewers. In fact, it expresses the capability of the system to reduce the amount of wastewater (graywater + rainwater) discharged into the drainage system. The lower *O* the better the impact of the HGRS on the environment.

The model was then used to estimate the potential for water savings for different cistern capacities. Fig. 9 shows the results in terms of both *E* and *O* index. *E* increases with the tank capacity, ranging from 72.46% with 4 m^3 to 76.38% with 20 m^3, the general trend of the curve highlights a linear increase of *E* as the storage fraction increases. Fig.9 shows how, despite the tank volume increases by 16m^3 (from 4 to 20 m^3), efficiency increases only by 3.92%.

Table 6. Precipitation statistics in Bologna between 2004 and 2016

Year	***Number of wet day***	***Consecutive dry weather day***		
		Avg	***Max***	***St.dev***
2004	116	3.087	37	23.48
2005	109	3.278	31	20.44
2006	89	4	24	26.86
2007	86	4.188	28	30.01
2008	103	3.559	29	28.84
2009	124	2.959	25	18.21
2010	141	2.571	21	8.16
2011	89	4.011	39	37.09
2012	87	4.174	60	80.14
2013	122	2.992	31	15.87
2014	131	2.754	21	12.24
2015	85	3.643	33	27.43
2016	111	3.218	17	12.96

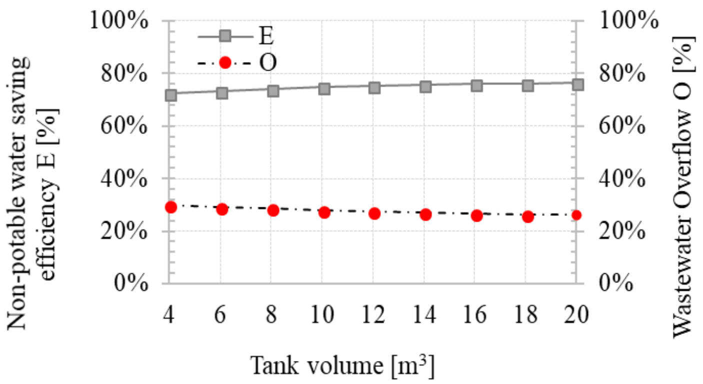


Fig. 9. Non-potable water saving efficiency -*E* and Overflow-*O* for different values of tank storage volume

This result is due to the contribution of two unfavorable factors: 1) the small size of the collection surface; and 2) the large extent of the areas to be irrigated during the summer. In summer, in order to supply only the non-potable demand for garden watering, a volume of 3368 l/d would be needed. It became clear that, the emptying rate, due to irrigation demand, is greater than the capacity of the self-loading system. Simulation results confirm the impact of HRGSs on wastewater mitigation: *O* values, evaluated for the 13 years rainfall, are respectively equal to 30.04% and 26.16% for 4 m^3 and 20 m^3 storage volumes. *O* does not decrease below such values because in winter, the daily production of gray water is higher than non-potable demand and therefore greywater spills are inevitable. To sum up, due to the building characteristics (small size of the roof), and the high non-potable demand in summer periods, simulations revealed a reduced water saving benefits as the tank size grows.

By considering the same building conditions, the model allows evaluating the hydraulic behaviour of other systems type such as for example a rainwater harvesting system or a greywater reusing system.

Thus, the model has been used to simulate the case study building, but under the hypothesis of replacing the hybrid system with a rainwater harvesting system. Results of simulations show (Fig. 10) that the non-potable water saving efficiency increases non-linearly as the storage volume increases. The *E* curve tends to flatten as the values of tank volume increase. This phenomena, already observed in other studies focussed on rainwater harvesting (Campisano and Lupia, 2017), reveals a reducing water saving benefit as the cistern size grows.

Fig. 10 reports two O curves indicated respectively with *O* and *O**. The first one has been obtained by using Eq. (2), and thus considering both greywater and rainwater inflows. On the contrary, *O** has been calculated by neglecting the greywater inflow. This allow *O** to provide information on stormwater runoff attenuation as the volume of the tank increases. The general trend of both curves shows the typical non-linear decrease of system overflows as the volume increases. O* decreases more rapidly than O demonstrating, as expected, an increasing efficiency on stormwater runoff attenuation as the cistern size grows. By considering the building, the RHS does not provide any benefit in terms of greywater reduction; however, it can reduce stormwater runoff by 86.8%with 4 m^3 cistern and by 97.84 with 20 m^3.

Finally, the model has been used to simulate the case study building, but under the hypothesis of replacing the hybrid system with a GRS. Fig. 11 shows the result of simulations. The *E* curves is almost flat, in fact efficiency stands at around 67% regardless of tank volume, demonstrating that is not possible to increase efficiency above this threshold.

The variations in *O* are minimal, demonstrating that, even in this case, it has been reached a benefit threshold beyond which, regardless of the volume of tank used, it is not possible to arrive.

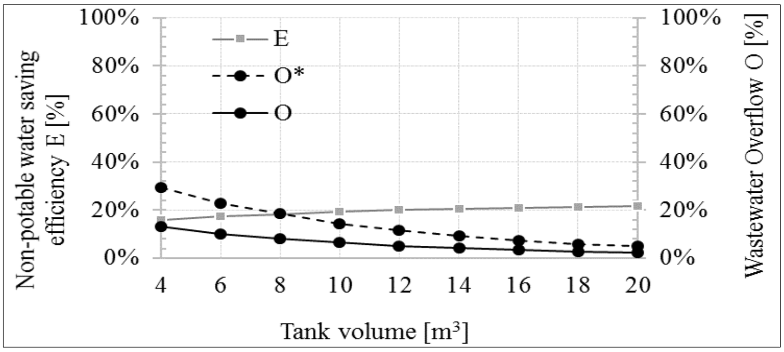


Fig. 10. Rainwater harvesting system: non-potable water saving efficiency -*E* and Overflow-*O* for different values of tank storage volume

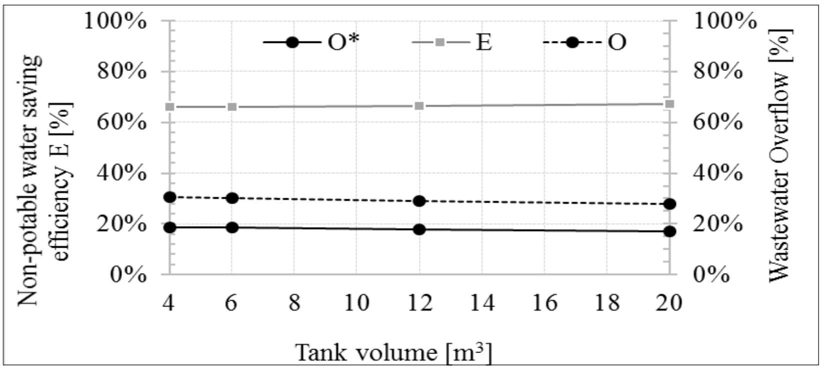


Fig. 11. Greywater reusing system: non-potable water saving efficiency -*E* and Overflow-*O* for different values of tank storage volume

In this case O* has been calculated by considering only the greywater inflow. This parameter allows to quantify the reduction of waste water (only greywater) sent into the sewer system, and its value range from 30.4 with 4 m^3 to 27.75 with 20 m^3 storage tank.

4. Conclusions

The study has quantified the non-potable water saving efficiency *E*, and system overflow *O* for an apartments building located in the city of Bologna (Italy). The first index provides information on the amount of non-water demand that can be effectively satisfied by on-site sources, while the second one provides an estimate of the reduction of volumes discharged into the sewer system. Both indexes were calculated for the real system configuration, and for a wide range of other scenarios obtained by varying the tank volume and the system type (Hybrid system, rainwater harvesting system, and greywater reusing system). Scenarios have been investigated by means of a long-term hydraulic/hydrological numerical model realised by means of SWMM software. To support the choice of the water end-use consumptions and of the greywater production, that were set up into the model, the water consumption (cold, hot, and recycled water) of four flats, located into the case study building, have been analysed.

Data were collected by the facility manager of the building for billing purposes Although they are not extremely accurate and referred to only 4 residential units, they provide several useful information. Data confirm that non-potable consumption accounts for almost a third of the total one, when considering only the toilet flushing water supply. Moreover, the monitoring of garden flats allowed to estimate the average irrigation needs. Measured data are comparable with those shown in other studies, validating the choice to use literature data for modelling purposes.

The performances of different systems configurations have been estimated by using 13 years of real daily rainfall data as input. The model shows that the real system configuration has a water saving efficiency of 75.86%, and that the volumes of wastewater (greywater + rainwater discharged into the combined sewer systems), are reduced by 73.29%. Model has then been used to estimate both *E* and *O*, for nine different tank volumes. Simulations revealed a marginal water saving benefits as the tank size grows, which is mainly attributable to the general characteristics of the building (small size of the roof, high number of inhabitants, and large extent of irrigated gardens). Despite this, the hybrid system, compared to a rainwater harvesting system or a greywater system, seems to be the most efficient because it is able to supply the highest water. From one hand, further researches might evaluate the possibility of using real time series or detailed parameterizations to estimate the non-potable water-end uses and greywater productions. On the other, to estimate others type of collection surfaces such as green roofs, permeable pavements, etc.

The presented model, here applied at the building scale, can also be applied at the district scale or at the city scale to evaluate the effectiveness of policy implementations both in terms of water saving efficiency and stormwater runoff mitigation.

The final goal of this paper, as a matter of fact, was to provide a simple tool to lay down the level of technical performance to be attained and define the minimum water saving efficiency of rainwater/greywater systems intended to benefit of the incentives or tax deduction promoted by the local authorities. The technical methods applied to achieve those goals are a matter of choice, but the minimal performances to be achieved themselves should be mandatory.

References

ABCB, (2016), Rainwater Harvesting and Use-research Report, Australian Building Codes Board on behalf of the Commonwealth of Australia and States and Territories of Australia, On line at: https://arrow.dit.ie/cgi/viewcontent.cgi?article=1003&context=engschcivrep.

Al-Zouby J.Y., Al-Zboon K.K., Kamel K., Al-Tabbal J.A., (2017), Low-cost treatment of grey water and reuse for irrigation of home garden plants, *Environmental Engineering and Management Journal*, **16**, 351-359.

Amos C.C., Rahman A., Gathenya J.M., (2018), Economic analysis of rainwater harvesting systems comparing developing and developed countries: A case study of Australia and Kenya, *Journal of Cleaner Production*, **172**, 196-207.

Antonopoulou G., Kirkou A., Stasinakis A.S., (2013), Quantitative and qualitative greywater characterization in Greek households and investigation of their treatment using physicochemical methods, *Science of the Total Environment*, **454-455**, 426-432.

Bitterman P., Tate E., Van Meter K.J., Basu N.B., (2016), Water security and rainwater harvesting: A conceptual framework and candidate indicators, *Applied Geography*, **76**, 75-84.

Campisano A., Modica C., (2012), Optimal sizing of storage tanks for domestic rainwater harvesting in Sicily, *Resources, Conservation and Recycling*, **63**, 9-16.

Campisano A., Modica C., (2015), Rain water harvesting as source control option to reduce roof runoff peaks to downstream drainage systems, *Journal of Hydroinformatics*, **18**, 23-32.

Campisano A., Lupia F., (2017), A dimensionless approach for the urban-scale evaluation of domestic rainwater harvesting systems for toilet flushing and garden irrigation, *Urban Water Journal*, **14**, 883-891.

Cipolla S.S., Maglionico M., (2014), Heat recovery from urban wastewater: Analysis of the variability of flow rate and temperature, *Energy and Buildings*, **69**, 122-130.

Cipolla S.S., Maglionico M., Stojkov I., (2016a), Experimental Infiltration Tests on Existing Permeable Pavement Surfaces, *Clean - Soil, Air, Water*, **44**, 89-95.

Cipolla S.S., Maglionico M., Stojkov I., (2016b), A long-term hydrological modelling of an extensive green roof by means of SWMM, *Ecological Engineering*, **95**, 876-

887.
De Gisi S., Casella P., Notarnicola M., Farina R., (2015), Grey water in buildings: a mini-review of guidelines, technologies and case studies, *Civil Engineering and Environmental Systems*, 1-20.
Domínguez I., Ward S., Mendoza J.G., Rincón C.I., Oviedo-Ocaña E.R., (2017), End-user cost-benefit prioritization for selecting rainwater harvesting and greywater reuse in social housing, *Water*, **9**, 516.
Dyballa C., Hoffman H.W., (2015), The Role of Water Efficiency in Future Water Supply, *Journal: American Water Works Association*, **107**, 35-44.
Failla B., Spadoni M., Stante L.D., Cimatti E., Bortone G., (2001), The Aquasave Project : an innovative water saving system in a residential building , Italy, *Integrated Water Resources Management*, 121-125.
Farreny R., Gabarrell X., Rieradevall J., (2011), Cost-efficiency of rainwater harvesting strategies in dense Mediterranean neighbourhoods, *Resources, Conservation and Recycling*, **55**, 686-694.
Ferraris M., De Gisi S., Farina R., (2016), Assessment of water consumptions in small mediterranean islands' primary schools by means of a long-term online monitoring, *Applied Water Science*, **7**, 3291-3300
Franchini M., Brunone B., (2016). Innovative and sustainable methodologies for smart water network management, *Civil Engineering and Environmental Systems*, **33**, 1-2.
Gambi G., Maglionico M., Tondelli S., (2011), Water management in local development plans: The case of the old fruit and vegetable market in Bologna, *Procedia Engineering*, **21**, 1110-1117.
Ghisi E., Mengotti de Oliveira S., (2007), Potential for potable water savings by combining the use of rainwater and greywater in houses in southern Brazil, *Building and Environment*, **42**, 1731-1742.
Imteaz M.A., Adeboye O.B., Rayburg S., Shanableh A., (2012), Rainwater harvesting potential for southwest Nigeria using daily water balance model, *Resources, Conservation and Recycling*, **62**, 51-55.
Lee K.E., Mokhtar M., Mohd Hanafiah M., Abdul Halim A., Badusah J., (2016), Rainwater harvesting as an alternative water resource in Malaysia: Potential, policies and development, *Journal of Cleaner Production*, **126**, 218-222.
Leong J.Y.C., Chong M.N., Poh P.E., Vieritz A., Talei A., Chow M.F., (2017a), Quantification of mains water savings from decentralised rainwater, greywater, and hybrid rainwater-greywater systems in tropical climatic conditions, *Journal of Cleaner Production*, **176**, 946-958.
Leong J.Y.C., Oh K.S., Poh P.E., Chong M.N., (2017b), Prospects of hybrid rainwater-greywater decentralised system for water recycling and reuse: A review, *Journal of Cleaner Production*, **142**, 3014-3027.
Maglionico M., Stojkov I., (2015). Water consumption in a public swimming pool, *Water Science and Technology Water Supply*, **15**, 1304-1311.
Marinoski A.K., Rupp R.F., Ghisi E., (2018), Environmental benefit analysis of strategies for potable water savings in residential buildings, *Journal of Environmental Management*, **206**, 28-39.
Mays L.W., (2014), Use of cisterns during antiquity in the Mediterranean region for water resources sustainability, *Water Science and Technology: Water Supply*, **14**, 38-47.
Oh K.S., Leong J.Y.C., Poh P.E., Chong M.N., Lau E.V., (2018), A review of greywater recycling related issues: Challenges and future prospects in Malaysia, *Journal of Cleaner Production*, **171**, 17-29.
Okoye C.O., Solyalı O., Akıntuğ B., (2015), Optimal sizing of storage tanks in domestic rainwater harvesting systems: A linear programming approach, *Resources, Conservation and Recycling*, **104**, 131-140.
Palla A., Gnecco I., Lanza L.G., (2011), Non-dimensional design parameters and performance assessment of rainwater harvesting systems, *Journal of Hydrology*, **401**, 65-76.
Palla A., Gnecco I., La Barbera P., (2017), The impact of domestic rainwater harvesting systems in storm water runoff mitigation at the urban block scale, *Journal of Environmental Management*, **191**, 297-305.
Pelak N., Porporato A., (2016), Sizing a rainwater harvesting cistern by minimizing costs, *Journal of Hydrology*, **541**, 1340-1347.
Penn R., Schütze M., Friedler E., (2013), Modelling the effects of on-site greywater reuse and low flush toilets on municipal sewer systems, *Journal of Environmental Management*, **114**, 72-83.
Rossman L., Huber W.C., (2016), Storm Water Management Model Reference Manual Volume I – Hydrology. US EPA Office of Research and Development, Washington, DC, EPA/600/R-15/162A.
Santos S.M. dos, de Farias M.M.M.W.E.C., (2017), Potential for rainwater harvesting in a dry climate: Assessments in a semiarid region in northeast Brazil, *Journal of Cleaner Production*, **164**, 1007-1015.
Silva C.M., Sousa V., Carvalho N.V., (2015), Evaluation of rainwater harvesting in Portugal: Application to single-family residences, *Resources, Conservation and Recycling*, **94**, 21-34.
Stephan A., Stephan L., (2017), Life cycle water, energy and cost analysis of multiple water harvesting and management measures for apartment buildings in a Mediterranean climate, *Sustainable Cities and Society*, **32**, 584-603.
TWDB, (2005), The Texas Manual on Rainwater Harvesting, On line at: http://www.twdb.texas.gov/publications/brochures/conservation/doc/RainwaterHarvestingManual_3rdedition.pdf.
UNI/TS 11445, (2012), Standard UNI/TS 11445:2012, Installations for use and collection of rainwater not intended for human consumption - Design, installation and maintenance, On line at: http://store.uni.com/catalogo/index.php/uni-ts-11445-2012.html?___store=en&josso_back_to=http%3A%2F%2Fstore.uni.com%2Fjosso-security-check.php&josso_cmd=login_optional&josso_partnerapp_host=store.uni.com&___from_store=it.
WWAP, (2015), The United Nations World Water Development Report 2015: Water for a Sustainable World, On line at: http://www.unesco.org/new/en/natural-sciences/environment/water/wwap/wwdr/2015-water-for-a-sustainable-world/.
Zanni S., Cipolla S.S., Di Fusco E., Lenci A., Altobelli M., Currado A., Maglionico M., Bonoli A., (2019), Modeling for sustainability : Life cycle assessment application to evaluate environmental performance of water recycling solutions at the dwelling level, *Sustainable Production and Consumption*, **17**, 47- 61.

Websites:

http://sustainabledevelopment.un.org.
http://www.arpae.it/dettaglio_generale.asp?id=3284&idlivello=1625.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2361-2372
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

FROM THE APPLICATION OF WATER SAFETY PLAN TO THE ACHIEVEMENT OF THE ISO 22000:2005 STANDARD: A CASE STUDY

Maria Cristina Collivignarelli[1], Alessandro Abbà[1], Sabrina Sorlini[2], Silvestro Damiani[1]*, Barbara Marianna Crotti[3]

[1]*DICAr, Department of Civil and Architectural Engineering, University of Pavia, via Ferrata 1, 27100 Pavia, Italy*
[2]*DICATAM, Department of Civil, Environmental, Architectural Engineering and Mathematics, via Branze 43, 25123 Brescia, Italy*
[3]*ASMia S.r.l., via Tiziano Vecellio 540, 27036 Mortara, Italy*

Abstract

The Water Safety Plan (WSP) model provides a completely new, cross-cutting and multidisciplinary approach for the risk assessment of drinking water pollution. The concept of "control" of the drinking water supply system (DWSS) is replaced by the concept of "under control", in order to protect human health. The key factor of the WSP approach is the identification and mitigation or, if possible, the elimination of all factors that may cause a chemical, physical, microbial and radiological risk for drinking water. Due to its characteristics, the WSP can be perfectly integrated with the Hazard Analysis Critical Control Points (HACCP) system, a food safety management system which has the same approach of the WSP for the control of CCPs in food and drink production. Based on the Codex Alimentarius indications, 7 main principles have to be followed in order to establish a HACCP plan. These 7 principles are resumed in the International Organization for Standardization (ISO) 22000:2005 management system. The aim of this study is to evaluate how the WSP implemented for the DWSS of Mortara, Italy, was integrated with the HACCP system, in order to achieve the ISO 22000:2005 standard. The novelty of this work is that this is one of the first nationwide application of the ISO 22000:2005 standard on the whole DWSS stages, from catchment to consumer. In this way, all the DWSS criticalities have been detected. Moreover, the drinking water quality control system has been improved so much to consider water by rights a food.

Key words: drinking water, Hazard Analysis Critical Control Points, ISO 22000:2005, Water Safety Plan

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

1.1. Water Safety Plan approach

Drinking water supply system (DWSS) utility managers have the responsibility of managing water quality risks to ensure the safety and quality of water supplied to their customers. Nowadays, managers rely on the Water Safety Plan (WSP), recently included in European Directive 2015/1787 (EC Directive, 2015). WSP is an innovative risk assessment and management approach introduced in 2004 by the World Health Organization (WHO) through guidelines for drinking water quality (Collivignarelli, 2017; Gunnarsdòttir et al., 2008; Khaniki et al., 2009; Sorlini et al., 2017; WHO, 2004; WHO, 2009; Yokoi et al., 2006). WSP ensures the safety of drinking water in the entire DWSS, from catchment to consumer (Collivignarelli, 2017; Sorlini et al., 2015, 2017). It identifies all factors that may cause a chemical, physical, microbial and radiological risk for water in order to reduce or eliminate these factors. Moreover,

* Author to whom all correspondence should be addressed: e-mail: silvestro.damiani01@universitadipavia.it; Phone: +39 0382985314; Fax: +39 0382985589

it prevents water re-contamination during storage and distribution (Collivignarelli, 2017; Giardina et al., 2016; Gibellini et al., 2017; Sorlini et al., 2017; WHO, 2009). This management intervention involves a continuous feedback loop of risk identification and evaluation of whether risks are under control, deriving from the approach used widely to ensure food safety (Setty et al., 2017).

In order to highlight the connection between drinking water and food is necessary to consider the Codex Alimentarius, i.e. the "Food Code". This is a collection of standards, guidelines and codes of practice adopted by the Codex Alimentarius Commission (CAC) in order to protect consumers' health and promote fair practices in food trade (Boutrif, 2002; Luber, 2010). Regarding to food safety, CAC has introduced the *"Hazard Analysis and Critical Control Point (HACCP) System and Guidelines for Its Application"* guideline (Dawson, 1995). According to Jayaratne (2008), at page 548: "HACCP is an internationally recognized process control system which involves identifying and prioritizing hazards and risks to product quality and controlling processes to reliably maintain the desired level of product quality".

The purpose of the HACCP system is to control potential hazards in food production and guarantee the safety of the products in the whole food chain (production, handling, treatment, transportation and storage), all the way to the consumer (Al-Busaidi et al., 2016; Allata et al., 2017; Bergström and Hellqvist, 2004; Casolani and Del Signore, 2016; Damikouka et al., 2007; Nordenskjöld, 2012). EC Directive (1993) and EC Regulation (2004) report that the application of HACCP system in a food production is mandatory in Europe (Damikouka et al., 2007; Khaniki et al., 2009; Nordenskjöld, 2012).

1.2. The HACCP principles and the ISO 22000:2005 standard

Based on the Codex Alimentarius indications, 7 main principles have to be followed in order to establish a HACCP plan (CAC, 1969):

- **Principle 1: perform a hazard analysis**. The target of this step is to obtain a comprehensive list of all biological, chemical and physical agents or conditions which have the potential to cause damage, the assessment and the severity of the risk associated with these hazards as well as the possible control measures for each hazard.
- **Principle 2: Determine the Critical Control Points (CCPs)**. The Codex, at page 26, defines CCP as: "A step at which control can be applied and is essential to prevent or eliminate a food safety hazard or reduce it to an acceptable level. The intent of the HACCP system is to focus control at CCPs" (CAC, 1969).
- **Principle 3: establish critical limit(s)** for each CCP. In some cases, more than one critical limit will be identified and measured.
- **Principle 4: establish a CCP monitoring plan** to verify that CCPs are always under control, in order to prevent the exceeding of critical limits.
- **Principle 5: establish the corrective action** to be taken when monitoring indicates that a particular CCP is no longer under control.
- **Principle 6:** establish procedures of verification to confirm that the HACCP system is working effectively.
- **Principle 7: introduce documentation** concerning all procedures **and records** appropriate to these principles and their application.

The systematically application of HACCP principles guarantees that water quality risks are controlled as close to their sources as possible (Jayaratne, 2008). The 7 principles can be applied through the implementation of 12 preparatory steps: (i) assemble HACCP team; (ii) describe product; (iii) identify intended use; (iv) construct flow diagram; (v) confirm flow diagram; (vi) conduct a hazard analysis; (vii) determine the critical control points (CCPs); (viii) establish critical limits for each CCP; (ix) establish a CCPs monitoring plan; (x) establish corrective actions; (xi) validation and verification of HACCP plan; (xii) establish documentation and record keeping. The 7 principles mentioned above are taken up in the ISO 22000 (2005) "Food safety management systems – Requirements for any organization in the food chain" quality management system, published by ISO Committee TC34 on the first of September 2005. Starting from the assumption that a consumer health hazard may occur at any stage of the production/distribution chain, ISO 22000 standard has been designed in order to ensure that there are no weak links in the food supply chain (Allata et al., 2017; Færgemand, 2008; ISO 22000, 2005). It therefore involves both the companies directly concerned (producers and distributors of the product) and those involved indirectly (i.e. packaging manufacturers or cleaning companies) (De Gregorio et al., 2010).

The structure of ISO 22000 (2005) standard is based on the combination of three elements: the principles of HACCP, the Prerequisite Programs (PRPs) and the operational Prerequisite Programs (oPRPs). PRPs, at page 16, are defined as "practices and conditions needed prior to and during the implementation of HACCP and which are essential for food safety" (ISO 22000, 2005). PRPs provide a foundation for an effective HACCP system and reduce the likelihood of certain hazards. Instead, the oPRPs are PRPs identified by the hazard analysis as essential in order to control the likelihood of introducing food safety hazards to and/or the proliferation of food safety hazards in the product(s) or in the processing environment. The system planning of the ISO 22000 (2005) standard is shown in Fig. 1.

The primary goal of this study is to highlight how the DWSS utility manager of Mortara, Italy, has adapted the already implemented WSP (2016) to the HACCP system, modifying and/or integrating the WSP hazard analysis with the principles reported in the Codex Alimentarius, in order to achieve the ISO 22000 (2005) standard. This upgrade process perfectly follows the objectives set by the European Commission.

As a matter of fact, at the beginning of February 2018, a proposal to amend EC Directive (1998) was presented. The focus of this proposal is to review the list of parameters to define drinking water as "safe". In particular article 10, now revised and entitled "Domestic distribution risk assessment", introduces the obligation to conduct a risk-based approach for the products and materials intended for contact with drinking water.

Furthermore, the proposal requires Member States to ensure regular monitoring of parameters such as lead and legionella and establishes rules on the admissible quantities of certain substances in water (EC Directive, 2018).

2. Material and methods

2.1. The HACCP system and the WSP: connection between drinking water and food

Access to drinking water, healthy and clean, is a human right and a fundamental health indicator. In Italy, the quality parameters to be observed for drinking water are defined in Legislative Decree 31 (2001), transposition of the Council Directive 98/83/EEC, which establishes the conformity compliance points, the control Bodies and the procedures by which the controls are to be carried out. Furthermore, as reported in Legislative Decree 31 (2001), DWSS utility managers and water kiosk managers must apply the HACCP system (EC Regulation, 2004) and must monitor the maintenance of water potability parameters through the adoption of self-control plans (MHC, 2011). In fact, HACCP is a food safety management system that can also be applied to drinking-water supply (Khaniki et al., 2009). In this perspective, the HACCP is a basic concept that underlies the WSP (Setty et al., 2017). Compared to food production chain, there are three main features in the drinking water treatment process:

1. *Variable qualitative features of raw water*. While quality checking of products and materials for food use can guarantee a qualifying level, which keeps constant along the whole food chain, water suppliers have to deal with a variation of water quality, based on the source of supply.

2. *Need for continuous treatment and supply*. Each food product is separately handled by production lots and is therefore easily traced. Instead, raw water is generally treated and supplied continuously to the consumer. Therefore, it is not possible to apply the lot concept as it is. Besides, re-contamination and re-growth could happen in the distribution system, after water treatment and purification.

3. *Respecting numerous qualitative and organoleptic parameters for drinking water*. Although the HACCP system covers only the health hazards, utilization hazards such as bad colour, bad taste and odour must be considered because they are unacceptable to water consumers (Yokoi et al., 2006).

2.2. Mortara (Pavia) drinking water supply system

A WSP was implemented for the DWSS of Mortara, a town of 15500 inhabitants located in northern Italy (province of Pavia). The water supply system consists of three drinking water treatment plants (DWTPs), each treating groundwater (drawn at 200 m depth, through wells, by a confined aquifer) containing the main following contaminants: arsenic, iron, manganese and ammonia. Two of the three DWTPs have the sequence of treatments reported in Fig. 2.

Pre-oxidation is carried out with air. This process allows to oxidize iron ($Fe^{2+} \rightarrow Fe^{3+}$) and ensure aerobic conditions for the next phase. Biofiltration is carried out on a quartzite support mixed with pyrolusite. The latter is produced by coating the sandy material with MnO_2, in order to catalyze the oxidation of manganese. The sandy support is also used for the development of nitrifying biomass that works on inorganic nitrogen compounds (NH_4^+). The iron precipitates ($Fe(OH)_3$) are also retained in this phase.

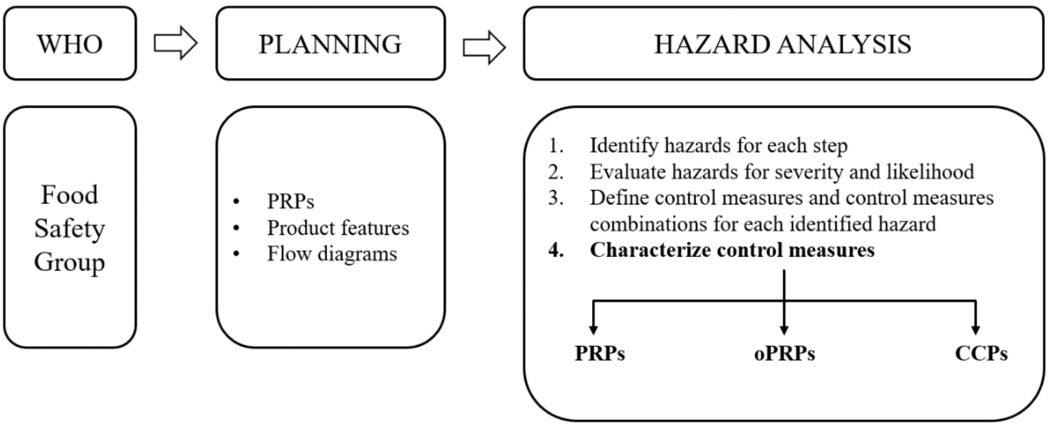


Fig. 1. System planning according to ISO 22000 standard

The $FeCl_3$ dosage ensures the arsenic and residual MnO_2 precipitation. These precipitates are retained in the mixed Granular Activated Carbon (GAC)/sand filtration. Finally, NaClO dosage guarantees chlorine coverage in the distribution network. The third plant does not have $FeCl_3$ dosage and mixed GAC/sand filtration treatment because the natural iron content in the raw water is enough for arsenic removal. The 2014-2017 averages of monitored data of the Mortara DWSS are reported in Table 1. Treated water flows into an 84-km interconnected distribution network (Sorlini et al., 2017). The implemented WSP was adapted to the HACCP system steps (described afterwards) in order to obtain the ISO 22000 certification for all the DWSS stages.

2.3. Description of the HACCP implementation steps

2.3.1. Assemble HACCP team (step 1)

The HACCP team is responsible for the planning, development, verification and implementation of the HACCP system. The DWSS utility manager has to appoint a Food Safety Group (FSG), consisting of Operative Director, Security Manager and Plants Foreman. The FSG composition owns a combination of knowledge and multidisciplinary experience in the development and implementation of the food safety management system relating to products, processes and hazards for food safety.

2.3.2. Describe product (step 2)

According to the implemented WSP, the DWSS utility manager has to describe and document drinking water features, building materials and products that may be in contact with water, in order to conduct the hazard analysis. The description includes: biological, chemical and physical features; raw water composition and characteristics of additives and processing aids; supply source; treatment methods; distribution methods; storage conditions; preparation and/or manipulation before use or processing; acceptance criteria relating to food safety or purchased materials specifications suitable for the intended use. For the choice of materials, the DWSS utility manager can take into account the legislative and regulatory requirements related to the drinking water distribution (Legislative Decree 31 (2001)).

2.3.3. Identify intended use (step 3)

The DWSS utility manager has to supply drinking water for both sanitary (toilet facilities) and food use, through the distribution network. Furthermore, the DWSS utility manager is responsible for the delivered service up to the end-user delivery point (counter). Poor post-counter handling could bring to a worsening in the distributed water potability features. The service is also aimed at particularly vulnerable users such as hospitals, old people's home, kindergartens, schools etc. In compliance with the provisions of Legislative Decree 31 (2001), the maintenance of water health parameters is considered in the risk assessment, as well as an adequate protection for the expected and predictable water uses.

2.3.4. Construct flow diagram (step 4 & step 5)

The FSG has to develop a flow diagram for the DWTPs, in order to describe the key steps in the water treatment process. Moreover, flow diagrams must be revised periodically.

2.3.5. Conduct a hazard analysis (step 6)

The FSG has the task of carrying out the hazard analysis in order to determine the hazards that need to be controlled, the degree of control needful to ensure food safety and which combination of control measures is required. For each phase identified through flow diagrams, the FSG detected all the hazardous events (i.e. any event that introduces hazards to the water supply) that may lead to a food safety water hazard. Furthermore, each hazardous event must be associated with the related hazards (i.e. any physical, chemical, biological or radiological agent that has the potential to cause harm to public health) that may cause a water physical, chemical, microbial or radiological contamination. In this assessment, the FSG has also to consider hazard events that are not readily apparent, such as changes in weather conditions or pipelines aging, also considering past events and historical information.

The risk associated with each hazard may be described by identifying the likelihood of occurrence (i.e. the frequency with which a hazard or hazardous event can occur) and evaluating the severity of the consequences (i.e. the severity or intensity of the impact that the hazard may cause on both human health and the sanitary quality of the distributed water).

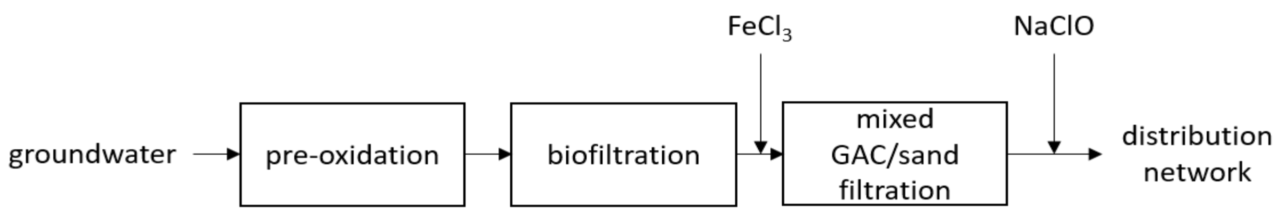


Fig. 2. Block diagram of Mortara DWTPs

Table 1. 2014-2017 averages of monitored data of the Mortara DWSS

2014-2017 Monitoring Data	*Raw Water*	*OUT Pre-oxidation*	*OUT biofiltration*	*OUT GAC/sand filtration*	*Italian Regulation Limits (EC Directive, 2001)*
Plant 1					
Fe [μg/L]	77	72	28.5	25	200
Mn [μg/L]	98	97	5.6	1.1	50
As_{TOT} [μg/L]	10.5	10	9.7	7.5	10
NH_4^+ [mg/L]	0.8	0.9	0.3	0.01	0.5
Plant 2					
Fe [μg/L]	69	66.5	10.5	44.3	200
Mn [μg/L]	94.5	95	1	1.03	50
As_{TOT} [μg/L]	9.7	10.1	9.6	7.5	10
NH_4^+ [mg/L]	0.7	0.8	0.03	0.01	0.5
Plant 3					
Fe [μg/L]	76.5	79.5	23	No GAC/sand filtration treatment	200
Mn [μg/L]	164.5	176.5	1		50
As_{TOT} [μg/L]	5.2	5.6	5.5		10
NH_4^+ [mg/L]	0.4	0.3	0.04		0.5

The likelihood of occurrence is assigned taking into account the DWSS utility manager experience, past events and monitoring data, both internal and external. The risk is calculated as the product of the likelihood and the severity of the consequences, according to the semi-quantitative risk matrix approach shown in Table 2.

The risk calculation is based on a semi-quantitative approach because it derives from a product between two factors, whose values are however established by the team taking into account the user's food safety requirements and the intended drinking water use. The risk assessment is initially carried out considering the worst possible scenario for the water system, i.e. assuming the absence of control measures and the absence of other downstream treatments, in order to highlight all the DWSS possible risks.

Based on the hazard analysis, the DWSS utility manager has to choose an appropriate combination of control measures to prevent, eliminate or reduce the food safety hazards. Therefore, based on the established control measures, the PRPs must be defined and cataloged within a monitoring plan.

Subsequently, the control measures are submitted to a validation process with the aim of verifying that they are effective and able (also in combination) to ensure the control of the identified hazards. In case of negative validation, the control measure and/or their combination are modified and evaluated again. Therefore, after identifying and appropriately validating all the control measures, the FSG reassess the risks considering the effectiveness of the control measures in place. The risks are recalculated in terms of the severity of consequences and likelihood of occurrence, considering that the latter, compared to the initial one, is as much smaller as the effectiveness of the control measures associated with each hazard is greater. *2.3.6. Determine the oPRPs and CCPs (step 7)*

After identifying and appropriately validating all the control measures, and after establishing which control measures can be considered as PRPs, the FSG has to divide them into categories to determine if they must be managed as oPRPs or as CCPs. The CCPs assessment is carried out using a logical approach, defined as "decision tree" and schematized through the flow chart shown in Fig. 3.

Table 2. Semi-quantitative risk matrix approach (adopted from WHO, 2009)

			Severity/consequence				
			Insignificant or no impact	*Minor impact*	*Moderate impact*	*Major impact*	*Catastrophic impact*
			1	*2*	*3*	*4*	*5*
Likelihood/ frequency	**Rare** (once every 5 years)	**1**	1	2	3	4	5
	Unlikely (once a year)	**2**	2	4	6	8	10
	Moderate (once a month)	**3**	3	6	9	12	15
	Likely (once a week)	**4**	4	8	12	**16**	**20**
	Almost certain (once a day)	**5**	5	10	15	**20**	**25**
Risk score			<6	6-9	10-15	**>15**	
Risk rating			Low	Medium	High	**Very high**	

If a PRP is classified as oPRP, it must be managed by identifying a control measure, a monitoring procedure and corrective actions.

2.3.7. Establish a CCPs critical limits (step 8), monitoring plan (step 9) and corrective actions (step 10)

For the identified CCPs, the FSG has to establish the critical limit and ensure the compliance with the level of acceptability, the measurability of the critical limit and the documentation relating to the criteria for the limit selection. The monitoring methods and their frequencies ensure that the critical limit is not exceeded in order to prevent the distribution of potentially polluted drinking water.

2.3.8. Validate/verify HACCP plan (step 11)

The FSG has to define a verification plan where, for each control measure, the methods, the phase or sampling point, the frequencies and the responsibilities for the verification activities are defined.

2.3.9. Establish documentation and record keeping (step 12)

The DWSS utility manager maintains hardcopy and electronic record keeping and tracking systems, asset information management databases and a water quality database in accordance with its ISO accreditation systems, as well as the traceability of the reagents used in DWTPs. The water distribution network is also documented by the indication of the traces, the pipeline diameters and of the construction materials.

3. Results and discussion

3.1 Results

As already reported, the hazard analysis applied for the WSP has been adapted to the HACCP system. The DWTPs flow diagram were constructed to describe the key steps in the water treatment process and include: sequence and interaction of all operational phases; water and reagents inlet in the flow; types of treatments and respective backwashes and discharge points in municipal sewage system. Processes stages are directly managed by DWSS utility manager or by accredited companies. Annually, through internal audits, the FSG verifies the accuracy of flow diagrams by on-site verification. An example of DWTP flow diagram is reported in Fig. 4.

For each phase identified through flow diagrams, the FSG detected all the hazardous events that may lead to a food safety water hazard. Tables 3 and 4 show an example of risk assessment, respectively before and after the validation of the control measures. Both tables reported the same hazardous events, chosen as examples.

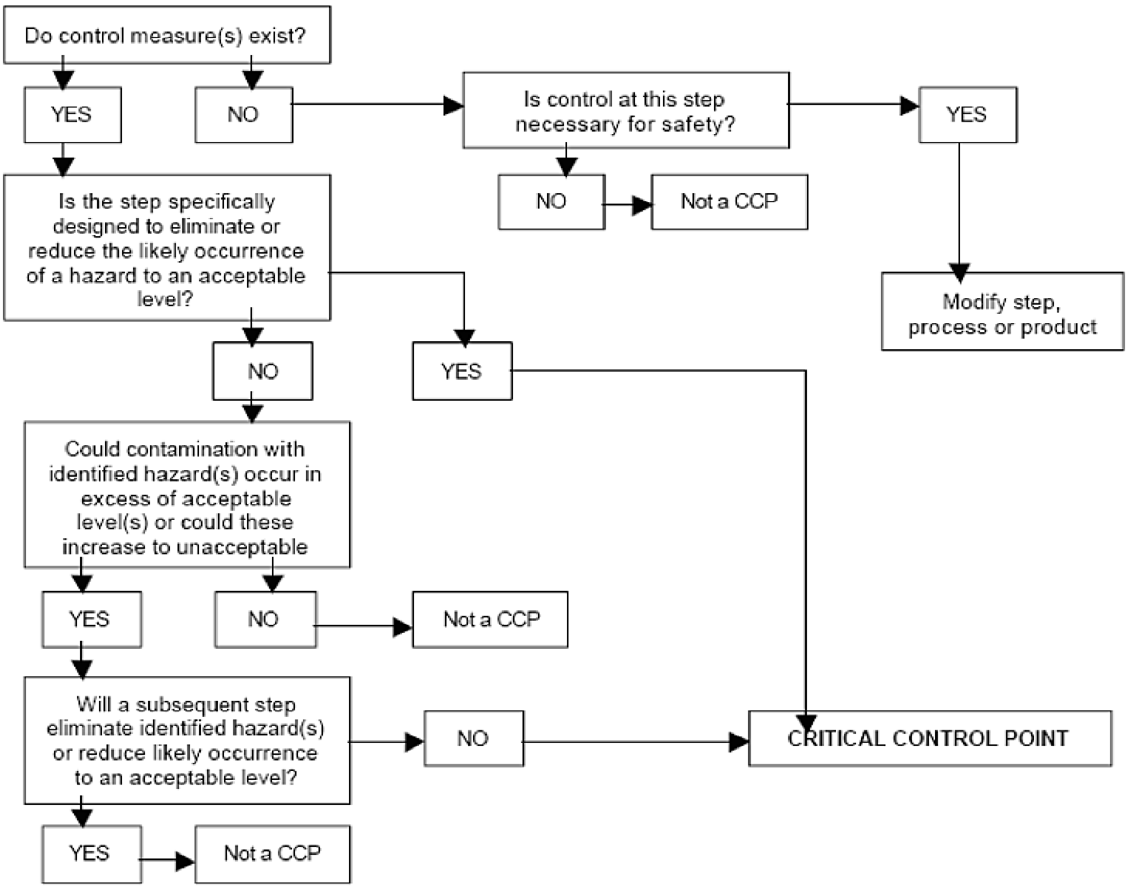


Fig. 3. The decision tree for determination of CCPs (adapted from CAC, 1969)

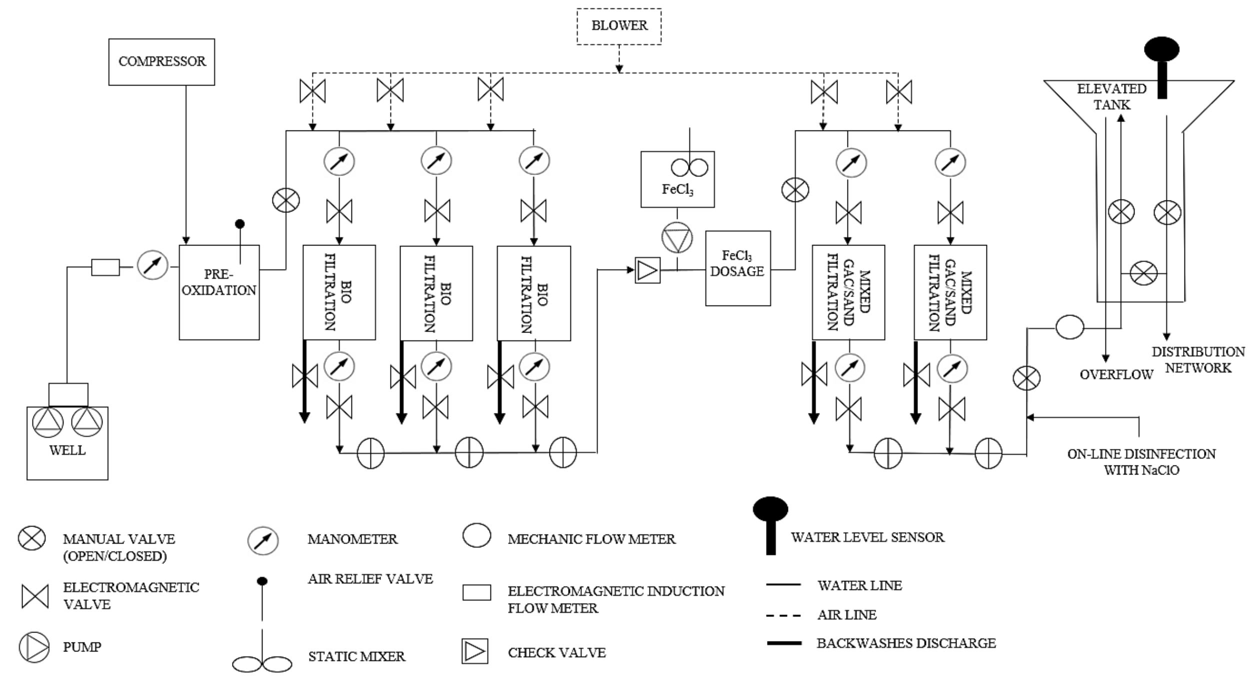


Fig. 4. Example of Mortara DWTP flow diagram

Table 3. Example of risk assessment before the validation of the control measures

Process step	*Hazardous event*	*Related hazard*	*L (a)*	*S (b)*	*R score (c)*	*R rating (before considering controls)*
Basin	Changes in weather conditions	Chemical	1	4	4	Low
Well	Pump failure	Insufficient water				Not applicable
Mixed GAC/sand filtration	Activated carbon exhaustion	Physical	3	2	6	Medium
		Chemical	3	4	12	High
Disinfection	Disinfectant underdosage	Microbial	2	5	10	High
Distribution network	Vandalism	Chemical/physical/microbial	1	5	5	Low

(a) L = likelihood; (b) S = severity; (c) R = risk

Table 4. Example of risk assessment after the validation of the control measures

Hazardous event	*R rating (before considering controls)*	*Control measure*	*Monitoring plan*	*Validation*		*L*	*S*	*R score*	*R rating (after considering controls)*
				E (d)	**NE (e)**				
Changes in weather conditions	Low (Chemical hazard)	Presence of a clay layer that waterproof the aquifer	Natural measure	X		1	4	4	Low
Pump failure	Not applicable	\	\	\		\	\	\	\
Activated carbon exhaustion	Medium (Physical hazard)	Periodic activated carbon replacements	PRP n.8: plants maintenance	X		1	3	3	Low
		in/out pressures verification	PRPo n.3: pressures verification	X					
		Downstream elevated tank that allows the sediment deposit	See downstream phase	X					

	High (Chemical hazard)	Periodic activated carbon replacements	PRP n.8: plants maintenance	X		1	4	4	Low
		in/out pressures verification	PRPo n.3: pressures verification	X					
Disinfectant underdosage	High (Microbial hazard)	Disinfectant dosing control	PRP n.1: continuous disinfection	X		1	5	5	Low
Vandalism	Low (Chem./Phys./Micro. hazard)	Active remote control	PRP n.2: site protection	X		1	5	5	Low
		Locked building that prevents unauthorized entry	PRP n.2: site protection	X					

(d) E = effective; (e) NE = not effective

As reported in the previous Tables 3 and 4, a hazardous event related to the catchment area may be the change in weather conditions. This event may involve both chemical and physical contamination, due essentially to rapid changes in the quality of the source water. According to the information reported by the DWSS utility manager, the likelihood of occurrence is once every 5 years (rare, 1). Instead, the severity of consequences is 4 (major regulatory impact). So, the calculated risk is low (1 x 4 = 4). In this case the control measure, that is the presence of a clay layer that waterproof the aquifer, is natural and cannot be classified as a PRP. Therefore, after the validation of this control measure, the risk remained unchanged.

Instead, at the catchment, the pump drawing water from the well to the treatment plant could malfunction. In this case, there is no water supply to the plant and is impossible to carry out a risk assessment: the supply interruption involves that there are no hazards for the food safety of water. Furthermore, at the disinfection, the reported hazardous event is the disinfectant underdosage. This event is associated with a microbial contamination hazard, due to the ineffectiveness of the treatment and the consequent presence of bacteria content in the water outlet from the disinfection step. The microbial contamination has a severity of consequences of 5 (public health impact). Moreover, according to the DWSS utility manager information, the likelihood of occurrence of the disinfectant underdosage is once a year (unlikely, 2). So, the calculated risk is high (2 x 5 = 10). The control measure applied in this case concerns the disinfectant dosing control, applied through the oPRP concerning the continuous disinfection process (described afterwards in the *step 7*). The effectiveness of this control measure has allowed to bring the risk to a level 5 (low), reducing the likelihood of occurrence to once every 5 years (rare, 1). After identifying and appropriately validating all the control measures, and after establishing which control measures can be considered as PRPs, the FSG had to divide them into categories to determine if they must be managed as oPRPs or as CCPs. Considering the examples reported in Table 5, the first detected oPRP is $FeCl_3$ dosing (Q1: yes; Q2: yes), the second is pressures verification (Q1: yes; Q2: yes; Q5: no) and the third is continuous disinfection process (Q1: yes; Q2: no; Q3: yes; Q4: no; Q5: no). The oPRPs are managed as shown in Table 5.

For example, the continuous disinfection process is carried out by using an automatic metering pump (0.1 mgNaClO/L ± 0,05 supplied). Further control measures are the exposure of pump settings, quantity of reagent and solution preparation methods in the DWTPs area. The monitoring procedure of the continuous disinfection process provides the pump connection to telecontrol, in order to verify the pump functionality. Furthermore, alarm triggering is sent to operators via e-mail notification. In addition, as further evidence of control, system accesses are recorded in the telecontrol system. Finally, Plants Foreman records the preparation of the solution, the maximum storage time and the settings of the metering pump on a dedicated document. The corrective actions are the restoring of the pump functionality (in presence of anomalies), water microbial analysis (if the dosage remains inactive for more than a week) and possible NaClO by hand dosage in the absence of normal dosage for more than one week. Comparing with the DWSS utility manager, the FSG has identified only one CCP, that is the monitoring of the residual chlorine in the distribution network (Q1: yes; Q2: no; Q3: yes; Q4: no; Q5: yes). In fact the continuous disinfection process, if not correctly managed, can lead to a chemical contamination of the water distributed to the users. This contamination can be determined by an excess of chlorine in the treated water or by the possible formation of disinfection by-products (THM) in the presence of precursors. The CCP is managed as shown in Table 6. As reported in Table 6, the FSG has established a CCP critical limit equal to 0.2 mgCl/L, as recommended by EC Directive (2001).

The FSG has also established a monitoring system for the control of residual chlorine in the distribution network. The calibration of the metering pump is carried out annually. Instead, the verification of the metering pump calibration by measuring the residual chlorine is carried out monthly, or as result of each variation of the chlorine dosage.

Table 5. oPRPs management plan

Hazardous event	***oPRP***	***Control measure/s***	***Monitoring procedure***	***Corrective actions***
Reagent overdosing	$FeCl_3$ dosing	● Automatic metering pump (1 mg$FeCl_3$/L ± 0.5 supplied)	● Pump connected to telecontrol	● Restoring pump functionality
			● Alarm triggering send via email to operators	● Chemical analysis of the water outlet from the treatment
			● Telecontrol system access registration	● Possible $FeCl_3$ by hand dosage in the absence of normal dosage for more than one week
			● Registration of the solution preparation, maximum storage time and metering pump settings	
Activated carbon exhaustion	Pressures verification	● DWTPs in/out pressures verification	● Pressure switch connected to telecontrol	● Backwash performance check or possible by hand backwash
			● Alarm triggering send by email to operators	● DWTPs performing test (pumps)
			● Telecontrol system access registration	● Possible filter material replacement
Disinfectant underdosage	Continuous disinfection process	● Automatic metering pump (0.1 mg NaClO/L ± 0.05 supplied)	● Pump connected to telecontrol	● Restoring of the pump functionality
		● Peristaltic pump settings exhibited in the DWTPs	● Alarm triggering sent by email to operators	● Water microbial analysis
		● Quantity of reagent and solution preparation methods exhibited in the DWTPs	● Telecontrol system access registration	● Possible NaClO by hand dosage in the absence of normal dosage for more than one week
			● Registration of the solution preparation, maximum storage time and metering pump settings	

Table 6. CCP management plan

CCP	Monitoring of the residual chlorine in the distribution network
Control measure	Chlorine dosage (max 0,2 mgCl/L) with calibrated metering pump
Critical limit	0,2 mgCl/L
CCP monitoring	Metering pump calibration
CCP verification	Calibration check with residual chlorine measure
Monitoring person in charge	Plants Foreman
Analysis results person in charge	Operative Director
Corrective actions	● chlorine dosage adjustment
	● metering pump calibration

The Operative Director undertakes the corrective actions listed in Table 6 if the critical limit is exceeded. The undertaken actions ensure the identification of the cause of non-compliance and the restoration of the control over the CCP. The FSG also prepares a documented procedure to prevent the consumption and/or the distribution of potentially polluted drinking water.

For the control measures identified, a verification plan was developed establishing the verification activity, method, phase/sampling point, the frequency of verification and the responsibility of verification. An extract of the verification plan adopted is reported in Table 7.

For example, regarding to CCP, the verification activities concern microbial parameters and chlorine dosage verification. The verification method of the microbial parameters is the sampling and laboratory sample analysis. Instead, the verification method of the chlorine dosage verification is the residual chlorine analysis. Both verification activity is carried out at the outlet of elevated tank and are under the responsibility of Plants Foreman.

3.2 Discussions

Tanks to the application of the WSP, the DWSS utility manager has obtained several benefits:

- reduction of public health risk, due to the identification of the criticalities of the DWSS;
- better compliance of water quality parameters with regulatory requirements, due to the passage from a retrospective to a preventive approach;
- greater confidence on health authorities and stakeholders, also thanks to the achievement of the ISO 22000:2005 standard;
- better management of resources due to intervention planning;
- better use of personnel, due to professional training courses.

Table 7. Extract of verification plan

Verification plan					
Control measure	***Verification activity***	***Method***	***Phase/ sampling point***	***Frequency***	***Responsibility***
$FeCl_3$ dosing (oPRP)	Chemical parameters	Sampling and laboratory sample analysis	Mixed GAC/sand filtration	See yearly analytical plan	Plants Foreman
Pressures verification (oPRP)	Chemical parameters	Sampling and laboratory sample analysis	Biofiltration - Mixed GAC/sand filtration	See yearly analytical plan	Plants Foreman
Continuous disinfection process (oPRP)	Microbial parameters	Sampling and laboratory sample analysis	Elevated tank outlet	See yearly analytical plan	Plants Foreman
Distribution network residual chlorine monitoring (CCP)	Microbial parameters	Sampling and laboratory sample analysis	Elevated tank outlet	See yearly analytical plan	Plants Foreman
	Chlorine dosage verification	Residual chlorine analysis	Elevated tank outlet	Monthly; after dosage adjustment	Plants Foreman

However, a WSP also presents a series of critical issues in the implementation procedure. The first critical issue concerned the difficulty in identifying all the hazard events and the related hazards, according to the indications provided by the WHO guidelines (WHO, 2009). The second critical issue concerns the definition of the risk score, performed by analyzing each DWSS treatment individually and assuming the absence of control measures and downstream treatments.

Finally, as the WSP model proposes a step-by-step risk assessment, the last critical issue concerns the lack of a "simplified" procedure, specific for Small Water Supplies (SWSs) where problems of scarcity of resources must be considered.

Certainly, the introduction of a WSP can support the identification of simple and cost-effective actions to be taken in order to protect and improve SWSs. However, specific WSPs that consider only the hazards that really can occur and, therefore, the respective control measures, might be more efficient in SWSs.

As stated above, it is clear that the most important common element to the WSP and HACCP is the risk analysis. As already reported by Mayes (1998), it must be stated that risk analysis and HACCP are two separate subjects with different outputs. The output of risk analysis is a numerical estimate of the occurrence of a particular hazardous event. The output of a HACCP study will be a list of significant hazards together with Critical Control Points, Critical Limits, Monitoring Procedures, Corrective Actions, etc. However, the potential benefits of the use of some elements of risk assessment in HACCP (i.e. increased scientific basis for hazard analysis, clear relationship between hazards, Critical Limits and public health impacts, greater transparency in decision making) cannot be achieved without the general application of validated risk assessment tools.

A possible critical issue of hazard analysis, as reported by Toropilová and Bystrický (2015), may be due to the fact that HACCP is implemented mainly with the objective of satisfying the requirement of authorities or is seen as a task that is mandatory. Establishing HACCP in such scenario gives very little chance of it becoming a meaningful exercise and there is a real risk that it will be seen as a burden by all personnel. In the situation when both the production and the consumer environments are changing, any lag in HACCP development may cause loss of its functionality.

In this perspective, the HACCP system can be compared with dikes built to protect against floods. If they are constructed poorly, it may not be visible but water would find its way. Therefore, constructions rules must be set and observed. If construction is built properly, it deteriorates in time anyway and therefore regular control and maintenance is vital to keep them functional. However, those poorly built will deteriorate faster (Toropilová and Bystrický, 2015).

4. Conclusions

The purpose of the WSP is to make tap water even safer, revolutionizing the control system on drinking water with a model that provides a global system of risk management extended to the entire water supply chain. This new approach allows to decide, on the basis of a concrete and accurate risk assessment, which parameters have to be monitored more frequently or how to extend the list of substances to be kept under control in case of public health concerns.

Thanks to the application of the WSP, the DWSS utility manager implemented a management system for food safety and hygiene according to the ISO 22000:2005 standard, through the application of the principles established in the Codex Alimentarius.

The ISO 22000:2005 standard was achieved in September 2017 for the whole DWSS of Mortara (Pavia). This is a particularly important aspect as it is one of the first nationwide application of the ISO 22000 quality management system on the whole DWSS stages, from catchment to consumer. The consumer satisfaction is a key-factor, but often taken insufficiently into account by the DWSS utility managers. The right of consumers to information about drinking water quality is essential and represents a regulatory obligation. Furthermore, questions raised by consumers, referring to the water quality or to other aspects of the water service, can identify specific aspects of improvement and highlight the effectiveness of the implemented management system. In this context, the active participation of consumer representatives is a particularly useful tool.

Finally, future goals concern the realization of supporting programs, i.e. activities that support the development of people's skills and knowledge, commitment to the WSP-HACCP approach and capacity to manage systems to deliver safe water.

References

Al-Busaidi M.A., Jukes D.J., Bose S., (2016), Hazard analysis and critical control point (HACCP) in seafood processing: An analysis of its application and use in regulation in the Sultanate of Oman, *Food Control*, **73**, 900-915.

Allata S., Valero A., Benhadja L., (2017), Implementation of traceability and food safety systems (HACCP) under the ISO 22000:2005 standard in North Africa: The case study of an ice cream company in Algeria, *Food Control*, **79**, 239-253.

Bergström M., Hellqvist R., (2004), *Quality and Environmental Management in the Food Industry*, 2nd Edition, Uppsala Bergström and Hellqvist AB.

Boutrif E., (2002), The new role of Codex Alimentarius in the context of WTO/SPS agreement, *Food Control*, **14**, 81-88.

CAC, (1969), Recommended international code of practice-general principles of food hygiene, Codex Alimentarius Commission, CAC/RCP 1-1969, Rev.4 – 2003, On line at: http://www.codexalimentarius.net/download/standards/23/cxp_001e.pdf.

Casolani N., Del Signore A., (2016), Managers' opinions of factors influencing HACCP applications in Italian hotel/restaurant/cafè (HoReCa) sector, *British Food Journal*, **5**, 1195-1207.

Collivignarelli C., (2017), Water safety: one of the primary objectives of our time, *Revista Ambiente and Àgua*, **1**, 1-7.

Damikouka I., Katsiri A., Tzia C, (2007), Application of HACCP principles in drinking water treatment, *Desalination*, **210**, 138-145.

Dawson R.J., (1995), The role of the Codex Alimentarius Commission in setting food standards and the SPS agreement implementation, *Food Control*, **6**, 261-265.

De Gregorio A., Dichiarante L., Focetola G., Pascale G., Prati R., Zarbà B., (2010), *The 22000:2005 ISO, Bureau Veritas detailed book, agri-food sector* (in Italian), Ed. May 2010, Bureau Veritas, Italy, On line at: http://www.inoptima.net/wordpress/wp-content/uploads/2012/05/LA_NORMA_ISO22000_BVhandbook2010.pdf

Færgemand J., (2008), The ISO 22000 series, Global standards for safe food supply chains, ISO Management Systems, Special report, On line at: https://www.newfoodmagazine.com/article/612/the-iso-22000-series-global-standards-for-safe-food-supply-chains/.

Giardina D., Sorlini S., Rondi L., (2016), Sanitation response in emergencies: Lessons learnt from practitioners in post-earthquake Haiti, *Environmental Engineering and management Journal*, **15**, 2029-2039.

Gibellini S., Sorlini S., Gomez A.P., (2017), Critical issues concerning drinking water and sanitation management in Vilanculos (Mozambique), *Environmental Engineering and Management Journal*, **16**, 1701-1708.

Gunnarsdòttir M.J., Gissurarson L.R., (2008), HACCP and water safety plans in Icelandic water supply: Preliminary evaluation of experience, *Journal of Water and Health*, **06.3**, 377-382.

ISO 22000, (2005), Food safety management systems-requirements for any organization in the food chain, International Organization for Standardization.

EC Directive, (1993), Council Directive 93/43/EEC of 14 June 1993 on the hygiene of foodstuffs, On line at: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex:31993L0043.

EC Directive, (1998), Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31998L0083.

EC Directive, (2001), Implementation of Directive 98/83/EC concerning the quality of water intended for human consumption, Legislative Decree n°31 of 2 February 2001, Official Gazette of the Italian Republic, On line at: https://www.ecolex.org/details/legislation/council-directive-9883ec-on-the-quality-of-water-intended-for-human-consumption-lex-faoc018700/.

EC Directive, (2015), Directive 2015/1787/EC of 6 October 2015 amending Annexes II and III to Council Directive 98/83/EC on the quality of water intended for human consumption, *Official Journal of the European Union*, L 260/6, 7.10.2015, Brussels.

EC Directive, (2018), Proposal for a Directive of the European Parliament and of the Council on the quality of water intended for human consumption (recast), European Commission, 2017/0332 (COD), 1.2.2018, Brussels, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1519210589057&uri=CELEX:52017PC0753.

EC Regulation, (2004), Regulation (EC) No 852/2004 of the European Parliament and of the Council of 29 April 2004 on the hygiene of foodstuffs, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32004R0852.

Jayaratne A., (2008), Application of a risk management system to improve drinking water safety, *Journal of Water and Health*, **06.4**, 547-557.

Khaniki G.R.J., Mokhtar M., Mohebbi M.R., (2009), HACCP application for treatment of drinking water for Germi in Iran, *Journal of Food, Agriculture & Environment*, **2**, 709-712.

Legislative Decree 31, (2001), The Legislative Decree no. 31 of February 2, 2001 Implementation of Directive 98/83 / EC on the quality of water intended for human consumption regulates the quality of water intended for human consumption in order to protect human health from the adverse effects associated with water, ensuring the healthiness and the cleaning, On line at: http://www.tifq.it/en/legislative-decree-no-31-of-february-2-2001/.

Luber P., (2011), The Codex Alimentarius guidelines on the application of general principles of food hygiene to the control of *Listeria monocytogenes* in ready-to-eat foods, *Food Control*, **22**, 1482-1483.

Mayes T., (1998), Risk analysis in HACCP: burden or benefit?, *Food Control*, **9**, 171-176.

MHC, (2011), Ministry of Health Circular 4283, On line at: https://mohfw.gov.in/circulars.

Nordenskjöld J., (2012), Implementation of a quality management system in food production, On line at: https://stud.epsilon.slu.se/4676/7/nordenskjold_j_120815.pdf.

Setty K.E., Kayser G.L., Bowling M., Enault J., Loret J.F., Serra C.P., Alonso J.M., Mateu A.P., Bartram J., (2017), Water quality, compliance, and health outcomes among utilities implementing Water Safety Plans in France and Spain, *International Journal of Hygiene and Environmental Health*, **220**, 513-530.

Sorlini S., Rondi L., Gomez A.P., Collivignarelli C., (2015), Appropriate technologies for drinking water treatment in Mediterranean countries, *Environmental Engineering and Management Journal*, **14**, 1721-1733.

Sorlini S., Biasibetti M., Abbà A., Collivignarelli M.C., Damiani S., (2017), Water Safety Plan for drinking water risk management: the case study of Mortara (Pavia, Italy), *Revista Ambiente & Àgua*, **4**, 513-526.

Toropilová J., Bystrický P., (2015), Why HACCP might sometimes become weak or even fail, *Procedia Food Science*, **5**, 296-299.

WHO, (2004), Guidelines for Drinking-water Quality, 3rd ed, World Health Organization, Geneva, On line at: http://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf;jsessionid=46D1CA6BEA993106F333B82F2B87F658?sequence=1.

WHO, (2009), Water Safety Plan Manual: step-by-step risk management for drinking-water suppliers, World Health Organization, Geneva, On line at: http://apps.who.int/iris/handle/10665/75141.

Yokoi H., Embutsu I., Waseda Y., Waseda K., (2006), Study on the introduction of hazard analysis and critical control point (HACCP) concept of the water quality management in water supply systems, *Water Science and Technology*, **4-5**, 483-492.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2373-2378
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

AN INTEGRATED HIGH TEMPORAL RESOLUTION APPROACH TO MONITOR VOCs CONCENTRATIONS AND ODOUR ANNOYANCE NEAR A PETROLEUM PLANT

Alessia Di Gilio[1]*, Jolanda Palmisani[1], Stefania Petraccone[1], Antonio Fornaro[2], Gianluigi de Gennaro[1]

[1]*Department of Biology, University of Bari, via Orabona 4, 70126 Bari, Italy*
[2]*Lab Service Analytica, via Emilia 51, Anzola dell'Emilia, Bologna, Italy*

Abstract

This study aims to monitor Volatile Organic Compounds (VOCs) and odour annoyance perceived by the exposed population living nearby a petroleum plant through an integrated high temporal resolution methodological approach. The area under investigation is considered one of the most critical industrial areas of the South of Italy (Basilicata) because of presence of the largest Italian petroleum plant, called the "Center Olio Val d'Agri" (COVA). In fact, VOCs and odours emitted from extraction processes, storage tanks and/or gas pipelines may have an adverse impact on health and life quality of population living near the plant. Therefore, in order to assess the potential impact on nearby urban settlements, two monitoring campaigns were carried out. The first campaign was conducted during 2011 and allowed to integrate the information about odours, monitored by means of electronic nose (e-nose), with meteorological data (wind speed and direction) and population complaints reported on questionnaires. In the second one (**from 1st January to 30th July 2017)**, the previous approach has been improved with an integrated system consisting of photoionization detector (PID) for VOCs monitoring, a video camera and a telephonic system able to systematize in real time the population complaints. Experimental data obtained revealed that there was correspondence between the VOCs concentration peaks, odour events and population complaints. Moreover, this study highlighted that technologies for high temporal resolution monitoring of both VOCs and odours integrated in a unique system are able to provide real time information about the emissive sources and odor annoyance and to promptly evaluate the impact on the exposed population.

Key words: electronic nose, gas and oil pre-treatment plant, odours, Photo Ionization Detector (PID), Volatile Organic Compounds (VOCs)

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The increasing interest of scientific community and stakeholders for airborne pollutants monitoring in Val d'Agri (Basilicata, Italy) is due to the presence of the largest Italian gas and oil pre-treatment plant, called the "Centro Olio Val d'Agri" (COVA), nearby the urban settlements. The large-scale plant extracts crude oil from the various wells placed in the surrounding territory and, afterwards, performs the desulphurization process (Calvello et al. 2015; 2017). Despite exhaustive data on chemical characterization of VOC emission from petrochemical plants and refineries are available in literature, limited information is to date available regarding emissions from industrial plants tailored to extraction and desulphurization processes (Cetin et al., 2003; Faruolo et al., 2014; Kalabokas et al., 2001; Kumar et al., 2017; Lin et al., 2004; Macey et al., 2014; Rodriguez-Espinosa et al., 2017; Tiwari et al., 2010; Wei et al., 2014; Zhang et al., 2017). Several studies highlighted that Volatile Organic Compounds (VOCs) represent

* Author to whom all correspondence should be addressed: e-mail: alessia.digilio@uniba.it; Phone: +390805443343

the main pollutants emitted from oil wells (Chen et al., 2016, Wei et al, 2014, Zhang et al., 2017). Main activities of petroleum plant affecting atmospheric VOCs airborne concentration are products handling, discharge and filling of tanks ant the treatment of industrial waste water. Specific classes of chemicals have been detected and related to potential sources: a) aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX); b) aliphatic alkanes, linear and branched, such as propane, butane, n-pentane, n-hexane, n-heptane, isobutane, isopentane; c) linear alkenes such as propene, 1-butene, 1-pentene and other branched alkenes (Calvello et al., 2017; EPA, 1995; Ryerson et al., 2003, Vega et al., 2011). Aromatic hydrocarbons emissions have been related to industrial waste water treatment whereas alkanes and alkenes emission to tank leaks. Moreover, it was observed that blow down system significantly contributes to CO_2, CO, NO_x and SO_x airborne concentrations as well as to VOCs concentrations (Nwakire, 2015). Fugitive emissions of hydrocarbons from storage tanks, gas pipelines and exhausted areas are also of concern. VOCs monitoring in industrial areas characterized by the presence of a petroleum plant is of great concern due to potential impacts on human health. In fact, several studies highlighted that VOC inhalation exposure could affect human health and in particular it could affect airway mucous membranes, provide feeling of sickness or dizziness and cause asthma, leukemia or brain cancer (Chen et al., 2017; Liu et al., 2008; Ye et al., 2017). Therefore, in order to evaluate the impact of emissions from petroleum plant in Val d'Agri on the surrounding territory, some actions have been made over the last years by the regional authorities. A network of five stations for air quality monitoring has been developed and installed by the Agency for Environmental Protection and Prevention of the Basilicata Region (ARPAB). This network provides concentrations of regulated pollutants (i.e. sulfur dioxide, carbon monoxide, nitrogen dioxide, nitrogen oxides, ozone, particulate matter and benzene) and of several pollutants specifically related to oil/gas extraction and treatment activities (i.e. hydrogen sulfide, methane, non-methane hydrocarbons, total hydrocarbons, toluene, ethylbenzene and isomers of xylene) (Calvello et al., 2017). Anyway, although the implementation of the regional monitoring network provides useful information, higher spatial and temporal resolution approach is needed to accurately identify short term pollution events e to evaluate their potential impact on the nearest area around the petroleum plant (Di Gilio, 2015). In fact, in high complexity industrial areas as the investigated one, fugitive emissions due to leaks from the tanks and/or the extraction process and to system over-charging cannot be neglected especially in the case the surrounding territory is populated (Amodio et al., 2013; Amodio et al., 2014; Dambruoso et al., 2014; Di Gilio et al., 2017). In addition, another key problem affecting the quality of life of the exposed population in Val d'Agri is the odour annoyance due to extraction and desulphurization processes. In fact, people that live around petroleum plant frequently complaint odour annoyance. Moreover, it often difficult identify the emission sources that determines odor annoyance events, because odor events last often short time. Therefore, this study aims to assess the potential impact of industrial emissions from petroleum plant on urban settlements in Val d'Agri monitoring VOCs and Odours with high spatial and temporal resolution.

2. Material and methods

In the first campaign VOCs and odour monitoring activity started on 1st October 2011 and was carried out for three months placing one electronic nose in a strategic position, downwind with respect the industrial petroleum plant in the investigated area (Fig. 1).

Fig. 1. Industrial area in Val d'Agri and gas-oil pretreatment plant COVA (red rectangle). Geographical position of Val d'Agri in the South of Italy (in the upper corner)

The position of the device was accurately chosen after a preliminary evaluation of the most predominant wind direction during the previous months. Research activity was mainly addressed to detect odour events produced by the industrial plant with a high temporal resolution and to relate the collected information with the perception of odour annoyance by the exposed population. Odour monitoring was carried out by using an electronic nose (PEN3, Airsense Analytics GmbH, Schwerin, Germany) placed near the petroleum plant at about 2.5 meters above the ground level. The electronic nose is a compact and lightweight portable olfactory system consisting of a gas sampling unit and a sensor array (Capelli et al., 2014). The sensor array is composed of ten thermo-regulated metal oxide thick film sensors (MOS) that are sensitive to several classes of chemical compounds (Table 1). The selectivity of the sensors is influenced by the dopant materials, the working temperature (in the range of 200°C-500°C) and the sensor geometry. When VOCs are adsorbed onto the MOS, there is an oxygen exchange resulting in a decrease in electrical conductivity, detectable by a transducer element (electrode) attached to each sensor. Through a pattern recognition software (Win Muster v. 1.6.2), the PEN3 allows visualization and analysis of the data collected in real time (1 second resolution). Anyway, for the study purpose the data were averaged on 1-minute base.

Table 1. Chemical compounds classes detectable by each MOS

Sensor	*Chemical compounds class*
1	Aromatic
2	Broadrange
3	Aromatic
4	Hydrogen
5	Aromatic - aliphatic
6	Broad methane
7	Sulphur-organic
8	Broad-alchol
9	Sulphur-chlor
10	Methane-aliphatic

Moreover, information regarding the odour annoyance perceived by the population living nearby the petroleum plant were collected through the compilation of suitable questionnaires. People were asked to provide detailed information on each perceived odour event in terms of occurence date, duration and intensity of annoyance, the latter specified on the basis of an odour intensity scale from level 1 (perceivable odour) to level 3 (very strong odour) passing through level 2 (strong odour). The odour intensity scale was associated to a chromatic scale: level 1 was associated to green colour, level 2 to yellow colour and level 3 to red colour. The information collected by questionnaires were integrated with meteorological data in order to have a more accurate interpretation of experimental results. On the basis of obtained results showing the correspondence between the odour events registered and the population complaints, and in order to have a comprehensive overview about the potential fugitive emission sources impacting on the territory, a second monitoring campaign from 1st January to 30th July 2017 was planned improving the methodological approach and coupling odour monitoring with VOCs measurements. The variation of the TVOCs concentration over the time was monitored by means of a high-time resolution photo-ionization detector (Corvus, Ion Science Ltd, UK), placed at about 2.5 meters above the ground level. The instrument was factory calibrated against Isobutylene, thus Total VOCs concentration was reported as ppm equivalent of this gas. The integrated system consisting of one electronic nose and one photoionization detector was installed in the area, downwind with respect the industrial plant. Both the sensors were remotely controlled through GSM-wireless network. In addition, metereological sensors for temperature, relative humidity, wind speed and direction monitoring as well as a video camera were placed close to the integrated system in order to collect data that could be considered representative of the monitoring site (Fig. 2).

(a)

(b)

Fig. 2. PID (Corvus), Electronic nose (PEN3) (a) and meterological sensors (b)

During the second campaign, conducted during 6 months from January to June 2017, instead of questionnaires, the odour impact assessment was carried out through a telephonic system called OdorLab (LabService Analytica srl) able to systematize population complaints. Each citizen (called receptor) was georeferenced on the territory map and, using a telephone switchboard, communicated the odour perception and its intensity choosing among 3 levels of intensity, visualized with different colors. The odour intensity scale and the chromatic association was the same used in the first campaign. The phone calls were promptly recorded and displayed on a real time map on a website, accessible from stakeholders.

3. Result and discussions

The analysis of high temporal resolution data from the 10 MOS of the electronic nose, during the first monitoring campaign, revealed that a significant response was particularly obtained for sensors n.7 and n. 9 (Table 1), sensitive to sulphur-organic compounds and sulphur-chlorinated compounds respectively (recognised as target pollutants emitted by the investigated source). For this reason, attention was mainly paid on the signal-time profiles of the aforementioned sensors. Data treatment and analysis consisted in integration of the electronic nose data with wind direction data as well as number and intensity of complaints from population derived from questionnaires. More specifically, the correlation beetween monitored data and wind direction coming from the source to the receptor (electronic nose downwind with respect the industrial plant) was condisered. As representative output from the first monitoring campaign, data collected from 11 October to 21 October are reported in Fig. 3. When most significant odour annoyance events occurred and peak signals of MOS 7 and 8 were registered from both sensors, correspondence was observed with the wind direction that promoted the transport of the emitted pollutants from the industrial source to the receptor. Moreover, the correspondence was also observed with the odour perception from the exposed population and the complaints noted, day by day, on the questionnaires.

Similarly to the results obtained from the first campaign, during the second one peak events of sulphurate and chlorinated compunds were registered by sensor 7 and 9 in correspondence of wind blowing from petroleum plant to receptor site. In addition sensors number 2 and 5 showed peaks in simultaneously to high concentrations of Total VOCs and population calls registered by OdorLab (three calls with level 3 of intensity). These results suggested the coherence of resulted obtained by different techonologies and devices and the importance of the integration of obtained information to identify the emission sources. In fact, peaks registered by sensor 2 and 5 suggest that the emissive finger print of the investigated source probably changed and became more complex over the time due to potentially increased fugitive emissions (e.g. tanks leaks) resulting in higher concentrations of VOCs, more specifically aromatic and aliphatic hydrocarbons. In Fig. 4 is reported for example one day when 5 events were registered and perceived by the exposed population.

Finally, the most significant odour events perceived by the population were also confirmed by images registered by the video camera showing the flame of gas flaring (Fig. 5). Therefore, as shown in Fig. 4, the methodological approach developed in the present study revelead to be a useful tool to both identify short term events and validate in real time warnings from the population living in the area around the petroleum plant. In fact, a conventional approach based on experimental mean data (averaged on longer time frame) doesn't allow to collect useful information to recognize the short term odor emissions determining annoyance events.

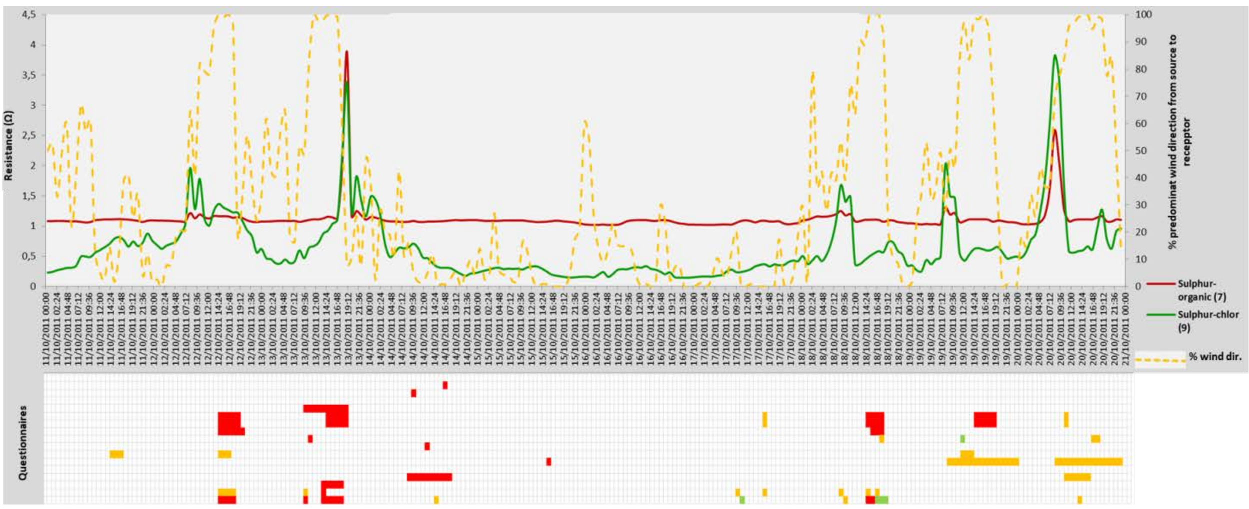


Fig. 3. Electronic nose (PEN 3) data (sensors n.7, 9) integrated with predominant wind direction (%) and information from questionnaires

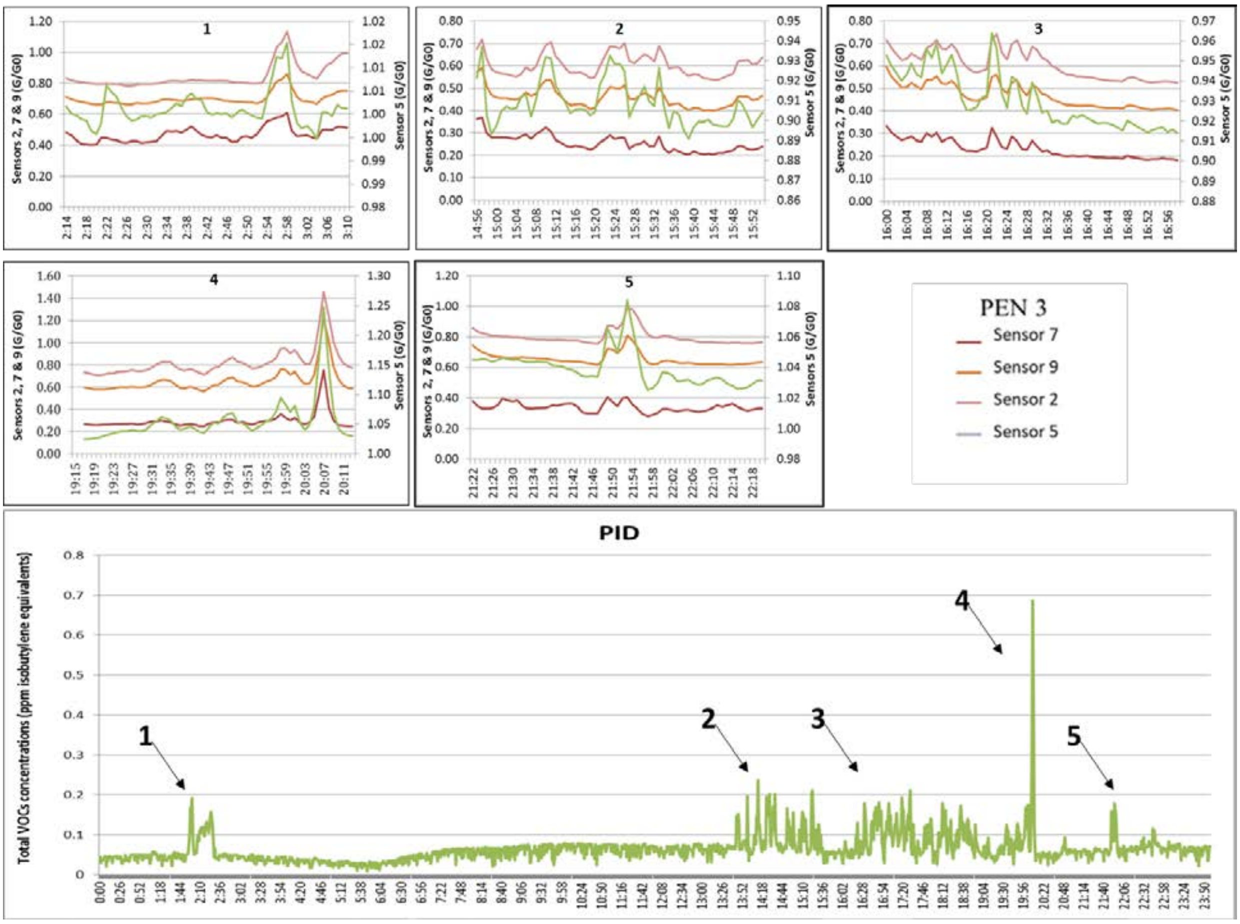


Fig. 4. VOCs Concentration (ppm) monitored by PID (Corvus) and electronic nose (PEN 3) data during 5 VOCs events occurring on one day – second monitoring campaign: 1-is the first event, of high VOCs concentrations, 2-is the second event, 3-the third event, 4-the fourth event and 5-the fifth event

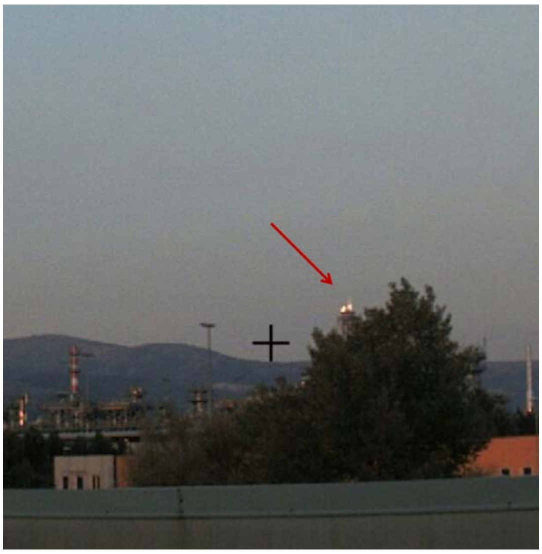


Fig. 5. Flame of gas flaring during the odour event number 4

4. Conclusions

The innovative and integrated approach for VOCs and odour monitoring in a complex industrial area characterized by the presence of the largest Italian gas and oil pre-treatment plant and its proximity to the urban settlements revelead to be a useful tool to collect real time information about the emission sources and their impacts on the urban settlement. Experimental data obtained showed correspondence between the VOCs concentration peaks, odour events and population complaints. This study highlights that technologies for high temporal resolution monitoring of both VOCs and odours integrated in a unique system are able to identify short term events and validate in real time warnings from the population that would not have been confirmed through a conventional approach.

References

Amodio M., Andriani E., Dambruoso P.R., de Gennaro G., Di Gilio A., Intini M., Palmisani J., Tutino M., (2013), A monitoring strategy to assess the fugitive emission from a steel plant, *Atmospheric Environment*, **79**, 455-461.

Amodio M., De Gennaro G., Di Gilio A., Tutino M., (2014), Monitoring of the deposition of PAHs and metals produced by a steel plant in Taranto (Italy), *Advances in Meteorology*, **2014**, Article ID 598301.

Calvello M., Esposito F., Lorusso M., Pavese G., (2015), A two-year database of BC measurements at the biggest European crude oil pre-treatment plant: a comparison with organic gaseous compounds and PM10 loading, *Atmospheric Research*, **164–165**, 156-166.

Calvello M., Caggiano R., Esposito F., Lettino A., Sabia S., Summa V., Pavese G., (2017), IMAA (Integrated Measurements of Aerosol in Agri valley) campaign: Multi-instrumental observations at the largest European oil/gas pre-treatment plant area, *Atmospheric Environment*, **169**, 297-306,

Capelli L., Sironi S., Del Rosso R., (2014), Electronic noses for environmental monitoring applications, *Sensor*, **14**, 19979-20007.

Cetin E., Odabasi M., Seyfioglu R., (2003), Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery, *Science of the Total Environment*, **312**, 103-112.

Chen M.-J., Lin C.-H., Lai C.-H., Cheng L.-H., Yang Y.-H., Huang L.-J., Yeh S.-H., Hsu H.-T, (2016), Excess lifetime cancer risk assessment of volatile organic compounds emitted from a petrochemical industrial complex, *Aerosol and Air Quality Research*, **16**, 1954-1966

Chen D., Zhang Z.-J., Gao F.-L., Li Q.-Q., Gu Y.-G., Wang B.-G., (2017), Study on health risk assessment of aromatic hydrocarbons from a typical oil refinery in Pearl River Delta, China, *China Environmental Science*, **37**, 1961-1970.

Dambruoso P., de Gennaro G., Di Gilio A., Palmisani J., Tutino M., (2014). The impact of infield biomass burning on PM levels and its chemical composition, *Environmental Science and Pollution Research*, **23**, 13175–13185

Di Gilio A., de Gennaro,G., Dambruoso P., Ventrella G., (2015), An integrated approach using high time-resolved tools to study the origin of aerosols, *Science of the Total Environment*, **530-531**, 28-37

Di Gilio A., Ventrella G., Giungato P., Assennato G., de Gennaro G., (2017), An intensive monitoring campaign of PAHs for assessing the impact of a steel plant, *Chemosphere*, **168**, 171-182.

Faruolo M., Coviello I., Filizzola C., Lacava T., Pergola N., Tramutoli V., (2014), A satellite-based analysis of the Val d'Agri (South of Italy) Oil Center gas flaring emissions, *Natural Hazards and Earth System Sciences*, **2**, 4101-4133.

Kalabokas P.D., Hatzaianestis J., Bartzis J.G., Papagiannakopoulos P., (2001), Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek oil refinery, *Atmospheric Environment*, **35**, 2545-2555.

Kumar S., Srivastava V.C., Nanoti S.M., (2017), Extractive Desulfurization of Gas Oils: A Perspective Review for Use in Petroleum Refineries, *Separation & Purification Reviews*, **46**, 319-347.

Lin T.-Y., Sree U., Tseng S.-H., Chiu K.H., Wu C.-H., Lo J.-G., (2004), Volatile organic compound concentrations in ambient air of Kaohsiung petroleum refinery in Taiwan, *Atmospheric Environment*, **38**, 4011-4122.

Liu C.C., Chen C.C., Wu T.N., Yang C.Y., (2008), Association of brain cancer with residential exposure to petrochemical air pollution in Taiwan, *Journal of Toxicological Environmental Health*, **71**, 310-314.

Macey G.P., Breech R., Chernaik M., Cox C., Larson D., Thomas D., Carpenter D.O., (2014), Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study, *Environmental Health*, **13**, 82.

Nwakire C., (2015), The impact of gas flaring on the air quality: A case study of izombe in earstern Nigeria, *Indian Journal of Environmental ProtectionVolume*, **35**, 1-9.

Ryerson T.B., Trainer M., Angevine W.M., Brock C.A., Dissly R.W., Fehsenfeld F.C., Frost G.J., Goldan P.D., Holloway J.S., Hübler G.R., Jakoubek O., Kuster W.C., Neuman J.A., Nicks D.K.Jr., Parrish D.D., Roberts J.M., Sueper D.T., Atlas E.L., Donnelly S.G., Flocke F., Fried A., Potter W.T., Schauffler S., Stroud V., Weinheimer A.J., Wert B.P., Wiedinmyer C., Alvarez R.J., Banta R.M., Darby L.S., Senff C.J., (2003), Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas, *Journal of Geophysical Research Atmospheres*, **108**, 24.

Rodriguez-Espinosa P.F, Flores-Rangel R.M., Mugica-Alvarez V., Morales-Garcia S.S., (2017), Sources of trace metals in PM10 from a petrochemical industrial complex in Northern Mexico, Air Quality, *Atmosphere and Health*, **10**, 69-84.

Tiwari V., Hanai Y., Masunaga S., (2010), Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan, *Air Quality Atmosphere and Health*, **3**, 65-75.

EPA, (1995), Profile of the petroleum refining industry, Enforcement and Compliance Assurance. EPA 310-R-95-013, US Environmental Protection Agency, Washington, DC, On line at: https://nepis.epa.gov.

Vega E., Sánchez-Reyna G., Mora-Perdomo V., Iglesias G.S., Arriaga J.L., Limón-Sánchez T., Escalona-Segura S., Gonzalez-Avalos E., (2011), Air quality assessment in a highly industrialized area of Mexico: Concentrations and sources of volatile organic compounds, *Fuel*, **90**, 3509–3520.

Wei W., Cheng S., Li G., Wang G., Wang H., (2014), Characteristics of volatile organic compounds (VOCs) emitted from a petroleum refinery in Beijing, China, *Journal of Environmental Sciences*, **26**, 332-342.

Ye D., Klein M.; Chang H.H., Sarnat J.A., Mulholland J.A., Edgerton E.S., Winquist A., Tolbert P.E., Sarnat S.E., (2017), Estimating Acute Cardiorespiratory Effects of Ambient Volatile Organic Compounds, *Epidemiology*, **28**, 197-206.

Zhang Z., Wang H., Chen D., Li Q., Thai P., Gong D., Li Y., Zhang C., Gu Y., Zhou L., Morawska L., Wang, B., (2017), Emission characteristics of volatile organic compounds and their secondary organic aerosol formation potentials from a petroleum refinery in Pearl River Delta, China, *Science of the Total Environment*, **584-585**, 1162-1174.

Environmental Engineering and Management Journal October 2018, Vol. 17, No. 10, 2379-2390
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

INFILTRATION/IRRIGATION TRENCH FOR SUSTAINABLE COASTAL DRAINAGE MANAGEMENT: EMILIA-ROMAGNA (ITALY)

Nicolas Greggio[1]*, Beatrice Maria Sole Giambastiani[2], Marco Antonellini[2]

[1]EMRG - Environmental Management Research Group, Via S. Alberto 163, 48123 Ravenna, University of Bologna
[2]BiGEA – Department of Biological, Geological and Environmental Sciences,
Via S. Alberto 163, 48123 Ravenna, University of Bologna

Abstract

The current trends in Mediterranean climate indicate longer periods of drought and hot temperature in summer and shorter and more intense precipitation in spring and autumn, which require reconsidering the current water management. The Emilia-Romagna coastal area (Northeastern Adriatic Sea, Italy) is entirely drained by a network of channels connected to more than 70 water pumping stations. Although drainage is fundamental in wet periods to keep the land dry, during long periods of stable weather, the fresh portion of drainage water could be reused for irrigation or managed aquifer recharge purposes. The proposed Managed Aquifer Recharge (MAR) project involves the reuse of drainage water towards infiltration trenches for both irrigation and natural infiltration purposes. Four possible locations in the Ravenna area were assessed and recommended for the implementation of drainage/irrigation/infiltration projects. It was estimated that, maintaining a raised level of +0.5 m respect to the current water level, a freshwater recharge of about 0.4 million m^3 could be achieved in 120 days of operation by the combined-use of the trenches (total length of 8200 m). If water level in the trench was maintained at +1 m respect to the current level, the freshwater amount available for the aquifer recharge could reach about 0.7 million m^3. This additional freshwater availability would allow irrigation for over 1500 hectares of land and could increase the agricultural gross marketable production of 50%.

Key words: aquifer, drainage, infiltration, MAR, water management

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

1.1. Research framework

Groundwater in coastal areas is one of the main freshwater supplies for both human activities and agro-ecosystems. Agricultural activities can cause groundwater quality degradation (due to nitrogen and phosphorus excess and pesticides) and, vice versa, groundwater quality can affect agricultural yield, especially in case of soil salinization (Mastrocicco et al., 2013). In the last decades, anthropogenic pressures have caused negative impacts on groundwater resources availability. Urbanization and over-drainage decrease aquifer natural recharge producing the conditions for saltwater intrusion in coastal aquifers, soil salinization with severe consequences in agriculture, and the deterioration of groundwater quality as well as the connected ecosystems, such as wetlands (Antonellini and Mollema, 2010; Greggio et al., 2012; Man et al., 2016). In particular, coastal areas of the Mediterranean basin are experiencing the greatest variations in water resources usage and strong conflicts for allocation and management, especially between agricultural and touristic purposes (Ferragina, 2010). Problems in water resource management are tackled by proposing solutions and alternative approaches that always generate heated debates related to their effectiveness and environmental sustainability (Cosgrove and Loucks, 2015). The construction of dams, for example, requires time and economic resources (even for the

* Author to whom all correspondence should be addressed: e-mail: nicolas.greggio2@unibo.it; Phone: +39 0544 937357; Fax: +39 0544 937411

social acceptability of design ideas) and, in addition, it occupies large portions of territory and causes population relocation. Furthermore, it does not guarantee an adequate solution to the problem of supply, since it is strictly dependent on precipitation (Rossetto and Bonari, 2014). Other options to face water scarcity and increasing requirements could be desalination plants even if there are still open issues related to production and disposal of brines and high construction costs, management and maintenance.

A real opportunity is the possibility to accumulate water into aquifers using non-drinking-quality water or water from periods of rainfall abundance. These technologies are known as Managed Aquifer Recharge (MAR). In recent years, an increased number of MAR projects were carried out around the world to store water from various sources, such as storm water, reclaimed water, desalinated seawater, rainwater or even groundwater from other aquifers (Dillon et al., 2009; Sprenger et al., 2017). MAR technologies, beside the advantage of storing water for later use, also contribute to increase the water quality characteristics of the infiltrated water. MAR techniques need to be adapted to the local situation and depend on the type of aquifer, topography, land use, water available for recharge, technical feasibility, and local population and administration acceptance. Currently, in Emilia-Romagna, only one case of MAR was set in place with the main objective to increase the piezometric level in the aquifer of the Marecchia alluvial fan that is strategically relevant for public water supply (Severi et al., 2014).

Since ancient times, water management in the Po River plain has always been of primary importance. In the II century BC, the Romans applied hydraulic techniques to distribute the water from the high lands in the Apennine foothills towards the low-lying lands of the Po River plain. They also made land cultivable thanks to artificial interventions (digging of canals and river dikes construction) on the natural river framework (Stefani and Zuppiroli, 2010). In the Middle Ages, marsh areas and wetlands in the low-lying zones were dried up by digging large canals which, leading the drainage water to the sea, allowed the establishment of a flourishing agriculture. During the ‘800s, land reclamation was performed by diverting natural streams and rivers into the areas to be reclaimed, so that sediment deposition allowed for the progressive increase in land elevation (Saltini, 2006). At the beginning of the ‘900, the availability of large steam and electrical pumps permitted the mechanical land reclamation that quickly drained the low-lying coastal lands (Antonellini et al., 2015). Nowadays, being most of the Ravenna area below or around 0 m a.s.l. in elevation, a drainage system, consisting in a network of drainage ditches and 12 water pumping stations, is required to keep the effective soil depth for agriculture practices and maintain land and infrastructure dry. The drainage ditches are also used as irrigation channels during summer (June-September) receiving surface water from nearby rivers via a system of pipes and sluice gates. The water management is accomplished by several Land Reclamation Authorities, which ensure the efficiency of irrigation distribution in support of the rural and industrial economy, urban, and civil activities. These Land Reclamation Authorities manage water scarcity emergencies in summer drought periods through water saving techniques and actions to reduce withdrawals and to rationalize the water distribution. The local economy is strongly related to agriculture and the production of high value crops, which require a considerable amount of irrigation water throughout late spring and the summer months.

In this context, the possibility to apply Managed Aquifer Recharge (MAR) techniques, specifically infiltration trenches, are investigated with the multiple objectives of reusing drainage water for irrigation and aquifer recharge by infiltration. In this paper, preliminary evaluations (not including yet a detailed economic assessment and environmental impact analysis) and recommendations for possible MAR multi-objective project locations in the low-lying coastal territory of Ravenna are presented. This study investigates the possibility to attribute an economic value to the drainage water that would otherwise no longer be used once it is lifted by the water pumping stations and collected into the final channel toward the sea. The presented MAR solution is adapted to the local territory and needs, in an area where these solutions are non-existent and their possibilities have not been investigated in detail, yet.

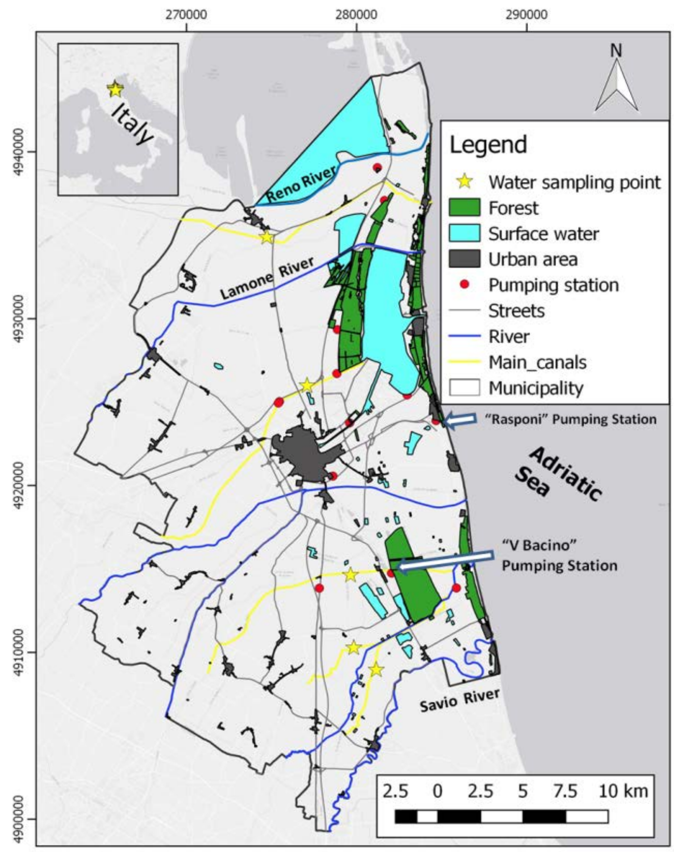
1.2. Regulatory framework of MAR: from Europe to Italy

The Water Framework Directive (WFD) (EC Directive, 2000/60) of the European Commission "requires that surface and groundwater achieve good status and a specific aspect of good status is the quantitative state of those water bodies". Over-abstraction and salinization are considered as major threats for European groundwater and, where this problem occurs, the WFD requires identifying and adopting measures to tackle the pressures. Among the measures aiming at reducing extraction and decreasing salinization, aquifer recharge with reuse of good quality water is one of the most promoted, especially because it can be seen as an alternative to conventional surface water storage and use. As reported by last EU guideline for water planning and management (EC Guideline, 2016), there are several advantages in artificial recharge: contrasting saltwater intrusion, decreasing evaporation, avoiding secondary contamination by animals and algal blooms, and limiting pipelines construction. Despite these benefits, the WFD sets out that artificial recharge needs a prior authorisation and imposes the use of sources that do not compromise the achievement of the environmental objectives established for recharged groundwater body (EC Directive 118, 2006). If at EU level the artificial recharge was regulated since 2000, not the same has been for Italy. Only with the national governmental decision n. 97/2013 (GD, 2013), in fact, the artificial recharge of groundwater bodies was allowed, changing art. 104 of the Legislative Decree 152/2006 (GD, 2006). Recently, thanks to the law n. 100/2016, the Italian Ministry of the Environment defined an authorization process (GD, 2016) for artificial recharge of water bodies. The Law identify in the Regional Water Authorities the administrative entities in charge of defining water bodies available for artificial recharge. Quality and quantity status of involved water bodies have to be constantly monitored pre- and post- intervention ensuring the maintenance of "good status" or the improvement for both water bodies. At the time of writing (2018), no database of water bodies potentially interested by MAR are available for the Emilia-Romagna Region.

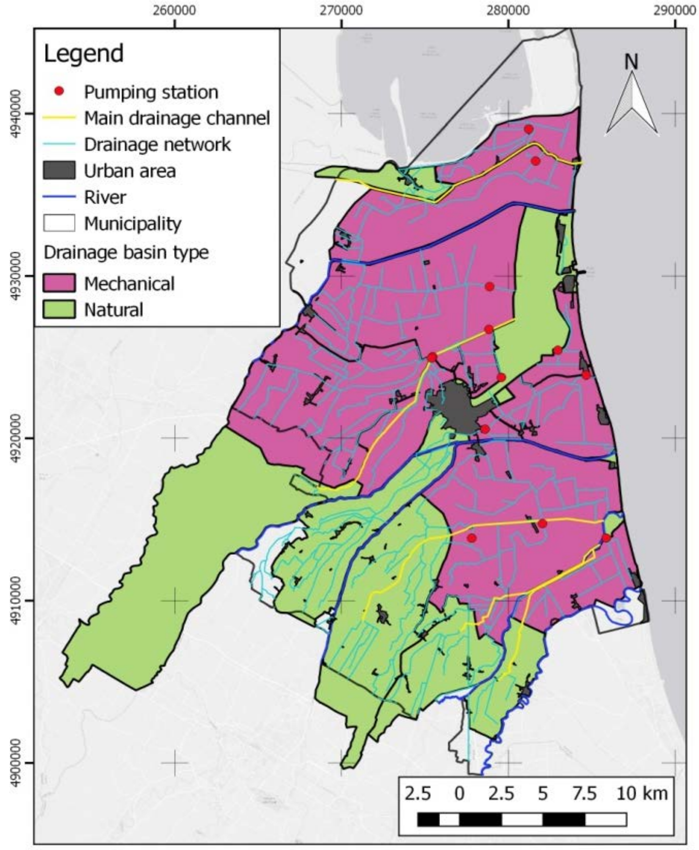
2. Local setting

The study area is in the Ravenna Municipality and extends from the mouth of the Reno River in the north, up to the Savio River's mouth in the south (Fig. 1a). The area is flat and comprises important natural areas within the *Po Delta Regional Park,* such as coastal forests and lagoons included in the Natura 2000 Special Areas of Conservation (SAC – Habitats Directive) (EC Directive, 1992/43). Large portions of the territory have topography ranging from 0.5 to -0.5 m a.s.l. In order to guarantee agriculture and all human activities, a dense network of drainage ditches and canals was set in place during the past century (Fig. 1b) (Antonellini et al., 2015). The whole area was separated in 15 drainage basins: eight basins require mechanical water drainage by pumping stations in order to discharge water toward the Adriatic Sea, while the other seven basins have natural hydraulic gradient (Fig. 1b). In the Ravenna Municipality there are nine pumping stations, which are active over the whole year; three additional pumping stations are activated in case of emergency. Two land Reclamation Authorities operate in this area: the Reclamation Consortium of Western Romagna for the northern area of the Lamone River, and the Reclamation Consortium of Romagna managing the southern zone. Basin extension ranges from 100 ha (closest basin to the Ravenna city), up to 10000 ha of the largest "V Basin" in the south (Mollema et al., 2012).

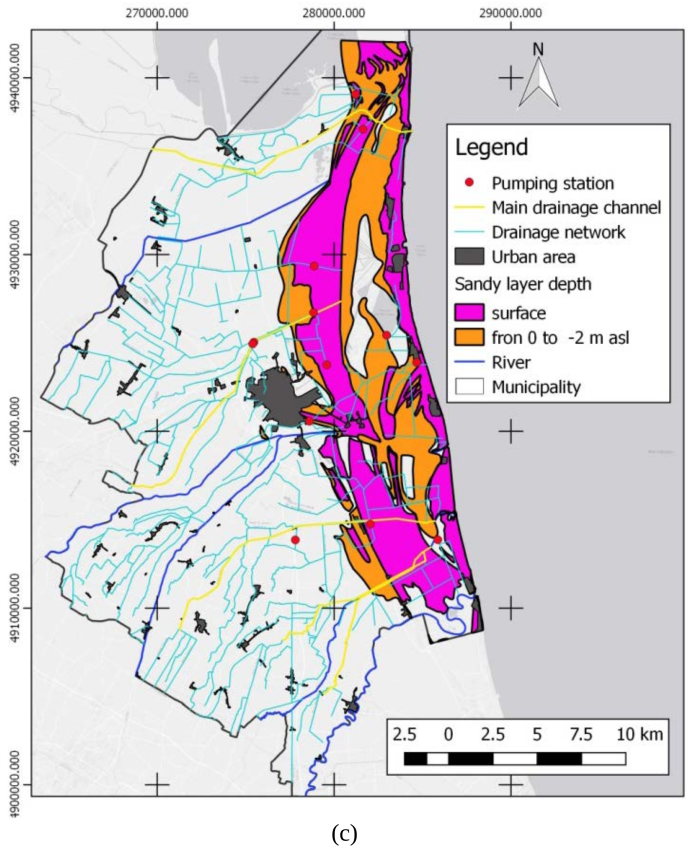
The hydrogeological setting of the shallow coastal aquifer consists of Holocene sediments (30 m in thickness) deposited during the last transgression-regression cycle started 18 ky ago (Greggio et al., 2017). The Pleistocene continental clays represent the impermeable unit and aquifer basement. From bottom to top, 2 - 3 m of transgressive fine-sand layer is overlapped by a thick prodelta unit ranging from 15 to 20 m in thickness; the uppermost unit consists of 7-10 m of sandy unit related to the ongoing beach progradation process (Amorosi et al., 1999). The aquifer is phreatic in the coastal portion, close to the Adriatic Sea, corresponding with the paleo- and current dune systems (Fig. 1c), while it becomes semi-confined by alluvial silty-clay layer westward, toward the Ravenna city (Antonellini et al., 2008; Greggio et al., 2012; Mollema et al., 2013a).



(a)



(b)



(c)

Fig. 1. (a) Study area location. The natural areas (pine forests, wetlands), surface water bodies, rivers and water sampling points are shown, (b) Drainage basins (mechanical and natural drainage), pumping stations, and drainage network, (c) Surface geology and coastal aquifer sandy unit depth

Many authors investigated the quality of the Emilia-Romagna coastal aquifer and pointed out that it is completely salinized (Antonellini et al., 2008; Giambastiani et al., 2007, 2013; Greggio et al., 2012; Mollema et al., 2013b). Generally, the water table is below or close to sea level, so that freshwater lenses in the dunes are seasonal and generally too thin to counteract regional groundwater and soil salinization processes. At a local scale, however, freshwater lenses can be important for irrigation purposes and sustainability of natural habitats (Cozzolino et al., 2017; Giambastiani et al., 2018; Vandenbohede et al., 2014).

2.1. Drainage system

The total water amount, which is drained by 12 water pumping stations across the Ravenna territory, is about 70 10^6 m^3/year with oscillations of ± 30 10^6 m^3 based on precipitation regime. The V Basin water pumping station (see Fig. 1a for location) serves the inland southern part of Ravenna (almost 9252 ha) and drains about 1/3 of the total yearly volume. By way of example, Fig. 2 shows the comparison between daily precipitation and drainage water volume of the V Basin and Rasponi water pumping stations for the 2015. The Rasponi pumping station serves a small reclamation area along the coast (2638 ha) (Fig. 1a for location). The water lifted by the pumping stations is higher during and just after strong rainfall events, but some pumping still takes place also in periods of no rainfall and during the dry summer months in order to keep the lowest coastal area dry.

Table 1 lists the average monthly precipitation and potential evapotranspiration over the period 1971-2015 and drainage averaged over the period 2000-2015. Drainage data are from the Land Reclamation Authority (http://www.bonificaromagna.it/); precipitation data (P) are from the Ravenna weather station (Regional Agency for environmental Protection database http://www.smr.arpa.emr.it/dext3r/), while potential evapotranspiration data (PET) are calculated by the Thornthwaite method according to the real length of the month and theoretical sunshine hours for local latitude. Data in Table 1 indicate a hydrological deficit (P-PET) in summer and water surplus in winter, when the drainage is at its peak. Over the entire period (1971-2015), average precipitation and evapotranspiration are 640 mm and 770 mm, respectively, in line with the previous water budget studies carried out in the same zone (Mollema et al., 2012, 2013a). The two pumping stations have drained together about 30 10^6 m^3 among which 5 10^6 m^3 during the summer period.

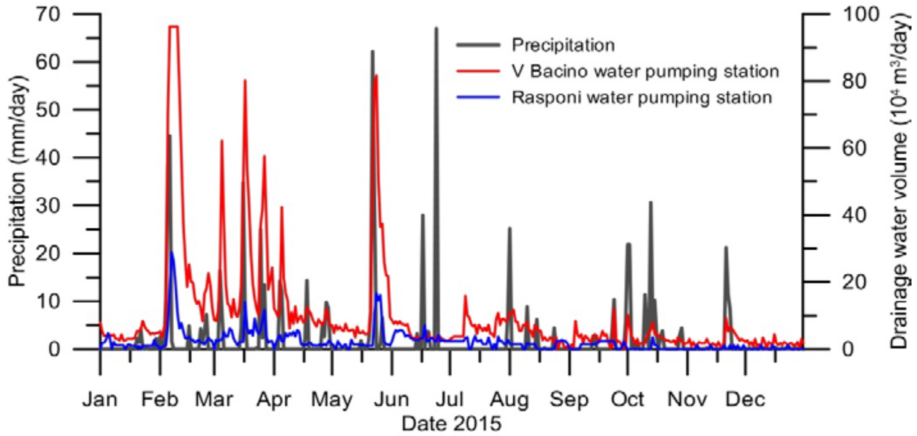


Fig. 2. Daily precipitation (mm) and daily drainage water volume (10^4 m^3) of "V Bacino" and "Rasponi" water pumping stations for the year 2015

Table 1. Average monthly drainage water (2000-2015), monthly precipitation and evaporation (1971-2015). The red colour indicates months characterized by hydrologic water deficit

	Month												***Total***
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***	
V Bacino water pumping station (mm/month)	22.2	30.8	36.1	28.7	22.6	14.6	15.4	13.2	13.0	15.4	15.7	22.4	**250.2**
Rasponi water pumping station (mm/month)	18.1	23.0	26.8	19.1	16.8	14.0	9.7	7.5	5.6	6.8	9.8	17.4	**174.6**
P (mm/month)	41.9	42.0	53.5	55.8	48.3	45.1	37.4	55.0	68.5	71.2	72.6	50.6	**642.0**
PET (mm/month)	4.6	9.5	27.1	49.8	93.3	126.5	153.1	138.1	89.9	53.2	20.1	6.2	**771.4**
P - PET (mm/month)	37.2	32.5	26.4	6.0	-45.0	-81.4	-115.7	-83.1	-21.3	18.1	52.5	44.4	**-129.4**

2.2. Water quality

The comparison of salinity values and chemical composition (Fig. 3) among different water samples collected from the main rivers and drainage channels across the study area (monitoring points in Fig. 1a) shows similar water composition in all samples. Although salinity of drainage water is slightly higher than salinity of natural bodies, it remains less than 1 g/l, far away from the values of 20-25 g/l of the Adriatic Sea, recorded in front of the coast and confirmed by previous studies (Cozzolino et al., 2017; Mollema et al., 2013b). The chemical composition of drainage water shows enrichments for all investigated species but chloride remains on average below 500 ppm. This ensures the possibility to reuse drainage water for irrigation and/or aquifer recharge by infiltration (GD, 2006).

3. Proposal – Technical solutions and requirements

The project assessment takes into account the local geology, water infrastructure availability, and drainage water quality. The water supply is drainage water that is annually released to the sea even during dry periods. The project would involve the excavation of a strategically located infiltration trench, which intercepts the top sandy units of the aquifer. The infiltration trench needs to be close to pumping station for the water supply and agricultural areas requiring irrigation.

Once the proper location is defined and the trench excavated, water will be collected from the main drainage channel, which currently brings drainage water from the water pumping stations to the sea, and delivered to the infiltration trench by a pipeline, following the natural hydraulic gradient. The infiltration trench will be kept full for four months from May to August and it would make water available for irrigation. Moreover, the water level in the trench will be higher than the surrounding water table, creating aquifer recharge. A preliminary case study in the Ravenna area considered an irrigation trench 1 km long, 5 m large and 2 m deep and calculated a recharge rate of 1 m^3 per day per unit length of channel, allowing an estimated aquifer recharge of 10^5 m^3 for summer operation (Vandenbohede et al., 2014). However, that situation is slightly different than the cases presented in this paper. In the site considered by Vandenbohede et al. (2014), in fact, aquifer recharge was totally accidental because location, trench size and operation time were completely based on agronomic needs (water-dependent and season crops). As a result, the trench was not continuously kept operative for four months as proposed in this paper. Besides, the geological setting in Vandenbohede et al. (2014) was different and not ideal for infiltration because of the presence of shallow silty-clay layers, which limited flow from trench to aquifer in the western trench bank. Given that many differences in management exist among the site of Vandenbohede et al. (2014) and the ones proposed here, in order to estimate the aquifer recharge, the following analytical solution for a drainage/recharge trench (Chiesa, 2004) is used (Eq. 1):

$$\frac{\partial^2 s}{\partial x^2} = \frac{S}{T}\frac{\partial s}{\partial t} \tag{1}$$

where: *s* [m] is the increase of water table (piezometric level) in the aquifer as a function of time *t* [days] and distance *x* [m] from the trench following a sudden water level increase s_0 [m] in the trench; *S* is the storativity [-] and *T* the aquifer transmissivity [m^2/day].

The analytical solution is for the transitory state and derived for confined aquifers. Since the aquifer thickness is considered close to the saturated thickness, Eq. (1) can be also used for phreatic aquifers (Chiesa, 2004). Using the initial condition $s(x, 0) = 0$ and boundary conditions $s(\infty, t) = 0$, $s(0, t) = s_0$ in Eq. (1), it is obtained (Eq. 2):

$$s = s_0\left(1 - erf\left(\frac{x}{\sqrt{\frac{4Tt}{S}}}\right)\right) \tag{2}$$

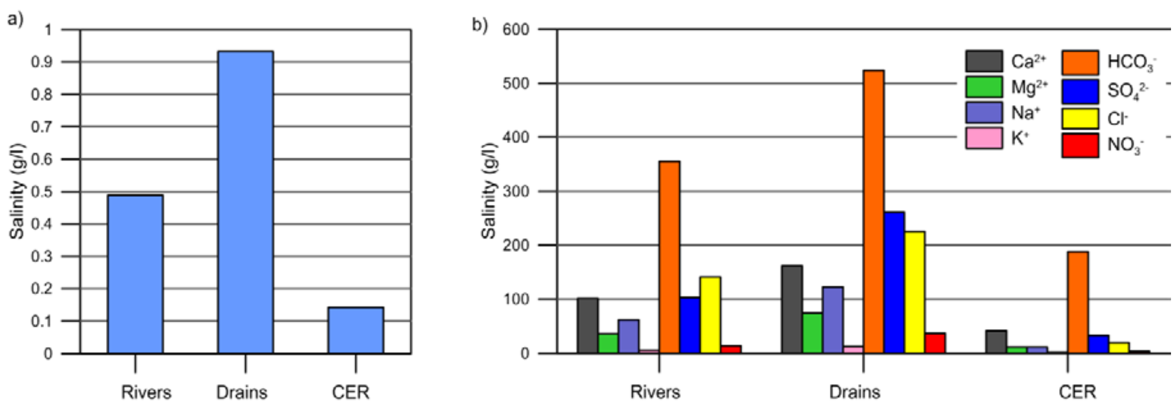


Fig. 3. Average salinity values (a) and chemical concentrations of the main ions (b) of river, drainage channels and CER water. Note: CER stands for "Canale Emiliano-Romagnolo" and represents a large regional irrigation infrastructure developed to guarantee delivery of high-quality water for agriculture. CER water is included in the analysis as irrigation water standard

For a phreatic aquifer, *s* can be set as (Eq. 3):

$$s = \frac{(H^2 - h^2)}{2b} \tag{3}$$

where: *b* is the saturated thickness of the aquifer [m], *H* and *h* are the current and increased hydraulic head in the trench, respectively [m]. The flow rate per unit length in the trench is (Chiesa, 2004) (Eq. 4):

$$Q_0 = s_0\sqrt{\frac{S_yT}{\pi t}} = \frac{K(H^2 - h^2)}{2\sqrt{\frac{Tt\pi}{S_y}}} \tag{4}$$

where *K* is the hydraulic conductivity [m/day], and, for the unconfined aquifer case, the storativity *S* is almost equal to the specific yield (S_y).

The amounts of water required to maintain a constant water increase of 0.5 m and 1 m in each proposed trench with respect to the current water table were calculated. These two proposed water levels in the trench are in line with the water table measurements conducted by Mollema et al. (2013a) in the coastal basin of Ravenna. The variable values used in the calculation and the total water requirements for 120 days of trench operation are listed in Table 3. It is important to note that the amounts of estimated water do not include water loss by direct evaporation processes, neither withdrawal for irrigation, and reflect only the quantity of drainage water infiltrating the aquifer.

In order to indicate possible benefits not only for groundwater and environment, but also for agriculture, simple calculation related to Gross Marketable Production (GMP) are performed. Based on what reported by Fanfani and Pieri (2015), the Gross Marketable Production (GMP) per ha for local extensive crops was about 1000 € in 2015, but four time higher in case of irrigated crops. For the estimates presented in this paper, an average of 2000 € GMP per ha for irrigated fields (Fanfani and Pieri, 2015) is adopted. It is also assumed that only half of current extensive crops could be converted in high value crops because of increasing need of manpower and technology by current agricultural companies.

4. Best sites identification

Based on the requirements listed in Table 2, four sites were selected as best locations for the infiltration trenches. Fig. 4 shows their locations and Table 3 lists the main characteristics of each project with the related estimates of recharge amounts.

Site 1 (Fig. 4) belongs to the “Casalborsetti” basin that drains more than 4700 ha of lowland. The Land Reclamation Water Authority of Western Romagna manages this basin. The withdrawal point is hypothesized immediately downstream of the pumping station, where the water is around 0 m a.s.l.

Table 2. Specific requirements considered to find the best locations for infiltration trenches in the Ravenna territory

Requirement	***Conditions***	***Advantage***	***Disadvantage***
Geological setting	The excavation must intercept the aquifer in its shallow sandy units (Fig. 1c) and the minimum size must be 5 m wide and 2 m deep (Vandenbohede et al., 2014)	Higher infiltration water rates and aquifer recharge. Development of shallow freshwater lenses above the saltwater (Cozzolino et al., 2017)	Not all territory is suitable for infiltration trenches because of potential waterlogging, presence of silty clay layers, and shallow water table
Water supply channel	The water supply is the channel that brings drainage water from the water pumping station towards the sea. Possibly the hydraulic head of this channel must be higher than the surrounding aquifer water level in order to have a natural hydraulic gradient.	No costs to lift up drainage water and fill the infiltration trench (the natural hydraulic gradient is used)	Not all channels are suitable as water supply channels.
Vicinity to water pumping station	Withdrawal point close to water pumping station.	Reuse of drainage water that, otherwise, would be delivered directly to sea without any other reuse. The economic value and cost of water in this point is at its lowest.	
Farmland	Proximity to farmland in need of irrigation	Availability of an infiltration trench for irrigation. Conversion from extensive agriculture to horticultural or fruit crops (higher marketable value).	Lack of stakeholder involvement. Lack of awareness between farmers.

Table 3. Summary of the characteristics of the selected sites and estimates of recharge amounts

Site	*Drainage basin name*	*Infiltration trench length (m)*	*Cumulative aquifer recharge (after120 days of trench operation) for 0.5 m water level increase (*) (m^3/120 day)s*	*Cumulative aquifer recharge (after120 days of trench operation) for 1 m water level increase (*) (m^3/120 day)*	*Agriculture area (ha)*	*GMP gain (k€/y)*
1	"Casalborsetti"	2400	$1.1\ 10^5$	$2.1\ 10^5$	350	175
2	"Canala-Valtorto"	2000	$9.0\ 10^4$	$1.8\ 10^5$	150	75
3	"V Basin"	2300	$1.0\ 10^5$	$2.1\ 10^5$	600	300
4	"Bevanella"	1500	$6.7\ 10^4$	$1.3\ 10^5$	400	200
TOTAL		**8200**	**$3.7\ 10^5$**	**$7.3\ 10^5$**	**1500**	**750**

(*) To be noted: Flow rate values are calculated based on Eq. 3 assuming: K = 10 m/day; S_y = 0.25 (Giambastiani et al., 2007; Mollema et al., 2013a), t = 120 days, H = 6 m; h= 6.5 m and 7 m in order to simulate the two scenarios s_o = 0.5 m and 1 m, respectively. This water would not include evaporative losses from the trench, trench filling water and any possible use of water for irrigation.

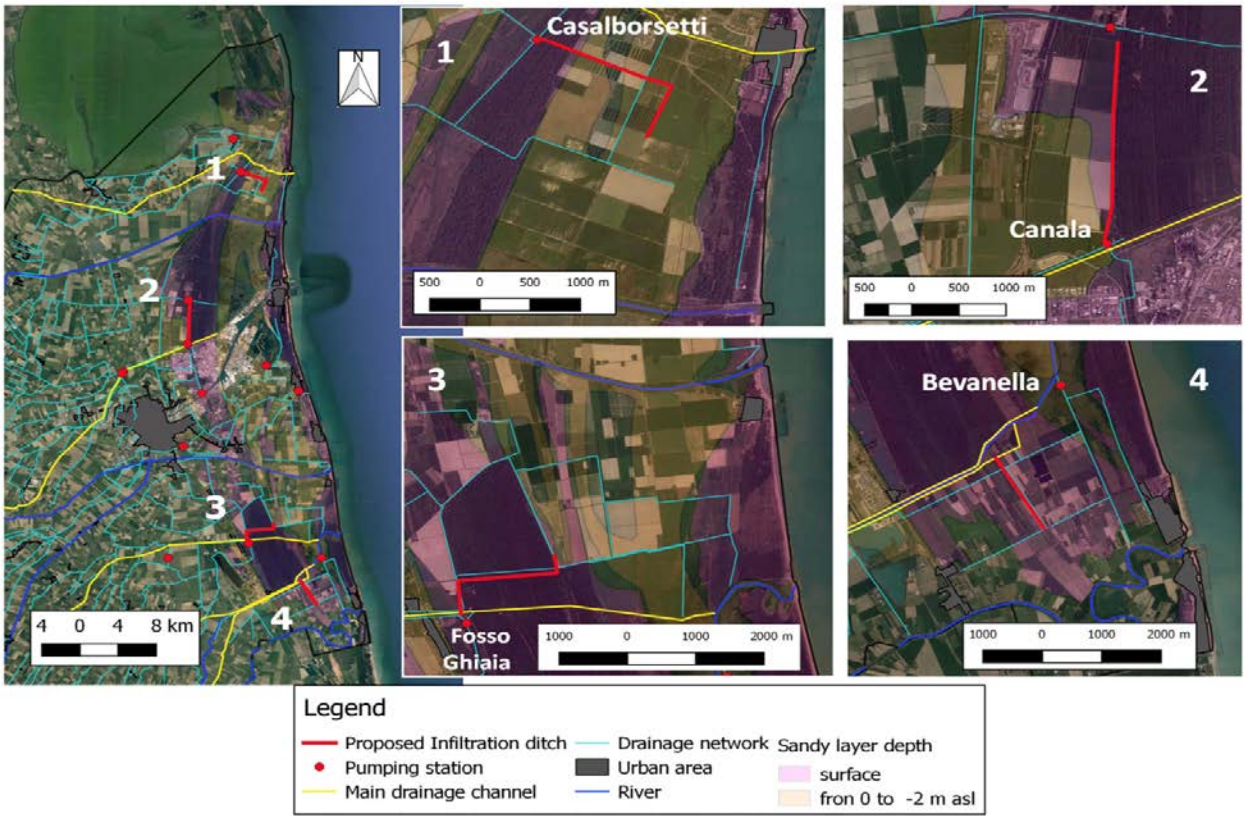


Fig. 4. Location of the four selected best sites (numbered as 1, 2, 3 and 4) for the proposed irrigation trenches. Pumping stations (named in figure) are indicated by red dots, rivers are in blue color, main drainage channels in yellow lines, while drainage network in cyan color

The agricultural area eastward to the channel is about 350 ha, entirely on extensive crops such as maize, grains and hay. The pumping station is located on the western border of a pine forest and the proposed trench starts from there and proceeds eastward, through the forest until the agricultural fields. The total length is over 2400 m, 500 m of which inside the pine forest. The aquifer is unconfined in the pine forest, and semi-confined by 1 m of shallow silty clay sediments in the cultivated area. Assuming to adopt trench dimensions as proposed by Vandenbohede et al. (2014) (5 m wide, 2 m deep) and considering 1.8 m of water column in the trench and a trapezoidal section (4.5 and 3 m for the two bases), the total trench volume would be around 16000 m^3. Based on Eq. (3), the amount of water required to maintain water level increases of 0.5 m and 1 m in the trench, with respect to the water table, are 1.1 10^5 and 2.1 10^5 m^3 of drainage water for 120 operation days, respectively. Based on the assumption described in chapter 3, the shifting from extensive crops to irrigated crops could generate a GMP increasing of 175 k€/y.

Site 2 is located near the water pumping station called "Canala" (Fig. 4); it is part of the inner "Canala-Valtorto" basin, which has an area of 7000 ha. In this site, the drainage channel has a natural gradient toward the sea and it can deliver water to the proposed infiltration trench without the installation of additional equipment. As shown in Fig. 4, the new trench should be excavated along the western border of a pine forest, where the aquifer is unconfined. The total planned trench length is about 2 km and trench shape and dimensions are the same as in the previous site (1). In this case, the trench volume is around 13000 m^3. About 150 ha of agricultural fields adjacent to the infiltration trench could be supplied by drainage water. The estimates point out that about 9 10^4 and 1.8 10^5 m^3 of reused water could be stored during 120 days of activity if the water level in the trench were constantly maintained 0.5 and 1 m higher than the current water table, respectively. At the same time, if farmers decided to replace half of the current crops with irrigated crops, an increase of 75 k€/y of GMP would be expected.

Site 3 is located in the southern part of the study area (Fig. 4). It is included in the V Basin, which is the largest of the area with an extension of more than 10000 ha. The water supply would be the ditch called “Fosso Ghiaia”. Also, in this case the water from the supply channel can naturally flow into the infiltration trench by natural hydraulic gradient without the use of additional equipment having this portion of the territory the lowest elevation and hydraulic level in Ravenna (-2 m a.s.l.). As in site 2, the vicinity of the withdrawal point to a coastal pine forest can add relevant environmental benefits in terms of improving groundwater quality and developing relevant freshwater habitats. The majority part of the proposed trench would be located inside the pine forest until the agricultural fields that border the eastern portion of the forest (Fig. 4). The trench would be 2.3 km long and, considering the same above-mentioned size, the volume of possible water storage would be about 15000 m^3, while the estimated aquifer recharge would be around 10^5 and 2.1 10^5 m^3 for 120 days of operation, considering 0.5 and 1 m of water level increase in the trench, respectively. Considering that more than 600 ha could be supplied by drained water and only 300 converted from extensive to irrigated crops, the estimated increase in GMP would be 300 k€/y.

Site 4 is within the “Bevanella” basin. The surface geology shows wide portion of unconfined aquifer with sandy units at the top (Fig. 4). The “Bevanella” drainage channel, which drains water from the inner part of the *Bevanella* basin, would supply water for the infiltration trench. The planned infiltration trench extends southward of the *Bevanella* channel for 1.5 km, potentially providing irrigation water for more than 400 ha of agricultural land. Based on the above-mentioned trench dimensions, infiltration rates and GMP values, water storage of about 10000 m^3 with an aquifer recharge of about 6.7 10^4 (s_0 = 0.5 m) and 1.3 10^5 (s_0 = 1 m) m^3 water for 120 days of operation are estimated, along with an increase of 200 k€/y in GMP.

5. Discussions

The current trends in Mediterranean climate indicate longer periods of drought and hot temperature in summer and shorter and more intense precipitation in spring and autumn, which lead to a deficit of freshwater resources to both agro- and natural ecosystems, requiring a reconsideration of the current water management (Mollema et al., 2012, 2013a). Decreasing natural aquifer recharge induces saltwater intrusion in coastal aquifers, soil salinization (crop yield reduction), and deterioration of groundwater-dependent natural ecosystems (Antonellini and Mollema, 2010; Greggio et al., 2012). As reported by Ferragina (2010) strong conflicts are rising for freshwater allocation between the need of drainage from one side and the irrigation water supply from the other side. Thanks to the advantage of storing water for later use, several MAR projects have been put in place around the world (Dillon et al., 2009; Sprenger et al., 2017; Stefan and Ansems, 2018).

The hydrogeological and anthropic settings in the study area, along with the previous findings by Vandenbohede et al. (2014), suggest the adoption of infiltration trench among the available MAR techniques. The advantages of this solution, compared to other MAR techniques, are well summarized by Bouwer (2002) and essentially include: low costs, reduced evaporative losses and clogging, as well as easy to be blended with surrounding agro-ecosystems. Other advantages here are the good quality of water supply for infiltration and the fact that the proposed trenches are identified as portion of already operating drainage network, which could be temporarily shifted from original drainage function and used as infiltration trench from May to August. This last point would reduce costs and need to expropriate land from farmers for trench excavation.

Four requirements have been identified in order to select the places for MAR implementations (Table 2). All identified locations are located within or in proximity of the historical paleodune systems (nowadays covered by historical pinewood of San Vitale and Classe) where the coastal aquifer is phreatic (Amorosi et al., 1999; Antonellini et al., 2008). The other fundamental requirements are the vicinity of drainage channel and pumping station. The closer they are, the lowest the cost for water supply. The last requirement of proximity to farmland has been easily solved being the area strongly agriculture-oriented.

Regarding the estimated benefits, the infiltration trenches could guarantee infiltration and storage into coastal aquifer of about 4 - 7 10^5 m^3/120 days of good quality drainage water, alternately wasted to the sea. The estimation does not include the irrigation water withdrawn from trenches. Based on the water irrigation demand projection for irrigated crops calculated by Gallo et al. (2012) of about 1000 m^3/ha*120 days, a rough estimate of saved water would reach 0.8 - 1.4 10^6 m^3/120 day. These data correspond to about 20% of the annual withdrawal from a local river (Lamone River) (CER, 2016). Considering that the Po Delta coastal plain has similar drainage infrastructure and groundwater is historically affected by salinization (Colombani et al., 2017a, 2017b), the application of the proposed MAR solution to the entire Delta area will allow reusing millions m^3 of drainage water for irrigation and aquifer recharge, avoiding withdrawals from rivers and deep groundwater abstraction.

The agricultural land potentially served by the proposed irrigation opportunities amounts to 1500 ha, about 2% of the Ravenna province. Based on the economic data by Fanfani and Pieri (2015), and considering that only half of current extensive crops could be converted into irrigated crops, the GMP gain is about 750 k€/y.

The infiltration trenches would also generate benefits for the adjacent pine forests (San Vitale and Classe pine forest), historically affected by groundwater salinization (Giambastiani et al., 2007). The forests could benefit from the groundwater freshening generated by the trenches with positive benefits in terms of freshwater habitat and biodiversity increase (Antonellini and Mollema, 2010; Janssen et al., 2016).

Apart from direct costs of the intervention, two main limitations would affect the wide implementation of this solution across the study area: water cost and maintenance/clogging of the trenches. Regarding drainage water cost, although the withdrawal point is supposed as close as possible to a pumping station, Land Reclamation Water Authority claims an economic compensation (lower than the common lease) for the volume of water derived from its channels. The designation of an equilibrate drainage water cost among farmers associations and Land Reclamation Water Authority is fundamental. The cost should take into account, firstly, the relevant environmental benefits for aquifer, and, secondly, agricultural uses.

The trench maintenance essentially depends on clogging of subsoil with consequent and gradual decrease of infiltration rates till complete trench obstruction (Masciopinto, 2013). Although trenches and ditches are less sensitive to clogging than other shallow methods (i.e. ponds) because of steep banks that increase water velocity, a once-a-year operation of trench reshaped should be accounted for clogged material removal and restoration of initial infiltration rate (Masciopinto et al., 2017).

6. Conclusions

In the low-lying coastal areas of Ravenna (Po River plain, Northern Adriatic Sea, Italy), the increasing demands for water supplies both as consumptive (irrigation, industry, domestic use) and non-consumptive (ecosystem services) commodity, force administrators to reconsider the current water management and find sustainable solutions. A recently introduced national regulatory network with specific indications and procedures for managed aquifer recharge (MAR) opens the possibility for the projects that are proposed in this paper. The discussed MAR projects plan the reuse of drainage water, which is annually released to the sea without any further reuse even during periods of high-water scarcity. This water could be intercepted immediately upstream of pumping stations and released in close infiltration trenches for both irrigation and aquifer recharge purposes. Chemical analysis performed on samples of drainage water reveal acceptable quality, suitable for irrigation and aquifer recharge according to the current regulations.

Since MAR system performance and efficiency depends upon site-specific conditions, four most important requirements are identified: geological setting, drainage channel (water supply) availability, proximity to water pumping station, and presence of agricultural fields in need of irrigation. The four proposed MAR sites comply with these requirements.

The infiltration trenches can operate for four months, from May to August, making water available during the irrigation season and guaranteeing aquifer recharge by infiltration. Overall, a total of 8200 m of infiltration trenches would provide storage of more than 0.7 million m^3 of water and irrigation for over 1500 ha of farmland. The water estimates do not include water loss by direct evaporation processes. Although no detailed economic analysis regarding setting-up and installation costs were reported in this work, the proposed MAR projects represent a relative low-cost intervention considering the resulting benefits in terms of water saving and storage.

The benefits for groundwater and agricultural sectors are evident and also nearby natural areas would benefit from the projects, with the possibility to create new freshwater habitats in coastal areas currently dominated by low-biodiversity brackish or saltwater habitats.

Costs are estimated to be about € 50000 for a 1000-m-long trench (RER, 2018), including: planning, design, excavation and monitoring instruments installation. Considering that water flows into infiltration trenches thanks to natural gradient and no more energy or additional equipment are required, this kind of intervention is cost-effective and win-to-win solution where compared with other MAR techniques. The main limitations of the proposed MAR project are water cost and clogging risk. The definition of an accessible water cost dedicated to irrigation need to be defined by farm associations and Land Reclamation Water Authority.

Future research directions include the development of a test-demonstration site where real costs are evaluated and stored water and crop yield increase measured in order to foster the adoption of this practice. At the same time the instauration of a periodic round table of all stakeholders is needed in order to overtake current different visions among users (farmers and environmental agencies) and water suppliers (Land Reclamation Water Authority and Municipalities). Despite a site-specific economic assessment and environmental impact analysis are required to complete the current proposal, this study could support the round table participants to improve water use efficiency and plan future water infrastructures.

References

Amorosi A., Colalongo M.L., Pasini G., Preti D., (1999), Sedimentary response to Late Quaternary sea-level changes in the Romagna coastal plain (northern Italy), *Sedimentology*, **46**, 99-121.

Antonellini M., Mollema P., Giambastiani B., Bishop K., Caruso L., Minchio A., Pellegrini L., Sabia M., Ulazzi E., Gabbianelli G., (2008), Salt water intrusion in the coastal aquifer of the southern Po Plain, Italy, *Hydrogeology Journal*, **16**, 1541-1556.

Antonellini M., Mollema P.N., (2010), Impact of groundwater salinity on vegetation species richness in the coastal pine forests and wetlands of Ravenna, Italy, *Ecological Engineering*, **36**, 1201-1211.

Antonellini M., Allen D.M., Mollema P.N., Capo D., Greggio N., (2015), Groundwater freshening following coastal progradation and land reclamation of the Po Plain, Italy, *Hydrogeology Journal*, **23**, 1009-1026.

Bouwer H., (2002), Artificial recharge of groundwater: hydrogeology and engineering, *Hydrogeology Journal*, **10**, 121-142.

CER, (2016), Rapporto Idrologico annuale del Consorzio del Canale Emiliano Romagnolo, On line at: http://www2.consorziocer.it/public/allegatifocus/RapportoCER_Giu_2016.pdf

Chiesa G., (2004), *Groundwater Hydraulics,* Dario Flaccovio Press, Italy.

Colombani N., Cuoco E., Mastrocicco M., (2017a), Origin and pattern of salinization in the Holocene aquifer of the southern Po Delta (NE Italy), *Journal of Geochemical Exploration*, **175**, 130-137.

Colombani N., Giambastiani B.M., Mastrocicco M., (2017b), Impact of climate variability on the salinization of the coastal wetland-aquifer system of the Po Delta, Italy, *Journal of Water Supply: Research and Technology-Aqua*, jws2017115.

Cosgrove W.J., Loucks D.P., (2015), Water management: current and future challenges and research directions. *Water Resources Research*, **51**, 4823-4839.

Cozzolino D., Greggio N., Antonellini M., Giambastiani B.M.S., (2017), Natural and anthropogenic factors affecting freshwater lenses in coastal dunes of the Adriatic coast, *Journal of Hydrology*, **551**, 804-818.

Dillon P., Pavelic P., Page D., Beringen H., Ward J., (2009), Managed aquifer recharge: An introduction, Australian Government – National Water Commission; Waterlines Report Series n. 13, On line at: http://webarchive.nla.gov.au/gov/search?q=Managed+aquifer+recharge.

EC Directive, (1992), Directive 1992/43/EEC of the European Council on the conservation of natural habitats and of wild fauna and flora, *Official Journal of the European Communities*, L 206/7-50, 21.05.1992, Brussels.

EC Directive, (2000), Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. *Official Journal of the European Communities.* L 327/1-72, 22.12.2000, Brussels.

EC Directive 118, (2006), Directive 2006//EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration. *Official Journal of the European Union*, L 372/19-31,12.12.2006, Brussels.

EC Guideline, (2016), Guidelines on Integrating Water Reuse into Water Planning and Management in the context of the WFD. On line at: http://ec.europa.eu/environment/water/pdf/Guidelines_on_water_reuse.pdf.

Fanfani R., Pieri R., (2015), *The agri-food system of Emilia-Romagna* (in Italian), Rapporto 2015, Maggioli Editore, On line at: http://www.ucer.camcom.it/osservatori-regionali/os-agroalimentare

Ferragina E., (2010), *The Water Issue in the Mediterranean*, In: *10 Papers for Barcelona 2010: Environmental and Sustainable Development in the Mediterranean*, Scoullos M., Ferragina E. (Eds.), 53-79.

Gallo A., Tomei F., Villani G., Pratizzoli W., Spisni A., Marletto V., (2012), Seasonal forecasts and climatic projections for the irrigation management in Emilia Romagna Region (Italy), *Journal of Agrometeorology*, **7**, 5-12.

GD, (2006), Italian Governmental Decision No. 152/2006 Environmental regulation (Norme in materia ambientale), On line at: http://www.gazzettaufficiale.it/atto/serie_generale/caricaDettaglioAtto/originario?atto.dataPubblicazioneGazzetta=2006-04-14&atto.codiceRedazionale=006G0171.

GD, (2013), Italian Governmental Decision No. 97/2013. On line at: http://www.gazzettaufficiale.it/eli/id/2013/08/20/13G00138/sg.

GD, (2016), Italian Governmental Decision No.100/2016. Regulation with criteria for the issue of the authorization for the artificial revitalization or augmentation of groundwater bodies in order to achieve the quality objective, On line at: http://www.gazzettaufficiale.it/eli/id/2016/06/13/16G00111/sg.

Giambastiani B.M., Antonellini M., Essink G.H.O., Stuurman R.J., (2007), Saltwater intrusion in the unconfined coastal aquifer of Ravenna (Italy): a numerical model, *Journal of Hydrology*, **340**, 91-104.

Giambastiani B.M.S., Colombani N., Mastrocicco M., Fidelibus M.D., (2013), Characterization of the lowland coastal aquifer of Comacchio (Ferrara, Italy): hydrology, hydrochemistry and evolution of the system, *Journal of Hydrology*, **501**, 35-44.

Giambastiani B.M., Greggio N., Nobili G., Dinelli E., Antonellini M., (2018), Forest fire effects on groundwater in a coastal aquifer (Ravenna, Italy), *Hydrological Processes*, **32**, 2377-2389.

Greggio N., Mollema P., Antonellini M., Gabbianelli G., (2012), *Irrigation Management in Coastal Zones to Prevent Soil and Groundwater Salinization*, In: *Resource Management for Sustainable Agriculture*, Abrol V., Sharma P. (Eds.), InTech, Rijeka, Croatia, DOI: 10.5772/50534.

Greggio N., Giambastiani B., Campo B., Dinelli E., Amorosi A., (2017), Sediment composition, provenance, and Holocene paleoenvironmental evolution of the Southern Po River coastal plain (Italy), *Geological Journal*, **53**, 914-928.

Janssen J.A.M., Rodwell J.S., Criado M.G., Gubbay S., Arts G.H.P., (2016), European Red List of Habitats, European Union. Report, On line at: http://ec.europa.eu/environment/nature/knowledge/pdf/terrestrial_EU_red_list_report.pdf.

Man Y.B., Chung A.K.C., Wong M.H., (2016), Changes in low molecular weight organic acids and antioxidative enzyme activities of wetland plants under metal stresses, *Environmental Engineering and Management Journal*, **16**, 1657-1663.

Masciopinto C., (2013), Management of aquifer recharge in Lebanon by removing seawater intrusion from coastal aquifers, *Journal of Environmental Management*, **130**, 306-312.

Masciopinto C., Vurro M., Palmisano V.N., Liso I.S., (2017), A suitable tool for sustainable groundwater management, *Water Resources Management*, **31**, 4133-

4147.
Mastrocicco M., Colombani N., Di Giuseppe D., Faccini B., Coltorti M., (2013), Contribution of the subsurface drainage system in changing the nitrogen speciation of an agricultural soil located in a complex marsh environment (Ferrara, Italy), *Agricultural Water Management*, **119**, 144-153.
Mollema P.N., Antonellini M., Gabbianelli G., Laghi M., Marconi V., Minchio A., (2012), Climate and water budget change of a Mediterranean coastal watershed, Ravenna, Italy, *Environmental Earth Sciences*, **65**, 257-276.
Mollema P.N., Antonellini M., Gabbianelli G., Galloni E., (2013a), Water budget management of a coastal pine forest in a Mediterranean catchment (Marina Romea, Ravenna, Italy), *Environmental Earth Sciences*, **68**, 1707-1721.
Mollema P.N., Antonellini M., Dinelli E., Gabbianelli G., Greggio N., Stuyfzand P.J., (2013b), Hydrochemical and physical processes influencing salinization and freshening in Mediterranean low-lying coastal environments, *Applied Geochemistry*, **34**, 207-221.
RER, (2018), Region Emilia Romagna, Regional prices database of public works and defense of the soil for the Emilia-Romagna Region, On line at: http://territorio.regione.emilia-romagna.it/osservatorio/Elenco-regionale-prezzi.
Rossetto R., Bonari E., (2014), The future of Managed Aquifer Recharge in Italy: the European FPVII MARSOL Project and the European Innovation Partnership on Water Mar to Market, *Acque Sotterranee - Italian Journal of Groundwater*, **3**, 9-12.
Saltini A., (2006), *Where man separated the earth from the waters. History of land reclamation in Emilia-Romagna*, Collana 'Terra d'acque. Padus', Diabasis Ed., 862 pp.
Severi P., Bonzi L., Ferrari V., Pellegrino I., (2014), Recharge in controlled conditions of the Marecchia River cone (Rimini), start of experimentation and first results, *Acque Sotterranee - Italian Journal of Groundwater*, **3**, 49-54.
Sprenger C., Hartog N., Hernández M., Vilanova E., Grützmacher G., Scheibler F., Hannappel S., (2017), Inventory of managed aquifer recharge sites in Europe: historical development, current situation and perspectives, *Hydrogeology Journal*, **25**, 1909-1922.
Stefan C., Ansems N., (2018), Web-based global inventory of managed aquifer recharge applications, *Sustainable Water Resources Management*, **4**, 153-162.
Stefani M., Zuppiroli M., (2010), The interaction of geological and anthropic processes shaping the urban growth of Ferrara and the evolution of the surrounding plain, *Alpine and Mediterranean Quaternary*, **23**, 355-371.
Vandenbohede A., Mollema P.N., Greggio N., Antonellini M., (2014), Seasonal dynamic of a shallow freshwater lens due to irrigation in the coastal plain of Ravenna, Italy, *Hydrogeology Journal*, **22**, 893-909.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2391-2399
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

ASSESSING THE CORRELATION BETWEEN CONTAMINATION SOURCES AND ENVIRONMENTAL QUALITY OF MARINE SEDIMENTS USING MULTIVARIATE ANALYSIS

Claudia Labianca[1]*, Sabino De Gisi[1], Michele Notarnicola[1]

Department of Civil, Environmental, Land, Building Engineering and Chemistry, Polytechnic University of Bari, Via E. Orabona no. 4, 70125 Bari, Italy

Abstract

Water sea pollution is influenced mainly by anthropogenic causes due to industrial and municipal activities which affect the quality of sea water, sediments and the whole ecosystem. In this paper, the correlation between contamination sources and the environmental quality of marine sediments was analyzed through multivariate analysis, in particular Principal Components Analysis (PCA), Cluster Analysis (CA) and Correlation Analysis. Considering the case study of Mar Piccolo in Taranto (Ionian Sea, Southern Italy), it was performed first a PCA on the total matrix consisting of 1023 samples 3m deep and 20 variables (moisture content, granulometry, metals, metalloids and nutrients). Then, a PCA only for the superficial layers (0-50cm) was performed to better understand correlations with anthropogenic and natural impacts. Cluster and correlation analyses corroborated PCA results, identifying sub-clusters among the variables. The assessment showed how the type of pollution in Mar Piccolo of Taranto is widespread on superficial layers with some particular areas (hotspots) with a heavy and deeper contamination. Correlation between nutrients and metals, validated by CA analysis, showed that the excessive presence of nutrients and organic matter, in the Mar Piccolo water, acts as carrier for many contaminants that concentrate in the fine fraction of sediments with high percentage of organic matter.

Key words: chemometric techniques, environmental management, heavy metals, remediation, Total Organic Carbon

Received: March, 2018; Revised final: May, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The presence of polluting loads in watercourses and the concentration of industrial and production activities may result in contamination of river sediments, port and marine areas.

Usually, sediments can be contaminated with metals (Aluminium, Arsenic, Cadmium, Chromium, Mercury, Nickel, Lead, Copper, Zinc, Vanadium), organic compounds (hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), aromatic solvents, polychlorinated biphenyls (PCBs)), microorganisms and other substances. In Italy, many coastal-marine areas coexist with large industrial and port settlements that have, over time, compromised the quality of the seabed in front of them. Some of these have been identified by the National Programme for Environmental Remediation and Recovery as contaminated Site of National Interest (SNI) (Ministerial Decree 468/01, 2002). As stated by Gabellini et al. (2011), recovery national activities are planned in these areas.

Contaminated sediment management strategies may consider in situ and ex situ techniques. In situ remedial alternatives normally involve Monitored Natural Recovery (MNR) (De Gisi et al., 2017a) and in situ containment and treatment (De Gisi et al., 2017b; Lofrano et al., 2016). Ex situ remedial

* Author to whom all correspondence should be addressed: e-mail: claudia.labianca@poliba.it; Phone: +39 3473886571

options include Stabilization/Solidification (S/S) (Todaro et al., 2016; Tang et al., 2015), Nano-scale Zero Valent Iron (nZVI) treatment (De Gisi et al., 2017c), landfarming (NSW EPA, 2014), composting (Mattei et al., 2017), sediment washing (Catianis et al., 2018; Stern et al., 2007), thermal desorption (Rumayor et al., 2017), vitrification (Colombo et al., 2009), biological treatment (Matturro et al., 2016) and/or their combination (Careghini et al., 2010). However, the definition of a remediation project requires a deepening of the study area. In this respect, the study of the sources of contamination is of great importance, especially for very complex contaminated sites.

Several statistical techniques and methodologies are available in literature, applied for different environmental problems. For example, Sabia et al. (2016) proposes a composite indicator-based methodology with the goal of identifying and then prioritising critical wastewater treatment plants, taking into account the territorial background issues. The alternatives were processed by analyzing the relationships between the sub-criteria and the dimensions of data coverage (i.e., collinearity, similarities/dissimilarities). The software Statistica (Statsoft) was used to evaluate the degree of correlation and the relative significance among the sub-indicators while, an explorative multivariate analysis (Factor Analysis FA) permitted to evaluate whether the alternative matrix was sufficiently supported by the statistical dimensions covered by the data. De Gisi et al. (2017d) used Multiple Correspondence Analysis (MCA) as a statistical exploratory technique to depict associations between categorical variables. The MCA was performed by using the software R-3.1.2 with the package "FactoMineR". Furthermore, in executing the analysis the eigenvalues and rates of variance were corrected by applying the Benzécri's method. Mali et al. (2017) combined chemometric tools for assessing hazard sources and factors acting simultaneously in contaminated areas. The study was aimed mainly at verifying the applicability of the methodologies adopted; in particular, Principal Component Analysis/Cluster Analysis (PCA/CA) and factorial Analysis of Variance (ANOVA) were exploited as complementary techniques for apprehending the impact of multi-sources and multi-factors considering the case study of Mar Piccolo in Taranto (Southern Italy).

The aim of the present study is to analyze by means of multivariate analysis (PCA, CA and correlation analysis) the correlation between contamination sources and the environmental quality of marine sediments, considering all the sub-areas of the First Seno of Mar Piccolo in Taranto, used as case study since it is one of the most industrialized and contaminated zones in the Mediterranean Sea. In particular, possible correlations between pollutant distribution and particle size characteristics, identification of areas of particular concern (hot spot) as well as areas characterized by geochemical anomalies (eventual natural presence of some substances) and/or strongly man-made areas, are identified and stressed.

2. Material and methods

2.1. Background information

Mar Piccolo is a semi-enclosed basin with a reduced water circulation, strongly influenced by human activities and with one of the most important areas in Italy for mussel farming. It is a typical polluted semi-enclosed basin characterized by scarce water circulation, which encourages organic matter sedimentation transport and accumulation of metals in sediments (Cardellicchio et al., 2006a). It has a surface area of 20.7 km^2 divided in two inlets, called First Seno and Second Seno, with a maximum depth of 13m and 9m, respectively. In particular, the first inlet is directly collected with the Mar Grande through two channels, one named Navigable Channel and the other one called Porta Napoli's Channel, while, the second one is connected only to the first inlet. Mar Grande is the area for incoming ships and it is separated from the Ionian Sea by a little archipelago. A particular characteristic of Mar Piccolo is the presence of some submarine freshwater springs called "citri", two of which are "citro Galeso" and "citro Citrello".

From several decades this area is subjected to chemical pollution deriving from the industrial activities carried out in the surroundings, the most important of which are ILVA, Cementir, Eni station and Military Arsenal. Contaminants presence and distribution in Mar Piccolo sediments already have been identified and documented. Between 2005 and 2009, first the Commissioner-Delegate for the waste emergency in Apulia and, then, the Commissioner-Delegate for the environmental emergency in Apulia, performed environmental characterizations aimed at area safety works and remediation. Later in 2014, the local environmental Authority (ARPA Puglia) and other public institutions performed additional analyses to complete previous results. One of the main objectives was the development of a standardized methodology to apply to other marine coastal areas of Mediterranean Sea by means of: mathematical models related to hydrodynamism, evaluation of sediment contamination, carbon exchanges to sediment–water interface, pollutant mobility by studying water–sediment interactions, PCBs anaerobic degradation and ecotoxicological effects of pollutants (Cardellicchio et al., 2016).

2.2. Sampling points and data input

The data set analyzed is the one obtained from the sampling campaign in the First Seno carried out by ISPRA in 2010, since it is one of the most complete, both for information and number of variables.

The considered matrix consists of 1023 samples, 3m deep (822 samples in the area external to mussel activities and 201 internal to it) and 20 variables (moisture percentage, granulometry, metals and metalloids Al, As, Cr, Cd, Hg, Fe, Ni, Pb, Zn, Cu, V and, lastly, nutrients concentrations, total nitrogen (N_{tot}), total phosphorus (P_{tot}) and total organic carbon (TOC)). Instead, PCBs, PAHs, organochlorine compounds and pesticides have been excluded from this analysis because their complex and different behavior needs a separate analysis.

In order to simplify the analyses, two secondary qualitative variables have been studied: the depth of surficial samples (S=Surficial = layers 0-10 cm (a), 10-30 cm (b), 30-50 cm (c); I=Intermediate = layers 100-120 cm; P=Deep = layers 180-200 cm, 280-300 cm); the different activities conducted on the specific area. The last qualitative variable has been created dividing the First Seno in the following areas: entry-exit channels; Military Arsenal area, mussels' area, citri, ILVA water-pump area and the remaining area (Fig. 1). In particular, during the 1970s, ILVA steel factory installed a large cooling water intake system that removes 120,000 m^3d^{-1} of water from Mar Piccolo and discharges it into the Gulf of Taranto (ILVA, 2009).

In addition to the industrial impact, other anthropogenic effects are widely spread along and within the study area (Buonocore et al., 2013; Annicchiarico et al., 2011; Calace et al., 2008): several urban sewages from Taranto and nearby cities are discharged into Mar Piccolo, streams and citri are the responsible for the drainage of the surrounding agricultural soils and, lastly, there is the shipyard of the Italian Navy, located on the southern shores of the First Inlet (Cardellicchio et al., 2004; 2006b; Lerario et al., 2003). Furthermore, the Mar Piccolo sustains the largest mussel production of Italy (about 30,000 t $year^{-1}$) over a total legal farm area of 10 km^2 (Caroppo et al., 2012).

2.3. Multivariate analysis and software

A multivariate analysis with a PCA (Principal Components Analysis) and a CA (Cluster Analysis) has been used. The PCA allows to reduce data and to describe multidimensional systems by means of a smaller number of new variables, through the linear combination of the original ones (Loska et al., 2003).

Instead, the combination of CA and correlation analysis allows to identify and confirm correlations between variables, grouped in clusters. Experimental data have been elaborated by multivariate statistical analysis to evaluate the possibility of differentiating sampling areas, according to the correlation between them and the several pollution sources. Three different types of software have been used to conduct multivariate analyses on the available data: the software Unscrumbler and the software SIMCA for the PCA analysis and the software Statistica10 for the CA and the Correlation analyses.

2.3.1. Software Unscrumbler®X

The Unscrambler®X software was originally developed in 1986 by Harald Martens and later by CAMO Software (v. 9.7 AS, Norway). Unscrambler®X was an early adaptation of the use of partial least squares (PLS). Other supported techniques include principal component analysis (PCA), 3-way PLS, multivariate curve resolution, design of experiments, supervised classification, unsupervised classification and cluster analysis. The software is used in several fields: chromatography, spectroscopy, quality control systems in sensory analysis and pharmaceutical and chemical industries.

2.3.2. Software Simca (Soft independent modelling by class analogy)

SIMCA allows to extract valuable information, structuring and finding hidden details, using data mining, process modeling and interactive graphics.

Whether it is large amounts of data, batch data, time-series data or other data, SIMCA transforms data into visual information for easy interpretation. It can work even with just 10 samples per class and there are no restrictions for the variables number per class, important aspect in chemical studies (chemometric techniques).

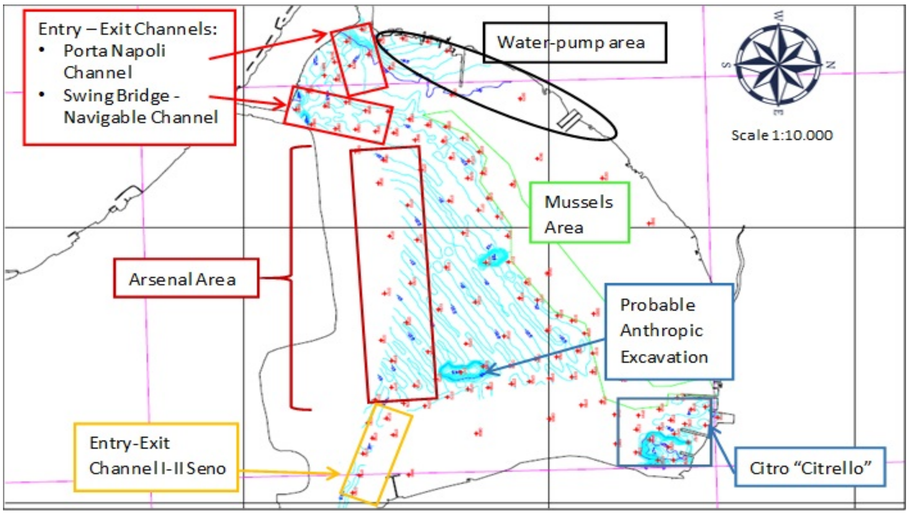


Fig. 1. First Seno sampling map with main anthropogenic and natural impacts

2.3.3. Software Statistica10

The software Statistica10 was created by StatSoft and can be considered one of the most powerful tools available today for data analysis, data mining, quality control, process monitoring, clustering and data visualization.

3. Results and discussion

3.1. Principal Components Analysis results

The paragraph is organized to reflect the main findings of the PCA, focusing on subgroups created by correlation. Firstly, a PCA was carried out on all data sets; secondly, attention was focused on the superficial layers in order to fully understand the influence and correlation between anthropogenic impacts and sediments.

3.1.1. PCA on total dataset

The considered model consists of three principal components PC1, PC2, PC3 covering 60% of the cumulative variance, with respectively variance of 31%, 19% and 10%. The loading plot of the variables on the first two principal components plan (Fig. 2) showed that all metals and nutrients are dominant variables on the variance of surficial layer data, while the variances of intermediate and deep layers were influenced mostly by geo-physical characteristics.

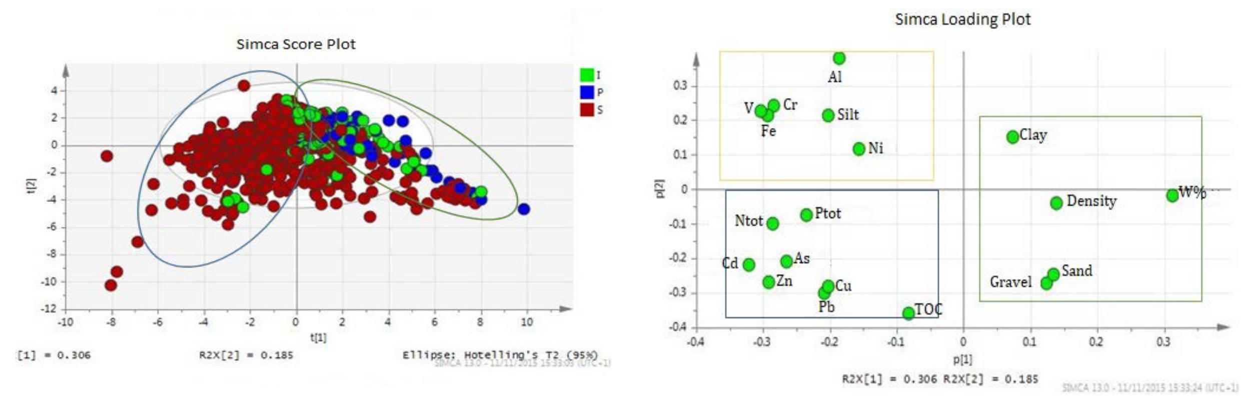
In particular, the surficial samples group was composed of two sub-groups of variables because of the different concentrations in metals, one in the space characterized by positive values in PC2 and negative in PC1 (concentrations of V, Cr, Al, Ni, Fe) and one characterized by negative values both in PC1 and PC2 (concentrations of Cd, As, Hg, Zn, Cu). It is assumed that V, Cr and Ni, associated to Al and Fe, natural elements in phyllosilicate minerals and ubiquitous in all marine sediments, appeared because of natural factors, while Cd, Cu, Hg, Pb, As were certainly added on account of anthropogenic activities and they were influenced by nutrients and organic matter (TOC, N_{tot} and P_{tot}).

Fig. 2 highlighted the presence of some samples from the deep layer in the space of the ones from the surficial area. In particular, they were samples adjacent to the Military Arsenal and the ILVA water-pump areas (Fig. 1) assuming that in such samples metal concentration has reached even deeper layers. At the same time, considering the few surficial samples among the deep ones analyzed, it was found that their variance was more influenced by physical-chemical characteristics and not by metal concentration. Most probably, they are all samples from an excavation area anthropologically generated, explained by the impact of sea currents in this area on the surficial layers, mobilizing the fine fraction of sediments in suspension. Same phenomenon occurred in the "citri" area: currents induced by fresh-water springs suspended the fine fraction of sediments, to which metal contaminants are associated, triggering a desorption process of the metals in the superficial layers through leaching of metals in the water column.

3.1.2. PCA on surficial data and different areas

The results from previous analyses have led to focus attention on surficial samples because of the widespread contamination. The PCA analysis was performed on different sub-clusters (Arsenal area; Citri; Entry-exit channels; Area between First and Second Seno; ILVA water-pump area; Remaining Fist Seno area), created according to the anthropogenic activities carried out in each area.

For the Arsenal area (Fig. 3) it was possible to notice that samples at *c* depth (from 30 to 50 cm, grouped in a green circle) had a negative value on PC1 and a maximum variance caused by the fine fraction (silt+clay). This means that the layer *c* of the Arsenal area presented an average contamination, compared to the dataset analyzed. A different situation occurred for the layer *b* (from 10 to 30 cm, grouped in a blue circle) with a positive value on PC1 and a negative one on PC2. In this case, contaminants that influenced this sub-group were Hg, Cu, Pb, Zn, Cd, As, which changed according to the organic matter (TOC) and all the previous ones according to $P_{tot,}$ as explained by M. Zhang and Zhang (2010).



(a) (b)

Fig. 2. Simca output: Total Dataset projection of (a) Score plot (samples) and (b) Loading plot (variables) on space PC1/PC2

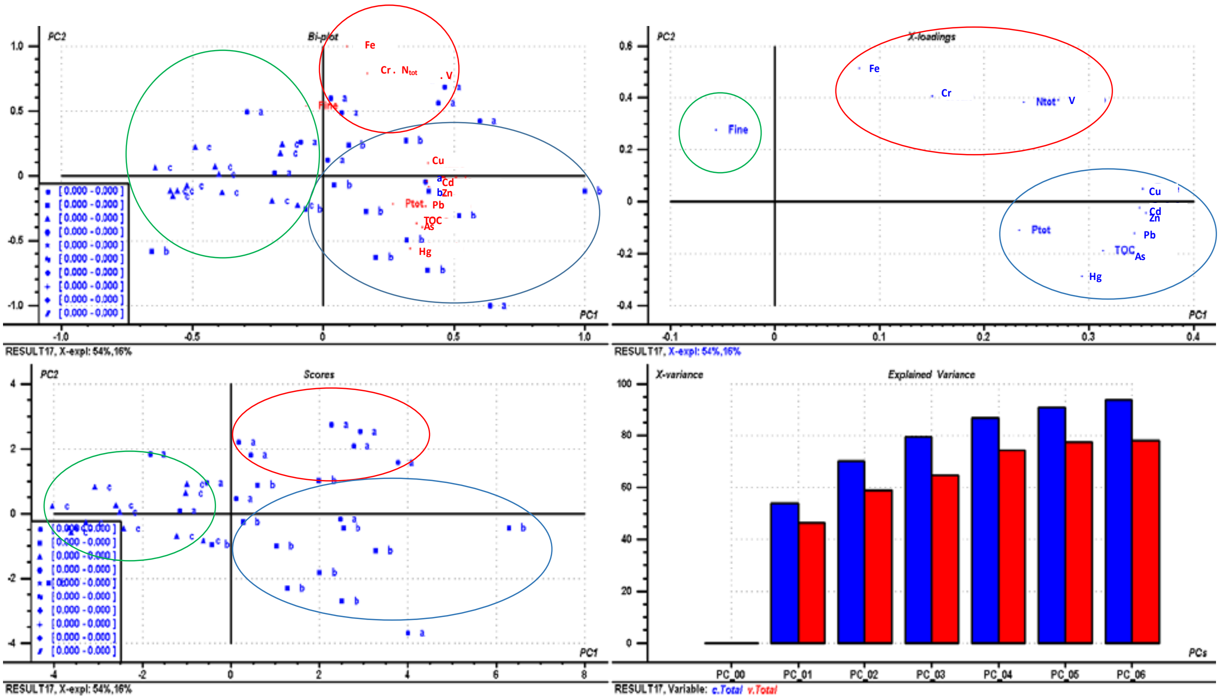


Fig. 3. Unscrambler output: Arsenal area

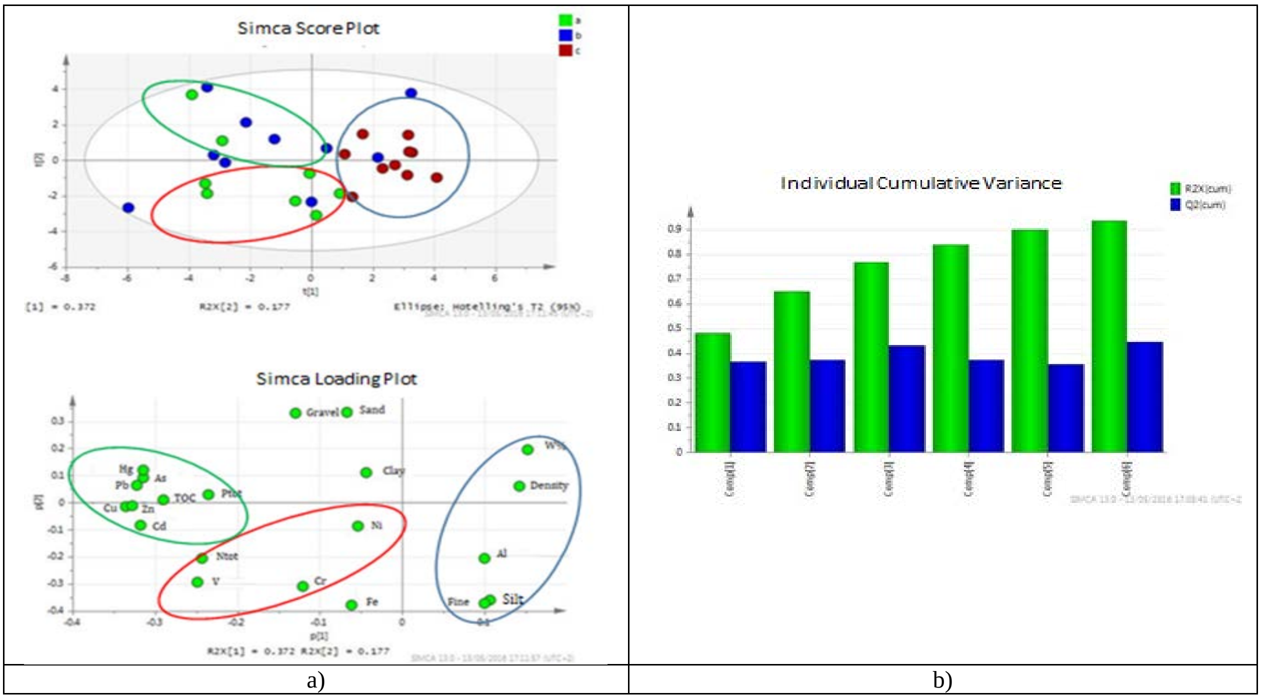


Fig. 4. Simca output: Arsenal area: a) projection of Score and Loadings plots on space PC1/PC2; b) PCs variance

It is possible to intuitively assume that TOC was the responsible mover of contaminants, since it behaves like carrier, but phosphorus has a central role too. Lastly, samples at *a* depth between 0-10 cm (grouped in red circle) were more influenced by Fe, Cr, V and N_{tot}. Using a 3 PCs model it was possible to reach an acceptable cumulative variance of 74%, with respectively 54% from PC1, 16% from PC2 and 4% from PC3. SIMCA was used to compare and confirm the previous results from Unscrumbler software, considering all the geo-physical parameters. Maintaining the separation between levels (a, b, c), the outputs are shown in Fig 4. Also in this case layer *b* was the one more affected by pollution from Hg, As, Cu, and Cd.

The surficial layer appeared to be affected by high concentrations of TOC which drive Cr, V and Ni into the fine fraction of sediments, while the layer *c* does not appear polluted. It is important to underline that pollution from As and Hg in this area was related to deeper layers (150-200 cm), in line with the previous results (paragraph 3.1.1).

Consequently, the area adjacent to the Arsenal was affected by: (i) Pollution in the layer 10-30 cm from Hg, As, Cd and Cu and in some spots even from Pb and Zn; (ii) Widespread pollution from Hg and As in the deeper layers (150-200 cm) driven by high-concentrated TOC and P_{tot}; (iii) High concentration of Cr and V, supposedly naturally present in surficial layers. The impact of industrial activities on Mar Piccolo occurred even indirectly by means of "citri", fresh-water springs spreading groundwater. As said, in the First Seno there are two "citri" called "Galeso" and "Citrello". From the PCA analysis of this area, results showed how most of samples *c* (at depth 30-50 cm) had the biggest influence on the variance only from the fine fraction (Table 1).

However, it was observed the presence in this group of some samples from the layer *b*. The remaining samples (all samples from layer *a* and two samples from layer *c*) were characterized by a high influence on the variance from the heavy metals group, divided in two sub-groups: (i) Hg, Pb, As, Zn, Cd, Cu; (ii) Cr, V, Fe, Ni. Therefore, the analysis of "citro Citrello" has shown widespread pollution that affects even the deepest layers, with particular peaks of Hg, Pb and As (found in all the layers considered).

For the entry-exit channels (Porta Napoli's natural channel, close to the commercial port, and Navigable channel) and the channel between First and Second Seno (Fig. 1), SIMCA application results emphasized how the Porta Napoli's channel and the surficial layer of the Swing Bridge area were influenced on the variance only by physical parameters. Instead, the layers *b* and *c* belonging to the Swing Bridge were part of the area characterized by a high variability with respect to all types of contaminants. Mali et al. (2017) pointed out that Pb and Hg can also result from oil spilling and ship-fuel losses. The area between First and Second Seno was characterized by a particular distribution since it is located between two deeply polluted areas, Arsenal and "citro Citrello".

More specifically, both Unscrumbler and Simca results showed how the layer *c* and part of *b* were in the area characterized by high variance from geo-physical parameters, while the layer *a* and the remaining part of *b* were more influenced on the variance by all nutrients and heavy metals. ILVA water-pump, on First Seno northwest coast, totally changed Mar Piccolo currents and increased the salinity level bringing a large amount of saltwater from Mar Grande. The Unscrambler outputs highlighted an irregular and widespread distribution of contaminants (in all the layers), reaching the layer *c* in some spots.

Table 1. Main results from PCA analysis on the different sub-areas

N.	*Sub-area*	*PCA Model (Unscrumbler/Simca)*	*Main influence on the variance (PCA analysis)*
1	Arsenal	PC1 54%, PC2 16%, PC3 4%	• layer *c* ONLY by geo-physical parameters, • layer *b* by P_{tot} → TOC → Hg, Cu, Pb, Zn, Cd, As (HEAVY METALS TRANSPORT EFFECT), • layer *a* by Fe, Cr, V and N_{tot}.
2	Citro "Citrello"	PC1 52%, PC2 20%, PC3 18%	• most of samples from layer *c* and few from layer *b* ONLY by Geo-physical parameters, • layer *a* totally, layer *b* partially and two spots from layer *c* by ALL the contaminants (two sub-groups Hg, Pb, As, Cd, Cu and Fe, Cr, Ni, V) D POLLUTION with HOT SPOTS).
3	Entry-Exit Channels (Porta Napoli's Channel, Swing bridge - Navigable Channel)	PC1 56%, PC2 14%, PC3 7%	• layers *a, b* and *c* of the Porta Napoli's Channel and the layer *a* of the Swing Bridge Channel ONLY by physical parameters, • layer *b* and *c* of the Swing Bridge Channel by ALL the contaminants (two sub-groups Hg, Pb, As, Cd, Cu and Fe, Cr, Ni, V) (POLLUTION IN DEEP LAYERS).
4	Channel I-II Seno	PC1 40%, PC2 27%, PC3 11%	• layer *c* and part of *b* ONLY by geo-physical parameters, • layer *a* and remaining part of *b* by ALL nutrients and heavy metals.
5	Ilva water-pump	PC1 50%, PC2 19%, PC3 13%	• some samples from layers *a, b* and *c* by geo-physical parameters, • some samples from layers *a, b* and *c* by ALL the contaminants (IRREGULAR POLLUTION IN ALL THE LAYERS)
6	Other areas	PC1 43%, PC2 19%, PC3 15%, PC4 7%, PC5 4%	• layer *c* and part of *b* ONLY by geo-physical parameters, • layer *a* and remaining part of *b* by a contamination pattern As, Pb, Cd, Cu, Zn, P_{tot}, N_{tot} and TOC, in particular layer *a* by Cu, Cd, Hg, V, Fe and Cr, while layer *b* more by Pb, As and Zn (information from space PC1/PC5)

For what concerns the samples in the remaining First Seno area, a new PCA analysis was performed. Results showed that all samples from layer *c* and some from layer *b* were not influenced on the variance by the concentration of contaminants, unlike the layer *a* and the remaining samples from layer *b,* associated to a contamination pattern composed of As, Pb, Cd, Cu, Zn, P_{tot}, N_{tot} and TOC.

The projection on space PC5/PC1 made it possible to understand the contamination pattern specifically for each layer. In particular, layer *a* was influenced on the variance more by Cu, Cd, Hg, V, Fe and Cr, while layer *b* more by Pb, As and Zn.

3.2. Cluster Analysis and Correlation Analysis results

In order to deepen and confirm PCA results, a CA was performed on the dataset. The software Statistica10, used for this type of analysis, allowed to identify sub-groups among the variables according to the correlation patterns (Table 2). The obtained dendrogram is shown in Fig. 5.

Table 2. Statistica output: correlation Table

1° Cluster	***TOC***	***As***	***Cd***	***Zn***	***Hg***	***Pb***	***Cu***
TOC	1.00						
As	0.30	1.00					
Cd	0.43	0.63	1.00				
Zn	0.44	0.67	0.87	1.00			
Hg	0.43	0.53	0.54	0.53	1.00		
Pb	0.40	0.70	0.68	0.76	0.49	1.00	
Cu	0.35	0.53	0.58	0.68	0.34	0.62	1.00
2° Cluster	P_{tot}	N_{tot}	***Al***	***Cr***	***Fe***	***Ni***	***V***
P_{tot}	1.00						
N_{tot}	0.50	1.00					
Al	0.11	0.21	1.00				
Cr	0.28	0.39	0.62	1.00			
Fe	0.28	0.53	0.78	0.60	1.00		
Ni	0.17	0.22	0.41	0.85	0.37	1.00	
V	0.37	0.56	0.61	0.92	0.64	0.74	1.00

It was possible to identify two macro clusters: (i) TOC, As, Cd, Zn, Hg, Pb, Cu, clay and gravel; (ii) P_{tot}, N_{tot}, Cr, Fe, Al, V and Ni. In the first cluster it was possible to intuit that the responsible correlating element was TOC, while in the second cluster the responsible ones were both the nutrients. One of the three correlation outputs from the software Statistica10 is shown in Fig. 6.

4. Conclusions

The chemometric techniques, used jointly with software Unscrumbler, Simca and Statistica10, allowed to clearly understand the correlation between contamination sources and the environmental quality of marine sediments as well as the existence and identification of hot spots within the study area. The analysis of the case study allowed to focus on the following main aspects:

- The strong correlation of TOC, Ptot and Ntot with As, Cd, Hg, Pb, Cu and Zn, suggested that the excessive presence of nutrients and organic matter in the water, acted as carrier for many contaminants that concentrate in the fine fraction of sediments with high percentage of organic matter. This situation was observed for some area of particular interest such as the Arsenal area, the "citri" area and the entry-exit one (with a peculiar distribution pattern due to hydrodynamic effects);
- All the surficial layer, the so-called fresh sediments, had a spread contamination; it suggested that the primary sources of contamination are still active;
- The presence of contamination even in the deeper layers (hot spots) led to hypothesize that those spots could become "secondary sources of contamination" where appropriate containment measures will not be taken;
- Areas with particular interest (entry-exit channels) suggested to investigate more on the influence of currents on the sediment quality.

Lastly, in methodological terms, the framework adopted could certainly be a powerful tool for the preliminary study of heavy metal pollution in coastal marine areas, because it is allowed to (i) identify the accumulation sites, (ii) evaluate the possible pollution sources and (iii) hypothesize one or more remediation techniques to use for the environmental restoration.

References

Annicchiarico C., Buonocore M., Cardellicchio N., Di Leo A., Giandomenico S., Spada L., (2011), PCBs, PAHs and metal contamination and quality index in marine sediments of the Taranto Gulf, *Chemistry and Ecology*, **27**, 21–32.

Buonocore M., Annicchiarico C., Cardellicchio N., Di Leo A., Giandomenico S., Spada L., (2013), Contribution to the knowledge of air quality in a highly industrialized site (Taranto City, Italy) by biomonitoring techniques, *Environmental Engineering and Management Journal*, **12**, 245-248.

Calace N., Cardellicchio N., Ciardullo S., Petronio B.M., Pietrantonio M., Pietroletti M., (2008), Metal distribution in marine sediments of the Mar Piccolo in Taranto (Ionian Sea, Southern Italy), *Toxicological and Environmental Chemistry*, **90**, 549–564.

Cardellicchio N., Annicchiarico C., Di Leo A., Giandomenico S., (2004), *Mercury in Marine Sediments and Mussel from Taranto Gulf (Ionian Sea, Southern Italy),* Proc. 7th Int. Conf. on Mercury as a Global Pollutant, Ljubljana.

Cardellicchio N., Buccolieri A., Di Leo A., Spada L., (2006a), Heavy metals in marine sediments from the Mar Piccolo of Taranto (Ionian Sea, Southern Italy), *Annali di Chimica*, **96**, 727-741.

Cardellicchio N., Buccolieri A., Giandomenico S., Lerario V.L., Lopez L., Pizzulli C., (2006b), Distribution and occurrence of polycyclic aromatic hydrocarbons (PAHs) in sediments from the Mar Grande and Gulf of Taranto (Ionian Sea, Southern Italy), *Annali di Chimica*, **96**, 51-64.

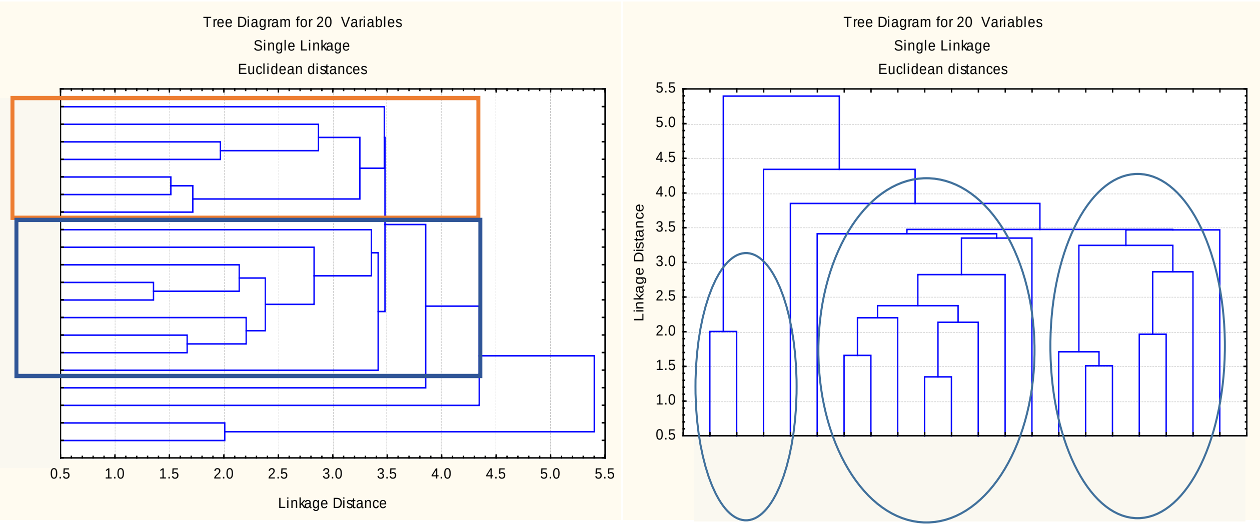


Fig. 5. Statistica output: dendrogram

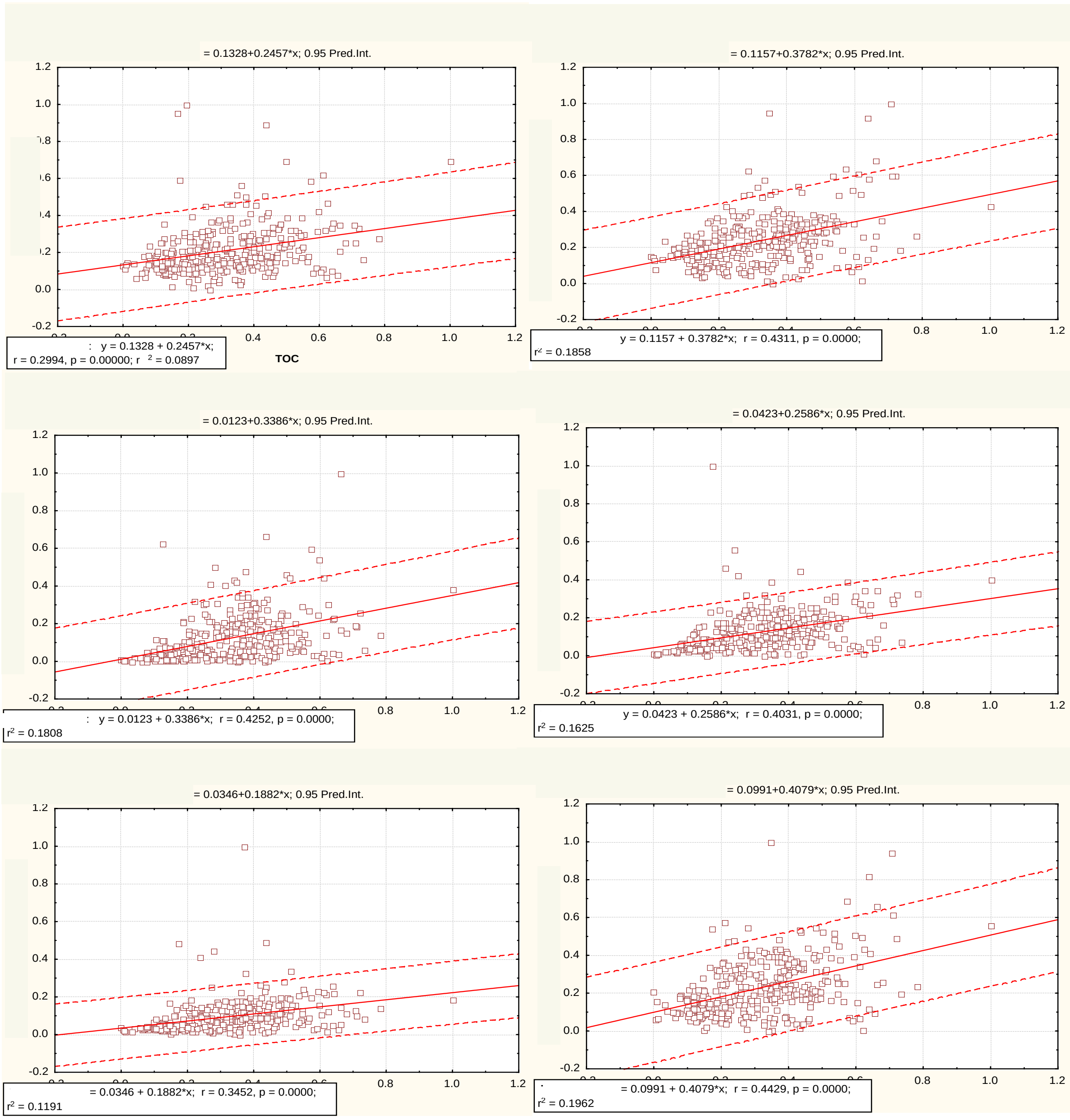


Fig. 6. STATISTICA10 output: 1st cluster correlation (TOC, As, Cd, Hg, Pb, Cu, Zn)

Cardellicchio N., Annicchiarico C., Di Leo A., Giandomenico S., Spada, L., (2016), The Mar Piccolo of Taranto: an interesting marine ecosystem for the environmental problems studies, *Environmental Science and Pollution Research*, **23**, 12495-12501.

Careghini A., Dastoli S., Ferrari G., Saponaro S., Bonomo L., De Propris L., Gabellini M., (2010), Sequential solidification/stabilization and thermal process under vacuum for the treatment of mercury in sediments, *Journal of Soils and Sediments*, **10**, 1646-1656.

Caroppo C., Giordano L., Palmieri N., Bellio G., Paride Bisci A., Portacci G., Sclafani P., Sawyer Hopkins T., (2012), Progress towards sustainable mussel aquaculture in Mar Piccolo, Italy, *Ecology and Society*, **17**, 10, http://dx.doi.org/10.5751/ES-04950-170310.

Catianis I., Magagnini L., Ghedini E., Bettoli D., Gherardi M., Sanibondi P., Ungureanu C., Ulazzi E., Stanica A., Bertoni A., (2017), Soil-washing and thermal plasma treatment for decontamination of dredged marine sediments from the Midia Port – Romania, *Environmental Engineering and Management Journal*, **17**, 1897-1908.

Colombo V., Ghedini E., Gherardi M., Mani M., Sanibondi P., Vazquez B., (2009), RF thermal plasma treatment of dredged sediments: vitrification and silicon extraction, *Journal of Physics*, **406**, 1-10.

De Gisi S., Minetto D., Todaro F., Lucia Lanzolla A.M., Notarnicola M., (2017a), *Monitored Natural Recovery of Contaminated Marine Sediments. Proposal of a Monitoring Plan for in Situ Continuous Testing and Sensing*, Proc. Int. Symp. on Instrumentation and Measurement Technology (I2MTC), Torino.

De Gisi S., Todaro F., Notarnicola M., (2017b), Effect of reactive mats on in-situ remediation of contaminated marine sediment, *Procedia Environmental Science, Engineering and Management*, **4**, 17-22.

De Gisi S., Minetto D., Lofrano G., Libralato G., Conte B., Todaro F., Notarnicola M., (2017c), Nano-scale zero valent iron (nZVI) treatment of marine sediments slightly polluted by heavy metals, *Chemical Engineering Transactions*, **60**, 139-144.

De Gisi S., Casella P., Sabia G., Farina R., Landolfo P., Notarnicola M., De Feo G., (2017d), Assessing the public perception of islanders regarding the implementation of new technologies to optimize the municipal solid waste management system: A Mediterranean case study, *Journal of Cleaner Production*, **164**, 1586-1601.

Gabellini M., Ausili A., Romano E., Geraldini S., Tornato A., Dastoli S., (2011), *Contaminated Sediments in Italy, State of the Art, Management and Remediation*, Proc. Nat. Conf. REMTECH, Ferrara, vol. 1, 221-226.

ILVA, (2009), Environment and Safety Report, ILVA of Taranto, Italy, On line at: http://www.ilvataranto.com/pdf/rapporto_ambiente_sicurezza_2009.pdf.

Lerario V.L., Giandomenico S., Lopez L., Cardellicchio N., (2003), Sources and distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from the Mar Piccolo of Taranto, Ionian Sea, Southern Italy, *Annali di Chimica*, **93**, 397-406.

Lofrano G., Libralato G., Minetto D., De Gisi S., Todaro F., Conte B., Calabrò D., Quatraro L., Notarnicola M., (2016), In situ remediation of contaminated marine sediment: an overview, *Environmental Science and Pollution Research*, **24**, 5189–5206.

Loska K., Wiechula D., (2003), Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir, *Chemosphere*, **51,** 723–733.

Mali M., Dell'Anna M., Notarnicola M., Damiani L., Mastrorilli P., (2017), Combining chemometric tools for assessing hazard sources and factors acting simultaneously in contaminated areas. Case study: “Mar Piccolo” Taranto (South Italy), *Chemosphere*, **184**, 784-794.

Mattei P., Pastorelli R., Rami G., Mocali S., Giagnoni L., Gonnelli C., Renella G., (2017), Evaluation of dredged sediment co-composted with green waste as plant growing media assessed by eco-toxicological tests, plant growth and microbial community structure, *Journal of Hazardous Materials*, **333**, 144–153.

Matturro B., Ubaldi C., Rossetti S., (2016), Microbiome Dynamics of a Polychlorobiphenyl (PCB) Historically Contaminated Marine Sediment under Conditions Promoting Reductive Dechlorination, *Frontiers in microbiology*, **7**, 1-4.

Ministerial Decree 468/01, (2002), National Program for the environmental restoration of polluted sites, Gazzetta Ufficiale Serie Generale n.13 of 16/01/2002 – Ordinary Supplement n.10, On line at: http://www.gazzettaufficiale.it/.

NSW EPA, (2014), *Best Practice Note: Landfarming, Environmental Guidelines and Codes of Practice*, Technical Press, New South Wales, Australia.

Sabia G., De Gisi S., Farina R., (2016), Implementing a composite indicator approach for prioritizing activated sludge-based wastewater treatment plants at large spatial scale, *Ecological Indicators*, **71**, 1-18.

Stern E.A., Jones K.W., Douglas W.S., Feng H.E., (2007), A *Proposal for Innovative Sediment Decontamination Technologies using a Cross Program*, Proc. Int. Symp. on WEDA Environmental Commission, San Diego (California), 267-276.

Rumayor M., Gallego J.R., Rodríguez-Valdés E., Díaz-Somoanoa M., (2017), An assessment of the environmental fate of mercury species in highly polluted brownfields by means of thermal desorption, *Journal of hazardous materials*, **325**, 1-7.

Tang I.Y., Yan D.Y.S., Lo I.M.C., Liu T., (2015), Pulverized fuel ash solidification/stabilization of waste: comparison between beneficial reuse of contaminated marine mud and sediment, *Journal of Environmental Engineering and Landscape Management*, **23**, 202-210.

Todaro F., De Gisi S., Notarnicola M., (2016), Contaminated marine sediments: waste or resource? An overview of treatment technologies. *Procedia Environmental Science, Engineering and Management*, **3**, 157-164.

Zhang M., Zhang H., (2010), Co-transport of dissolved organic matter and heavy metals in soils induced by excessive phosphorus applications, *Journal of Environmental Sciences*, **22**, 598–606.

Environmental Engineering and Management Journal October 2018, Vol.17, No.10, 2401-2408
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

SPENT COFFEE GROUNDS FROM COFFEE VENDING MACHINES AS FEEDSTOCK FOR BIOGAS PRODUCTION

Ciro Vasmara, Rosa Marchetti*

Research Centre for Animal Production and Aquaculture of Council for Agricultural Research and Economics; CREA, Via Beccastecca 345, 41018, San Cesario sul Panaro (Modena), Italy

Abstract

Large amounts of spent coffee grounds (SCG) are currently available all over the world due to the enormous increase in coffee consumption. This increase has in turn to be related to the even greater diffusion of coffee vending machines. The aim of this study was to evaluate the biomethanation potential (BMP) of SCG alone or in co-digestion with pig slurry (PS). Pig slurry was chosen because it is frequently utilized as feedstock for biogas production from agricultural waste. The raw material was obtained from the SCG-collecting tank of a commercial coffee vending machine. Compared treatments were: SCG, PS and SCG+PS. Depending on the treatment, each reactor (100 mL) contained: 1 g (2%) SCG volatile solids (VS) and 50 mL of hydration medium (in SCG) or PS (in SCG+PS); 50 mL of PS (in PS). A lab-prepared inoculum (10% v/v) was added to each reactor. Biogas production at 35 °C and composition were monitored until exhaustion of the anaerobic digestion (AD). The BMP of SCG was 290 mL CH_4 g^{-1} VS, a value comparable to that of other substrates currently used as ingredients in anaerobic digestion. Using PS instead of hydration medium increased the CH_4 production per reactor. We conclude that SCG are a suitable feedstock for biogas production. Our in-batch results suggest also the potential for increasing biogas yields from pig slurry using spent coffee grounds as co-substrates, in continuous systems.

Key words: biomethanation potential, co-digestion, methane, pig slurry, spent coffee grounds

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The coffee water extract is a beverage widely spread all over the world. The world coffee beans production in the 2017/18 biennium is estimated to be around 9.5 million tons (USDA, 2017). The European Union imports nearly 40% of the whole world coffee production, and this quantity is practically constant since 2012 (USDA, 2017). It is therefore not surprising that 17 of the 20 countries in the world with the highest per capita consumption of coffee are European (ICO, 2017). As the EU imports exclusively coffee beans (USDA, 2017), their roasting is carried out in the EU territory. Two kinds of waste are produced in the coffee roasting process: the residues of the roasting process and the solid residues from the extraction process, the so-called "spent coffee grounds" (SCG). These residues can derive either from brewed or from expresso coffee preparation (in a 50 to 50 proportion; Cruz et al., 2012b). Regardless of the extraction procedure, the mean per capita consumption in the EU is 7 kg. With reference to the consumption data, Europe can be divided into 3 macro areas: the Mediterranean-Balkan area with an average consumption per capita of 5.4 kg, Central Europe (6.1 kg per capita, on average) and Northern Europe (9.4 kg per capita, on average). When taking into account the population of the various States, it can be concluded that SCG are widely available throughout Europe.

Currently, most of the SCG are disposed of in landfills, despite their high organic load (Franca and

* Author to whom all correspondence should be addressed: e-mail: rosa.marchetti@crea.gov.it; Phone: +39 059926268; Fax: +39 05928371

Oliveira, 2009). Spent coffee grounds are considered eco-toxic (Ciesielczuk et al., 2017) due to their high content in caffeine, tannins and polyphenols (Buerge et al., 2003; Mussatto et al., 2011). In recent years, several alternative uses of SCG have been evaluated, for example as ruminant feeds (Givens and Barber, 1986), or as ingredients of bakery goods in human nutrition (Martinez-Saez et al., 2017). Their use as crop fertilizers or soil amendments has also been suggested (Campos-Vega et al., 2015; Cruz et al., 2012a). Other authors have emphasized the interest of SCG as a source of bioactive molecules. According to Machado et al. (2012) SCG can be used as a feedstock for fungal strains capable to extract polyphenolic compounds (*Penicillium purpurogenum*, *Neurospora crassa* and *Mucor*). Other authors (Acevedo et al., 2013; Cruz et al., 2012b; Scully et al., 2016) report that remarkable amounts of chlorogenic acids and caffeine can be obtained from SCG, which are particularly requested by the food and pharmaceutical industry.

Spent coffee grounds can also been exploited for energy production. In fact, they can be directly burned (Silva et al., 1998), or pyrolysed (Li et al., 2014; Luz et al., 2018a), or they can be used as raw material for production of liquid fuels, such as bioethanol (Kwon et al., 2013; Mussatto et al., 2012) and biodiesel (Calixto et al., 2011; Kondamudi et al., 2008; Oliveira et al. 2008; Somnuk et al., 2017). However, these types of exploitation are involved in particulate emissions into the atmosphere (Kim and Choi, 2010).

Anaerobic digestion (AD) can represent an interesting alternative to direct combustion of SCGs or to their transformation into liquid biofuels. In the past, several authors suggested the possibility of obtaining biogas from SCG both in mesophilic (Lane, 1983) and in thermophilic (Kida and Sonoda, 1992) conditions, but the system, in both cases, did not have adequate long-term stability. More recently, Luz et al. (2017) obtained interesting results by feeding an anaerobic reactor with the liquid fraction deriving from the spent coffee filtration. To overcome the problem of digestion stability, Luz et al. (2018b) also proposed the hydrothermal carbonization of SGC as a pretreatment before anaerobic digestion. This pre-treatment allowed a remarkable increase in CH_4 production. However, a longer lag phase duration was observed in the pre-treated samples. Moreover, the pre-treatment application requires an additional energy input, which can make the process economically unsustainable. Vitez et al. (2016) carried out mesophilic AD using SCG from a coffee shop as feedstock, without detecting any problems of process stability. The same authors however conclude that, although the biogas production by SCG is a viable solution, the limiting factor to its application is the lack of a system of collection and transport suitable for this kind of waste.

In recent years, in the EU and especially in Italy there has been an increase in the spreading of coffee vending machines. Currently there are in the EU 2.2 million of coffee vending machines (EVA, 2017), installed mainly in public areas such as airports, railway stations, hospitals, universities, etc. The maintenance (supply and discharge of the SCG) is entrusted to the installer companies; this means that SCGs are collected and transferred to a single centre that belongs to a specific geographical area. It follows that, in the face of a widespread diffusion of coffee vending machines, there is a concentration of SCG in a few areas, and this can represent a solution to the problem of the collection and transport of SCG.

The aim of this study was to evaluate the biomethanation potential (BMP) of SCG collected from a commercial coffee vending machine, with particular attention to its possible use as co-ingredient in the AD of pig slurry, a feedstock frequently utilized in biogas production from agricultural waste.

2. Materials and methods

2.1. Feedstock

Spent coffee grounds were collected from the coffee vending machine at our Research unit. The operation of the machine is completely automatic: the roasted coffee beans are freshly ground at the time of delivery of the coffee to the customer, and the SCG are automatically transferred to a plastic bag placed in the lower part of the machine. A maintenance worker periodically picks up the full bag and takes it to the vending machine-producing company. The samples of SCG were collected on one of these occasions, and frozen until use. They were used as they are, without any pre-treatment or sterilization.

Fresh pig slurry was collected from the first collection tank of our experimental farm in S. Cesario sul Panaro (MO), after mechanical homogenisation, and it was used immediately after collection. Selected analytical characteristics of these materials are reported in Table 1.

2.2. Experimental design

Compared treatments were: SCG, PS and SCG+PS, with 3 replications, for a total of 9 reactors. Anaerobic digestion was carried out in batch, in mesophilic conditions (35 °C). Biogas volume and composition were determined for each reactor during the incubation period (3 months).

2.3. Inoculum preparation

The inoculum was prepared according to Vasmara et al. (2015), using pig slurry as raw material. The liquid fraction of pig manure after solid separation was used for this purpose. It was withdrawn from the main farm storage tank, at two-thirds depth. Pig slurry was mixed with hydration medium (sterilized phosphate buffered basal medium without energy sources, HM) in a 1:1 volume ratio, in modified atmosphere (N2-CO2, 80:20). This mixture was left to incubate at 35 °C, in strictly anaerobic conditions (degassing phase)

.

Table 1. Selected composition characteristics of the materials used in the experiment.

Parameter	***Unit***	***Pig slurry***	***Spent coffee grounds***
Total solids (TS)	%	1.42	47.35
Volatile solids	% FW	1.04	46.46
pH		7.2	6
Kjeldahl N	% FW	0.093	0.147
Total P	% FW	0.029	0.067
Organic carbon	% TS	39.48	50.61
Neutral Detergent Fibre (NDF)	g kg^{-1} TS	300	647
Acid Detergent Fibre (ADF)	g kg^{-1} TS	175	362
Acid Detergent Lignin (ADL)	g kg^{-1} TS	82	168
Crude Fat	% TS	6.00	9.08
Total polyphenols (Folin-Ciocalteu method)	% TS	0.134	0.200
Caffeine	mg kg^{-1} TS	n.d.	30.3

FW= fresh weight; n.d.= not determined

The inoculum was considered as ready for use when gas production had stopped, indicating the complete exhaustion of endogenous energy sources. At the end of the degassing phase it was centrifuged, and the pellet was resuspended in HM (inoculum to HM ratio: 10:1), in anaerobic conditions. A fixed volume of this suspension (10% of the liquid phase in the reactor, v/v) was used to inoculate each digestion reactor. As the inoculum did not produce CH_4 anymore when ready for use, it gave no contribution to the final amount of cumulated CH_4. The inoculum VS content was 5.72% FW.

2.4. Anaerobic digestion

Anaerobic digestion was carried out in 100-mL reactors (118.5 mL effective volume) according to Owen et al. (1979). The headspace of the reactors was gassed with 100% N_2 throughout the preparation steps before inoculation. Reactors were plugged with butyl rubber stoppers and aluminum seals and they were incubated at 35 °C for 91 days. During the incubation period they were randomly distributed on the incubator shelves. Biogas was collected by means of 100 mL glass syringes as described in Vasmara and Marchetti (2016). The incubation period was completed when there was no more biogas production in any of the reactors. Three reactors containing only inoculum and HM were also included as blanks. No methane production was detected in the blank reactors.

In this experiment, 3 digestion times were assumed as representative of the CH_4 production curve: the start of the linear phase of CH_4 production (4 d after inoculum); the time when all the reactors were in the linear phase of CH_4 production (14 d after the start of the incubation); and the time when all the reactors had joined the stationary phase, at the end of the incubation period (91 days). As the lag phase was practically lacking, the amount of CH_4 produced 4 and 14 d after the start of the incubation can be considered as an estimate of the rate of CH_4 production, whereas the cumulated amount of CH_4 at the end of the digestion period is identified as the maximum CH_4 production (Mmax). The BMP value is given by the ratio of Mmax to the VS content of the substrate. Blanks did not produce any CH_4, therefore no CH_4 subtraction to the CH_4 production of the samples was needed.

2.4.1. Monodigestion conditions

Anaerobic digestion was carried out using SCG as substrate. The reaction mixture included 1 g of SCG VS in 50 mL HM. The initial pH of the mixture was adjusted to 7. pH adjustment at the desired level was made in each reactor before inoculation, with NaOH 32%, using a syringe equipped with a sterile filter (pore size 0.2 μm). Since in each reactor 1 g of SCG VS had been added, on the basis of the VS inoculum content the inoculum to substrate VS ratio in monodigestion was 0.29.

2.4.2. Co-digestion conditions

In co-digestion with pig slurry (SCG+PS), 1 g SCG VS was added in each reactor to 50 mL of non-sterilized pig slurry (0.5 g VS), for a total of 1.5 g VS per reactor. Since in each reactor 1.5 g of SCG VS had been added, on the basis of the VS inoculum content the inoculum to substrate VS ratio in co-digestion was 0.19.

Three reactors with 50 mL PS alone (0.5 g VS) were included as controls. The initial mean pH value was on average equal to 7. Since in each reactor only 0.5 g of PS VS had been added, on the basis of the VS inoculum content the inoculum to substrate VS ratio in the control reactors was 0.57.

Due to the solid matter contribution, the final volume of the SCG treatment, in monodigestion or in co-digestion with PS, was 53 mL, corresponding to a 6% increase of the overall feedstock suspension volume (feedstock + hydration medium).

2.5. Analytical methods

Methane concentration in the biogas was determined by means of a MicroGC Agilent 3000 gas-chromatograph, equipped with 2 columns: Molsieve and Plot U; detector: TCD. Carrier gas: argon. Methane volume was expressed in standard conditions of temperature and pressure (STP; 273 °K and 760 mm Hg).

The total solid (TS), volatile solid (VS), organic C, Kjeldahl N, and total P contents and pH were determined in SCG and PS according to APHA (1992). Total solids and ashes were determined gravimetrically, after thermal treatment respectively in an oven at 105 °C at constant weight, and in a muffle furnace at 550 °C for 10 hrs. The VS content was calculated as the difference between TS and ashes. Organic C was determined with the dichromate reflux method. Total N was determined with the Kjeldahl apparatus. Total P was determined on ashes by colorimetry with ammonium molibdate, after solubilisation by means of HCl 1 N. pH was measured potentiometrically (dry matter: water ratio, 1:10; 2-h stirring and sedimentation). The fat content was determined gravimetrically, after extraction of 1 g TS by means of a Soxhlet extractor. Fiber fractions (neutral detergent fiber, NDF; acid detergent fiber, ADF; and acid detergent lignin, ADL), were determined on SCG and PS according to Van Soest et al. (1991). Caffeine was determined by spectrophotometry, at 271 nm (Salihović et al., 2014), using caffeine from Sigma (Sigma–Aldrich GmbH, Sternheim, Germany) for the preparation of the standard solutions (0, 2, 4, 6, 8, 10 mg caffeine L^{-1} distilled water). Caffeine was extracted from the SCG samples according to the method of Cruz et al. (2012b) with some modifications. Five hundred milligrams of SCG were suspended in 50 mL of distilled water and left to boil for 10 min in continuous stirring. The suspension was then centrifuged at 4000 rpm for 10 min. The supernatant was kept aside and the pellet suspended again in 50 mL distilled water, left to boil for 10 min in continuous stirring, and centrifuged. This procedure was repeated two more times. Eventually, the supernatants were filtered and combined into a single 200-mL volumetric flask. After cooling, the volume was adjusted at 200 mL. The samples were appropriately diluted before spectrophotometric analysis. Total polyphenols were determined colorimetrically, using the Folin–Ciocalteu reagent (Singleton and Rossi, 1965) and expressed as percent gallic acid per g of dry matter.

2.6. Statistical analyses

The analysis of variance was carried out using the SAS package procedures. The PROC MIXED procedure (Littell et al., 1996) was used to test the significance of the treatment effects on BMP and on the CH_4 volumes produced 4, 14 and 91 days (Mmax) after the start of the incubation. Multiple comparisons of the means were carried out using the SAS LSMEANS statement. Factor effects were considered significant at $P < 0.05$. The Tukey Honestly Significant Difference (HSD) at $P = 0.05$ was used to compare the treatment mean values.

3. Results and discussion

The CH_4 concentration in biogas produced from SCG during the whole incubation period (Fig. 1) was very similar, on average, to the CH_4 concentration obtained from PS (41 ± 1.9% vs 44 ± 1.5%, n = 14). The lowest value of CH_4 concentration for SCG was 18%, measured 4 days after the start of incubation, and the highest CH_4 concentration was 58%, measured at the 14th day of incubation. These values are in agreement with those reported by other autors (Luz et al., 2017; Vitez et al., 2016).

Even though the adopted inoculum to substrate ratio was relatively low when compared to those usually reported in the literature (more frequently 1.5 or 2), and it changed depending on the treatment, however, due to the method of inoculum preparation, the cell load and activity were always high enough to ensure a prompt substrate degradation, and AD started nearly immediately after the start of incubation (Fig. 2). Conversely, 2 d of lag phase were detected for the AD of SCG by Vitez et al. (2016), whereas Luz et al. (2017) estimated a lag time >9 d for the AD of soluble SCG in co-digestion with cow manure.

The AD of SCG allowed CH_4 production, both in monodigestion and in co-digestion (Fig. 2). In co-digestion, a higher CH_4 production from nearly the same volume of reaction mixture (50 mL in monodigestion, and 53 mL in co-digestion) was possible, because more VS were present in the reactor.

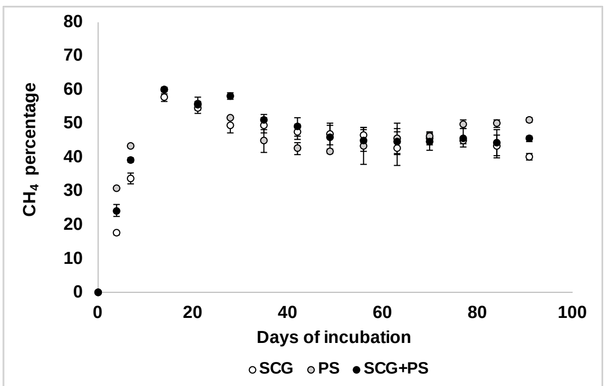


Fig 1. Methane concentration in biogas during anaerobic digestion of spent coffee grounds in monodigestion (SCG) and in co-digestion with pig slurry (SCG+PS). Pig slurry alone (PS) was included as feedstock for comparison.
At each measurement time, vertical bars are the standard deviation of the mean

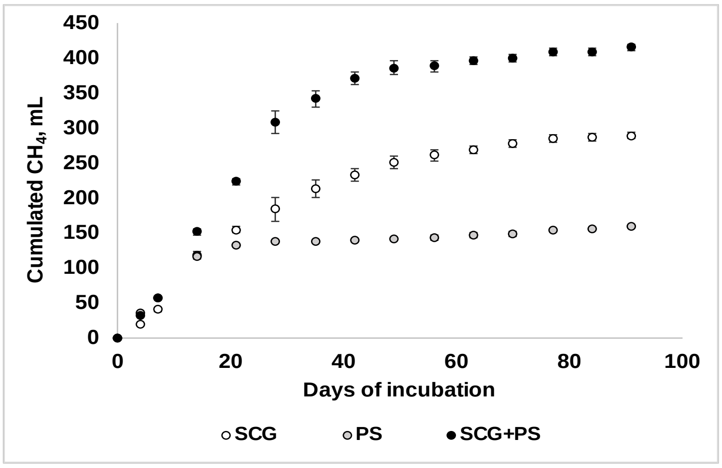


Fig 2. Cumulative CH_4 production during anaerobic digestion of spent coffee grounds in monodigestion (SCG) and in co-digestion with pig slurry (SCG+PS). Pig slurry alone (PS) was included as feedstock for comparison. At each measurement time, vertical bars are the standard deviation of the mean.

Table 2. Volume of CH_4 accumulated 4, 14, and 91 days after the start of the anaerobic digestion, and biomethanation potential (BMP) of spent coffee grounds in monodigestion (SCG) or in co-digestion with pig slurry (SCG+PS). Pig slurry alone (PS) was included for comparison.

Treatment	***Cumulated CH_4 (mL) after***						***BMP***	
	4 d		***14 d***		***91 d (Mmax)***		***mL CH_4 g^{-1} VS***	
SCG	19.4	b	119	b	290	b	290	ab
PS	36.0	a	116	b	159	c	318	a
SCG+PS	31.9	a	152	a	415	a	278	b

3.1. Monodigestion conditions

In our experiment, the initial rate of CH_4 production in SCG (Table 2) was lower than in PS, as only 19.4/1 = 19.4 mL $CH_{4(STP)}$ g^{-1} VS were produced 4 d after the start of incubation, much less than in the PS treatment (36/0.5 = 72 mL $CH_{4(STP)}$ g^{-1} VS). Equally, the CH_4 production rate, as estimated by the measurements 14 d after the start of incubation (Table 2), was the same in the SCG and PS reactors, when the comparison was based on the amount of gas produced per reactor. However, when related to the initial VS content, the amount of CH_4 produced in the SCG reactors in the linear phase of CH_4 production was 119 mL $CH_{4(STP)}$ g^{-1} VS, that is lower than that calculated for PS (116/0.5 = 232 mL $CH_{4(STP)}$ g^{-1} VS). Reasons can be identified with the need for microorganisms to multiply and adapt to an environment richer in VS. Alternatively, an initial inhibitory effect of some SGC component can be considered. Sousa et al. (2015) reported that SCG can have an inhibiting effect towards selected microbial pathogenic species (*S. Aureus*, *E. Coli* and *Candida* sp.) beacuse they are rich in bioactive molecules. However, the amount of gas produced per reactor at the end of AD (91 d after the start of incubation; Table 2) was higher in SCG than in PS, and the BMP of the two feedstocks did not differ significantly.

The BMP value for SCG in monodigestion was on average 290 mL CH_4 (Table 2). This amount is in agreement with those reported by Vitez et al. (2016), who used SCG from a coffee shop; it was slightly lower than that reported by Kim et al. (2017) and Valero et al. (2016), who worked on SCG coming from a cafeteria, obtaining 314 and 318 mL CH_4 g^{-1} VS, respectively. The amount of CH_4 that can be produced from SCG, being of the same order of magnitude of that obtainable from other, frequently used, feedstocks, makes it a good feedstock for AD. In fact, a part from PS, which in our experiment allowed a BMP of 318 mL CH_4 g^{-1} VS (Table 2), from grass silage it is possible to obtain 320 mL CH_4 g^{-1} VS (Luna-delRisco et al., 2011), from wheat straw, 276 mL CH_4 g^{-1} VS (Bauer et al., 2010), from maize residues, 317 mL CH_4 g^{-1} VS, from barley straw, 229 mL CH_4 g^{-1} VS, and from rice straw, 195 mL CH_4 g^{-1} VS (Dinuccio et al., 2010).

3.2. Co-digestion-conditions

In co-digestion, 152 mL of CH_4 per reactor were accumulated 14 days after the start of the incubation in the SCG+PS treatment (Table 2), that is, +29%, on average, in comparison with monodigestion. This amount corresponds to a daily methane production of 10.9 mL CH_4 d^{-1} for SCG+PS treatment, vs 8.5 and 8.3 mL CH_4 d^{-1} for SCG and PS, respectively. Thus, co-digestion can increase the daily rate of CH_4 production.

Equally, the co-digestion with PS allowed an increase (+85%, on average) in the total amount of CH_4 produced per reactor at the end of the AD period (Table 2), in comparison with monodigestion treatments. In fact, 415 mL CH_4 (1.5 g VS) could be obtained per reactor in co-digestion, instead of 290 mL CH_4 in SCG (1 g SV) and 159 mL in PS (0.5 g VS), compared to an increase of only 6% in the volume of the feedstock.

The theoretical BMP expected from co-digestion is: 290*0.67 + 318*0.33 = 299 mL CH_4, when considering the VS contribution of SCG to the VS weight unit (1/1.5 = 0.67), and that of PS (0.5/1.5 = 0.33). This theoretical BMP is not significantly different from that measured in co-digestion, on the basis of a t-test.

The type of substrate selected for co-digestion of SCG can significantly influence the fate of the AD process. Kim et al. (2017) evaluated several substrates in co-digestion with SCG, and found differing trends depending on the substrate type. When SCG were digested with differing percentages of cheese whey, the BMP was never affected by the recipe, whereas when they were co-digested with food waste the BMP decreased for increasing percentages of SCG. The SCG inclusion in the recipe with *Ulva* (marine macroalgae) or waste activated sludge remarkably increased the BMP of AD. Qiao et al. (2013), working in thermophilic conditions, noticed a positive effect when SCG was in co-digestion with waste activated sludge. As no difference between theoretical and actual BMP could be detected, our results demonstrate that, in this experiment, a negative as well as a positive interaction between co-ingredients can be excluded.

3.3. Relationship between SCG composition and anaerobic digestion

Spent coffee grounds are rich in caffeine and polyphenols (Tab.1). These compounds have a recognized antimicrobial activity (Daglia, 2012; Nonthakaew et al., 2015). Caffeine can easily penetrate the bacterial cell walls and inhibit DNA synthesis, in so interfering with bacterial growth (Sundarraj and Dhala, 1965). Polyphenols are known to affect microbial growth by acting on enzyme activity or on signal transduction pathways to cell receptors (Daglia, 2012; Field et al., 1989). Several authors have reported polyphenol toxicity on methanogens (Field and Lettinga, 1987; Kayembe, 2013), to the point of proposing polyphenols as an ingredient in the diet of ruminants to reduce the emissions of CH_4 from the rumen of these animals (Patra and Saxena, 2010). Battista et al. (2014) report that the inhibiting action of polyphenols against methanogens increases for increasing amounts of polyphenols in the waste derived from olive oil production. On the contrary, no evidence exists on the inhibition of methanogenesis by caffeine. In fact, some authors suggest the possibility to produce CH_4 from caffeine, athough in specific digestion conditions (Chen et al., 2018; Prabhudessai et al., 2009).

In our experiment, the presence of inhibitory compounds in the SCG reactors affected the digestion performances at the start and in the linear phase of CH_4 production. The lower, even though not significantly different, BMP in the SCG than in the PS treatment confirmed the initial trend. This is due to the intrinsic characteristics of the feedstock in the recipe. Spent coffee grounds have shown a different behaviour, in comparison with PS, due to their different composition. However, in the end, the BMP of SCG+PS was not significantly different from the theoretical one. Therefore, in co-digestion, the lower AD performances of SCG were compensated by the contribution of PS to CH_4 production, and the co-digestion solution was the best, both on an absolute basis (volume of CH_4 produced per reactor) and in relation to the VS content of the feedstock.

It remains to be ascertained which component in the SCG feedstock had a delaying effect on the start of AD.

Marchetti et al. (2016), studying the effect of selected feedstock components on CH_4 production from wetland biomass, did not find any negative correlation between polyphenols, in concentrations similar to those in this paper (15 mg tannic acid g^{-1} dry matter, on average) and CH_4 production.

Among SCG components, lipids represent an important fraction (>9%, Table 1). Lipids can interfere with anaerobic digestion of SCG (Qiao et al. 2013) due to the release of long-chain fatty acids (LCFA) in consequence of triglyceride hydrolysis. A negative effect of LCFA on AD has been recognized on the acetogenic activity of syntrophic bacteria (Alves et al., 2009). However, Valero et al. (2016) did not find any limiting effect of lipids on the anaerobic digestion of SCG.

Based on data of Table 1, 16.8% of SGC TS was in the ADL fiber fraction, mainly containing lignin. Lignin content in feedstock has been repatedly and negatively correlated to CH_4 production (El Achkar et al., 2016; Marchetti et al., 2016). Our samples contained 19% cellulose, as estimated by subtracting the ADL to the ADF fiber fraction (Table 2). The presence of lignin impedes the cellulose utilization, because cellulose, when linked to lignin, becomes completely recalcitrant (Jimenez et al., 1990). Based on the amount of biogas produced per reactor, our results are in agreement with those of Vitez et al. (2016), who observed no inhibition for AD due to the presence of materials such as caffeine, tannins, and polyphenols, whereas different conclusions can be drawn on the basis of biogas production per VS unit.

4. Conclusions

The biological methane production from spent coffee grounds can represent an interesting alternative to landfill disposal. The biomethanation potential of this feedstock amounts indeed to 290 mL CH_4 g^{-1} VS, which is comparable to that of other substrates currently used as ingredients in anaerobic digestion, even though lower than BMP of pig slurry (318 mL $CH_{4(STP)}$ g^{-1} VS). Co-digestion of spent coffee grounds with pig slurry did not seem to involve any inhibition effect, as in this case BMP (278 mL $CH_{4(STP)}$ g^{-1} VS) was not statistically different from the theoretical one.

Our in-batch results suggest the possibility on the one hand of increasing biogas yields from pig slurry using spent coffee grounds as co-substrates, while keeping nearly constant the reactor volume. On the other hand, pig slurry could be conveniently utilized as hydration medium, as requested by the low moisture content of spent coffee grounds, that need resuspension when digested in wet anaerobic digestion processes. Clearly, the hypothesis of using pig slurry in co-digestion with spent coffee grounds needs to be substantiated by in-continuous experiments, specifically devoted to the study of chemical and physical interaction effects between feedstock ingredients on the parameters more appropriately describing the performances of the anaerobic digesters.

Acknowledgements
We are grateful to Anna Orsi for the contribution to the laboratory analyses.

References

Acevedo F., Rubilar M., Scheuermann E., Cancino B., Uquiche E., Garcés M., Inostroza K., Shene C., (2013), Spent coffee grounds as a renewable source of bioactive compounds, *Journal of Biobased Materials and Bioenergy*, **7**, 420-428.

Alves M.M., Pereira M.A., Diana Z., Sousa D.Z., Cavaleiro A.J., Picave M., Smidt H., Stams A.J.M., (2009), Waste lipids to energy: how to optimize methane production from long chain fatty acids (LCFA), *Microbial Biotechnology*, **2**, 538-550.

APHA, (1992), *Standard Methods for the Examination of Water and Wastewater*, 18th Edition. American Public Health Association, Washington D.C.

Battista F., Fino D., Ruggeri B., (2014), Polyphenols concentration's effect on the biogas production by wastes derived from olive oil production, *Chemical Engineering Transactions*, **38**, 373-378.

Bauer A., Leonhartsberger C., Bösch P., Amon B., Friedl A., Amon T., (2010), Analysis of methane yields from energy crops and agricultural by-products and estimation of energy potential from sustainable crop rotation systems in EU-27, *Clean Technologies and Environmental Policy*, **12**, 153-161.

Buerge I.J., Poiger T., Müller M.D., Buser H.-R., (2003), Caffeine, an anthropogenic marker for wastewater contamination of surface waters, *Environmental Science & Technology*, **37**, 691-700.

Calixto F., Fernandes J., Couto R., Hernandez E. J., Najdanovic-Visak V., Simoes P.C., (2011), Synthesis of fatty acid methyl esters via direct transesterification with methanol/carbon dioxide mixtures from spent coffee grounds feedstock, *Green Chemistry*, **13**, 1196-1202.

Campos-Vega R., Loarca-Piña G., Vergara-Castañeda H.A., Oomah B.D., (2015), Spent coffee grounds: A review on current research and future prospects, *Trends in Food Science & Technology*, **45**, 24-36.

Chen R., Jiang H., Li Y-Y., (2018), Caffeine degradation by methanogenesis: Efficiency in anaerobic membrane bioreactor and analysis of kinetic behaviour, *Chemical Engineering Journal*, **334**, 444-452.

Ciesielczuk T., Rosik-Dulewska C., Poluszyńska J., Miłek D., Szewczyk A., Sławińska I., (2017), Acute toxicity of experimental fertilizers made of spent coffee grounds, *Waste and Biomass Valorization*, 1-8, Doi: https://doi.org/10.1007/s12649-017-9980-3.

Cruz R., Baptista P., Cunha S., Pereira J.A., Casal S., (2012a), Carotenoids of lettuce (*Lactuca sativa* L.) grown on soil enriched with spent coffee grounds, *Molecules*, **17**, 1535-1547.

Cruz R., Cardoso, M.M., Fernandes, L., Oliveira M., Mendes E., Baptista P., Morais S, Casal S., (2012b), Espresso coffee residues: A valuable source of unextracted compounds, *Journal of Agricultural and Food Chemistry*, **60**, 7777-7784.

Daglia M., (2012), Polyphenols as antimicrobial agents. *Current Opinion in Biotechnology*, **23**, 174-181.

Dinuccio E., Balsari P., Gioelli F., Menardo S., (2010), Evaluation of the biogas productivity potential of some Italian agro-industrial biomasses, *Bioresource Technology*, **101**, 3780-3783.

El Achkar J.H., Lendormi T., Hobaika Z., Salameh D.N., Louka N., Maroun R.G., Lanoisellé J.-L., (2016), Anaerobic digestion of grape pomace: Biochemical characterization of the fractions and methane production in batch and continuous digesters, *Waste Management*, **50**, 275-282.

EVA, (2017), Market Report on European OCS & Vending, The European Vending Association, On line at: http://vending-europe.eu/en/consumer--market-reports/market-report/.

Field J.A., Kortekaas S., Lettinga G., (1989), The tannin theory of methanogenic toxicity, *Biological Wastes*, **29**, 241-262.

Field J.A., Lettinga G., (1987), The methanogenic toxicity and anaerobic degradability of a hydrolyzable tannin, *Water Research*, **21**, 367-374.

Franca A.S., Oliveira L.S., (2009), *Coffee Processing Solid Wastes: Current Uses and Future Perspectives*, In: *Agricultural Wastes*, Ashworth G.S., Azevedo P. (Eds.), Nova Publishers, New York, 155-189.

Givens D.I., Barber W.P., (1986), In vivo evaluation of spent coffee grounds as a ruminant feed, *Agricultural Wastes*, **18**, 69-72.

ICO, (2017), International Coffee Organization, On line at: http://www.ico.org/new_historical.asp?section=Statistics

Jimenez S., Cartagena M.C., Arce A., (1990), Influence of lignin on the methanization of lignocellulosic wastes, *Biomass*, **21**, 43-54.

Kayembe K., Basosila L., Mpiana P.T., Sikulisimwa P.C., Mbuyu K., (2013), Inhibitory effects of phenolic monomers on methanogenesis in anaerobic digestion, *British Microbiology Research Journal*, **3**, 32-41.

Kida Ikbal K., Sonoda Y., (1992), Treatment of coffee waste by slurry-state anaerobic digestion, *Journal of Fermentation and Bioengineering*, **73**, 390-395.

Kim H., Choi B., (2010), The effect of biodiesel and bioethanol blended diesel fuel on nanoparticles and exhaust emissions from CRDI diesel engine, *Renewable Energy*, **35**, 157-163.

Kim J., Kim H., Baek G., Lee C., (2017), Anaerobic co-digestion of spent coffee grounds with different waste feedstocks for biogas production, *Waste Management*, **60**, 322-328.

Kondamudi N., Mohapatra S.K. Misra M., (2008), Spent coffee grounds as a versatile source of green energy, *Journal of Agricultural and Food Chemistry*, **56**, 11757-11760.

Kwon E.E, Yi H., Jeon J., (2013), Sequential co-production of biodiesel and bioethanol with spent coffee grounds, *Bioresource Technology*, **136**, 475-480.

Lane A.G., (1983), Anaerobic digestion of spent coffee grounds, *Biomass*, **3**, 247-268.

Li X., Strezov V., Kan T., (2014), Energy recovery potential analysis of spent coffee grounds pyrolysis products, *Journal of Analytical and Applied Pyrolysis*, **110**, 79-87.

Littell R.C., Milliken G.A., Stroup W.W., Wolfinger R.D., (1996), *SAS system for Mixed Models*, SAS Inst. Inc., Cary, NC.

Luna-delRisco M., Normak A., Orupõld K., (2011), Biochemical methane potential of different organic wastes and energy crops from Estonia, *Agronomy Research*, **9**, 331-342.

Luz F.C., Cordiner S., Manni A., Mulone V., Rocco V., (2017), Anaerobic digestion of coffee grounds soluble fraction at laboratory scale: Evaluation of the biomethane potential, *Applied Energy*, **207**, 166-175.

Luz F.C., Cordiner S., Manni A., Mulone V., Rocco V., (2018a), Biomass fast pyrolysis in screw reactors: Prediction of spent coffee grounds bio-oil production through a monodimensional model, *Energy Conversion and Management*,**168**, 98-106.

Luz F.C., Volpe M., Fiori L., Manni A., Cordiner S., Mulone V., Rocco V., (2018b), Spent coffee enhanced biomethane potential via an integrated hydrothermal carbonization-anaerobic digestion process, *Bioresource Technology*, **256**, 102-109.

Machado E.M.S., Rodriguez-Jasso R.M., Teixeira J.A., Mussatto S.I., (2012), Growth of fungal strains on coffee industry residues with removal of polyphenolic compounds, *Biochemical Engineering Journal*, **60**, 87-90.

Marchetti R., Vasmara C., Florio G. Borin M., (2016), Biomethanation potential of wetland biomass in codigestion with pig slurry, *Waste and Biomass Valorization*, **7**, 1081-1089.

Martinez-Saez N., García A., Pérez I., Rebollo-Hernanz M., Mesías M., Morales F., Martín-Cabrejas M., del Castillo M., (2017), Use of spent coffee grounds as food ingredient in bakery products, *Food Chemistry*, **216**, 114-122.

Mussatto S.I., Ballesteros L.F., Martins S., Teixeira J.A., (2011), Extraction of antioxidant phenolic compounds from spent coffee grounds, *Separation and Purification Technology*, **83**, 173-179.

Mussatto S.I., Machado, E.M.S., Carneiro L.M., Teixeira J.A., (2012), Sugars metabolism and ethanol production by different yeast strains from coffee industry wastes hydrolysates, *Applied Energy*, **92**, 763-768.

Nonthakaew A., Matan Na., Aewsiri T. Matan Ni., (2015), Caffeine in foods and its antimicrobial activity, *International Food Research Journal*, **22**, 9-14.

Oliveira L.S., Franca A.S., Camargos R.R.S., Ferraz V.P., (2008), Coffee oil as a potential feedstock for biodiesel production, *Bioresource Technology*, **99**, 3244-3250.

Owen W.F., Stuckey D.C., Healy Jr. J.B., Young L.Y., McCarty P.L., (1979), Bioassay for monitoring biochemical methane potential and anaerobic toxicity, *Water Research*, **13**, 485-492.

Patra A. K., Saxena J., (2010), A new perspective on the use of plant secondary metabolites to inhibit methanogenesis in the rumen, *Phytochemistry*, **71**, 1198-1222.

Prabhudessai V., Ganguly A., Mutnuri S., (2009), Effect of caffeine and saponin on anaerobic digestion of food waste, *Annals of Microbiology*, **59**, 643-648.

Qiao W., Takayanagi K., Shofie M., Niu Q., Yu H.Q., Li Y.-Y., (2013), Thermophilic anaerobic digestion of coffee grounds with and without waste activated sludge as co-substrate using a submerged AnMBR: system amendments and membrane performance, *Bioresource Technology*, **150**, 249-258.

Salihović M., Šapčanin A., Pazalja M., Alispahić A., Dedić A., Ramić E., (2014), Determination of Caffeine in Different Commercially Available Green and Black Teas, *Bulletin of the Chemists and Technologists of Bosnia and Herzegovina*, **43**, 1-4.

Scully D.S., Jaiswal A.K., Abu-Ghannam N., (2016), An investigation into spent coffee waste as a renewable source of bioactive compounds and industrially important sugars, *Bioengineering*, **3**, 1-13.

Silva M.A., Nebra S.A., Machado Silva M.J., Sanchez C.G., (1998), The use of biomass residues in the Brazilian soluble coffee industry, *Biomass and Bioenergy*, **14**, 457-467.

Singleton V.L., Rossi Jr J.A., (1965), Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents, *American Journal of Enology and Viticulture*, **16**, 144-158.

Somnuk K., Eawlex P., Prateepchaikul G., (2017), Optimization of coffee oil extraction from spent coffee grounds using four solvents and prototype-scale extraction using circulation process, *Agriculture and Natural Resources*, **51**, 181-189.

Sousa C., Gabriel C., Cerqueira F., Manso M.C., Vinha A.F., (2015), *Coffee Industrial Waste as a Natural Source of Bioactive Compounds with Antibacterial and Antifungal Activities*, In: *The Battle Against Microbial Pathogens: Basic Science, Technological Advances and Educational Programs*, Méndez-Vilas A. (Ed.), Formatex Research Center. Badajoz, 131-136.

Sundarraj C.V., Dhala S., (1965), Effect of naturally occurring xanthines on bacteria (I). Antimicrobial action and potentiating effect on antibiotic spectra, *Applied Microbiology*, **13**, 432-436.

USDA, (2017), Coffee: World Markets and Trade, United States Department of Agriculture, On line at: https://www.fas.usda.gov/data/coffee-world-markets-and-trade

Valero D., Montes J.A., Rico J.L., Rico C., (2016), Influence of headspace pressure on methane production in Biochemical Methane Potential (BMP) tests, *Waste Management*, **48**, 193-198.

Vasmara C., Cianchetta S., Marchetti R., Galletti S., (2015), Biogas production from wheat straw pre-treated with ligninolytic fungi and co-digestion with pig slurry, *Environmental Engineering and Management Journal*, **14**, 1751-1760.

Vasmara C., Marchetti R., (2016), Biogas production from biodegradable bioplastics, *Environmental Engineering and Management Journal*, **15**, 2041-2048.

Van Soest P.J., Robertson J.B., Lewis B.A., (1991), Methods for dietary fiber, neutral-detergent fiber and non-starch polysaccharides in relation to animal nutrition, *Journal of Dairy Science*, **74**, 3583-3597.

Vitez T., Koutný T., Šotnar M., Chovanec J., (2016), On the Spent Coffee Grounds Biogas Production, *Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis*, **64**, 1279-1282.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2409-2419
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

TOWARDS THE OPTIMAL DESIGN AND OPERATION OF MULTI-ENERGY SYSTEMS: THE "EFFICITY" PROJECT

Matteo Zatti[1,2], Marco Gabba[2], Michele Rossi[3], Mirko Morini[4], Agostino Gambarotta[4], Emanuele Martelli[1]*

[1]Politecnico di Milano, Department of Energy, Via Lambruschini 4 - 20133, Milano, Italy
[2] Energy & Environment Laboratory Piacenza, Via Nino Bixio 27/c – 29121, Piacenza, Italy
[3]SIRAM, Milano, Italy
[4]University of the Studies of Parma, Interdepartmental Center for Energy and the Environment, Parco Area delle Scienze, 181/a – 43124, Parma, Italy

Abstract

The development of Multi-Energy Systems (MES) or District Energy Systems (DES) requires suitable design and operation optimization tools, in order to assess their feasibility and economic profitability. These tools can be helpful in choosing the proper technologies and also in the perspective of defining proper incentive or taxation schemes. A critical result of the analysis of MES is that, when optimizing their design, the operation strategy and the part load behavior of the units must be considered in the optimization model. This way, the model is to be formulated as a two-stage problem, where the design and the operation variables are optimized in the first and in the second stage, respectively. In order to guarantee the computational tractability, the scheduling/operation problem is solved for a limited set of typical and extreme periods. We have developed a Mixed Integer Linear Programming model to solve this design optimization problem, for which we have linearized the off-design and the size effects of performances and costs for the technologies considered in the case study. The model has been applied to optimize the design of a district energy system for the University of Parma Campus in Northern Italy.

Key words: carbon tax, design optimization, district energy systems, tri-generation

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Multi-Energy Systems (MES) and District-Energy Systems (DES) have been considered as promising solutions to lower the costs and the environmental impact of the energy production, distribution and use in urban areas (Weber et al., 2007). The fundamental concept is the integration of the energy networks – i.e. electricity, heating and cooling – operating in residential, commercial and industrial districts, so as to maximize the possible synergies among them. Examples of these possible synergies are represented by the combination of photovoltaic panels with heat pumps or refrigeration cycles and/or CHP internal combustion engines with absorption refrigeration cycles (tri-generation).

Both local and national institutions are growing an interest and taking initiatives in this field, hence research projects and investments arise, involving both private and public subjects. An example of this is the "Efficity" project – Efficient Energy Systems for Smart Urban Districts (www.efficity-project.it), co-funded by Emilia-Romagna Region (Italy), whose objective is the development of a software platform able to optimize the design, scheduling and control of smart energy networks – both conventional and renewables-based – serving urban districts, public and commercial buildings. Indeed, the first step towards

* Author to whom all correspondence should be addressed: e-mail: emanuele.martelli@polimi.it; Phone: +3902 23993908

the aforementioned synergy maximization is the validation of its technical feasibility and economical profitability through mathematical optimization models, whose results could give important indications about which driving forces would play a major role – either positive or negative – in the development and diffusion of such systems.

When dealing with MES and DES design optimization, both centralized and distributed generation solutions should be taken into account; thus, a design optimization model has to accommodate for the possibility of installing multiple energy conversion units of variable size in many different locations of the district, making the problem extremely more difficult to solve than a single site problem. Moreover, in order to avoid operational issues and/or poor energy performances of the units, the optimal design has to take into account the part-load performances and operational limitations (e.g., start-up/shut-down time and costs, ramp-up rates etc.) that characterize the operation of the energy conversion units (Yokoyama et al., 2002).

The characterization of the off-design performances of the units, together with the size effects on the nominal performances and costs, introduces many non-linearities, leading to challenging nonconvex Mixed Integer Nonlinear Program (MINLP) problems. To tackle such problems, two main approaches can be found in literature: the first one features a decomposition of the entire problem into a design and an operation subproblem, the second one entails the linearization of the nonlinear relations so as to convert the MINLP into a large-scale Mixed Integer Linear Program (MILP) problem.

A thorough literature review about the methods developed by various research groups following either approach can be found in (Elsido et al., 2017). On one hand, the MILP formulation introduces a larger approximation error in modelling the nonlinear part-load performances and the size effects, but, on the other, tackling a MILP has the following advantages: i) there are global optimality guarantees, ii) the solution accuracy is constantly known and returned by the solver as the branch and bound gap, iii) extremely effective commercially MILP solvers are available, e.g. CPLEX (https://www.ibm.com/analytics/cplex-optimizer) and Gurobi (http://www.gurobi.com), which can successfully tackle large scale problems with thousands of binary variables. In light of these aspects, we have chosen the second approach. The MILP design optimization problem that we have developed has a two-stage structure: the design decisions (first stage) are taken in light of the optimal operation strategy (second stage).

In order to guarantee the computational tractability, the operation problem is solved for a limited set of typical periods (e.g., days or weeks), for which the hourly profiles of energy demands, energy prices and energy production from Renewable Energy Sources (RES) are usually considered. The selection of these typical periods has been widely studied in literature (Kotzur et al., 2018) and, in a previous work, we analyzed the impact of these selection techniques on the design (Zatti et al., 2018). In this work, a case study has been developed to assess the optimal retrofit for a district energy system represented by a University Campus in Northern Italy, which features electricity, heating and cooling demands. The MILP optimal design problem is solved with state-of-the-art MILP solvers. The impacts of different strategies as concerns the possibility of having energy load outages, CO_2 taxation and tri-generation implementation have been assessed.

2. Material and methods

2.1. Case study description

Within the "Efficity" project, besides the development of the novel algorithms for the optimization of the design and the operation of MES, there is a great interest in assessing the potential of practical economic and environmental benefits from the spread of such systems. Thus, both research institutes and private companies have been involved. Thanks to this, we have the chance to test our algorithms on real data, made available by the partners of the project. In this work, we determine the retrofit design of energy supply system which minimize the total annual cost in a University Campus in Northern Italy, featuring electricity, heating and cooling demands. The University Campus features in total about 30 buildings spread over an area of approximately 0.77 km^2. The fulfilment of the heating and cooling demands of buildings in the Campus of the University of Parma is provided by a district heating and cooling network.

The network is fed by five natural gas boilers and four compression refrigeration cycles located in the central site: the heating and cooling networks reach all the other buildings through four independent water loops, as shown in Fig. 1. The mass flow rate in each building heat exchanger is regulated by means of a bypass valve in order to maintain the temperature inside the building equal to 20 °C during working hours. The test case is relevant since it is representative of a medium scale district heating and cooling network which serves buildings with different sizes, envelope characteristics and destinations (offices, sport facilities, classrooms, etc.) in the tertiary sector. Moreover, the location in the north of Italy implies a quite high variability of external temperature during the heating period, and therefore sizing and management of the energy systems is of utmost importance.

The objective of this study is to determine the retrofit design of the energy supply system which minimizes the total annual cost (annualized capital costs + operating costs). We assume that all the existing units (boilers and refrigeration cycles) are to be replaced by new installations, whereas, in order to limit the capital cost of the retrofit, the layout of the heating and cooling networks are kept fixed.

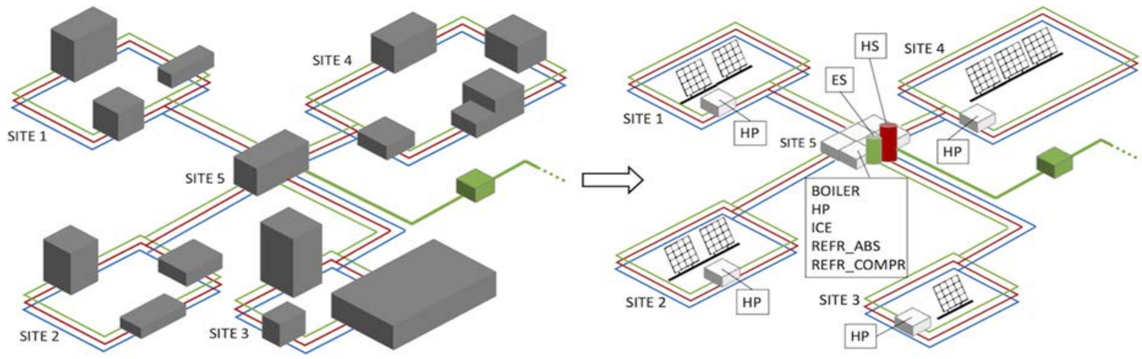


Fig. 1. From a generic district to the actual Campus: conceptual sketch. The algorithm is bounded to install each technology only in the pre-specified sites. Networks: blue = cooling, red = heating, green = electricity. The district is connected to the national electricity grid (green box). HP = heat pumps, ICE = internal combustion engine, REFR_ABS = absorption refrigeration cycle, REFR_COMPR = compression refrigeration cycle, ES = electrical storage, HS = heat storage

One of the main advantages of using the approach proposed within the "Efficity" project is the ability to explore several configurations, trying to exploit possible synergies between different technologies to achieve the desired objective.

Thus, we give our algorithm the faculty to choose among several technologies: cogeneration internal combustion engines (ICE), natural gas boilers (BOILERS), compression refrigerators (REFR_CMPR), absorption refrigeration cycles (REFR_ABS), heat pumps (HP), photovoltaic (PV) panels and solar heating (SH) panels, heat storage (HS) tanks and electrical storage (ES), that is batteries. According to the site characteristics, it has been assumed that internal combustion engines, natural gas boilers and compression refrigerators can only be located in the central site. The number of machines that can be installed in each site and the surface available for the installation of PV and SH panels are also parameters of the model.

The heat produced by both heat pumps and solar heating panels can be used only in the site where they are installed: the heat is exchanged with the secondary loop in order to exploit its lower temperature (leading to a higher efficiency of the units) compared with the one of the primary loops. The algorithm has also the possibility to install heat storages in the central site. The presence of internal combustion engines, compression and absorption refrigeration cycles and heat pumps in the technology roster is very challenging, since they produce couplings between energy networks. If on one hand this set-up adds complexity to the system, on the other it allows for larger optimization, especially with respect to the current situation.

Hourly values for one year of heating, cooling and electricity demand have been used as input of the model. As concerns heating and cooling, data were made available for each building in the campus as results of both data collection and physical models, as described in (Gambarotta et al., 2017). As regards the electricity demand, only measures of the total monthly demands of the campus were available. They have been allocated to the different buildings considering that during evening hours, weekends and holidays the buildings are closed; thus, they feature very low and constant electricity demand. This assumption is confirmed by the characteristic daily and weekly profiles of schools, which can be found in the literature (RSE, 2009).

In addition to the energy demand profiles, hourly values for ambient temperature and solar irradiation have been retrieved and used for the identification of the typical and extreme days. Global horizontal irradiance and beam horizontal irradiance data have been used to calculate the global irradiance on a tilted surface (angle = 35°, commonly used value at these latitudes), assumed to be directed towards south, so as to maximize the daily and yearly production. Finally, hourly electricity prices have been collected from the Italian power exchange website. The one-year time series for the relevant attributes (normalized between 0 and 1) are reported in Fig. 2.

2.2. Formulation of the optimization model

The design optimization problem considered in this work has been formulated as a two-stage MILP problem, involving investment decisions (first stage) and operation decisions (second stage). This two-stage structure is represented by the following compact formulation, Eqs. (1 - 5):

$$\min_{x_u^{(1)} x_{u,t}^{(2)}} TAC = \sum_{u \in U} C^{INV} \cdot x_u^{(1)} + \sum_{t \in T} C^{OP} \cdot x_{u,t}^{(2)} \tag{1}$$

Subject to:

$$A^{(1)} x_u^{(1)} + A^{(1)} y_u^{(1)} = b_u^1 \tag{2}$$

$$A^{(2)} x_u^{(2)} + A^{(2)} y_u^{(2)} = b_u^2 \tag{3}$$

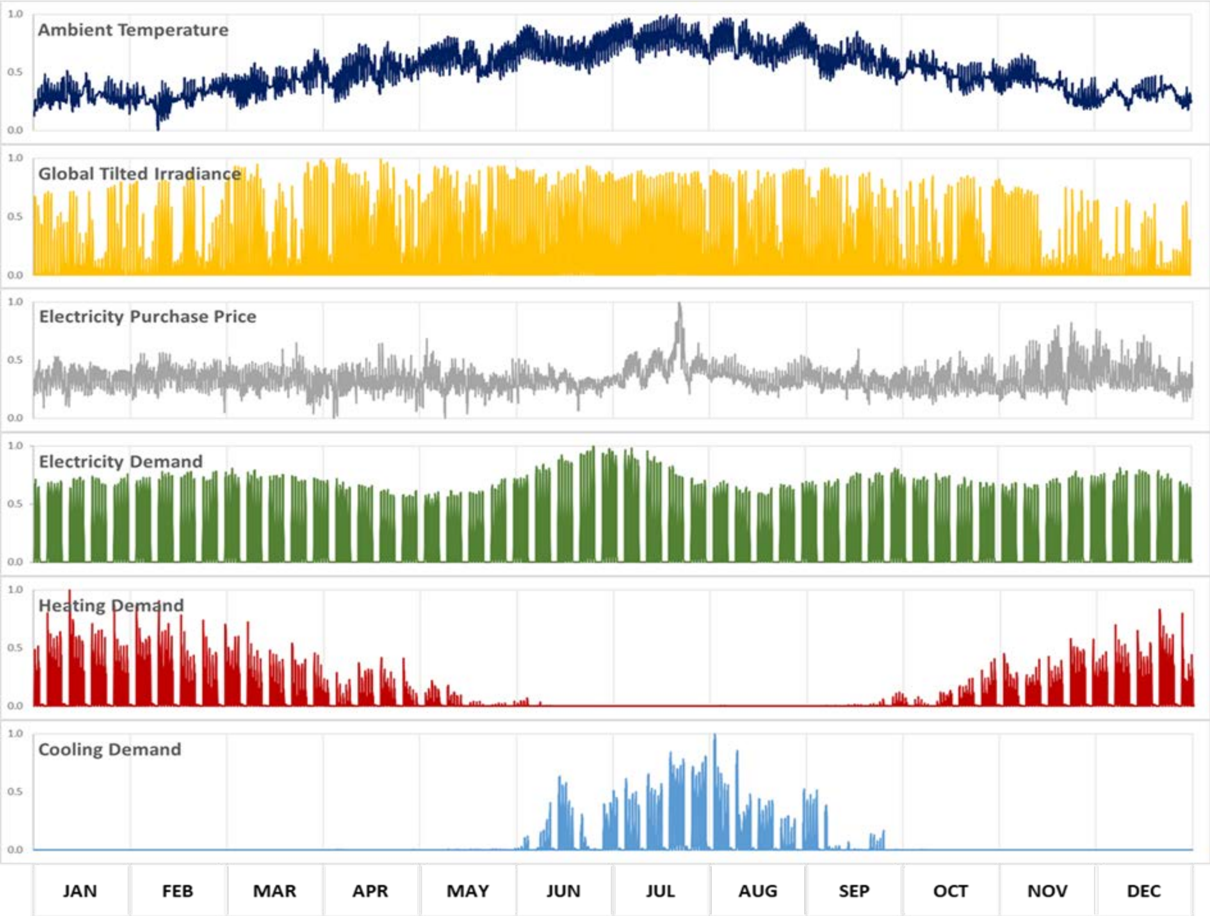


Fig. 2. One-year original data set of heating, cooling and electricity demands (the profiles report the total of the five sites), electricity purchase price, ambient temperature and the irradiance on a tilted surface (35°) oriented towards south

$$A^{(1)}x_u^{(1)} + A^{(1)}y_u^{(1)} + A^{(2)}x_{u,t}^{(2)} + A^{(2)}y_{u,t}^{(2)} = b_{u,t}^{(1,2)} \qquad (4)$$

$$x_u^{(1)} \in R, \quad x_{u,t}^{(2)} \in R, \quad y_u^{(1)} \in \{0,1\} \quad y_{u,t}^{(2)} \in \{0,1\} \qquad (5)$$

where $TAC = CAPEX + OPEX$ is the total annualized costs; $u \in U$ is the sets of energy conversion and storage units and $t \in T$ is the set of time steps considered in the operation. $x^{(1)}$ and $y^{(1)}$ are, respectively, the continuous (unit sizes, storage capacities, network branches capacities) and binary (unit/storage/network branch selection and installation) investment variables, and $x^{(2)}$ and $y^{(2)}$ are the continuous (unit load, storage level, network branch power flow) and binary (unit on/off status) operation variables.

As seen from Eq. (5), there are real and binary variables in both stages making the problem structurally similar to a two-stage stochastic problem with integer recourse (Birge and Louveaux, 2011). There are constraints that accounts only for the investment stage, as in Eq. (2), e.g. the minimum and maximum unit sizes or the available locations for the installation of the units. There are also constraints referring only to the operation stage, as in Eq. (3), e.g. the balances between the energy production and demand. Finally, as in Eq. (4), there are constraints that bind the first and the second stage variables, e.g. the performance maps of the units which depend on their size. This model presents many similarities with the methods described in (Bracco et al., 2016; Buoro et al., 2014; Gabrielli et al., 2018; Yang et al., 2015; Yokoyama et al., 2002; Yokoyama and Ito, 2006), which linearize the part-load performances of the units. Yet, our model is characterized by the simultaneous presence of three elements, which is not the case for the aforementioned works: i) a multisite structure, ii) the capacities of the units to be chosen by the algorithm are continuous variables for all the possible technologies and the size effects on performances are linearized with the approach proposed by Yokoyama et al. (2002), iii) the part load behavior of the units is modelled using the convex hull formulation (Lahdelma and Hakonen, 2003). These characteristics make it more general.

The problem is solved assuming that the energy production system serving the Campus nowadays is at the end of its life and the new energy conversion and storage units chosen by the design optimization model, once installed, have to work for the following 20 years, without any replacement or further intervention, except for the ordinary maintenance. The TAC are computed with respect to such time horizon, assuming an interest rate equal to 0.08. The district energy system is connected to the national gas and eletric grids, with the possibility of withdrawing or injecting electrical energy whenever it prefers. Finally, the charge/discharge cycle of the thermal storage is considered to be of 24 hours, that is the level of water in the hot water tank at the beginning and the end of the day has to be the same.

2.3. Modelling and performance linearization of energy technologies

We have modelled the performance and the costs of the aforementioned energy technologies by using: Thermoflex (Thermoflow®) for internal combustion engines and data derived from commercially available catalogues for heat pumps (Gabrielli et al., 2017) and for refrigeration cycles. Moreover, we have used the approaches available in SDH (2012) and Skoplaki and Palyvos (2009) for solar thermal and PV panels), respectively, together with data found in commercially available catalogues. Finally, concerning hot water heat storage systems we have used the approach proposed in Barbaro (2009) and data available in Turton et al. (2008). Such models account for: 1) economies of scale on capital costs 2) nonlinear size effects on nominal performances and 3) part-load operation of the units.

To be able to model within a MILP problem the performance of the energy technologies, we have linearized all the size effects on costs and efficiency of generation units. As for the performance at part loads and size effects, the correlation between the output (i.e. thermal, electrical or cooling power) and the input of the machine (i.e. fuel, electric or thermal power) has been linearized following the approach described by Yokoyama et al., (2002) and the convex hull formulation described in (Lahdelma and Hakonen, 2003), which results in the following formulation, Eqs. (6 – 11):

$$p_{u,t} = k^{1P} \cdot in_{u,t} + k^{2P} \cdot S_u + k^{3P} \quad (6)$$

$$q_{u,t} = k^{1Q} \cdot in_{u,t} + k^{2Q} \cdot S_u + k^{3Q} \quad (7)$$

$$r_{u,t} = k^{1R} \cdot in_{u,t} + k^{2R} \cdot S_u + k^{3R} \quad (8)$$

$$k^{IN}_{MIN} \cdot S_u \le in_{u,t} \le k^{IN}_{MAX} \cdot S_u \quad (9)$$

$$in_{u,t} = \sum\nolimits_{v=1}^{Nv} \alpha_{u,v,t} \cdot k^{IN}_{v} \cdot S_u \quad (10)$$

$$\sum\nolimits_{v=1}^{Nv} \alpha_{u,v,t} = z_{u,t} \quad (11)$$

where: $p_{u,t}$, $q_{u,t}$ *and* $r_{u,t}$ are, respectively, the electrical, thermal and cooling output of machine u at time t. $in_{u,t}$ is the input of the unit, which is: 1) fuel for boilers and ICEs, 2) electricity for heat pumps and compression refrigeration units and 3) thermal power for absorption refrigeration units. S_u is the size of the unit. $\alpha_{u,v,t}$ is the variable used for the convex hull formulation (where v are the vertexes) and $z_{u,t}$ is the binary on/off variable. Thanks to Eq. (11), the product of the two variables in Eq. (10) can be linearized.

The k^{1P}, k^{2P} and k^{3P} coefficients are used to linearize the size effect and the part load performances of the electrical output in Eq. (6), and similarly for thermal output in Eq. (7) and cooling output in Eq. (8). Eq. (9) is meant to set the minimum and maximum load of a unit, as a function of its size.

As an example of the methodology used to calculate the set of coefficients, we illustrate here the results concerning the internal combustion engine performance linearization; the other technologies follow similar patterns. We have collected – from catalogues and Thermoflex - thermal and electric efficiencies, both for on- and off-design conditions, for engines between 1500 kW_e and 18000 kW_e of electric power output. On the basis of these data, engines can be classified into two families, as shown in Fig. 3: "small" engines, with efficiency depending on the nominal electric power output, and "large" engines, for which the efficiency is independent from the nominal electric power output.

We have evaluated the set of coefficients required in Eqs. (6 – 10) for both engine families. To do so, we have selected a single producer with engine covering the whole "small" size range. The fitting of the available data results in the coefficient sets in Table 1, suitable for modeling all the range of "small" engines as shown in Fig. 4a, Fig. 4b and Fig. 4c. A similar fitting procedure has been carried out to linearize the off-design thermal power output map for the same engines.

Similarly, we have calculated the linearization coefficients for the other technologies included in our model. Coefficient values are reported in Table 1. As it can be seen in Fig. 4d and Fig. 4e, in order to model the part-load performances of the compression refrigeration units, it is better to use a piece-wise formulation entailing two segments; thus, two sets of coefficients are required.

As for the operational limits of the units, in the model we have enforced minimum up-time constraints in order to avoid abrupt turn-on and shut-down of the machines during the day, which would drastically diminish the life time of the units.

Costs are evaluated based on data available from commercial catalogues using the function reported in Eq. (12).

$$C_u = C_{u,0} \cdot \left(\frac{S_u}{S_{u,o}} \right)^{fu} \quad (12)$$

where C_u is the total investment cost of unit u of size S_u. $C_{u,0}$ is the total investment cost of unit u at the reference size and f_u is the proper scale factor.

We linearize these costs using piecewise functions featuring three segments; the breakpoints for each technology are reported in Table 2, together with the specific costs we have assumed for heat storage tanks (Euro/m^3) and solar heating panels (Euro/m^2).

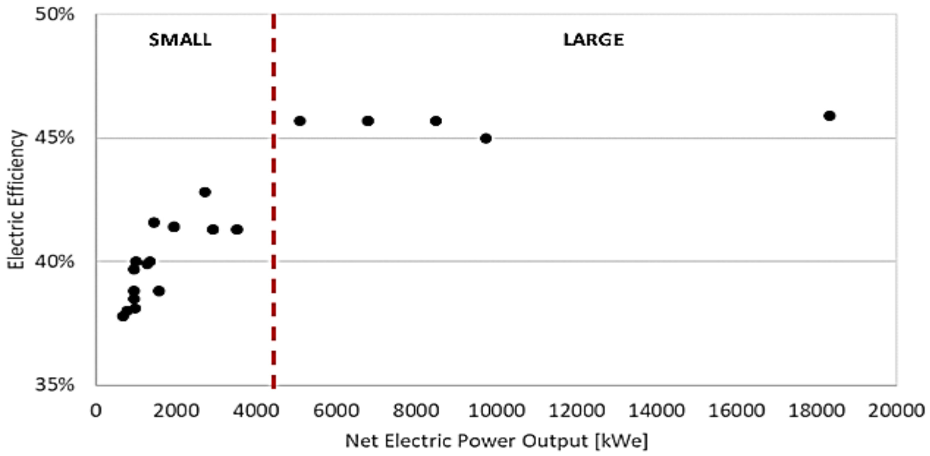


Fig. 3. Classification of engines based on the correlation between electric efficiency and net electric power output

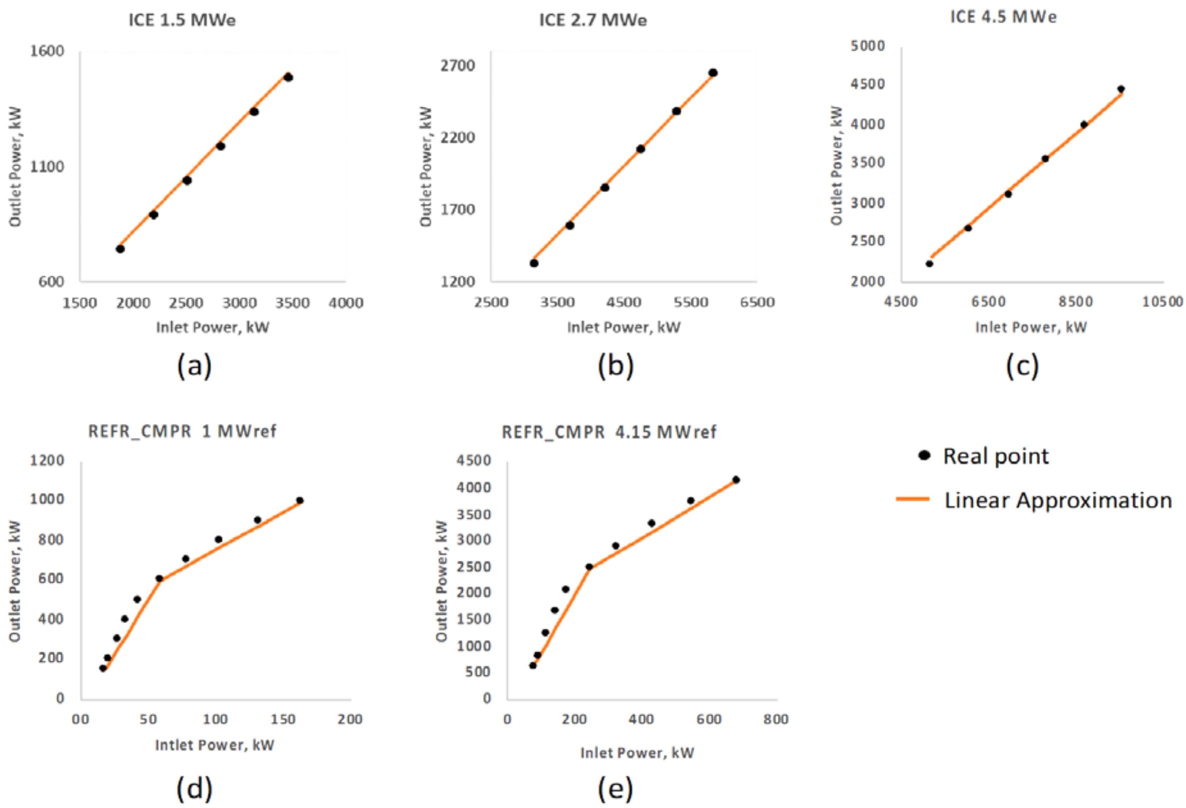


Fig. 4. Piecewise linearization of the performances of the internal combustion engines (ICE) and the compression refrigeration cycles (REFR_CMPR): (a), (b), (c) are three relevant sizes for the ICEs in the "small" range and (d), (e) are two relevant sizes for the REFR_CMPRs

Table 1. Linearization coefficients sets for the technologies considered in the case study (ICE = internal combustion engine; REF_CMPR = compression refrigeration cycle, REF_ABS = absorption refrigeration cycle, HP = heat pump)

UNIT TYPE	***Electricity Output***			***Thermal Output***			***Cooling Output***		
	k^{1P}	k^{2P}	k^{3P}	k^{1Q}	k^{2Q}	k^{3Q}	k^{1R}	k^{2R}	k^{3R}
HP				3.590	-0.080	0.000			
BOILER				0.976	-0.032	4.338			
"SMALL" ICE	0.490	-0.017	-128.830	0.439	-0.005	108.180			
"LARGE" ICE	0.507	-0.043	0.000	0.429	0.015	0.000			
REF_CMPR (1st segment)							11.103	-0.324	0.000
REF_CMPR (2nd segment)							3.806	2.295	0.000
REF_ABS							0.781	0.000	0.000

Table 2. Cost evaluation: breakpoints for piecewise linearization and specific costs. The size is expressed in terms of the input as indicated in unit type, the cost is expressed in kEuro; the specific cost is expressed in Euro and is specific to the unit of measure of the unit type (HP = heat pump, ICE = internal combustion engine, REF_CMPR = compression refrigeration cycle, REF_ABS = absorption refrigeration cycle, SH = solar heating, HS = heat storage, ES = electrical storage)

UNIT TYPE	***SIZE***				***COST [kEuro]***				***SPECIFIC COST***
	1	***2***	***3***	***4***	***1***	***2***	***3***	***4***	
HP, kW_{el}	100	500	2000	10000	254	778	2039	6239	
BOILER, kW_{fuel}	100	1000	10000	50000	8	69	554	2387	
ICE, kW_{fuel}	1328	13783	26237	38692	247	2296	4242	6145	
REF_CMPR, kW_{el}	165	337	508	680	248	428	587	733	
REF_ABS, kW_{th}	192	2348	4505	6661	136	385	505	594	
HS, m^3	1	2000	5000	10000	5	626	1131	1770	
ES, kWh									500
SH, m^2									350

2.4. Selection of typical and extreme days

Since optimizing the operation in the whole set of time steps (e.g., 8760 hours to evaluate the total annual cost) would make the problem computationally intractable, due to the large number of binary on/off variables, time series aggregation must be used to find a few representative operating profiles (Fazlollahi et al., 2014) or to group the binary operational variables (Gabrielli et al., 2017) and reduce the problem size. The required feature of such aggregation is to be representative of the original time series, in such a way that: 1) the operational feasibility is preserved and 2) the operational costs appearing in the objective function resemble properly the actual operational costs. For the first task, extreme periods are usually added to the input data set, while for the second one, clustering techniques are commonly used.

As thoroughly explained in (Kotzur et al., 2018), the aim of time series aggregation techniques is to gather a set of periods $i \epsilon \{1, \dots, N_i\}$ (e.g. the 365 days of a year), each consisting of the same number of time steps $h \epsilon \{ 1, \dots, N_h\}$ (e.g. the 24 hours), with N_a attributes (e.g. heating demand, irradiance, etc.), into a pre-defined N_k number of groups such that the group members are as similar as possible.

Usually, the aggregation is performed by minimizing a distance measure of the attributes between each group member. The groups are then represented by a single period. The selection of the representative period, often called *typical periods*, depends on the specific techniques. Moreover, since the typical periods are the most representative profiles of the clusters, extreme periods are not included and need to be added so as to enforce the operational feasibility of the system throughout the year.

In this work, the attributes considered for the clustering are: the heating, electricity and cooling demands, the irradiance, the ambient temperature and the electricity prices.

Moreover, based on the periodicity of the energy demand profiles, of the physical phenomena (sun irradiance) and the typical usage of the storage systems, the time step basis we have chosen for the typical periods is 24 hours, that is we have considered *typical days*.

In order to determine typical and extreme days, the systematic MILP-based clustering method proposed in Zatti et al. (2018) has been used. It is an improvement of the k-medoids clustering approach in which: 1) it is possible to bound the maximum violation of the total yearly value of each attribute (e.g., the sequence of selected typical days and actual days must have similar total yearly electricity/heat/cooling demand), 2) the most atypical days are automatically identified as "extreme days" – see further details in Zatti et al. (2018).

To preserve computational tractability of the optimization problem, 6 typical and 6 extreme days have been considered to represent the whole operating year. Their normalized profiles are reported in Fig. 5 (values have been normalized between the minimum and maximum value reached by each profile).

2.5. Investigated scenarios

The MILP design optimization model has been applied to the case study considering 6 different scenarios:

- Scenario 1: outages are not allowed (the heat and cooling demand must always be satisfied by the installed units).
- Scenario 2: if the energy systems supplying heat and cooling power cannot meet the users' demands in a certain hour of the day, a fixed fee of 5000 Euro/hour must be paid plus a fee proportional to the load shedding (100 and 200 Euro per MWh of, respectively, heating and cooling demand not met).
- Scenario 3: in case of outages, only a variable fee of 100 and 200 Euro per MWh of, respectively, heating and cooling demand not met is paid.
- Scenario 4: same assumptions as Scenario 2 with the addition of a CO_2 emissions tax equal to 100 Euro/tCO_2. In this scenario, cogeneration and renewable technologies should be favored compared to the use of natural gas boilers.

Scenario 5: same techno-economic assumptions as scenario 4 but with the additional possibility of installing an absorption refrigeration unit in site 5

.

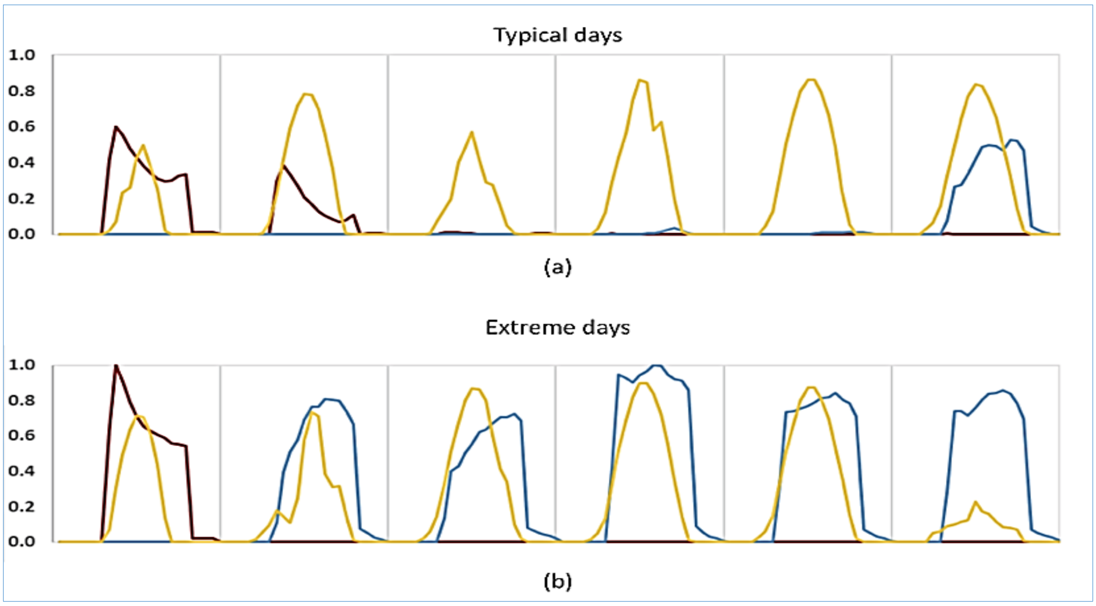


Fig. 5. Normalized profiles for heating demand (red curve), cooling demand (light blue curve) and irradiance (yellow curve) of: (a) the 6 typical days and (b) the 6 extreme days

- Scenario 6: same assumptions as scenario 5 but with the possibility to use the thermal power produced by the solar heating in the whole districts through the primary heat distribution network; this lowers the average yearly efficiency of the SH panels because of the higher temperature of the water to be heated up (95 °C) compared to the secondary internal building loops (45-60 °C).

For all the above-listed scenarios, a natural gas price of 0.039 Euro/kWh_{LHV} has been assumed.

3. Results

3.1. Design results

Table 3 and Table 4 report the design optimization results in terms of selection of installed units and annualized costs respectively. As it can be seen, in scenario 1, the optimal design must feature 3 boilers (a large one covering approximately 56% of the peak heating demand and two much smaller ones), a large ICE covering between 58% of the peak electricity demand, 3 refrigeration cycles (two large ones covering 45-50% of the demand and a smaller one) and a heat storage system (100 m^3 volume) to be installed in site 5, plus a heat pump to be installed in site 1. The peak demand of heating is met by using all the boilers, the ICE and discharging the heat storage system. Thanks to the thermodynamic advantage of the cogeneration engine, the optimized management of the storage system and the optimized layout and sizing, the retrofit solution generates 21% less CO_2 emissions than the current design. This result is remarkable considering that no CO_2 emission taxes or incentives for renewable energy technologies is considered. In scenarios 2 and 3, the optimal design exploits the possibility of making outages to save some capital costs and, thus, it reduces the capacity of installed boilers. In scenario 2, the designed system is not able to meet 0.85% of the requested heat demand while in scenarios 3, due to the lower outage fees, this fraction rises to 2.5%. Similarly, to scenario 1, also in scenarios 2 and 3 the optimal solution essentially resembles the centralized paradigm to exploit economies of scale. Even if in scenario 3 outages are allowed and not expensive, renewable technologies (solar PV and solar thermal panels) are not exploited because of their higher costs compared to conventional fossil-fired technologies (boilers and ICEs).

It is worth noting that the actual TAC of scenario 2 (TAC assessed by optimizing the operation day-by-day for the whole year) is worse than that of scenario 1, even though scenario 2 features a relaxation of the constraints of scenario 1 (i.e., it should feature a TAC equal or lower than scenario 1). This is due to the approximation caused by the typical periods which, within the design optimization problem, underestimate the number of outage hours compared to the actual operating profiles.

In Scenario 4, the capacity of the boilers is decreased and that of the CHP ICE is increased so as to lower the CO_2 emissions thanks to the fuel saving effect of cogeneration. When possible, peaks of heat demand are met by discharging the heat storage system. On average, 0.82% of the heat demand is not met across the whole year (i.e. during the peak demand hours, occurring only a few hours per year). Cooling power is provided by refrigeration cycles, which are sized to meet the peak demand. Given the assumed CO_2 emissions tax, solar PV panels are not installed because less cost-effective than CHP ICEs (the installed ICE cogenerates useful heat in addition to the electricity).

Table 3. Selection of the units (S1.S5 is the site number; SH = Solar Heating; HP = Heat Pump; ICE EL = electricity produced by Internal Combustion Engine; ICE TH = Heat produced by Internal Combustion Engine; REF_CMPR = compression refrigeration cycle, REF_ABS = absorption refrigeration cycle, HS = Heat Storage**)**

SCENARIO	***S1***	***S2***		***S5***												
	SH [m²]	***HP***	***SH [m²]***	***BOILERs***			***ICEs EL***		***ICEs TH***		***REF_CMPRs***			***REF_ABSs***		***HS [m³]***
1		0.147		0.564	0.023	0.006	0.585		0.158		0.502	0.456	0.167	n.a.		100
2		0.132	9	0.248	0.023	0.007	0.603		0.163		0.484	0.474	0.167	n.a.		100
3		0.131		0.181	0.004	0.004	0.602		0.163		0.450	0.122		n.a.		100
4		0.139	9	0.236	0.004	0.004	0.754		0.205		0.496	0.461	0.167	n.a.		77
5	265	0.132	2	0.228			0.684	0.081	0.185	0.022	0.131			0.586	0.297	100
6		0.147	441	0.266	0.005		0.701		0.190		0.328	0.122		0.586		100

Table 4. Annualized costs, heating and cooling demand outages, fossil CO_2 emissions for the six scenarios. Capex: Capital expenditures, Opex: operation expenditures, TDs: typical days, TAC: Total Annualized Costs = Capex + Opex. All the economic values have been normalized with respect to the TAC calculated considering TDs of the first scenario. The outages are reported as fraction of the corresponding total energy demands

	COSTS					***OUTAGES***		***FOSSIL CO₂ EMISSIONS***
SCENARIO	***Annualized Capex***	***Opex TDs***	***Opex 365 days***	***TAC TDs***	***TAC 365 days***	***heating***	***cooling***	
1	0.30	0.70	0.69	1.00	0.98	0.00%	0.00%	0.79
2	0.27	0.71	0.77	0.98	1.04	0.85%	0.00%	0.78
3	0.22	0.72	0.71	0.94	0.94	2.48%	8.65%	0.78
4	0.29	1.06	1.12	1.35	1.41	0.82%	0.00%	0.77
5	0.28	1.06	1.14	1.34	1.41	0.86%	0.00%	0.78
6	0.28	1.05	1.09	1.33	1.38	0.52%	0.00%	0.77

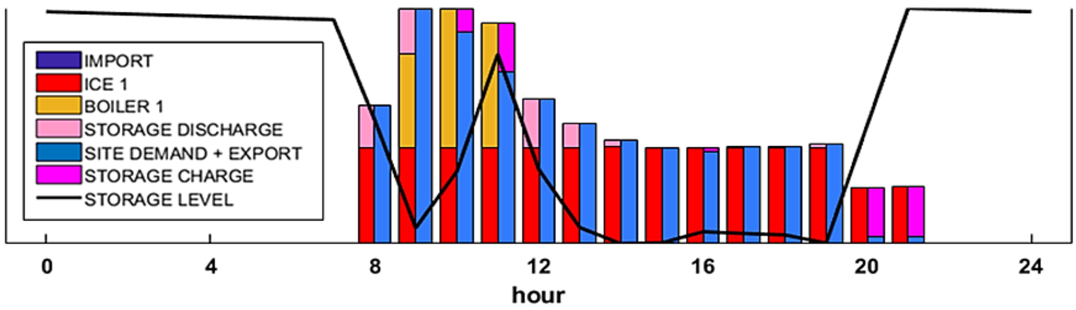
Likely, solar PV panels would be installed if higher CO_2 emission taxes would be assumed. Although the assumed taxes on CO_2 emissions cause a total annual cost increase by 40% compared to scenario 1, the yearly total CO_2 emissions are only 2% lower.

In scenario 5, the optimal solution features two absorption chillers (of different capacity) which, during summer, convert the heat produced by two CHP ICEs into cooling power. The absorption chiller allows using the CHP ICE also during summer with a slight capital cost saving compared to the installation of refrigeration cycles (Table 4). Thermal power for heating purposes is generated by a boiler and two CHP ICE placed in the central site (site 5), and a heat pump placed in site 2. A considerable extent of solar thermal panels is placed on the buildings of site 1 to contribute to the heat generation system (saving CO_2 emissions). Compared to the previous ones, this scenario features a higher share of renewable sources and a more decentralized energy production system.

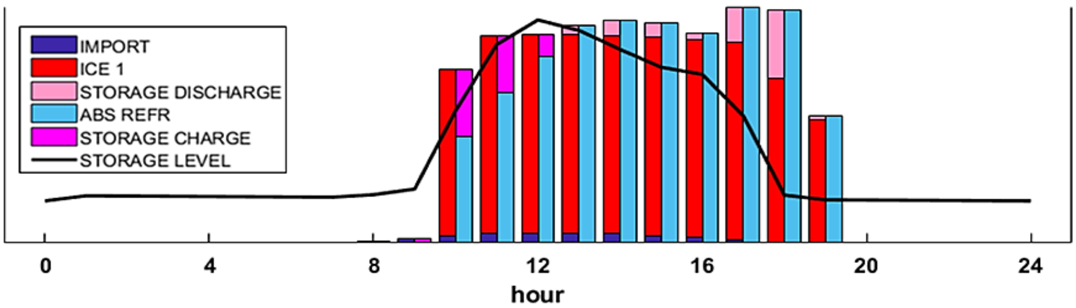
In Scenario 6, solar thermal panels can be installed to provide heat to the primary heat distribution system. Thus, their thermal power can be transferred from one site to the others via the existing heating network and, when necessary, converted into cooling power by the absorption chiller. This solution allows to use solar heating to contribute to the heat required by the absorption chiller, thus considerably increasing the utilization factor of the panels. As a result, the optimal design features 441 m^2 of thermal solar panels in site 2. On the other hand, due to the intermittency of solar radiation, only one absorption chiller is installed and it is capable of covering only half of the cooling demand. The remaining cooling power is provided by two refrigeration cycles, which guarantee operation also during cloudy days. For the assumed cost of CO_2 emissions tax, Scenario 6 turns out to be less expensive (i.e., leading a 3% lower total annual cost) and less carbon intensive (-1.5% total yearly CO_2 emissions) than scenario 5 thanks to the lower operating costs.

3.2. Operation results

Fig. 6 shows the optimized operation of the installed units for the design solution of scenario 6 in a typical winter day (Fig. 6a) and a typical summer day (Fig. 6b). In the typical winter day, the integration of the ICE and the larger boiler together with an appropriate discharge of the thermal storage allows to cover the total heating demand of the district. In order to meet the minimum up time constraint, the ICE is used to charge the thermal storage in the evening so as to use the stored heat in the morning peak hours, together with the boiler. In the typical summer day, the ICE and the thermal storage are synergistically used to produce the heat required by the absorption chiller to match the cooling demand of the district. In the morning hours, the ICE is used to charge the thermal storage so that the latter can be used in the evening, when the district cooling demand reaches the peak values. Thanks to this strategy, the system can also benefit from the higher morning electricity sale prices.



(a)



(b)

Fig. 6. Optimized operation of the installed units for the design of scenario 6. The plot reports the heat generated by the units installed in the central site of the campus (site 5) at each hour of the day, during: (a) a winter typical day and (b) a summer typical day. The left-hand bars show the positive contributions to the heat balance, that is the heat produced by the units, the heat storage discharge and the import from the solar panels located in site 2. The right-hand bars show the negative contributions to the heat balance, that is the site demand (please notice that the heating demand of site 5 is very low), the heat storage charge, the heat absorbed by the absorption chiller and the heat exported to the other sites of the campus. The bars are normalized with respect to the peak values reached within the day

4. Conclusions

The paper presents the systematic design methodology for multi-energy systems and smart energy districts developed in the framework of the "Efficity" project. The optimal design problem of multi-energy systems (MES) serving districts of buildings is formulated as a multi-period multi-site Mixed Integer Linear Program. The model includes accurate linearized cost and performance models of conventional and renewable energy technologies as well as energy storage systems. The approach has been applied to identify the best retrofit design for the energy system serving the Campus of University of Parma. Six interesting scenarios were considered featuring different costs of outages, CO_2 emission taxes and retrofit options. For the scenarios without CO_2 emission taxes (or incentives), the minimum cost solution essentially resembles a centralized paradigm with three boilers and a CHP ICE producing most of the required thermal power. Peak demands of heat are satisfied with the aid of a hot water storage tank. Renewable technologies are not selected because of their high specific capital costs (being no incentives). The optimal size of the required boilers depends on the fee to be paid for the heating outages. Even though CO_2 emission taxes are not considered, the retrofit design allows saving from about 21 to 22% of CO_2 emissions compared to the current design, thanks to the fuel saving advantage of CHP engines and the optimized layout.

If CO_2 emission taxes equal to 100 Euro/t are considered, the optimal solution from an economic and CO_2 emissions point of view is the one of scenario 6 which includes two boilers, an internal combustion engine, an absorption chiller, two refrigeration cycles and a hot water tank in the central site (S5), plus a heat pump and more than 400 m^2 of solar thermal panels in site 2. Solar thermal panels generate hot water for the primary distribution networks between sites which can be used during winter/spring/autumn for space heating and domestic hot water, and during summer to generate cooling power with the absorption cycle of site 5. Thus, the optimal solution calls for two-way heat flows between the sites, like in decentralized multi energy systems. Due to the assumed taxes on fossil CO_2 emissions, the total annual cost rises by about 40% compared to the scenario without emissions penalties. On the other hand, the optimized design of scenario 6 allows saving only 2% more fossil CO_2 emissions compared to scenario 1 (which is already quite efficient in reducing CO_2 emissions thanks to the fuel savings effect of the CHP engine). In order to achieve higher CO_2 emission savings, higher CO_2 emission taxes (or incentives for solar PV or solar heating panels) should be set, but this would lead to a considerable penalty on the total annual cost.

An interesting result is that in all the considered scenarios solar PV panels are not selected to generate electric power because of their relatively higher investment costs (without incentives) compared to CHP engines (which have also the advantage of cogenerating useful heat).

Acknowledgments

The authors acknowledge SIRAM for the useful techno-economic information and the key data of the case study. This work was supported by the "Efficity - Efficient energy systems for smart urban districts" project (CUP E38I16000130007) co-funded by Regione Emilia-Romagna through the European Regional Development Fund 2014-2020.

References

Barbaro C., (2009), *Optimization of poligeneration units and energy μ–grids for applications in the residential sector* (in Italian), PhD Thesis, Università degli Studi di Palermo, Palermo, Italy.

Birge J.R., Louveaux F., (2011), *Introduction to Stochastic Programming*, 2nd Edition, Springer, New York.

Bracco S., Dentici G., Siri S., (2016), DESOD : A mathematical programming tool to optimally design a distributed energy system, *Energy*, **100**, 298-309.

Buoro D., Pinamonti P., Reini M., (2014), Optimization of a Distributed Cogeneration System with solar district heating, *Applied Energy*, **124**, 298-308.

Elsido C., Bischi A., Silva P., Martelli E., (2017), Two-stage MINLP algorithm for the optimal synthesis and design of networks of CHP units, *Energy*, **121**, 403-426.

Fazlollahi S., Bungener S.L., Mandel P., Becker G., Maréchal F., (2014), Multi-objectives, multi-period optimization of district energy systems: I. Selection of typical operating periods, *Computers and Chemical Engineering*, **65**, 54-66.

Gabrielli P., Gazzani M., Martelli E., Mazzotti M., (2018), Optimal design of multi-energy systems with seasonal storage, *Applied Energy*, **219**, 408-424.

Gambarotta A., Morini M., Rossi M., Stonfer M., (2017), A library for the simulation of smart energy systems: The case of the campus of the University of Parma, *Energy Procedia*, **105**, 1776-1781.

Kotzur L., Markewitz P., Robinius M., Stolten D., (2018), Impact of different time series aggregation methods on optimal energy system design, *Renewable Energy*, **117**, 474-487.

Lahdelma R., Hakonen H., (2003), An efficient linear programming algorithm for combined heat and power production, *European Journal of Operational Research*, **148**, 141-151.

RSE, (2009), Definition of indicators and classes of energy requirements of the different energy consumption centers in the educational buildings – energy consumption of primary and secondary schools, (in Italian), Report by RSE (Ricerca Sistema Elettrico), On line at: http://www.enea.it/it/Ricerca_sviluppo/documenti/ricerca-di-sistema-elettrico/governance/rse119.pdf.

Skoplaki E., Palyvos J.A., (2009), On the temperature dependence of photovoltaic module electrical performance: A review of efficiency/power correlations, *Solar Energy*, **83**, 614-624.

SDH, (2012), Solar district heating guidelines: Collection of fact sheets, Report, Solar District Heating, On line at: http://solar-district heating.eu/Portals/0/Factsheets/SDH-WP3-D31-D32_August2012.pdf.

Turton R., Bailie R.C., Whiting W.B., Shaeiwitz J.A., (2008), *Analysis, Synthesis and Design of Chemical Processes*, 3rd Edition, Prentice Hall International Series, Upper Saddle River.

Weber C., Maréchal F., Favrat D., (2007), Design and optimization of district energy systems, *Computer Aided Chemical Engineering*, **24**, 1127-1132.

Yang Y., Zhang S., Xiao Y., (2015), Optimal design of distributed energy resource systems coupled with energy distribution networks, *Energy*, **85**, 433-448.

Yokoyama R., Hasegawa Y., Ito K., (2002), A MILP decomposition approach to large scale optimization in structural design of energy supply systems, *Energy Conversion and Management*, **43**, 771-790.

Yokoyama R., Ito K., (2006), Optimal design of gas turbine cogeneration plants in consideration of discreteness of equipment capabilities, *Journal of Engineering for Gas Turbines and Power*, **128**, 336-343.

Zatti M., Gabba M., Rossi M., Balestrieri G., Gambarotta A., Morini M., Martelli E., (2018), *A Systematic Approach for the Selection of the Typical and Extreme Days for the Optimal Design of Multi Energy Systems*, Proc. ECOS 2018 – the 31st Int. Conf. on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Guimaraes, Portugal.

Web sites:

www.efficity-project.it
https://www.ibm.com/analytics/cplex-optimizer
http://www.gurobi.com

2420

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2421-2425
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

REUSE AND VALORIZATION OF SILT FROM AGGREGATES CRUSHING OF ALLUVIAL GRAVEL AND SAND, FOR THE MANUFACTURING OF CEMENT BASED BUILDING ELEMENTS

Marco Migliore[1]*, Giancarlo Paganin[2], Massimo Senini[3], Cinzia Talamo[1]

[1]*Department of Architecture, Building Environment and Construction Engineering (ABC), Politecnico di Milano, via Ponzio 31, 20133 Milano, Italy*
[2]*Department of Architecture and Urban Studies (DASTU), Politecnico di Milano, via Bonardi 3, 20133 Milano, Italy*
[3]*Senini S.p.a., via Erculiani 192, 25018 Novagli di Montichiari, Italia*

Abstract

The development of Multi-Energy Systems (MES) or District Energy Systems (DES) requires suitable design and operation optimization tools, in order to assess their feasibility and economic profitability. These tools can be helpful in choosing the proper technologies and also in the perspective of defining proper incentive or taxation schemes. A critical result of the analysis of MES is that, when optimizing their design, the operation strategy and the part load behavior of the units must be considered in the optimization model. This way, the model is to be formulated as a two-stage problem, where the design and the operation variables are optimized in the first and in the second stage, respectively. In order to guarantee the computational tractability, the scheduling/operation problem is solved for a limited set of typical and extreme periods. We have developed a Mixed Integer Linear Programming model to solve this design optimization problem, for which we have linearized the off-design and the size effects of performances and costs for the technologies considered in the case study. The model has been applied to optimize the design of a district energy system for the University of Parma Campus in Northern Italy.

Key words: carbon tax, design optimization, district energy systems, tri-generation

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The materials studied in this paper are the "silt washing", that represent the residues from the processing of aggregates (extracted from alluvial sand and gravel quarries), conduct in some production centers defined crushers. In these production centers different processes are carried out on quarry aggregates: crushing, mechanical screening (winnowing), decanting and washing with water (Fig. 1).

The aggregates "silt washing", byproduct of these processes, show up in the form of aqueous suspension containing clay, silt and fine sand in different grain sizes. Currently, the silt resulting from washing phase of the aggregates production process, represents a good product suitable for environmental requalification or for other purposes. Obviously for the activation of a systematic recovery, it is essential to observe the provisions of the rules relating to the recycling of waste (Decree in Force of Law, 1997, 2006). However, although there is a tendency to consider the silts washing as wastes, there are different interpretations that, according to their origin, agree with their definition as byproducts of processing. The Court of Cassation in its judgment of 2 March 2015 # 8982 clarifies that to the waste from mining activities should not be applied the discipline of General waste, but the special discipline referred to Decree in Force of Law (2008).

* Author to whom all correspondence should be addressed: e-mail: marco.migliore@polimi.it; Phone: +39 02.2399.5172

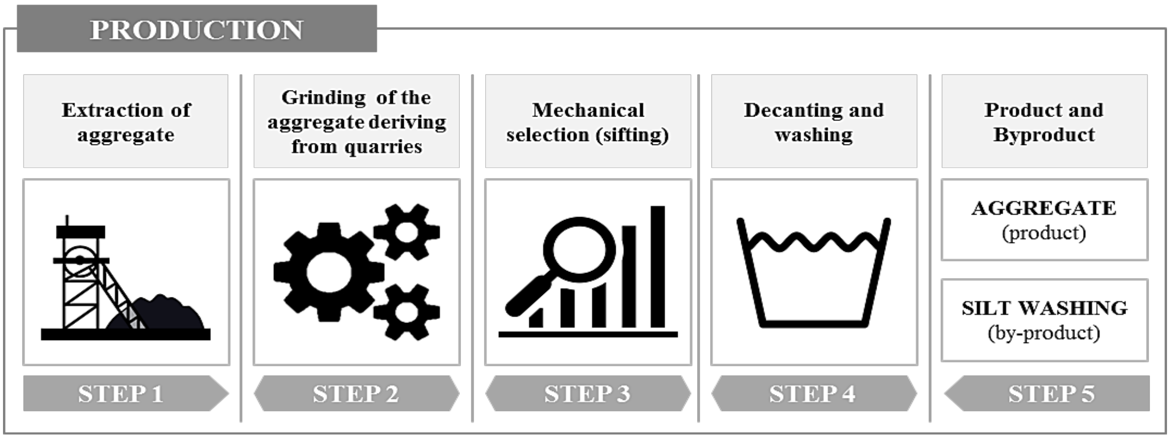


Fig. 1. Scheme of the process that generates silt washing

Therefore "*the silts from washing of aggregates deriving from quarry (sludge from mining activities) fall outside the scope of application of the guidelines on waste only when they remain within the production cycle of mining and associated cleanup, while when it is activated a subsequent and different processing activities, they are subject to General rules about waste disposal, storage depots and dump*". Discriminating factor, for the correct identification of the applicable legislation, is the classification of cleanup of aggregates extracted as internal activities of the production process considered.

From the point of view of technological features and capabilities, the "silts washing" can be considered an equivalent to the aggregates themselves resulting from the processing of materials extracted from the quarry (Migliore et al., 2015; Sansone, 2016). Several international studies (Chang et al., 2010; Lupo et al., 2007a) showed that the performance of the "silts washing" are within the parameters set by international technical standards for materials that can be used in construction. Therefore, the use of silts becomes possible even without any preliminary processing, because it is clear that their potential use qualifies them as by-product. Based on these premises, the purpose of the article is to highlight the potential derived from their recovery and their exploitation. So was chosen as a case study an Italian company that produces cement products, in which a systematic recovery of this by-product could be activated.

2. Case studies

2.1. Quarries issue in Italy, impacts and sustainability perspectives

The quarries report of Legambiente (2017) every year provides data on the state of the quarries in Italy and highlights the data about the number of active quarries, quantities of materials extracted, and predicts the perspectives on this sector (both in economic and in environmental point of view). The data published in the report of 2017 have highlighted that the quarries of aggregates constitute the largest percentage among the active quarries; it is estimated that they represent approximately 61% of the total active quarries in Italy (Legambiente, 2017) for a total figure of about 2900 quarries. In quantitative terms (Table 1), for the aggregate quarries is registered a movement of 53 million cubic meters of material (sand and gravel), which currently are focused mainly on three regions in Italy (Lombardia, Puglia and Piemonte). These regions detain the 60% of national amount extracted (only aggregates), for a quantity of approximately 32 million cubic meters of material extracted.

Table 1. Annual amount extracted by Region [cm] (Legambiente, 2017)

Region	*[cm]*	*%*
Lombardia	19.585.433 cm	36,95%
Puglia	7.024.137 cm	13,25%
Piemont	4.804.258 cm	9,06%
Other regions	21.591.430 cm	40,74%
Italy	53.005.073 cm	100%

These quantities have been reduced in the years of the economic crisis that has hit Europe; indeed, the crisis in the construction industry has forced the closure of many quarries (20% of open quarries) and decreased the amount of material extracted (about 40% in reduction). However, the values of the material extracted, remain high and attention shall be given in order to reduce the use of resources, even in respect of what is asked by the Community Directives (EC Directive, 2011a; 2011b; 2014; 2015) on environmental sustainability. Some ways to contain these large consumptions of raw materials are represented on one side by the reduction of the use of resources and on the other side by the progressive recovery of scraps/waste resulting from the extraction and processing.

With reference to the sand and gravel quarries, the scraps (silt washing etc.) can be quantified in about 5/8% of the total extracted. Considering the entire national context, the overall quantity of about 4 million cubic meters of material unless otherwise used (restoration and enhancement as inert material in different purpose) would be destined to landfill.

2.2. Reuse of silt washing of aggregate

Reuse of silt washing of aggregates is an important opportunity to promote processes of circular economy, and several studies have shown that this by-product is adequate to replace virgin raw materials in different production cycles. A study Gonzalez-Corrochano et al. (2009a) has shown that the silt washing (along with used motor oil and fly ash) can be used to produce lightweight aggregates with high insulating capacity. This is an alternative use of this by-product that highlights so far unexploited features that can increase the business value, qualifying the reuse as a process of up-cycling.

A similar result has emerged from another research work (Lupo et al., 2007b) funded by DEFRA (Waste and Resources R&D Programme UK), which intended to produce a lightweight aggregate in the form of pellets using scraps of washing of aggregates. Always as lightweight aggregate (Gonzalez-Corrochano et al., 2009b) was studied its reuse as a product for agriculture and building industry, in this case, it is worked with other by-products and/or non-contaminated waste and compatible with the proposed uses. On the quality of scraps resulting from the extraction (Tutumluer et al., 2015) has also expressed a study conducted in Illinois Institute of Transportation, who sees in this by-product an excellent material to stabilize the subgrade.

2.3. Case study

Based on the assumptions made, it emerges clearly that the proposal of systematic strategies for the enhancement of silt washing, can result in significant environmental benefits. Benefits may arrive in terms of reduction in the use of natural resources (by turning scraps into secondary raw material for further processing and avoiding landfill disposal) and in terms of environmental benefits with reduced impacts of the supply chain.

Focusing the attention to the Italian context, and specifically to the Lombardy region, it is clear that strategies to obtain a systematic recovery of this by-product can lead to the activation of processes of circular economy with a considerable impact on territory. It can be estimated that only in the Lombardy region it is produced a quantity of silt washing of about 1/1.5 million cubic meters, not negligible compared to the data of national production.

The need to undertake a requalification of what is generated (in terms of scrap/waste) from industrial processes is an important objective and the same regional authority (Region Lombardia, 2016) support initiatives aimed at better environmental protection and respect for natural resources. These initiatives have resulted in significant improvements in waste management, aligning with the European averages. To highlight the potential in terms of valorization of the resources a case study is presented referred to an Italian manufacturer that produces concrete elements. The company studied is Senini Spa that operates on the Lombard territory from many years; its main production consists in concrete elements such as masonry units, curbs, paving, block paving etc. However, over the years it has innovated by putting in new products such as hemp brick manufacture.

Actually, the production of Senini Spa regards approximately 90,000 tons of aggregates (derived from alluvial sand and gravel quarries located in Lombardy) that are treated for the manufacturing of finished products. The treatment of the raw aggregates can generate about 7,000 tons of silt washing that, if properly managed, could become an additional resource. The hypothesis under study is the transformation of the washing silt in substrate for the gardening, hypothesis already pursued in other contexts (Gonzalez-Corrochano et al., 2009b) and that if further investigated could turn the current type of process into a zero waste production.

The idea of being able to follow this direction stems from the fact that the aggregates processed by Senini are free from contamination (Table 2) (several laboratory tests have been performed) and therefore the washing silt can be considered as virgin raw material. Its use does not need to take action to treat it or to decontaminate it; on the contrary it is a fertile material (enriched by years of sedimentation) that could establish itself as a product with many powerful features for target sector. Also, if the silts are properly added and blended with other materials (fertilizers etc.) they may be enriched for more specific purposes (Fig. 2).

Table 2. Chemical tests conducted on samples of material used (data from Senini Spa)

***Level of contaminant* mg/kg s.s.**	***Results***	***Limit value max***
Arsenic [As]	4.6	20
Cadmium [Cd]	0.4	2
Cobalt [Co]	4.4	20
Chrome total [Cr]	11.2	150
Chrome VI [Cr]	<1	2
Mercury [Hg]	<0.1	1
Nickel [Ni]	12.6	120
Lead [Pb]	8.7	100
Copper [Cu]	16.0	120
Zinc [Zn]	56.8	150

The proposal represents a perfect example of circular economy, which provides the possibility to establish systemic cycles between different sectors. In this case the transfer is from the construction sector to agricultural sector. These cross-sectorial transfers are the basis of the circular economy: providing some form of systematic reuse within consolidated production contexts (like industrial districts) they make the reuse of the scraps/by-product/waste easier and promote forms of industrial innovation both incremental and disruptive.

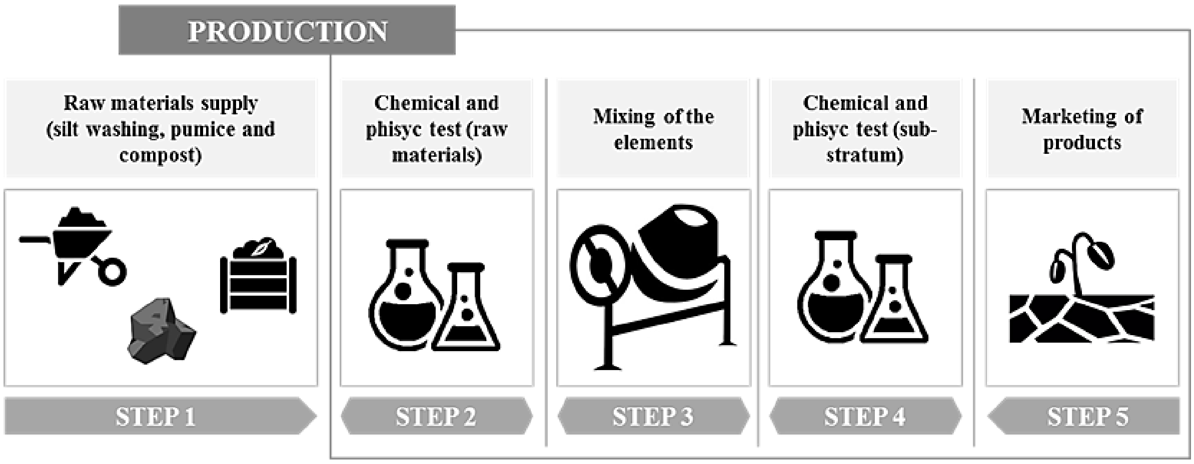


Fig. 2. Scheme of the hypothetical production process of the soil

3. Conclusions

The paper is intended to highlight the negative effects associated with unsuccessful recovery and valorization of the outputs of the processes related to the extraction and processing of aggregates for the construction sector. Quantitative data reported have revealed that this is a problem not marginal and therefore deserving of thorough investigations. The context of region Lombardia appears as a perfect case study for the implementation of initiatives aimed at recovering these scraps; the huge amount of material gives the possibility to operate with continuity over time (continuous supply of resources).

The proposal made by referring to the context of Senini spa represents an incentive to proceed in different directions to encourage the reuse and recovery of silt washing; therefore, are underlined the peculiarities emerged about the investigation conducted on silt washing and the prospects for feasible recovery.

References

Chang F., Lee M., Lo S., Lin J., (2010), Artificial aggregate made from waste stone sludge and waste silt, *Journal of Environmental Management*, **91**, 2289-2294.

Sansone C., (2016), Cave esauste (exhausted quarries), *Modulo*, **401**, 100-101.

Decree in Force of Law (1997), Legislative Decree of February 5th 1997, No. 22, Implementation of the directives 91/156/CEE on the waste, 91/689/CEE on the hazardous waste and 94/62/EC on packaging and packaging waste, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A62007CJ0387.

Decree in Force of Law (2006), Legislative Decree of 3th April 2006, No. 152, Environmental Legislation, On line at: https://www.ecolex.org/details/legislation/legislative-decree-no-152-approving-the-code-on-the-environment-lex-faoc064213/.

Decree in Force of Law (2008), Legislative Decree of 30th May 2008, No 117, Implementation of directive 2006/21/EC on the management of waste from the extractive industries and amending directive 2004/35/EC, On line at: http://www.europarl.europa.eu/sides/getDoc.do?pubRef=-//EP//TEXT+WQ+E-2006-2960+0+DOC+XML+V0//EN&language=SL.

EC Directive, (2011a), COM (2011) 21 final - Communication from the Commission to the European Parliament, the Council and the Committee of the Regions: A resource-efficient Europe - Flagship initiative under the Europe 2020 Strategy, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52011DC0021.

EC Directive, (2011b), COM (2011) 571 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Roadmap to a Resource Efficient Europe, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52011DC0571.

EC Directive, (2014), COM (2014) 398 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Towards a circular economy: A zero waste programme for Europe, On line at: https://eur-lex.europa.eu/resource.html?uri=cellar:aa88c66d-4553-11e4-a0cb-01aa75ed71a1.0022.03/DOC_1&format=PDF.

EC Directive, (2015), COM (2015) 614 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Closing the loop - An EU action plan for the Circular Economy, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52015DC0614.

Gonzalez-Corrochano B., Alonso-Azcarete J., Rodas M., (2009a), Characterization of lightweight aggregates manufactured from washing aggregate sludge and fly ash, *Resources, Conservation and Recycling*, **53**, 571-581.

Gonzalez-Corrochano B., Alonso-Azcarete J., Rodas M., (2009b), Production of lightweight aggregates from mining and industrial wastes, *Journal of Environmental Management*, **90**, 2801-2812.

Legambiente, (2017), Quarry report. The numbers and the economic and environmental impacts of mining activities in the Italian territory. Opportunities and challenges in the direction of the circular economy, On line at: https://www.legambiente.it/contenuti/comunicati/ecosistema-urbano-2017-dati-performance-ambientali-comuni-capoluogo.

Lupo R., Tyrer M., Cheeseman C.R., Donatello S., (2007a), *Manufactured Aggregate from Waste Materials*, Proc.

1st Int. Conf. on Sustainable Construction Materials and Technologies, , London, 763-767.

Lupo R., Tyrer M., McKeever F., Tsang N., Cheeseman C. (2007b), *Manufacture of Aggregates from Waste Silt and Fines*, Resource Efficiency Knowledge Transfer Network Conference "Designing Out Waste" 15th & 16th February 2007 Reading, UK.

Migliore M., Campioli A., Lavagna M., Oberti I., Paganin G., Talamo C., (2015), Intersectorial reuse of waste and scraps for the production of building products: strategies and valorization of waste, *Environmental Engineering and Management Journal*, **14**, 1675-1681.

Region Lombardia, (2016), Environmental sustainability: waste management in Lombardy. Waste: problem or resource?, (in Italian), Regione Lombardia, Milano. On line at: http://www.regione.lombardia.it/wps/portal/istituzionale/HP/DettaglioPubblicazione/servizi-e-informazioni/cittadini/tutela-ambientale/gestione-dei-rifiuti/pubblicazione-la-gestione-dei-rifiuti-in-lombardia/pubblicazione-la-gestione-dei-rifiuti-in-lombardia

Tutumluer E., Ozer H., Hou W., Mwumvaneza V., (2015), Sustainable aggregates production: Green applications for aggregate by-products. A report of the findings of ICT R27-125, Illinois Center for Transportation Series No. 15-012, Research Report No. FHWA-ICT-15-012, On line at: https://www.ideals.illinois.edu/handle/2142/78188

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2427-2436
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

ECO-INNOVATION IN VALCUCINE FOR A CIRCULAR ECONOMY

Veronica Novelli*, Paola Geatti, Luciano Ceccon, Alberto Bettarel

Department of Economics and Statistics, University of Udine, Via Tomadini, 30/A, 33100 Udine, Italy

Abstract

Recently, more and more companies are implementing good environmental practices. Environmental certifications, besides being valuable management tools for companies, given the opportunity to strengthen their role on the market. An example of such virtuous behavior is the case of Valcucine, an enterprise of the Livenza furniture district in Northern Italy. Valcucine focuses its care in the production of furniture, in particular of kitchen units, characterized by sustainable production, eco-compatibility of materials and the lowest possible environmental impacts. Valcucine wishes to transfer its philosophy to customers by improving product quality, rationalizing the use of recyclable virgin raw materials, employing also recycled materials and reducing dangerous emissions into the environment. For this reason, Valcucine obtained several certifications, such as ISO 14001, Forest Stewardship Council (FSC), F**** (4 stars) Japanese Standard and Leadership in Energy and Environmental Design (LEED). In particular, the LEED certification, obtained for the Invitrum and Meccanica production lines, allows the enterprise both to differentiate from the competitors and to enter new segments of the market, such as the Arab Countries, where the LEED certification is renowned and appreciated. This gives a strong competitive advantage to Valcucine, working in a production field which has been saturated for many years. This virtuous behavior of the enterprise fits well in the principles inspiring circular economy and perfectly embraces the Goals 6 (Clean and Water Sanitation), 7 (Affordable and Clean Energy), 8 (Decent Work and Economic Growth), 12 (Responsible Consumption and Production) and 15 (Life on Land).

Key words: formaldehyde emissions, FSC, ISO 14001, LEED certification, Valcucine

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The 2030 Agenda is a global strategic action plan subscribed in September 2015 by the governments of 193 countries, UN members. It consists of 17 goals for Sustainable Development to be achieved within 2030 (United Nations, 2015).

According to EC Communication (2014), some transformations in the perspective of Circular Economy (CE) are durability of a product, efficiency, eco-design, industrial symbiosis. For a firm, waste reduction is essential for developing a sustainable economy, causing less CO_2 emissions, utilizing the resources in an efficient manner and remaining competitive (EC Communication, 2015; Novelli et al., 2017). The CE realization fits well in the Goals 6 (Clean and Water Sanitation), 7 (Affordable and Clean Energy), 8 (Decent Work and Economic Growth), 12 (Responsible Consumption and Production) and 15 (Life on Land) (Shroeder et al., 2018). CE represents a continuous and positive development cycle: it is a regenerative economy, reproducing nature, optimizing the systems connected each other (Ellen MacArthur Foundation, 2017; Federico, 2015). In few words, CE minimizes the consumption of resources by the adoption of cleaner technologies (Andersen, 1997, 1999) and the application of the Best Available Technologies (BAT).

Eco-innovation can be defined as "innovation that consists of new modified processes, practices, systems and products which benefit the environment and contribute to environmental sustainability" (Rennings, 2000), or "a change in economic activities that improve both the economic performances and the

* Author to whom all correspondence should be addressed: e-mail: veronica.novelli@uniud.it; Phone +39 0432 249335; Fax +39 0432 249229

environmental performances" (Kemp, 2010), or "the production, the introduction or the use of a product, a process, a service, a management system, or a company methodology which is new for the company itself or for consumers, and which guarantees, during its life cycle, a reduction of environmental risk, of pollution and of other negative impacts due to the use of resources (including energy) with respect to other possible expectations" (Sala and Castellani, 2011).

The environmental policy, the competitive pressure, the wish to reach a better position on the market by employing a cleaner production are the main drivers pushing a firm to be eco-innovative (Kemp, 2010), with the aim of satisfying the interests of the consumers towards less harmful products, built with a greater respect for environment (Davenport, 1993). According to Sala and Castellani (2011), eco-innovation may concern the following dimensions: process, product, packaging, organization, logistics and distribution, purchasing, communication, network building.

The eco-innovation application to the planning step is called eco-design and it is finalized to improve all the aspects related to a product, from the provenance of raw materials to the final packaging, through all the phases of product life cycle (Radonjič et al., 2015). To assess the sustainability of their activities the wood-based products companies can adopt several voluntary environmental instruments, as: ISO 14001 (Ruddell and Stevens, 1998), EMAS Registration (CML, 2006; Merli et al., 2016; Novelli et al., 2018), LEED certification (Ugur and Leblebici, 2018), F**** certification (Salem and Bohm, 2013), certification of forest products (Chen et al., 2011; Wingate and McFarlane, 2005), eco-labelling (Donatello et al., 2017), LCA (Krystofik et al., 2018; Rinawati et al., 2018). In particular, the LEED (Leadership in Energy and Environmental Design) certification refers to a system of evaluation of the energy and environmental characteristics of a building, for establishing how much it integrates with the environment, by defining its level of eco-compatibility during the steps of planning, building and management (Steinemann et al., 2017; Wei et al., 2015). The system is based on the assignment of a score to each requisite characterizing the building sustainability. The degree of sustainability is obtained by the sum of the scores. Therefore, not only the structural and plant-engineering components, but also the internal elements, as furniture and kitchen unit, contribute to the definition of the degree of sustainability.

Particulate matter from fireplaces, cigarette smoke, dust, food cooking, can pollute indoor air in close spaces, but also building materials and furniture may cause emissions of dangerous substances for human health. The Volatile Organic Compounds (VOC) are easily released into the air for a definite period of time, while formaldehyde is continuously emitted because it is generated inside the panels (Bulian and Fragassa, 2016). Many epidemiological studies on cancer risk for humans classified formaldehyde as "probably carcinogenic to humans" (IARC, 1982; 1987; 1995), while the most recent studies defined formaldehyde as "carcinogenic for humans" (Cogliano et al., 2004, 2005; IARC, 2006). Formaldehyde is a colorless gas with an acrid odor; it is used in many industrial productions, like adhesives for wood, floorings, paints, walls, ceilings, carpets, furniture, plastics and textiles and for producing chemical compounds (Bosetti et al., 2008; Missia et al., 2010).

Formaldehyde emissions are dangerous not only during the phases of working, but also during the phase of product use (National Cancer Institute, 2017). Even if formaldehyde is not the only substance that can be emitted by wood-based materials, it is an important parameter to evaluate the environmental health status due to the presence of a particular type of furniture. The F**** certification, required by the Japanese legislation, foresees a limit of 0.3 mg/L, the lowest limit for formaldehyde emissions, with respect to other standard methods (Risholm-Sundman et al., 2007).

The FSC certification, promoted by Forest Stewardship Council, guarantees that the certified wood and wood products come from sustainably managed forests and harvested in accordance with the laws of the Country of origin. In particular, the FSC Chain of Custody (FSC-CoC) certification ensures the traceability of raw materials, by identifying the chain across which products are traded, starting from their origin and passing through all manufacture processes, until the sale. According to the FSC-CoC certification, final products are labelled:

- FSC 100%, if the product is made entirely by materials (wood or paper) coming from certified forests,
- FSC Recycled, if wood or paper in the products come from re-used materials,
- FSC Mix, if certified wood or paper have been supplemented with non-certified materials (Forest Stewardship Council, 2017; Masiero and Zorzi, 2006; Vidal et al., 2005).

The aim of this study is to present a case study of a Northeastern Italian eco-innovative firm that considers CE themes as fundamental drivers of the company policy. The case under examination could be a model not only for other industries of the furniture sector, but also a point of reference for consumers with attitude towards sustainable purchases. The objectives of the paper are to underline the environmentally virtuous choices of the firm and to suggest possible sustainable tools to be adopted by the enterprise, in the perspective of continuous improvement.

In this paper the case study of Valcucine is presented: a small firm operating in the Livenza furniture district, in the province of Pordenone (Italy), producing kitchen units with a particular attention to long product life, low toxic emissions of the paints used, recycling of the finished products, a sustainable use of materials (Bettiol et al., 2012).

2. Material and methods

After an in-depht analysis of CE and eco-innovation themes with particular attention to the furniture sector (Gonzales-Garcia et al., 2012; Krystofik et al., 2018) a territorial firm census has been done, to put in light the most interesting suitable ones for our study. Our scientific interests have been satisfied by Valcucine, located in the first Italian district that in 2006 obtained the EMAS registration, the Livenza Furniture district, in the province of Pordenone (Italy) (CML, 2006; Novelli et al., 2018).

This step was followed by the firm visitation, with the supervision of the Quality Control manager and the Communication manager. In the meantime, the sustainability information, acquired by literature, was compared with the firm reality and data about the production activities were collected. These data are shown in Tables 1-5. Furthermore, some calls and e-mails with the firm managers have been necessary for acquiring other material for organizing this paper.

In November 2017 an interesting congress about the quality of indoor air, within the big fair of Ecomondo in Rimini (Italy), allowed us to know not only the national legislation regulating the wood-based products emissions, but also the technologies adopted to assess them and the situation in Italy.

3. Case study presentation

Valcucine is an enterprise of the Livenza furniture district located in the municipality of Pordenone (Italy). Valcucine makes modular kitchen units and other wood furniture destined to customers of a medium-high target. Exports represented nearly 40% of sales in 2014, thanks to the company policy of growth of its catchment area. Valcucine carries on the only activity of planning and assembly of the components, with some additional workings on the semi-finished boards such as drilling, sectioning, beading and customization of worktops. The enterprise has concentrated on the topics of sustainability and of protection of customers' health, by devoting attention in particular to:

- shortage of raw materials,
- management of waste and of products at the end of their life cycle,
- energy consumption,
- environmental pollution.

The goals of Valcucine are:

- the decrease of consumption of both energy and virgin raw materials employed in the production process,
- the decrease of the use of dangerous materials, environmental pollution,
- the development of technological innovations directed to environmental safeguard.

Valcucine obtained the ISO 14001 certification in 2001, in 2008 the FSC-CoC certification for some of its products, in 2006 the F**** certification for the ennobled panel, in 2013 the LEED certification for the Invitrum and Artematica models: it can be considered an exemplary firm strengthening its environmental strategies for a competitive advantage in the furniture sector, able to improve the quality of the environment in which it is located and, at the same time, to enter markets in which the care towards environment and health is particularly real (De Marchi et al., 2013).

4. Results

Our analysis showed that Valcucine managing strategies use CE paradigm as business driver, improving its industrial position by eco-innovation initiatives. In fact, the guidelines of Valcucine's management are:

1. Product dematerialization. Valcucine obtained a notable saving of wood, of rolled sections and of energy in particular by reducing the thickness of the "Riciclantica" mono-material aluminum door to only 2 mm. From the managerial point of view, this policy aiming at dematerialization led to reduce storage spaces, weight of finished products, energy consumption and waste production.

2. Material recyclability. Valcucine introduced recyclable materials, as glass and aluminum, and recycled components for structural pieces in its products. With a view to reuse at the end of the life cycle, the firm plans its products so that the components can be easily identified and separated at the time of discarding (Bergamaschi, 2010). Product components are assembled with mechanical joints, without employing glues or adhesives, to be easily disassembled and recycled. This fact allowed Valcucine to commit itself in the free collection of its products at the end of their life cycle. The aluminum components, present in the structural frames of the doors and in the supports of worktops, are completely recyclable. Their reclamation is economically advantageous, since energy needed to obtain recycled aluminum is about 5-10% in respect of energy needed to obtain primary aluminum from ores (Quinkertz et al., 2001; Smith, 2006). Plastic components are labelled to favour their identification and possible reuse at the time of discarding. Furthermore, Valcucine has committed itself in reclamation of doors and their components, as rolled stratified section boards, which are reused for the production of dashboards in the car field when they are cast-off. In 2009, Valcucine was able to make a kitchen unit which is 100% recyclable and 80% reusable, thanks to the use of the Invitrum glass structural basis, together with a glass worktop with an aluminum support and the "Riciclantica" door (Galli, 2015). The characteristics of recyclability and reusability of some components made by Valcucine are shown in Table 1.

3. Reduction of dangerous emissions. Valcucine has identified in particular three aspects to be monitored:

- varnishes containing synthetic solvents,
- artificial radioactivity,
- formaldehyde emissions.

Table 1. Characteristics of recyclability and reusability of some components made by Valcucine

Component	***Material***	***Characteristics***
Draw plates	Recycled aluminum	100% recyclable, 80% reusable
Backs	Primary aluminum sheets	100% recyclable, 100% reusable
Legs	Recycled iron, plastic	100% recyclable
Bottom bases (structural area/part)	Temperated glass	100% recyclable, 90% reusable
Sides	Temperated glass	100% recyclable, 90% reusable
Spacers	Recycled aluminum	100% recyclable, 100% reusable

Furniture treated with varnishes containing synthetic solvents continues to emit harmful substances for a long time after buying, with risks for health of final users. To limit solvent emissions, Valcucine uses water varnishes, by realizing a superficial finish based on oils and natural polishes. Artificial radioactivity is due to the radioactive substances emitted into the environment by the accidents of nuclear plants, which can be absorbed by trees and subsequently be released during time by wood. For this reason, Valcucine carries on analyses to check the presence of radioactivity in the timber utilized. In the sector of wood processing, the wood elements for obtaining panels, like chipboard, plywood and laminated wood, are stucked by resins and adhesives based on urea-formaldehyde, melamine-formaldehyde and melamine-urea-formaldehyde. Valcucine does not carry out panel realization, which is the step characterized by the highest release, but only handles the semi-finished products. Furthermore, Valcucine realizes final products without chipboard, thanks to the use of high-pressure laminates; however, frames made by melamine-faced particle boards are used for some kitchen units, which respect standards and limits imposed by the Japanese F**** normative, the most severe in the world.

*4. Product durability.*Valcucine products are planned to last for a long time, with a consequent reduction of environmental impacts.

As a consequence of the policy adopted by the company, Valcucine has obtained notable improvements, in particular in terms of reduction of consumption of raw materials, working scraps, waste production, emission of harmful substances and energy consumption. This has allowed the achievement of some environmental certifications.

4.1. Certifications obtained

4.1.1. ISO 14001

In 2001, Valcucine obtained the ISO 14001 certification. The parameters monitored by the environmental management system are: water consumption, electricity consumption, fuel consumption, use of raw materials, use of chemicals, emissions into the atmosphere, waste management and indirect environmental aspects.

Water consumption. Water is not used for the production process, but only for sanitary use and for irrigation of the green areas of the plant. Water consumption in the period 1999-2016 is presented in Table 2. As can be noted, consumptions showed significant yearly variations. It is not possible to control the consumption of water for irrigation, which substantially depends on atmospheric precipitations, whereas the reduction of consumption of sanitary water has been achieved with a careful maintenance of supply facilities.

Table 2. Water consumption (m^3) in Valcucine plant

Year	***Water consumed, m^3***
1999	12,488
2000	13,365
2001	12,790
2002	6,811
2003	4,836
2004	4,403
2005	4,635
2006	7,459
2007	5,620
2008	2,233
2009	6,559
2010	5,818
2011	9,320
2012	10.532
2013	5,383
2014	3,074
2015	3,603
2016	6,178

Electricity consumption. In 2010, the lighting installation of production departments was rationalized. Furthermore, in 2010 the installation of photovoltaic panels (1450 m^2) was completed, as well. Electricity consumption, including the requirements of the manufacturing process, offices and other operational activities, is presented in Table 3. Fuel consumption.

Until winter 2009-2010, diesel oil was used to heat the plant; since the following year, diesel oil has been replaced by natural gas. Natural gas is also used in the laboratory for material testing. Fuel consumption relative to the period 1998-2016 is reported in Table 4.

Table 3. Electricity consumption (kWh) in Valcucine plant

Year	***Electricity from the grid***	***Electricity produced by the photovoltaic plant***	***Self-consumed electricity***	***Total consumption***
1999	586,266			586,266
2000	596,000			596,000
2001	638,200			638,200
2002	627800			627,800
2003	640,606			640,606
2004	720,861			720,861
2005	675,878			675,878
2006	797,610			797,610
2007	877,152			877,152
2008	855,661			855,661
2009	749,447			749,447
2010	803,347	18,558		821,905
2011	615,424	207,610		823,034
2012	630,969	187,494		818,463
2013	566,505	233,489	188,665	755,170
2014	535,698	180,640	138,000	716,338
2015	554,168	193,920	149520	703,688
2016	615,200	211,404	171,840	787,040

Table 4. Fuel consumption in Valcucine plant

Period (July-June)	***Year***	***Diesel oil (L)***	***Natural gas (m^3)***
1998/1999		65,000	
1999/2000		74,000	
2000/2001		68,000	
2001/2002		70,000	
2002/2003		70,000	
2003/2004		71,000	
2004/2005		82,900	
2005/2006		68,732	
2006/2007		60,398	
2007/2008		81,110	
2008/2009		67,720	
2009/2010		78,640	
	2010		27,455
	2011		63,479
	2012		63,015
	2013		56,954
	2014		43,751
	2015		64,702
	2016		79,239

Use of raw materials. The main materials are chipboard and fiberboard panels, laminated wood panels, glass, aluminum and steel, which come to the company as semi-finished materials.

The planning activity is addressed to reduction of not-renewable raw material consumption and to employment of composite materials which, despite being characterized by a high energy consumption for their production (glass, aluminum and steel), have a long-life cycle and a complete recyclability.

Use of chemicals. The main products used are solvents, bonding agents and adhesives. The used amounts have not varied much over years, and are so low, that the risk associated may be classified as irrelevant for the safety of workers and the effects on the environment.

Emissions into the atmosphere. As regards the exposure of Valcucine workers to wood dust, measurements carried out in 2014 in 10 workstations showed amounts included in the range 0.10 – 0.65 mg/m^3, below the limit value of 5 mg/m^3 (EC Directive, 2004). Nevertheless, wood dust produced during the manufacturing process is captured by an air extraction and filtration equipment and then disposed, in order not to be released into the atmosphere.

Waste management. Most packaging originates from kitchen equipment suppliers' wrappings and are composed mainly of paperboard and plastics (PE, PS and PET). Glass, granite, aluminum and steel are also present in discarded materials, both as processing waste and as parts coming from kitchen furniture taken back from customers when disused, or when old or defective parts are substituted. Moreover, Valcucine produces Electric and Electronic Equipment Waste (EEEW) because it assembles and disposes components for lighting. Hazardous waste is produced as the result of the use of varnishes, mostly water paints, and oils and emulsions for machine tools, compressors and pantograph maintenance.

Indirect environmental aspects. Valcucine purchases semi-finished materials from external suppliers, who manage all phases from raw material acquisition up to painting. Consequently, Valcucine asked suppliers improvements in environmental matters, in particular with regard to the reduction of industrial solvents in varnishes, with the use of water paintings, for all wood and glass panels since 2005; the use of components with extremely low formaldehyde emissions; the use of sustainable timber. Valuable information are collected for each supplier to monitor its environmental performances; gathered data are used to set an "indirect environmental impact" value, which might constitute a parameter for the qualification of suppliers.

4.1.2. FSC Chain of Custody certification

Valcucine uses wood as the main material for the realization of its products. The company is not involved in wood processing, except marginally in short finishing operations: it mostly purchases semi-finished products as doors, panels, seat backs, structural parts and accessories from external suppliers.

With the aim of maintaining a high product quality and protecting the environment, Valcucine started the FSC-CoC certification process. To obtain the certification, all production phases along the supply chain need to be identified, to ensure the traceability of the material; so it is necessary to identify in an appropriate matrix the following issues: type of incoming material, supplier from which the material is purchased and validity of supplier certification, type of incoming material certification (e.g. FSC 100%; FSC Mix Credit, etc.), contractor chosen by the supplier for possible processing and kind of processing, type of certification which will be affixed on the product at the end of processing or after assembling. Likewise, the material supplier has to fill out a similar matrix by indicating previous phases, up to the phase of wood cutting, in order to guarantee traceability and certification characteristics (Masiero and Zorzi, 2006).

An important topic is the allocation of certification standard of finished products, output, (FSC 100% or FSC Mix Credit) in relation to incoming products, input. FSC regulation provides for three types of assessment systems based on: the type of transferred materials; the percentages of certified and not certified materials; assigned credits (rare).

In case of a single type of material, the initial label is assigned to the final product. In the other cases, the FSC certification of the final product changes on the basis of the percentage of incoming material of one or more types: the allocation is done with a weighting of incoming material. Valcucine properly evaluated this issue because of small not certified parts (a very small proportion of the overall amount), slowing down the whole certification process. On the occasion of the various renewals of the certification, Valcucine has widened the range of certified products. In 2008, in compliance with the FSC STD-40-004 standard, Valcucine obtained the FSC 100% certification for solid maple pieces, corresponding to the so-called "internal drawer". In 2014 the FSC 100% certification was obtained for doors and back panels, as well as the FSC Mix for parts made of melamine faced chipboard panel (material normally used for cabinet sides and bottom panels). The products which obtained the certification are listed in Table 5.

Table 5. Present FSC certified Valcucine's products

Product	***Certification***
Internal solid maple drawer	FSC 100%
Door	FSC 100%
Cabinet back panel	FSC 100%
Cabinet side panel, cabinet bottom panel, wooden worktop	FSC Mix

Special investments were not needed for the certification process of Valcucine's products; costs met were mainly related to consultancy services and certification process itself. Because of FSC certification, which led to an improved product quality and facilitated access to markets in which FSC-CoC standard is a compulsory element and competition is reduced, the company improved its environmental sustainability reputation.

*4.1.3. The F**** certification*

4.1.3.1. Formaldehyde: indoor air quality and effects on human health

We spend the major part of our life inside houses, offices, schools etc., so indoor air quality (IAQ) is very important. Many chemical substances can be emitted by furniture, walls, carpets, with dangerous consequences for human health. Modern buildings, built with energy saving insulating systems, could increase the concentration of pollutants in indoor environments. In particular, formaldehyde and other substances can be released during time.

Among the European Countries, national regulations for construction products are different, and this can create some problems when firms have to export their products from a Country to another (Bulian and Fragassa, 2016).

In the last years, IAQ has become a very important matter under discussion (Böhm et al., 2012; de Blas et al., 2012; Gilbert et al., 2006; Mølhave et al., 1995; Vassura et al., 2015). The frame study European Indoor Air Monitoring and Exposure assessment (AIRMEX) is related to the bound between indoor air and chronic human exposure to VOCs in public buildings during the years 2003-2008 (Geiss et al., 2011; Kotzias, 2005).

4.1.3.2. Wooden panels: the European and Japanese rules

Wooden panels are classified on the basis of formaldehyde emissions, according to the technical regulation UNI EN 13986 (2015). Panels can be classified in one of the two classes E1 and E2. For E1 (low emissions), the beginning test refers to the emissions that have to be less or equal to 0.124 mg/m^3 air, measured with the chamber analysis method UNI EN 717-1 (2004). The raw panels, Medium-Density Fibreboard (MDF) or Oriented Strand Board (OSB), have to emit less or equal to 8 mg/100g of oven dried panel, measured with the method UNI EN ISO 12460-5 (2016). The other panels, varnished panels, melamine-faced particle boards or plated panels have to emit less or equal to 3.5 mg/m^2 h, measured with the gas analysis method UNI EN 717-2 (1995), substituted by the UNI EN ISO 12460-3 (2015). The E1 limit of emission (0.1 ppm) is in accordance with the limit recommended by WHO (Federlegnoarredo, 2017).

According to the changes for improving the integrity of new houses, after the Kobe earthquake in 1995, the Japanese government introduced some countermeasures for reducing indoor formaldehyde pollution. In fact, the Housing Quality Assurance Act (HQAA) required the improvement of the quality and performance of residential houses, including air quality. The Sick House Regulations regulated formaldehyde emissions in houses, schools and clinics. Among the countermeasures for formaldehyde emissions there was the F**** rating of materials for products, including wooden building materials. For the F**** rating system, formaldehyde emission levels have to be less or equal to 0.005 mg/m^{2}h, an added value for the above-mentioned wooden products (Eastin and Mawhinney, 2011).

*4.1.3.3. Valcucine toxic emissions control (F**** normative)*

In October 2006, Valcucine obtained the F**** certification for its chipboard panels. The panels observe the formaldehyde emission limits required by the Japanese normative, which is the most severe in the world: this limit is less than the half of the European standard E1 (Federlegnoarredo, 2017). In Italy, the Ministerial Decree of October 10, 2008, foresees a limit of 0.1 ppm, as recommended by WHO (Ministerial Decree, 2008).

4.1.4. The LEED certification

Valcucine had set itself entering the market of Arab Countries as a goal; in that Countries, the topics of eco-sustainability of buildings and the LEED certification are renowned and appreciated. This is partly due to the local market habits of proposing the sale of buildings already furnished inside. For this reason, who takes part in a LEED project in the Arab Countries looks for suppliers of products compliant with the parameters required for the awarding of the various scores. Therefore, in 2013 Valcucine started the process of evaluation of some of its products with the aim of awarding of LEED credits. The products to which LEED credits have been awarded belong to the Invitrum and Meccanica models. The credits obtained by Valcucine are (Valcucine, 2017):

- MR Credit 2_Construction Waste Management
- MR Credit 3_Material Reuse
- MR Credit 4_Recycled Content
- MR Credit 7_Certified Wood
- EQ Credit 4.1_Low-Emitting Materials: Adhesives and Sealants

For many years, Valcucine had already implemented an environmental management system, with a consequent decrease of the utilization of raw materials and energy and of environmental impacts. Therefore, Valcucine had to introduce only small changes to planning and making of its products in order to obtain the LEED credits.

5. Discussions

As can be deduced from the above findings, Valcucine business is set in the perspective of CE through:

- the efforts to lower energy and water consumption and waste production;
- the design and production of components made from recycled materials and which can be easily disassembled and recycled at the time of discarding;
- the use of renewable certified materials;
- the lowering of components thickness;
- the extension of products life.

The above listed items fit well in the guidelines proposed by EC Communication (2014; 2015).

The results obtained by Valcucine are surely important. However, the environmental strategy of the firm could be improved by a tool as Life Cycle Assessment (LCA), for example applied to a kitchen furniture production, (e.g. Artematica or Invitrum). In fact, LCA allows the assessment of the environmental impact of entire life cycle of the product considering raw materials exploitation, production, transport and distribution, use and maintenance, re-use, re-cycle and final disposal (waste management) (Baldo et al., 2008). Several are the studies on LCA in the furniture sector (Gonzales-Garcia et al., 2012; Krystofik et al., 2018; Iritani et al., 2015). The study could be "from cradle to gate", firstly, where cradle refers to the acquisition of raw materials and gate refers to the steps inside the firm, before distribution. LCA is a mandatory methodology for the obtainment of eco-labels of Type (I) and (III), that need a third part for the verification (Cobut et al., 2013) and are defined for several products, also for furniture. In particular LCA for Environmental Product Declaration (EPD), eco-label of Type (III), needs the so-called Product Category Rules (PCR) for assuring a correct comparison among products made by different companies (Fullana et al., 2008).

The EU-Ecolabel, a Type (I) (EC Regulation 66, 2010) logo, on furniture informs the consumer on sustainable materials used, limited use of hazardous substances, low formaldehyde and VOC emissions, product eco-design (Cobut et al., 2013). More than 90% of European people think that the environmental protection is important and 27% of the interviewed sample knows and appreciate the mark Eu-Ecolabel, considering its role important for purchasings (Eurobarometer, 2017). Considering the growing attitude of consumers towards green products, the EU-Ecolabel certification could be for the firm an important tool of marketing.

6. Conclusions

Valcucine, a company operating in the Livenza furniture district, carries out its activity with particular care towards the environment. This policy allowed Valcucine to obtain some certifications, such as ISO 14001 in 2001, F**** in 2006, FSC in 2008 and LEED in 2013. Consequently, Valcucine could differentiate from the competitors and enter new segments of the market.

"Innovation for life" is the Valcucine slogan, representing the three key-words: wellbeing, long life products and innovation. The firm's focus is the realization of a product, beautiful to see, but also practical, by a planning activity that allows the ergonomic study of the kitchen units produced. The innovation can be considered a necessary tool of eco-management.

If the F**** certification can push the sales of the firm in Japan, the LEED certification in Arab countries, the EU-Ecolabel obtainment, on some products, could increase the sales in the European countries.

The adoption of clear environmental labels by the producers, permits an easy orientation of the consumers in their purchasings. In our opinion the Valcucine case can be taken into consideration by other firms that want to improve their market position.

Acknowledgements
The authors contributed equally in idea conception, acquisition of information, data analysis and comment, drafting of the manuscript.

References

Andersen M.S., (1997), Evaluation of the cleaner technology programme, *Environmental Review*, **14**, Environmental Protection Agency, Copenhagen, On line at: https://pure.au.dk/ws/files/86521632/cleanertechn_uk.pdf

Andersen M.S., (1999), Governance by green taxes: implementing clean water policies in Europe 1970-1990, *Environmental Economics Policy Study*, **2**, 39-63.

Baldo G.L., Marino M., Rossi S., (2008), *Life Cycle Assessment, LCA. Materials, Products, Processes*, (in Italian), Edizioni Ambiente, Milano.

Bergamaschi I., (2010), From cradle to cradle, eco-design in the kitchen, (in Italian), *Ecoscienza*, **2**, 88.

Bettiol M., Di Maria E., Finotto V., (2012), Marketing in SMEs: the role of entrepreneurial sensemaking, *International Entrepreneurial Management Journal*, **8**, 223-248.

Böhm M., Salem M.Z.M., Srba J., (2012), Formaldehyde emission monitoring from a variety of solid wood, plywood, blockboard and flooring products manufactured for building and furnishing materials, *Journal of Hazardous Materials*, **221-222**, 68-79.

Bosetti C., McLaughlin J.K., Tarone R.E., Pira E., La Vecchia C., (2008), Formaldehyde and cancer risk. A quantitative review of cohort studies through 2006, *Annals of Oncology*, **19**, 29-43.

Bulian F., Fragassa C., (2016), VOC emissions from wood products and furniture: A survey about legislation, standards and measures referred to different materials, *FME Transactions*, **44**, 358-364.

Chen J., Innes J.L., Kozak R.A., (2011), An exploratory assessment of the attitudes of Chinese wood products manufactures towards forest certification, *Journal of Environmental Management*, **92**, 2984-2992.

Cobut A., Beauregard R., Blanchet P., (2013), Using life cycle thinking to analyse environmental labeling: the case of appearance wood products, *International Journal of Life Cycle Assessment*, **18**, 722-742.

Cogliano V., Grosse Y., Baan R., Straif K., Secretan B., El Ghissassi F., Gérin-Chair M., Demers P., Hughes K., Krewski D., Hansen J., Goldberg M., Reynier M., Andrae U., Shaham J., Soffritti M., Feron V., Grafström R., Burge S., Cocker J., Coggon D., Chhabra R., Conolly R., Eastmond D., Faustman E., Goldstein B., Hauptmann M., Junghans T., Olin S., Stayner L., Stewart P., Wolf D., (2004), Advice on formaldehyde and glycol ethers, *Lancet Oncology*, **5**, 528.

Cogliano V.J., Grosse Y., Baan R.A., Straif K., Secretan M.B., El Ghissassi F., Andrae U., Burge S., Chhabra R., Cocker J., Coggon D., Conolly R., Demers P., Eastmond D., Faustman E., Feron V., Gérin M., Goldberg M., Goldstein B., Grafström R., Hansen J., Hauptmann M., Hughes K., Junghans T., Krewski D., Olin S., Reynier M., Shaham J., Soffritti M., Stayner L., Stewart P., Wolf D., (2005), Meeting report: summary of IARC monographs on formaldehyde, 2-butoxyethanol, and 1-ter-butoxy-2-propanol, *Environmental Health Perspectives*, **113**, 1205-1208.

CML, (2006), Consortium of Mobile Livenza, Territorial Environmental Analysis Report of the Mobile District of Pordenone, 2006, (in Italian), On line at: http:// www.distrettodelmobilelivenza.it.

Davenport T.H., (1993), *Process Innovation: Reengineering Work through Information Technology*, Harvard Business Press, Cambridge.

de Blas M., Navazo M., Alonso L., Durana N., Gomez M.C., Iza J., (2012), Simultaneous indoor and outdoor on-line hourly monitoring of atmospheric volatile organic compounds in an urban building. The role of inside and outside sources, *Science of the Total Environment*, **426**, 327-335.

De Marchi V., Di Maria E., Micelli S., (2013), Environmental Strategies, Upgrading and Competitive Advantage in Global Value Chains, *Business Strategy and the Environment*, **22**, 62-72.

Donatello S., Moons H., Wolf O., (2017), Revision of EU-Ecolabel criteria for furniture products, European Commission, On line at: http://ec.europa.eu/environment/ecolabel/documents/technical_report_furniture.pdf.

Eastin I.L., Mawhinney D.E., (2011), Japanese F-4Stars Formaldehyde rating process for value-added wood products, Working paper, Center for International Trade in Forest Products, School of Forest Resources, University of Washington, Box 352100, Seattle, WA 98195-2100, On line at:

http://www.cintrafor.org/publications/workingpapers/WP120.pdf.

EC Communication, (2014), Communication 2014/398/EC, Towards a circular economy: A zero waste programme for Europe, On line at: https://eur-lex.europa.eu/resource.html?uri=cellar:50edd1fd-01ec-11e4-831f-01aa75ed71a1.0001.01/DOC_1&format=PDF.

EC Communication. (2015), Communication 2015/614/EC, Closing the loop. An action plan for the Circular Economy, On line at: https://ec.europa.eu/transparency/regdoc/rep/1/2015/EN/1-2015-614-EN-F1-1.PDF.

EC Directive, (2004), Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work, *Official Journal of the European Union*, L 158, 30.04.2004, Brussels.

EC Regulation 66, (2010), Regulation 66 of the European Parliament and of the Council of 25 November 2009 on Eu-Ecolabel, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010R0066&rid=10.

Ellen MacArthur Foundation, (2017), What is a circular economy?, On line at: https://www.ellenmacarthurfoundation.org/circular-economy/overview/concept

Eurobarometer, (2017), People Attitudes towards Environment, (in Italian), On line at: https://www.arpae.it/dettaglio_notizia.asp?id=9419&idlivello=474

Federico T., (2015), The foundings of circular economy, (in Italian), Fondazione per lo Sviluppo Sostenibile, On line at: https://www.scribd.com/document/348986799/FEDERICO-Appunti-Di-Economia-Circolare-250315

Federlegnoarredo, (2017), On line at: http://www.federlegnoarredo.it/it/servizi/normativa/normative-per-categoria-di-prodotto/pannelli-e-semilavorati/pannelli-a-base-di-legno-e-emissioni/classi-di-emissione-di-formaldeide-in-europa

Forest Stewardship Council, (2017), Chain of Custody Certification FSC-STD-40-004 V3-0, On line at: https://us.fsc.org/en-us/certification/chain-of-custody-certification

Fullana P., Frankl P., Kreissig J., (2008), Communication of life cycle information in the building and energy sectors, United Nations Environment Programme, Nairobi, On line at: http://www.unep.fr/shared/publications/pdf/DTIx1090xPA-CommunicationofLCInfoinBuildingandEnergy.pdf

Galli A., (2015), The design furniture is more and more careful to eco-sustainability, (in Italian), Il Sole 24ore, On line at: https://www.ilsole24ore.com/art/casa/2015-04-22/larredo-design-sempre-attento-134856.shtml.

Geiss O., Giannopoulos G., Tirendi S., Barreo-Moreno J., Larsen B.R., Kotzias D., (2011), The AIRMEX study-VOC measurements in public buildings and schools/kindergartens in eleven European cities: statistical analysis of the data, *Atmospheric Environment*, **45**, 3676-3684.

Gilbert N.L., Gauvin D., Guay M., Heroux M.E., Dupuis G., Legris M., Chan C.C., Dietz R.N., Levesque B., (2006), Housing characteristics and indoor concentrations of nitrogen dioxide and formaldehyde in Quebec City, Canada, *Environmental Research*, **102**, 1-8.

Gonzales-Garcia S., Lozano r.G., Moreira M.T., Babarrell X., i Pons J.R., Feijoo G., Murphy R.J., (2012), Eco-innovation of a wooden childwood furniture set: An example of environmental solutions in the wood sector, *Science of the Total Environment*, **426**, 318-326.

IARC, (1982), Formaldehyde, In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans-Some Industrial Chemicals and Dyestuffs, **29**, IARC Ed., Lyon, France, 345-390, On line at: http://monographs.iarc.fr/ENG/Monographs/vol1-42/mono29.pdf

IARC, (1987), Formaldehyde, In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans-Overall evaluation of carcinogenicity. An updating of IARC Monographs, **1-42**, IARC Ed., Lyon, France, Suppl. 7, 211-215, On line at: http://monographs.iarc.fr/ENG/Monographs/suppl7/Suppl7.pdf

IARC, (1995), Formaldehyde, In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans-Wood Dust and Formaldehyde, **62**, IARC Ed., Lyon, France, 217-368, On line at: http://monographs.iarc.fr/ENG/Monographs/vol62/mono62.pdf

IARC, (2006), Formaldehyde, In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans-Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol, **88**, IARC Ed., Lyon, France, 37-326, On line at: http://monographs.iarc.fr/ENG/Monographs/vol88/mono88.pdf

Iritani D.R., Silva D.A., Saavedra Y.M.B., Grael P.F.F., Ometto A.R., (2015), Sustainable strategies analysis trough Life Cycle assessment: A case study in a furniture sector, *Journal of Cleaner Production*, **96**, 308-318.

Kemp R., (2010), Eco-innovation: definition, measurement and open research issues, *Economia Politica*, **XXVII** 397-422.

Kotzias D., (2005), Indoor air and human exposure assessment-needs and approaches, *Experimental and Toxicologic Pathology*, **57**, 5-7.

Krystofik M., Luccitti A., Parnell K., Thurston M., (2018), Adaptive remanufacturing for multiple lifecycles: A case study in office furniture, *Resources, Conservation and Recycling*, **135**, 14-23.

Masiero M., Zorzi G.M., (2006), Quality and certification in the wood chain: the chain of custody. Guide for enterprises (in Italian), Camera di Commercio, Industria, Artigianato, Agricoltura di Padova, On line at: http://www.innovazionepadova.it/public/doc/32-catenacustodia.pdf

Merli R., Preziosi M., Ippolito C., 2016, Promoting sustainability through EMS application: A survey examining the critical factors about EMAS registration in Italian Organizations, *Sustainability*, **8**, 197-210.

Ministerial Decree, (2008), Ministerial Decree of October 10, 2008. Provisions suitable for prescribing formaldehyde emissions from wood-based panels and manufactured articles made by wood-based panels in living and stay environments (in Italian), *Official Journal of the Republic of Italy*, L 288, 10.12.2008, Rome.

Missia D.A., Demetriou E., Michael N., Tolis E.I., Bartzis J.G., (2010), Indoor exposure from building materials: A field study, *Atmospheric Environment*, **44**, 4388-4395.

Mølhave L., Dueholm S., Jensen L.K., (1995), Assessment of exposures and health risks related to formaldehyde emissions from furniture: A case study, *Indoor Air*, **5**, 104-119.

National Cancer Institute, (2017), Formaldehyde and Cancer Risk, On line at: https://www.cancer.gov/about-cancer/causes-prevention/risk/substances/formaldehyde/formaldehyde-fact-sheet

Novelli V., Geatti P., Ceccon L., Toscani L., (2017), Low environmental impact of alternatively supplied cars. Results of an investigation carried out in the north-east of Italy, *Environmental Engineering and Management Journal*, **16**, 1751-1759.

Novelli V., Geatti P., Bianco F., Ceccon L., Del Frate S., Badin P., (2018), *The EMAS Recognition of the Livenza Furniture District in the Province of Pordenone*, Int. Conf. on Sustainable Development Research Society (ISDRS), 2018, Messina, Italy.

Quinkertz R., Rombach G.M., Liebig D., (2001), A scenario to optimise the energy demand of aluminum production depending on the recycling quota, *Resource, Conservation and Recycling*, **33**, 217-234.

Radonjič G., Pisnik A., Krajnc D., (2015), Product ecodesign in companies with ISO 14001 certified environmental management system, *Environmental Engineering and Management Journal*, **14**, 167-181.

Rennings K., (2000), Redefinition innovation-eco-innovation research and the contribution from ecological economics, *Ecological Economics*, **32**, 319-332.

Rinawati I.D., Sriyanto, Sari P.D., Prayodha C.A., (2018), Eco-efficiency analysis of furniture product using life cycle assessment, *E3S Web of Conference*, **31**, 08005, 1-5.

Risholm-Sundman M., Larsen A., Vestin E., Weibull A., (2007), Formaldehyde emission - Comparison of different standards methods, *Atmospheric Environment*, **41**, 3193-3202.

Ruddell S., Stevens J.A., (1998), The adoption of ISO 9000, ISO 14001, and the demand for certified wood products in the business and institutional furniture industry, *Forest Products Journal*, **48**, 19-26.

Sala S., Castellani V., (2011), *Atlas of Eco-Innovation: Methods and Experiences For Innovation, Enterprise Environmental Competitiveness and Sustainable Development*, (in Italian), Franco Angeli Press, Milan, Italy.

Salem M.Z.M., Bohm M., (2013), Understanding of formaldehyde emissions from solid wood: An overview, *BioResources*, **8**, 4775-4790.

Shroeder P., Anggraeni K., Weber U., (2018), The relevance of circular economy practices to the sustainable development goals, *Journal of Industrial Ecology*, 1-19.

Smith C., (2006), *Handbook of Aluminum Recycling*, Vulkan-Verlag GmbH, Essen, Germany.

Steinemann A., Wargocki P., Rismondi B., (2017), Ten questions concerning green buildings and indoor air quality, *Building and Environment*, **112**, 351-358.

Ugur L.O., Leblebici N., (2018), An examination of the LEED green building certification system in terms of construction costs, *Renewable and Sustainable Energy Reviews*, **81**, 1476-1483

UNI EN 717-2, (1995), Wood-based panels. Determination of formaldehyde release. Part 2: Formaldehyde release by the gas analysis method, canceled standard, superseded by EN ISO 12469-5:2015, On line at: https://www.iso.org/standard/64064.html.

UNI EN 717-1, (2004), Wood-based panel- Determination of formaldehyde release. Part 1: Formaldehyde emission by the chamber method, On line at: https://www.iso.org/standard/2564.html.

UNI EN 12460-3, (2015), Wood-based panels - Determination of formaldehyde release - Part 3: Gas analysis method, On line at: https://infostore.saiglobal.com/preview/is/en/2015/i.s.eniso12460-3-2015.pdf?sku=1841030.

UNI EN 13986, (2015), Wood-based panels for the use in constructions-Characteristics, assessment of conformity and marking, On line at: https://www.pdistribution.pl/pdf_Amroc/Norma%20EN%2013986-2004%20%20jezyk%20angielski.pdf.

UNI EN ISO 12460-5, (2016), Wood-based panels- Determination of formaldehyde release- Part 5: Extraction method, On line at: https://www.iso.org/standard/63066.html.

United Nations, (2015), Transforming our world: the 2030 agenda for Sustainable development, On line at: https://sustainabledevelopment.un.org/content/documents/21252030%20Agenda%20for%20Sustainable%20Development%20web.pdf

Vassura I., Venturini E., Bernardi E., Passarini F., Settimo G., (2015), Assessment of indoor pollution in a school environment through both passive and continuous samplings, *Environmental Engineering and Management Journal*, **14**, 1761-1770.

Vidal N., Kozak R., Cohen D., (2005), Chain of custody certification: an assessment of the North American solid wood sector, *Forest Policy and Economics*, **7**, 345-355.

Wei W., Ramalho O., Mandin C., (2015), Indoor air quality requirements in green building certifications, *Building and Environment*, **92**, 10-19.

Wingate K.G., McFarlane P.N., (2005), Chain of custody and eco-labelling of forest products: A review of the requirements of the major forest certification schemes, *International Forestry Review*, 342-347.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2437-2445
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

APPLICATION OF LCA METHODOLOGY IN THE ASSESSMENT OF A PYROLYSIS PROCESS FOR TYRES RECYCLING

Esmeralda Neri[1], Beatrice Berti[2], Fabrizio Passarini[1,2]*, Ivano Vassura[1,2], Loris Giorgini[2,3], Giorgio Zattini[2,3], Cristan Tosi[4], Massimo Cavazzoni[4]

[1] *"Energy and Environment" Interdepartmental Center of Industrial Research, University of Bologna, Via Dario Campana 71, Rimini, Italy*
[2] *"Toso Montanari" Department of Industrial Chemistry, University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*
[3] *"Advanced Applications in Mechanical Engineering and Materials Technology" Interdepartmental Center of Industrial Research, CIRI-MAM, V.le del Risorgimento, 2, 40136 Bologna, Italy*
[4] *CURTI S.p.A., Divisione Energia, Via Emilia Ponente, 750, Castel Bolognese, Ravenna, Italy*

Abstract

According to recent estimations, the total yearly amount of end-of-life tyres (ELTs) arising in Europe exceeds 3 million tons; more than 95% are managed through mechanical and thermal treatments because ELTs represent a useful resource both of materials and energy. For this purpose, the goal of the present work is the assessment of the environmental impacts of a novel pyrolysis process and the comparison with alternative ELTs valorisation or disposal scenarios. Life Cycle Analysis (LCA) methodology has been applied to determine the most critical stages of the process under study, assessing the environmental benefits arising from the recovery of material and energy and the impacts, compared to the technologies already on the market, taking into account treatment processes, materials recovery and disposal of wastewater/residues. The chosen functional unit (FU) is 1 ton of ELTs treated by the plant. The different scenarios investigated have been analyzed through ReCiPe impact assessment method. Considering the pre-treatment, the pyrolysis process results in a lower environmental impact compared to the others, with the 1/3, 1/10 and 1/20 of energy consumption compared to the alternatives considered. The analysis of pyrolysis process showed that the avoided impact due to the recovery of carbon black, steel, oil and syngas exceeds the impact generated by the process, related to the energy consumption and to the emissions into the atmosphere. Compared to other energy-recovery scenarios, a greater advantage results from the pyrolysis process, mostly due to the recovery of valuable materials. Then, comparing it to other material recovery scenarios, a variable influence is given by the different options of recovery, considering which materials could actually be replaced and the commercial value of the materials that is replaced.

Key words: energy, life cycle assessment, material, recovery, tyres

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The flows of end of life tyres (ELTs) managed all around Europe has been recently quantified at more than 3 Mt in 2016 (about 3.51 Mt in EU-28, and 3.93 considering also Norway, Switzerland and Turkey) (ETRMA, 2018). Of this amount, more than 95% has been treated for the recovery of energy or materials. As for Italy, Ecopneus (National consortium company for ELTs collection and treatment) (Ecopneus, 2017) reports that approximately 265 kt of new tyres were introduced in the national market in 2015. The total collection of ELTs in 2015 amounted to about 252 Kt and, of these, about 245 kt were properly managed, according to the national legislation.

After collection, ELTs are subdivided between recycling and recovery plants; ELTs constitute an important source of valuable materials (about the 40%

* Author to whom all correspondence should be addressed: e-mail: fabrizio.passarini@unibo.it; Phone/Fax: +39 051 2093863

in weight of the tyre is composed of rubber, about the 30% is carbon black, while the third major component by weight is steel) and energy, with a lower calorific value similar to that of coal. The main treatments for ELTs are based on mechanical and thermal processes.

Mechanical processes generally start with the crushing of the tyres and the physical separation of its components, without changes in the chemical composition. The degree of grinding is a function of the desired final application. For low added value manufacturing, simple shredding technologies are adopted, which return chips varying in size from 20-50 mm up to 300 mm. They are suitable as coarse materials used in civil engineering works like modified asphalts or bitumen production (ETRMA, 2018; Ecopneus, 2017). Otherwise, a further grinding process, for example using mill technologies followed by sieving, allows to obtain homogeneous streams of granules and powders of different size (from 0.8 to 20 mm for granules and <0.8 mm for powders). These secondary raw materials can be used for a wide number of applications including elastic modifiers for sports and playgrounds surfaces or compound additives for new tyres manufacturing, insulation materials and urban furniture (ETRMA, 2018; Ecopneus, 2017). The use of specific process devices for cleaning the ELTs fed into the recycling plants, as well as other downstream technologies (granulators for the separation of steel from rubber, magnetically or gravimetrically, or of textile fibres through controlled aspiration), allows high quality in terms of purity of the recovered materials.

Thermal processes involve the use of the entire or crushed ELTs as alternative fuels for energy production, exploiting their high calorific value. Therefore, ELTs can be co–incinerated in cement kilns, paper mills, lime manufacturing plants and thermal power plants, i.e. in all the highly energy-intensive plants (ETRMA, 2018; Ecopneus, 2017).

An interesting alternative for treating ELTs is pyrolysis (a chemical process which is carried out at moderately high temperature and in the absence of oxygen) which allows the decomposition of the organic material. The resulting products are divided into three streams (Quek and Balasubramanian, 2013):

- solid fraction: this is a carbonaceous residue (char) in which it is also possible to find metals or inorganic fillers, if these were contained in the input material;
- liquid fraction: this is an oil rich in organic molecules (aliphatic and aromatic) having different molecular weight, such as alcohols, aldehydes, acids and ketones and also aromatic compounds;
- gaseous fraction: this is syngas composed of light hydrocarbons (C2-C6), in addition to CO, CO_2, H_2O and H_2.

The pyrolysis process generally requires an initial phase of shredding to reduce tyres at 2 to 10 cm in size. These pieces are then loaded into the reactor, in which the pyrolysis reactions take place at temperature above 450°C, leading to the formation of a solid residue (coal and metals), gases and vapours. Vapours are then condensed and separated from the gases to obtain a pyrolytic oil, which can be furtherly refined. As regards the non-condensable compounds, these are burned to obtain electric and thermal energy. The exhaust gases are carried in a burner, in which a reduction of NO_x by selective non-catalytic reduction (SNCR) with urea and a reduction of sulfur oxides and HCl with soda are made. Once purified, the fumes are released into the atmosphere. The solid residue needs further treatment to separate the metal fraction from coal (Andreola et al., 2016).

For this purpose, the Life Cycle Assessment methodology (LCA) has been applied to determine the most critical stages of the process under study, the environmental benefits arising from the recovery of materials and energy and the greater or lower impact compared to the mechanical or thermal technologies on the market. Different previous works studied the environmental impact of recovery of tyres, through LCA methodology (ISO 14040, 2006; ISO 14044, 2006), comparing alternative scenarios of ELTs management (Corti and Lombardi, 2004; Li et al., 2010; Rafique, 2012). The assessment was performed considering the indirect impacts caused by energy production stage, the direct impacts caused by ELTs treatment process and the avoided impacts caused by valuable products (recycled materials and energy). Bartolozzi et al. studied the case of rubberized asphalt pavement in comparison to a conventional asphalt (Bartolozzi et al., 2015). In another paper (Clauzade et al., 2010) a comparative environmental evaluation of the various recovery alternatives was carried out, aimed at identifying the strengths and weaknesses of each recovery method. Even in Feraldi et al. (2013) and Ortiz-Rodrìguez et al. (2017) different treatment options have been compared as material recycling and tire-derived fuel combustion through co-incineration, finding that the material recycling scenario provides a greater impact reduction than the energy recovery scenario, but they did not analyze the case of pyrolysis process (Feraldi et al., 2013; Ortiz-Rodrìguez et al., 2017).

As for Italy (according to Ecopneus, 2017), about 150 kt of CO_2 eq. were emitted by the combustion of ELTs in cement plants, 57% of which in Italy (where there are 5 plants, mostly in the North) and 43% in foreign cement plants (located in Romania, Morocco, Turkey, Austria, Germany and Hungary (Torretta et al., 2015). This treatment allows the saving of other fossil fuels, such as coal and petroleum coke (56.8% of avoided emissions). On the other hand, emissions from ELTs recovery in power stations (11.6%) are not offset by the benefits resulting from the avoided production of an equal amount of electricity generated in Italy (Ciacci et al., 2014), considering the national energy mix.

As regards the resources balance (material footprint), 54% of their consumption is associated with collection and transportation of ELTs to the treatment systems, which involves the use of fossil fuels to feed hundreds of vehicles and dozens of ships, which annually cover millions of kilometres to carry

ELTs. In a scenario in which the treatment of ELTs is exclusively performed within the national territory, it would lead to a lower resources consumption and therefore greater environmental benefits.

Finally, ELTs recycling results in significantly greater water savings, compared to the energy recovery scenario, while carbon and material footprint show values of the same order of magnitude.

The goal of the study is the assessment of the environmental impacts of the pyrolysis process of ELTs performed with a novel plant (owned by the company Curti S.p.A., located in Northern Italy) (Bortolani et al., 2014) and to compare it with alternative valorisation and/or disposal scenarios.

2. Material and methods

2.1. Goal and scope definition

This novel pyrolysis plant is an upgraded version of a pilot plant designed and built by Curti S.p.A. The pilot plant was tested with ELTs (Giorgini et al., 2015a), glass fibres reinforced polymers (GFRPs) (Giorgini et al., 2016) and carbon fibres reinforced polymers (CFRPs) (Giorgini et al., 2015b). These experimentations have been crucial to obtain useful data required for the design of the new plant object of the study here proposed.

The environmental impacts associated to the life cycle of ELTs were evaluated giving credit to recycling for the avoided production from primary sources (Eckelman et al., 2014; ISO 14040, 2006; ISO 14044, 2006). For instance, the use of ELTs as a fuel in cement factory would avoid the use of coal and petroleum coke. Yet, steel and the combustion ash are incorporated into the cement, thus permitting a further saving of filler material. Similarly, sending ELTs to power plants for the production of electrical energy would avoid to produce the same amount of electricity from the national grid. The steel that is obtained by crushing ELTs and by combustion in power stations supplements the avoided impact, being recyclable as scrap iron. The ashes resulting from the combustion in power stations can be recycled as a binder for cement or as material for road infrastructure. Lastly, the rubber recycled as granules and powder, coming from a mechanical treatment of ELTs, avoids the consumption of virgin rubber for the creation of new compounds.

The boundaries of the system are “from gate to gate”, considering the life cycle phases regarding the following operations:

- treatment process (including all input and output streams for the supply and distribution of materials and energy);
- materials recovery (sent to recycling plant);
- disposal of wastewater/residues.

The functional unit is the physical quantity to which all flows and impacts (input and output) are reported: 1 ton of ELTs treated by the plant of pyrolysis has been chosen as the functional unit, dimensioned on a 4 tons/h capacity (according to the primary data provided by the plant). As regards the alternative scenarios, they also have been evaluated with the same reference unit in such a way that they can be compared in a univocal way.

2.2. Life Cycle Inventory (LCI)

In the Life Cycle Inventory step all mass and energy flows of the processes investigated were considered. First of all, steps and material flow of the pyrolysis plant managed by the company Curti s.p.a. has been analyzed, considering the flow diagram shown in Fig. 1.

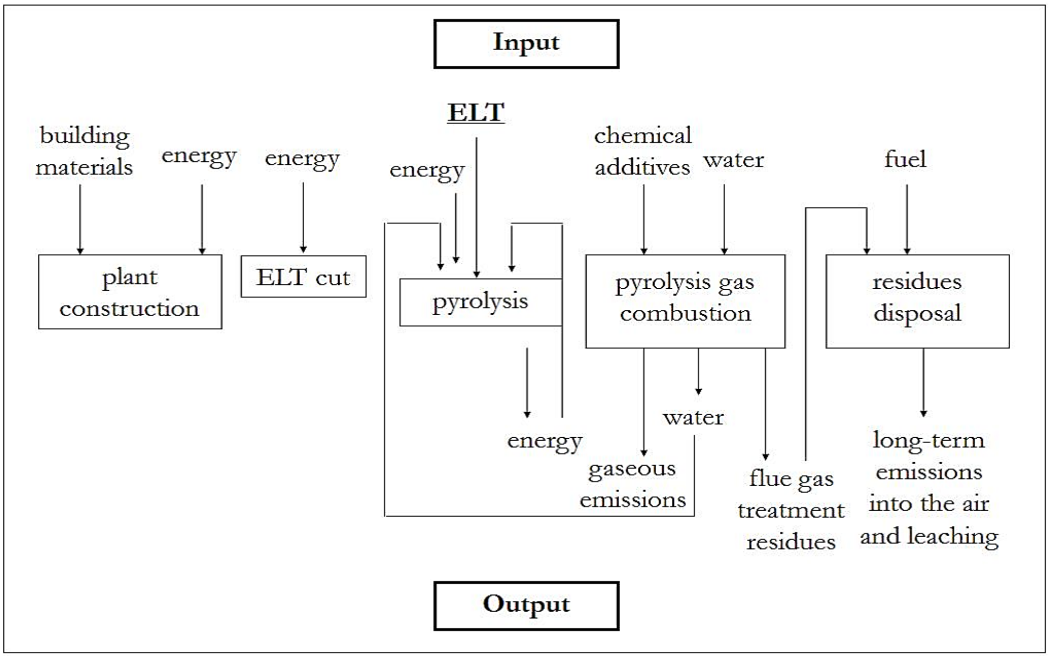


Fig. 1. Flow diagram of the pyrolysis plant studied

This is a pyrolysis process for the recovery of ELTs able to recover three main products having a commercial value: carbon black, oil and steel. The peculiarity of this process is that, in contrast to the common pyrolysis processes, in the pre–treatment step it is not necessary to crush the whole tyre, but only a circumferential cutting of ELTs (a “single cut”) is needed (the diameter must be less than 1400 mm), (Bortolani et al., 2014; Giorgini et al., 2015a).

Input and output flows included in the model are shown in Table 1.

Table 1. Input and output of the PFU pyrolysis process by Curti S.p.A.

Flows	***Quantity***	***Unit***
Input		
PFU	1.00E+00	t
Electricity for pre treatment	1.41E+01	kWh
Electricity for pyrolysis	5.69E+01	kWh
Air	1.20E+04	kg
$CO(NH_2)_2$	1.33E+00	kg
$NaHCO_3$	2.67E+00	kg
Output		
Carbon black	3.15E+02	kg
Oil	2.57E+02	kg
Steel	1.30E+02	kg
CO_2	8.08E+02	kg
NO_2	2.03E-01	kg
SO_2	1.40E+00	kg
H_2O	1.16E+01	kg

By this system it is possible to obtain the recovery of the following materials:

- carbon black. In the modelled scenario an equal amount of *Carbon black, at plant/GLO U* has been inserted as an “avoided product” (process already present in the reference database, Wernet et al., 2016);
- oil (a low sulphur diesel). In the modelled scenario an equal amount of *Diesel, low-sulphur, at refinery/CH U* has been considered (Wernet et al., 2016);
- steel. In the modelled scenario an equal amount of *Steel, low-alloyed, at plant/RER U* has been accounted (Wernet et al., 2016).

In the model, the consumption of air, sodium carbonate and urea (necessary for the SNCR treatment) has been inserted, as well as two different input flows of electricity consumption, one necessary for the circumferential cut of ELTs and the other for the pyrolysis process considering the national energy mix (Electricity, medium voltage, production IT, at grid/IT U).

Moreover, the emissions of CO_2, NO_2 and SO_2 into the air due to the combustion step, and the wastewater output were considered.

After the analysis of this process, a comparison between different pre-treatment scenarios has been performed, considering different processing steps (Corti and Lombardi, 2004; Rafique, 2012):

- a single circumferential cut realized by the new pyrolysis plant;
- grinding, with the production of ground particles of about 7-10 cm, that could be used for energy recovery (eg. electricity production, cement plant; Ecopneus Report, 2017);
- crushing, that is a further grinding to a size of about 2 cm, that could be used for energy and material recovery purposes too;
- pulverization, to a size lower than 1 mm, that could be aimed at material recovery (eg. sports floors, insulating, rubber goods).

In every scenario, the electricity consumption and the steel consumption related to the wear of the cutting blades have been considered, referred to 1 ton of ELTs treated.

After this step, the pyrolysis process under investigation was compared to other scenarios of recovery of energy or material.

Considering the energy recovery processes, the management of 1 ton (the functional unit) of ELTs has been compared amongst:

- pyrolysis plant;
- cement plant;
- waste-to-energy plant.

In the cement plant scenario, the following input and output have been considered (Corti and Lombardi, 2004):

- the avoided use of coal (as *Hard coal supply mix/IT U*) and iron (as *Iron scrap, at plant/RER U*) due to the use of ELTs (already containing the steel necessary as reinforcement for the cement);
- the input of energy necessary for the co-combustion (diesel and electricity) and the electricity for the grinding step;
- atmospheric emissions of CO, chromium, lead, NOx and non-methane volatile organic compound (NMVOC).

Concerning the waste-to-energy process scenario, a previous life cycle assessment model containing primary data regarding a municipal solid waste (MSW) incineration process (Passarini et al., 2014) has been used.

In the second step, the comparison of different scenarios for material recovery through the pyrolysis process was carried out. Since the recovery of secondary rubber from ELTs could result in different uses (e.g., modified asphalts, sports surfaces, anti-trauma surfaces for playgrounds, etc.), its recycling could substitute different kinds of material, and cannot be simply considered as a replacement of an equivalent amount of primary (synthetic or natural) rubber (which has a very versatile use, in many different applications). However, the recovery of secondary rubber from ELTs has been considered as an extreme hypothesis of recycling, which can settle the highest benefit deriving from mechanical recovery. In order to take into account, the avoided impact by the recycling of ELTs two different scenarios were considered and compared to the pyrolysis process under investigation:

- Scenario 1. In the first scenario the avoided impacts associated to the following recovery processes were considered:
  - o recovery of iron (*Iron scrap, at plant/RER U*);
  - o recovery of polymeric material as an avoided production of synthetic rubber (*Synthetic rubber, at plant/RER U*);
  - o recovery of the fibers as an avoided production of material for road paving such as bitumen (*Bitumen, at refinery/RER U*).
- Scenario 2. In the second scenario the avoided impacts associated to the following recovery processes were instead considered:
  - o recovery of iron (the same as above);
  - o recovery of the polymeric material and of the fibre as an avoided production of an equivalent amount of synthetic rubber, bitumen and sand (with the proportion of one third, each).

All the two scenarios have been modelled considering the same functional unit (1 ton of recovered ELTs); in all models, the input of electricity necessary for the pulverization step and the emission of particulate matter into the air were included.

3. Results and discussion

The Life Cycle Impact Assessment (LCIA) stage was carried out using the ReCiPe analysis method (Goedkoop et al., 1999; Goedkoop et al., 2008; Goedkoop et al., 2012), considering five impact categories at the midpoint level (Climate Change, Human Toxicity, Particulate Matter Formation, Fossil Fuels Depletion and Metal Depletion) and three damage categories at the endpoint level (Human Health, Ecosystem Quality and Resources Depletion). According to the methodology, to each input and output of the models created, one or more "midpoint" impacts have been associated, using the method of analysis ReCiPe and the software SimaPro. Following ReCiPe procedures of normalisation and weighting (hierarchical perspective) a single score (Pt) was calculated, that is an index summarising the global impact of each scenario (Goedkoop et al., 2012). In the following paragraphs, the results related to different scenarios are reported and discussed (Fig. 2 and Fig. 3).

Results show that electricity consumption for tyres cutting and co-combustion accounts for about 10% of the total impacts of the process, while atmospheric emissions are responsible for the most of the total impacts generated. However, the avoided impact due to the recovery of carbon black, steel and oil fuel exceeds widely the impacts estimated (more than an order of magnitude), with a gain associated to the damage category "Resources Depletion" (Fig. 3). Therefore, environmental benefits are greater than impacts, especially considering the impact categories of Climate Change, Fossil Fuel Depletion and Metal Depletion (directly related to the recovery of steel). Fig. 4 shows the results from the scenario analysis

Considering only the pre-treatment, the process consisting of a single cut got an environmental impact equal to 1/3, 1/10 and 1/20 respectively of the alternatives considered (i.e., grinding, crushing and pulverization). In particular, lower impact resulted for the categories related to Climate Change and Fossil Depletion. This is likely due to the very low consumption of electricity required by the single cut step (130 MJ/t.

For the other recovery and recycling processes, a finer grinding is required, with a higher consumption of electricity, from a size of few centimeters to less than 2 millimeters (the finest fraction is generally employed for material recycling for which 2.81E+03 MJ/t are required). Considering energy recovery processes, the management of 1 ton of ELTs in the pyrolysis plant investigated was compared with a cement factory and a waste-to-energy plant (Figs. 5 - 6).

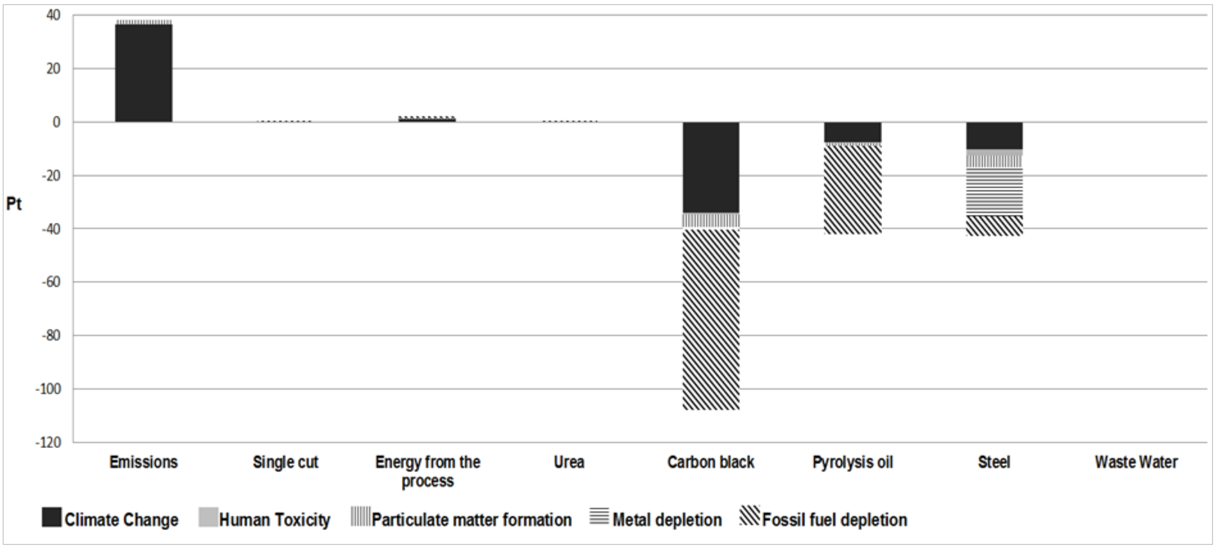


Fig. 2. Impacts of the pyrolysis process (Single Point, midpoint impact categories)

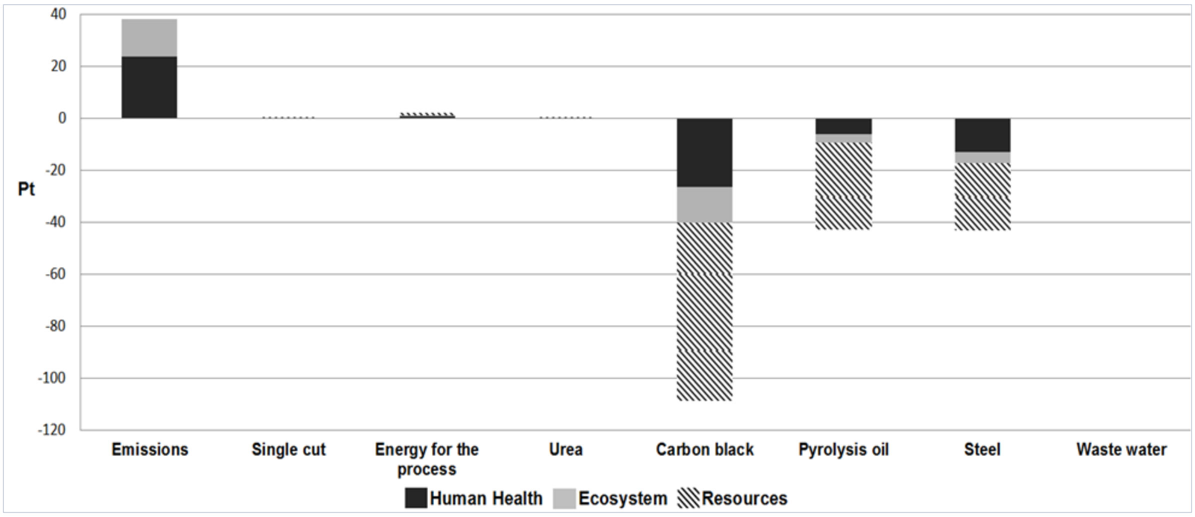


Fig. 3. Impacts of the pyrolysis process (Single Point, endpoint impact categories)

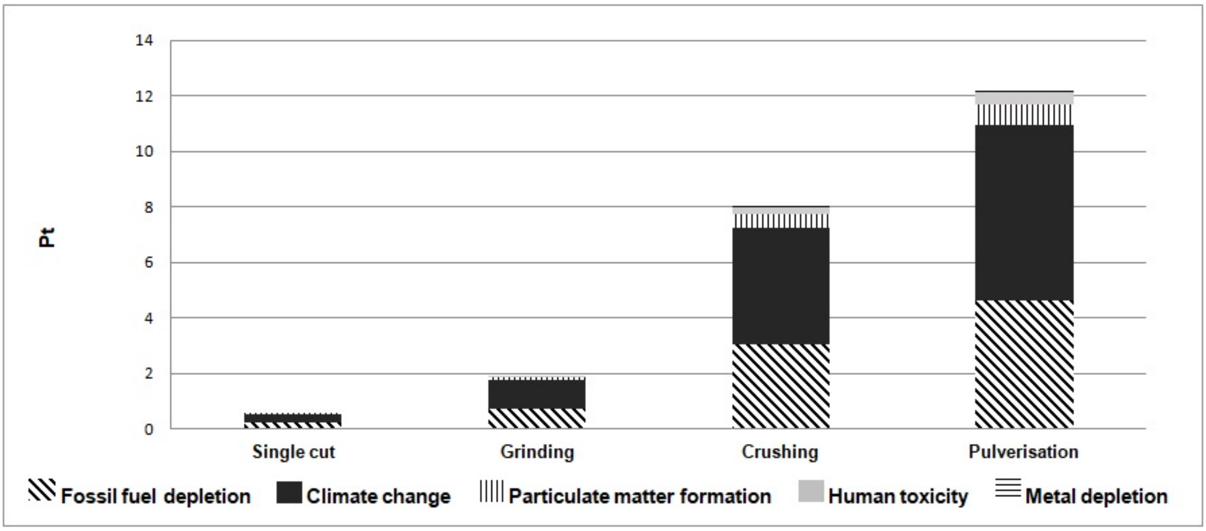


Fig. 4. Impacts of different pre-treatment process (Single Point, midpoint impact categories)

Compared to other energy-recovery scenarios (recovery in cement plant and in a solid waste incineration plant) the environmental preference is given to the pyrolysis process, especially for the Fossil Fuel Depletion midpoint category (Fig. 5) and the Resources Depletion endpoint category (Fig. 6) thanks to the recovery of diesel performed. It is worth noting that for energy recovery in a cement factory, coal was considered as energy carrier providing the same amount of energy; this has been considered as an avoided impact. If another fuel less impacting than coal was considered, the avoided impact would be likely lower for the categories Fossil Fuel Depletion and Human Toxicity. The avoided impact for the Fossil Fuel Depletion category is due to the partial replacement of the diesel with ELTs, while that of Human Toxicity is the result of the avoided emission of NO_x and NMVOC during the production of the clinker in the cement plant.

It can be observed, on the other hand, that the waste to energy process results in a net-positive impact since the energy recovery with an avoided impact for the category Fossil Fuel Depletion does not offset the damages coming from the different emissions and consumptions. A higher impact for the category Climate Change (722 $kgCO_{2eq}/t$) was computed. Considering the endpoint categories (Fig. 6), the waste-to-energy of ELTs has a higher damage related to Human Health and the pyrolysis resulted in the lower environmental burden thanks to the recovery of material and the avoided damage for Resources Availability.

Then, a comparison of the pyrolysis process with different recovery of material scenarios was performed (Figs. 7 - 8). Compared to other material recovery scenarios, a better performance is due to the different recovery options of the granulate/powder, depending on which materials they could actually replace. The efficient recovery of rubber (to replace the same amount of synthetic rubber), and metals would bring to a greater environmental benefit especially related to the impact categories of Climate Change and Fossil Depletion (Fig. 7). However, as previously said, this could be considered an extreme hypothesis: even though a quantitative recovery of secondary rubber could be reached, a complete substitution of primary synthetic rubber would also depend on comparable quality of the recycled material for the same range of applications. A more realistic option, which considers that only a part of material could effectively replace primary synthetic rubber, would generally bring to a lower gain from the environmental point of view, compared to the pyrolysis technology.

4. Conclusions

The LCA analysis carried out on a new pyrolysis plant for ELTs treatment highlighted the effective influence of the added value of recycled products in determining the environmental sustainability of a process. Taking the case of the scenarios investigated in this study, carbon black, oil, steel and pulverized ELTs ready for material recovery have all a high added value, as they can be reused as secondary raw materials in many applications. In order to optimize a process, it is therefore essential to analyse the industrial demand to ensure the use of the recycled products and thus the accounting of avoided impacts.

The study identified the most environmentally sustainable solutions among the pre-treatments and the recovery processes investigated, and performed preliminary assessments to support the design phase of a new pyrolysis pilot plant. At the end of the analysis, it was possible to identify the critical aspects and the strengths of each scenario, computing the associated environmental impacts.

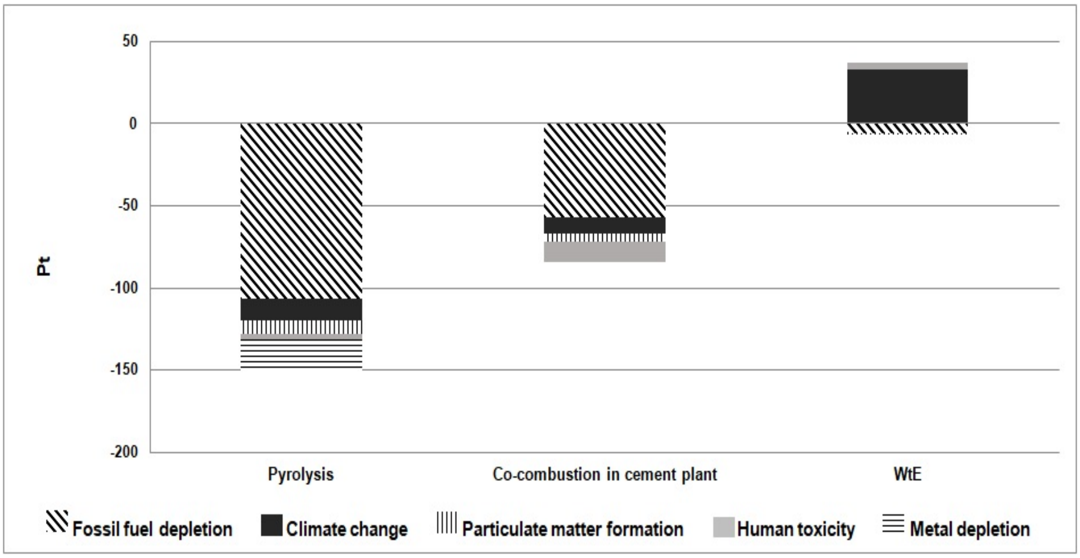


Fig. 5. Impact of the energy recovery processes (Single Point, midpoint impact categories)

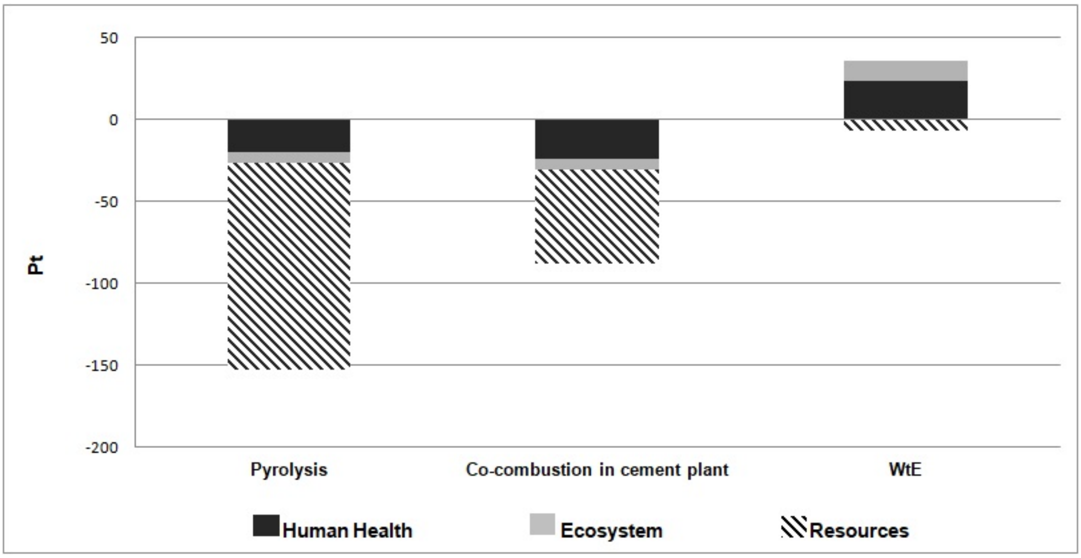


Fig. 6. Impacts of the energy recovery processes (Single Point, endpoint impact categories)

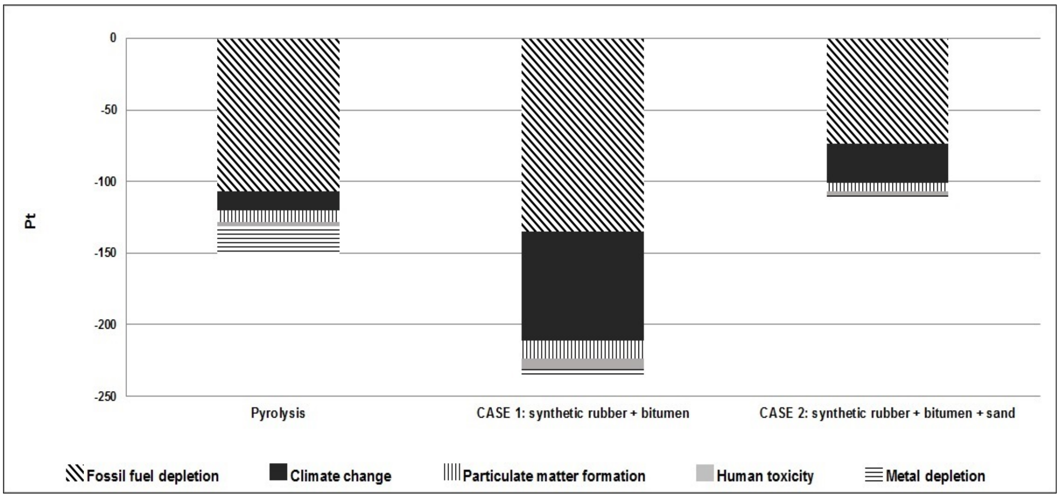


Fig. 7. Impacts of the material recovery processes (Single Point, midpoint impact categories)

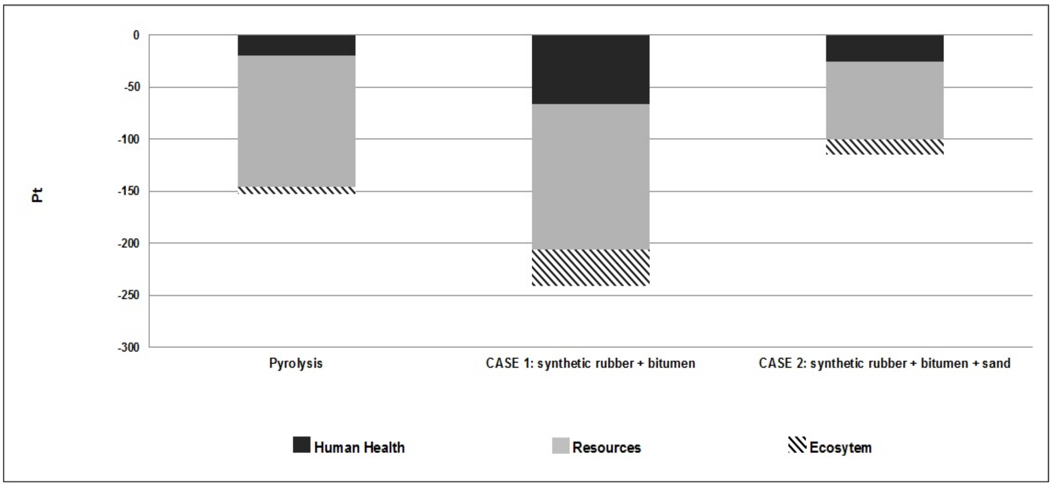


Fig. 8. Impacts of the material recovery processes (Single Point, endpoint impact categories)

The pyrolysis process investigated resulted in lower environmental impacts if compared to different energy recovery options thanks to lower energy requirements for the pre-treatment phase (only "single cut", with a cumulative energy demand of 1.30E+02 MJ_{eq}/ton, with respect to the classical crushing of the tyres, with a cumulative energy demand of 1.83E+03 MJ_{eq}/ton), and to a more efficient recovery of secondary materials (carbon black, oil and steel). The same process resulted also competitive, in terms of environmental performance, with other recyclingtechniques, even if it is important to understand which materials the recovered resource can replace (sand, bitumen or synthetic rubber) and in which fraction. However, quality issues of the recovered materials can affect the replacement of primary resources for given applications.

LCA confirmed to be a very useful methodology investigate the environmental performance of industrial processes and to compare alternative technologies. Identifying of the most advantageous options for material and energy recovery provides an evidence-based knowledge for safeguarding the environment, natural resources and the human health.

References

Andreola F., Barbieri L., Lancellotti I., (2016), Valorization of tyres waste pyrolysis residue in lightweight materials, *Environmental Engineering and Management Journal*, **14**, 1907-1914.

Bartolozzi I., Mavridou S., Rizzi F., Frey M., (2015), Life cycle thinking in sustainable supply chains: The case of rubberized asphalt pavement, *Environmental Engineering and Management Journal*, **14**, 1203-1215.

Bortolani G.N., Giorgini L., Tosi C., Bianchi M., (2014), Plant for transforming into secondary raw material, or disposing used tires, made of rubber or other carbon matrices comprising pyrolysis chamber, comprises first hydraulic sealing means, first evacuating means, and second evacuating means. Italy Patent, No. *WO2014057430-A1*.

Ciacci L., Eckelman M.J., Passarini F., Chen W.Q., Vassura I., Morselli L., (2014), Historical evolution of greenhouse gas emissions from aluminum production at a country level, *Journal of Cleaner Production*, **84**, 540-549.

Clauzade C., Osset P., Hugrel C., Chappert A., Durande M., Palluau M., (2010), Life cycle assessment of nine recovery methods for end-of-life tyres, *The International Journal of Life Cycle Assessment*, **15**, 883-892.

Corti A., Lombardi L., (2004), End life tyres: Alternative final disposal processes compared by LCA, *Energy*, **29**, 2089-2108.

Eckelman M.J., Ciacci L., Kavlak G., Nuss P., Reck B.K., (2014), Life cycle carbon benefits of aerospace alloy recycling, *Journal of Cleaner Production*, **80**, 38-45.

Ecopneus, (2017), Sustainability Report 2016, Rome, Italy, On line at: www.ecopneus.it/_public-file/Rapporto%20Ecopneus%202016.pdf

ETRMA, (2018), End-of-life Tyre Management 2016, European Tyre & Rubber manufacturers' association, On line at: http://www.etrma.org/uploads/Modules/Documentsmanager/20180502---2016-elt-data_for-press-release.pdf.

Feraldi R., Cashman S., Huff M., Raahauge L., (2013), Comparative LCA of treatment options for US scrap tires: material recycling and tire-derived combustion, *The International Journal of Life Cycle Assessment*, **18**, 613-625.

Giorgini L., Benelli T., Leonardi C., Mazzocchetti L., Zattini G., Cavazzoni M., Montanari I., Tosi C., (2015a), Efficient recovery of non-shredded tires via pyrolysis in an innovative pilot plant, *Environmental Engineering and Management Journal*, **14**, 1611-1622.

Giorgini L., Benelli T., Mazzocchetti L., Leonardi C., Zattini G., Minak G., Dolcini E., Cavazzoni M., Montanari I., Tosi C., (2015b), Recovery of carbon fibers from cured and uncured carbon fiber reinforced composites waste and their use as feedstock for a new composite production, *Polymer Composites*, **36**, 1084-1095.

Giorgini L., Leonardi C., Mazzocchetti L., Zattini G., Cavazzoni M., Montanari I., Tosi C., Benelli T., (2016), Pyrolysis of fiberglass/polyester composites: Recovery and characterization of obtained products, *FME Transactions*, **44**, 405-414.

Goedkoop M.J., Hofstetter P., Müller-Wenk R., Spriensma R., (1999), The ECO-indicator 98 explained, *The International Journal of Life Cycle Assessment*, **3**, 352-360.

Goedkoop M., De Schryver A., Oele M., (2008), Introduction to LCA with SimaPro 7, Prè Consultant, On line at: https://www.pre-sustainability.com/download/SimaPro8IntroductionToLCA.pdf

Goedkoop M., Heijuns R., Huijbregts M., De Schryver A., Struijs J., van Zelm R., (2012), ReCiPe 2008- A life cycle impact assessment method which comprises harmonized category indicators at the midpoint and the endpoint level, First edition (revised), Ministry of Housing, Spatial Planning and the Environment (VROM), Netherlands, On line at: https://www.leidenuniv.nl/cml/ssp/publications/recipe_characterisation.pdf

ISO 14040, (2006), Environmental management, life cycle assessment, principles and framework, National Institution for Italian Unification, Second edition 2006-07-01, Switzerland, On line at: https://web.stanford.edu/class/cee214/Readings/ISOLCA.pdf.

ISO 14044, (2006), Environmental management, life cycle assessment, requirements and guidelines, National Institution for Italian Unification, First edition 2006-07-01, Switzerland, On line at: https://www.iso.org/standard/37456.html.

Li X., Xu H., Gao Y., Tao Y., (2010), Comparison of end-of-life tire treatment technologies: A Chinese case study, *Waste Management*, **30**, 2235-2246.

Ortiz-Rodrìguez O.O., Ocampo-Duque W., Duque-Salazar L.I., (2017), Environmental impact of end-of-life tires: Life cycle assessment comparison of three scenarios from a case study in Valle Del Cauca, Colombia, *Energies*, **10**, 1-13.

Passarini F., Nicoletti M., Ciacci L., Vassura I., Morselli L., (2014), Environmental impact assessment of a WtE plant after structural upgrade measures, *Waste Management*, **34**, 753-762.

Quek A., Balasubramanian R., (2013), Liquefaction of waste tires by pyrolysis for oil and chemicals, *Journal of Analytical and Applied Pyrolysis*, **101**, 1-16.

Rafique R.M., (2012), *Life cycle assessment of waste car tyres at Scandinavian Enviro Systems*, MsC Thesis, Chalmers University of Technology, Göteborg, Sweden.

Torretta V., Cristina E., Ragazzi M., Trulli E., Istrate I.A., Cioca L.I., (2015), Treatment and disposal of tyres: Two EU approaches. A review, *Waste Management*, **45**, 152-160.

Wernet G., Bauer C., Steubing B., Reinhard J., Moreno-Ruiz E., Weidema B., (2016), The ecoinvent database version 3 (part I): overview and methodology, *The International Journal of Life Cycle Assessment*, **21**, 1218-1230.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2447-2453
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

EFFECT OF PARTICLES SIZE OF CRT GLASS WASTE ON PROPERTIES OF POLYMER CONCRETES

Paolo Pozzi

Engineering Department E.Ferrari, University of Modena and Reggio, 10 Vivarelli Street, Modena, 41125, Italy
E-mail: paolo.pozzi@unimore.it

Abstract

The research has been focused on concretes in which the continuous phase is some kind of polymeric resin and the discrete phase is some type of mineral aggregate. Such composite materials are known as Polymer concretes (PC) and boast several advantages such as lower weights, higher resistance to corrosive environments and chemical attacks, faster curing and lower permeabilities. In PC the inorganic fraction can reach up to 90% of the total and is made up of aggregates such as sand and gravel. The aim of this work is to study how to use glass waste CRT to replace sand and gravel, from to made a recycled glass polymer concretes. In particular it has been investigated the effect of particle size distribution of CRT recycled glass on properties of PC obtained. The first step is the chemical/physical characterization of recycling materials through XRF, XRD, particle size and microstructural analysis (SEM). This is followed by the realization and optimization of laboratory prototypes prepared with glass wastes and unsaturated polyester resin. The performances of material have been evaluated with different tests: microstructural analysis (SEM, packing factor), chemical/physical analysis (chemical resistance, water adsorption), and mechanical analysis (bending test, impact test, scratch test). The results obtained showed how it is possible to obtain a concrete polymer composed only of recycled glass. The results also showed the structural limits of the materials obtained allowing the relative percentages between coarse and fine fractions of glass to use to achieve PC with recycled glass.

Key words: glass waste, polymer concrete, recycling, unsaturated polyester

Received: March, 2018; Revised final: May, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Polymer concretes (PC) are composite materials formed by incorporating inorganic aggregates into polymers, they are used in a range of civil and structural applications such as bridge decking, concrete crack repair materials, pavement overlays, hazardous waste containers, sewer pipes and decorative constructional panels. Due to their specific properties including; higher mechanical strengths, and lower weights, excellent bonding to different substrates, higher resistance to corrosive environments and chemical attacks, faster curing and lower permeabilities. The aggregates can be silicates, quartz, quartz sand, crushed stone, gravel, limestone, calcareous, granite, clay, etc. In the composition different types of fine materials such as: fly ash, silica fume, glass fiber, carbon fiber, etc. can be used to improve the properties of polymer concrete. The aggregates in weight percentages between 60% and 95% are used, for example are used sand and gravel between 60 and 80% to produce pipes and structural components, while is used quartz sand in percentage up to 95% to produce kitchen tops, desks tops, and worktops. Various polymers have been used in fabrication of PCs such as unsaturated polyesters, epoxies, acrylics, polyuretan (Agavriloaia et al. 2012). During hardening, the polymer react through their unsaturated groups, the chemical reaction is isothermal and is called cross-linking (Lipovsky, 2006). The production process associated with it is referred to as curing, and the resulting polymer binder is a thermosetting polymer (Elalaoui et al., 2012). In concrete polymers the use of recycled materials is widely studied, both with the introduction of inorganic and organic recycled materials (Barbuta et al., 2016; Hodul et al., 2016; Shi-Cong et al., 2013; Pozzi et al., 2013; Taurino et al., 2015; Saribiyik et al., 2013; Shao et al., 2000). This research has investigated on how to use waste glass ground from cathode ray tubes (CRT panel glass) for the realization of polymer concretes. CRT glass originate from the treatments carried out on television sets and computer monitors permit the separation of the cathode-ray tube (CRT) which is two thirds of the entire weight of these apparatus and consists for 85% of glass (Andreola et al., 2010). Color CRTs generally are composed by four different glasses each one having a particular chemical composition. Panel (screen, the front part) a very homogeneous barium (9-11 wt%) –strontium (8-10 wt%) glass, of a greenish-blue color whose weight is about two-third of the whole CRT. Cone (the hidden part inside the TV set) a lead (18-20 wt%) glass, whose weight is about one-third of the whole CRT. Neck a glass with a very high lead content enveloping the electron gun. Frit (the junction between the panel and the cone) a low melting lead glass, included only in color CRTs. The separated glasses after reclaiming process become a not dangerous residue and represent a useful raw material not only in closed-loop recycling but also in open-loop one.

In the polymer concretes both glass from screens (panel) are potentially acceptable even if they must be supplied with particular characteristics of homogeneity, cleanliness, etc. The research was developed in collaboration with Stena Technoworld, a company specializing in the recycling of waste glass from cathode ray tubes. Analyzing the recycled glass produced by Stena, it was decided to direct research into the production of kitchen tops, desk tops and worktops using Stena glass instead of quartz sand. These materials industrialmente classificati come quartz composites are produced whit unsaturated polyester resins (5-8% by weight), quartz (95-92% by weight) and colored pigments (Fugazzi,1999; John, 2006). The choice of working on these products was made because the recycled glass produced by Stena has a particle size distribution compatible with the quartz sand used for quartz composites.

2. Case studies

2.1 Materials

The materials used for the realization of new polymer concretes are the unsaturated polyester resin, glass wastes from cathode ray tube and quarz sand. Unsaturated polyester resin (UP) is a category of thermosetting polymers which is widely used in fabrication of quartz composites.

Such due to their suitable processing characteristics, thermal stabilities, chemical resistance and comparatively low prices. The polymeric matrix is an unsaturated polyester resin dispersed in styrene and methacrylate, provided by Carlo Riccò Company (Correggio Italy). Table 1 shows the characteristics before curing.

Table 1. Characteristic of the unsaturated polyester resin before curing

Content methacrylate	5±1 %
Content styrene	27-31 %
Viscosity at 25°C	450–550 mPa·s
Appearance liquid resin	Limpid, Green
Stability at 80°C	24hours

This unsaturated polyester is accelerated with a complex of cobalt, and catalyzed with methyl ethyl ketone peroxide (MEKP) therefore the crosslinking occurs at room temperature with the simple addition of a peroxide. In Table 2 are reported the Gel Time and Curing of the resin and the temperature range in which the reaction exothermic peak may occur.

Table 2. Gel time and curing of unsaturated polyester resin

Gel time	20 – 38 (min.)
Exothermic peak	185° – 205 °C
Curing time	28 – 53 (min.)

For glass wastes, two granulometric fractions obtained by dry milling of CRT glass were used, one with a coarse granulometry and one with fine granulometry. Stena Technoworld, a factory in Angiari (It), has provided the coarse and fine CRT panel glass wastes. The composition of glass fractions of CRT panel glass has been obtained by XRF analysis, the data show a barium glass with a low concentration of dangerous elements (Table 3).

Table 3. Chemical composition (% in weight) of the CRT panel glass by XRF analysis

Oxides	***% in weight***
SiO_2	**56.87**
Na_2O	**12.89**
SrO	**8.52**
BaO	**7.95**
K_2O	**7.29**
Al_2O_3	**3.76**
ZrO_2	**1.41**
ZnO	**0.63**
TiO_2	**0.38**
Fe_2O_3	**0.22**
NiO	**0.03**
PbO	**0.02**
CoO	**0.01**
CaO	**0.01**
MgO	**0.01**
Tot.	**100**

Coarse CRT panel glass has been used to produce the coarse fraction of the filler, used to make the composites. The particles size distribution of the coarse CRT panel glass is resulted to be a monomodal (Fig. 1), with a peak around 200 microns. The particles size distribution has achieved with the use of a Micromeritics MASTERSIZER 2000 laser particle analyzer. The fine CRT panel glass is used to produce the fine fraction of the filler, used to make the samples. In this glass the particles size distribution shows a peak around 20 micron (Fig.2) and the microstructure of the particles are visible in Fig. 4, where the presence of very fine particles is very high. The quartz sand used show a bimodal particles size distribution (Fig. 3) with the peaks at 300 and 35 microns.

The first peak represents particles size the coarse fraction that gives the main structure to the composite. The second peak represents particles size the fine particles that gives to the structure a good level of compaction. The chemical analysis carried out with XRF showed a content of SiO_2 of 99.98%.

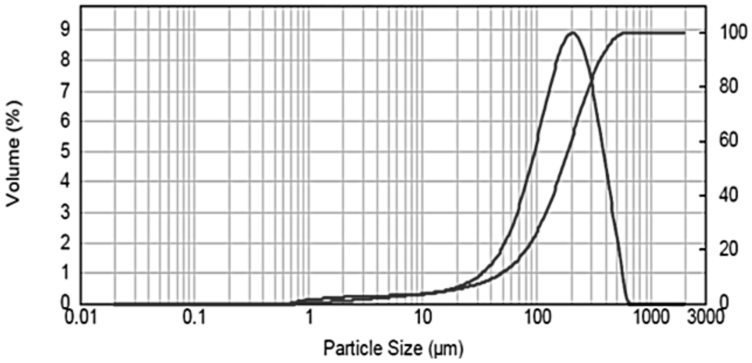


Fig. 1. Particle size distribution coarse CRT panel glass, is show a peak at 200μm

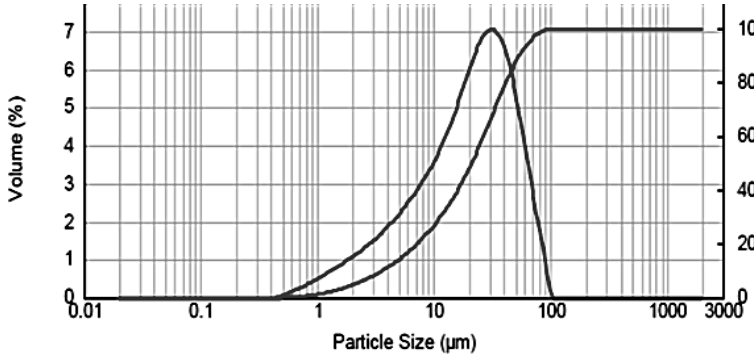


Fig. 2. Particle size distribution of fine glass CRT

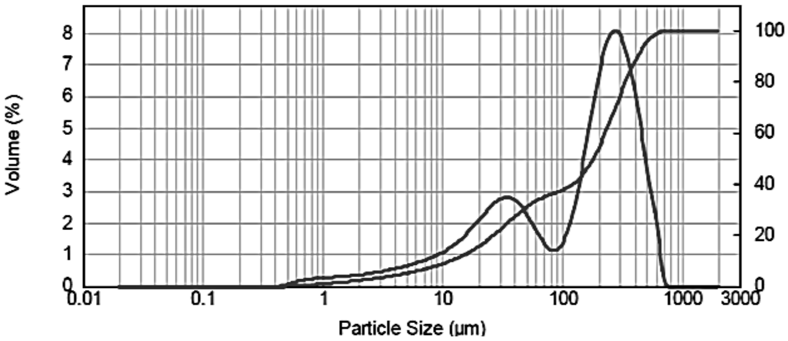
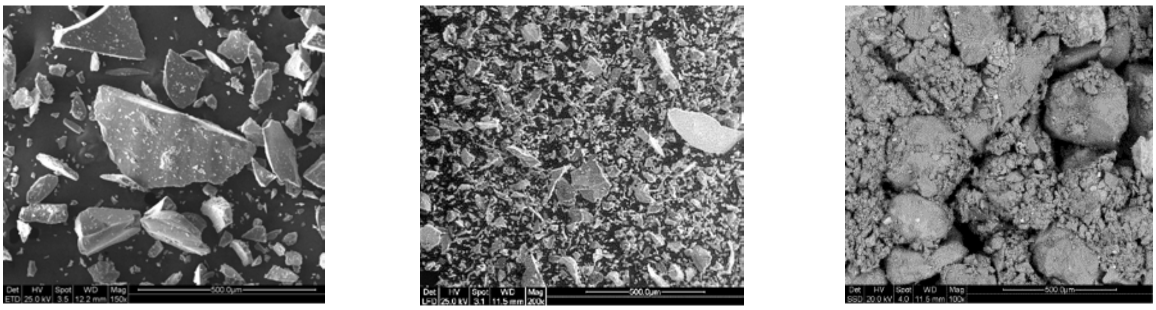


Fig.3. Quartz sand particle size distribution, peaks at 300 and 35μm



(a) (b) (c)

Fig. 4. ESEM micrographs of coarse (a), fine (b) CRT panel glass and quarz sand (c)

On the glasses and sand used, a morphological analysis was performed using an electron microscope (ESEM).The micrographs (Fig. 4) they showed that the glass is made up of particles with heterogeneous diameter and morphology with sharp edges of the grains, due to the dry grinding of the glass carried out in the CRT treatment plant. On the other hand, the quartz sand has a more rounded morphology of the particles, evident effect of the different processing phase to which it is subjected.

2.2. Sample preparation

Four sets of CRT glass samples were produced for the work, and a series of quartz sand was used as reference (code samples QSL). Samples with the glass were prepared by adding the fine CRT glass to the coarse CRT glass up to a percentage of 30%. Samples prepared with quartz sand were made to reproduce quartz compounds in the laboratory, these samples were used as reference samples. In consideration of the average percentage used in industrial quartz composites, the samples were made with a ratio between filler and unsaturated polyester resin to 92/8 by weight. The samples have been prepared by mixing the filler with resin using a mechanical mixer. The suspension obtained has been casting at 25°C into a 10x10x2.5 cm metal mold, and for cross-linking pressed at 10 bar at 25°C for 1 hour, using one Carver hydraulic press. After the hardening phase the samples have been cured to 80°C for 4 hours in a stove to complete cross-linking. To improve the adhesion between polymer and filler, a silane coupling agent (vinyltriethoxysilano) has been added to the samples. This addition has been made at 1% in weight on the filler. The composition of samples is shown in Table 4, with percentages in weight of glass, quartz sand and unsaturated polyester resin. Five samples have been made for every composition.

2.3 Testing on samples

On the produced samples we have carried out the following analyzes:

- Water absorption by immersion test in distilled water for 24 hours at 25° C.
- Chemical resistance in hydrochloric acid (10% w/w) and potassium hydroxide (10% w/w) by immersion test for 24 hours at 25° C.
- True density measured with the helium pycnometer ACCUPYC 1330, Micromeritics instrument.
- Packing factor
- Drop weight test performed to the standard ASTM D3029 using Dynatup 9250HV, Instron.
- Three points bending test performed to the standard UNI EN ISO 178, using a testing machines Instron 3340.
- Microstructural analysis with ESEM-Quanta200-FEI.

3. Results and discussion

3.1. Microstructural analysis

As we expected, the first result we have observed that the addition of fine fraction up to 30% in weight creates samples with a good level of compaction. The microstructural analysis with SEM (Scanning Electron Microscope) to show us the gradual addition of fine fraction (with particle size around 35 microns) decreases the porosity with a good compaction in the sample, with 30% in weight of fine fraction (sample Vg*/Vf/R 62/30/8) (Fig.5).

If we compare the particles size distribution of the quartz sand samples (QSL) with the glass samples we can see that only the sample Vg*/Vf/R 62/30/8 (Fig. 6) has a particles size distribution similar to the quartz composite, while the other samples have a smaller fine fraction.

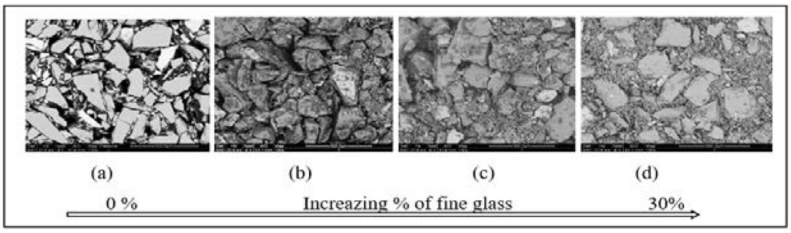


Fig. 5. ESEM micrographs of glass samples: (a) 0%; (b) 10%; (c) 20%; (d) 30% of fine glass

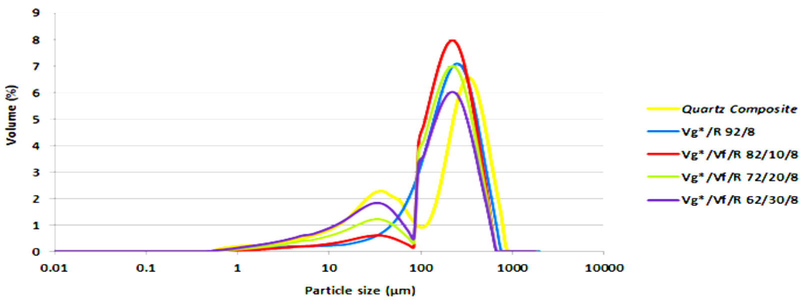


Fig. 6. Comparison particle size distribution of samples glass and quartz composite

3.2. Packing factor

The packing factor indicates the fraction of the volume of the structure occupied by particles. It is a dimensionless number and its values run between 0 and 1. The packing factor is calculated by assuming that each particle is represented as a rigid sphere and in particular, it is obtained from the ratio between the apparent density and the real density of the powder. Table 5 shows the data obtained from the density measurement and the value of the packing factor. The packing factor reaches the highest value with the sample at 30% of fine glass and the values are similar to those observed for the QSL samples.

Table 5. Density data and packing factor

Samples	*Apparent Density (g/cm^3)*	*True Density (g/cm^3)*	*Packing factor*
QSL	2.91	2.93	0.99
Vg*/R 92/8	1.98	2.60	0.76
Vg*/Vf/R 82/10/8	1.99	2.57	0.78
Vg*/Vf/R 72/20/8	2.08	2.57	0.81
Vg*/Vf/R 62/30/8	2.81	2.87	0.98

3.3. Chemical resistance and water adsorption

The chemical resistance has been evaluated in hydrochloric acid and potassium hydroxide with an immersion test of 24 hours at 25°. Table 6 shows the weight loss data obtained with the samples and other values, added as a comparison, obtained with a sample of pure resin. The increase of glass fine fraction in the glass composites decreases the chemical resistance, in contrast, the chemical resistance observed for the QSL samples was the highest.

All the samples have a better resistance in acidic medium (HCl), with lower removal rates compared to the attack in the basic environment (KOH). The unsaturated polyester resins, in fact, have a low resistance in a basic environment. It should be noted that with 30% of fine glass there is a strong increase in weight loss, especially in an acid environment.

Table 6. Chemical resistance data

	% weight loss HCl	*% weight loss KOH*
Resin	**0.04**	**0.45**
QSL	**0.05**	**0.49**
Vg*/R 92/8	**0.13**	**1.14**
Vg*/Vf/R 82/10/8	**0.33**	**2.31**
Vg*/Vf/R 72/20/8	**0.40**	**3.18**
Vg*/Vf/R 62/30/8	**2.35**	**7.87**

The most interesting data have been the increase of water absorption that is observed by adding fine glass in the samples (Table.7). This data is not related to the improvement of the packing factor, which increases with the growth in the percentage of fine glass in the samples.

Table 7. Water absorption of samples

	Water absorption %
QSL	2.54
Vg*/R 92/8	3.08
Vg*/Vf/R 82/10/8	4.97
Vg*/Vf/R 72/20/8	8.84
Vg*/Vf/R 62/30/8	9.79

The increase of the fine fraction glass makes possible to increase the level of compaction and the paking factor. The result is a very low residual porosity and consequently the decrease in water absorption. It is evident that this mechanism is valid for the samples produced only with quartz sand, while for the glass composites it is necessary to consider the interaction with the resin. The resin penetrates into the pores of the composite and the cross-linking closes the pores, sealing the composite and making it waterproof. When the cross-linking is blocked or the resin does not bind the particles, the porosity remains open and the composite results permeable. The data of water absorption on chemical degradation seem to indicate that the fine glass fraction interferes with the cross-linking mechanism, while with quartz sand there is no interference with the cross-linking reaction.

3.4. Mechanical analysis

The mechanical analysis data confirm the strong correlation with the percentage of fine glass used in the glass samples. The increase in the fine glass fraction leads to a decrease in the values observed in the bending tests (Fig. 7) and in the drop weight test (Table 8) compared to the QSL samples data. Only samples without fine glass present interesting results, with bending load values and impact energy better than the QSL samples. these results can be interpreted using the considerations made previously on the block of the mechanism of cross-linking. Only the development of a good cross-linking of the thermosetting resin allows obtaining good results in the mechanical tests.

Table 8. Data drop weight test

Sample	*Maximum load (N)*	*Energy at maximum load (J)*
QSL	1608 ± 25	1.51 ± 0.85
Vg*/R 92/8	1633 ± 30	1.56 ± 0.86
Vg*/Vf/R 82/10/8	1198 ± 24	1.02 ±0.10
Vg*/Vf/R 72/20/8	862 ± 9	0.44 ± 0.16
Vg*/Vf/R 62/30/8	852 ± 10	0.49 ± 0.23

3.5. Optimization polymer concrete

The observed behaviors of the mechanical and chemical properties are related to the partial inhibition of the formation of the lattice structure, that must bind the resin to the fine glass particles, with a consequent decrease of the chemical/physical and mechanical parameters. This is because the structure and chemical composition of the CRT panel glass particles do not allow an effective interaction between the glass surface and the polyester resin. To solve this problem, we have decided to increase the percentage of coupling agent from 1% to 4% in weight on glass. In this way, the compatibility between the glass surface and the resin tends to increase, allowing the formation of the lattice structure between particles and resin.

The results obtained show an increase in the chemical and mechanical properties of the samples obtained by increasing the silane (as observed in Table 9 for the KOH attack, Table 10 for the HCl attack, e Table 11 for water absorbption). The table shows the percentage change between the measured values before and after the percentage increase of the coupling agent. In particular, it is interesting to analyze this datum by observing that the major variations are recorded with the attack in KOH, while they are very limited in case of water absorption. The marked improvement in KOH resistance is an indication of an improvement in resin crosslinking, but the result of water absorption indicates that the porosity is not influenced.

Table 9. Chemical resistance in KOH.

Sample	*weight loss % (1% silane)*	*weight loss % (4% silane)*	*percentage variation*
QSL	0.49	/	/
Vg*/R 92/8	1.14	0.98	**14%**
Vg*/Vf/R 82/10/8	2.31	1.64	**29%**
Vg*/Vf/R 72/20/8	3.18	1.97	**38%**
Vg*/Vf/R 62/30/8	7.87	3.58	**54%**

Table 10. Chemical resistance in HCl.

Sample	*weight loss % (1% silane)*	*weight loss % (4% silane)*	*percentage variation*
QSL	0.05	/	/
Vg*/R 92/8	0.13	0.06	**54%**
Vg*/Vf/R 82/10/8	0.33	0.24	**27%**
Vg*/Vf/R 72/20/8	0.40	0.36	**10%**
Vg*/Vf/R 62/30/8	2.35	1.97	**16%**

The exception is the sample with 10% of fine glass, which shows a reduction in the absorption of 44%. Therefore, the increase in the percentage of coupling agent increases crosslinking in all the samples, but it develops a greater interaction between glass and resin only at a low percentages of fine glass. In the mechanical tests, we have an increase of the properties in the bending tests (as shown in Table 12), due to the fact that increases crosslinking.

Table 11. Water absorbption data

Sample	*absorbed water % (1% silane)*	*absorbed water % (4% silane)*	*Percentage variation*
QSL	2.54	/	/
Vg*/R 92/8	3.21	3.08	**4%**
Vg*/Vf/R 82/10/8	8.80	4.97	**44%**
Vg*/Vf/R 72/20/8	9.57	8.84	**8%**
Vg*/Vf/R 62/30/8	11.27	9.79	**13%**

Table 12. Stress bending data

Sample	*Stress bending 1% Silane (MPa)*	*Stress bending 4% Silane (MPa)*	*Stress Increasing %*
QSL	31 ± 3	/	/
Vg*/R 92/8	34 ± 4	39 ± 3	**13%**
Vg*/Vf/R 82/10/8	17 ± 1	22 ± 4	**23%**
Vg*/Vf/R 72/20/8	9 ± 3	15 ± 2	**40%**
Vg*/Vf/R 62/30/8	4 ± 1	6 ± 1	**33%**

4. Conclusions

The results obtained allow us to make the following conclusions.

The first conclusion is that it is possible to develop polymer composites loaded with CRT glass only if the percentage of fine glass is limited (<100μm). Comparing the results obtained with the specifications required for the various types of commercial composites, we can assume that it is possible to use our produced composites as thin panels usable as coatings. The composites for internal and external coatings have, as only requested property, a good resistance to bending, that can obtain by using only coarse CRT glass panel.

The second conclusion concerns the use of CRT fine glass. The data show a considerable criticality related to the interaction that this material develops with the resin. The use of coupling agents can partially solve the problem, in particular if the percentage of fine glass is used in low quantity (about 10%).

The third consideration points out that the structure of the glass particles is very irregular and because of it, it interferes with the formation of the lattice particles resin. This is a limiting factor, especially for the use of fine glass.

Finally, the fourth consideration regards the possibility of improving the properties of CRT glass/polymer composites. We believe that this is possible by working on crosslinking catalysts and coupling agents specifically selected to solve the criticality observed in the glass resin interaction.

References

Agavriloaia L., Oprea ST, Barbuta M, Luca C., (2012), Characterization of polymer concrete with epoxy polyurethane acryl matrix, *Construction and Building. Matererial*. **12**, 190-196.

Andreola F., Barbieri L., Lancellotti I., (2010), *End of Life-Materials: WEEE Glass Recovery in Construction Sector*, Proc. of the 2nd Int. Conf. on Sustainable construction materials and technologies, Ancona, Italy.

Barbuta M. Rujanu M. Nicuta A., (2016), Characterization of polymer concrete with different wastes additions, *Procedia Technology*, **22**, 407–412.

Barbuta M, Harja M, Baran I., (2010), Comparison of mechanical properties for polymer concrete with different types of filler, *Journal Materials Civil Engineering*, **22**, 696–701.

Elalaoui O, Ghorbel E, Mignot V, Ben Ouezdou M,. (2012), Mechanical and physical properties of epoxy polymer concrete after exposure to temperatures up to 250 C, *Construction and Building. Matererial*, **27**, 415–24.

Fugazzi R.A., (1999), Solid surface composite and method of production. USA Patent No. *5976670*.

Garbacz A. Sokolovska J.J., (2013), Concrete like polymer composite with fly ash-Comparative study. *Construction and Building Materials*, **38**, 689-699.

Golestaneh M. Amini G. Najafpour D. Beygi M.A., (2010), Evaluation of mechanical strength of epoxy polymer concrete with silica powder as filler, *World Applied Science Journal*, **9,** 216-220.

Haidar M., Ghorbel M., Toutanji H., (2011), Optimization of the formulation of micro-polymer concretes, *Construction and Building Materials* **25**, 1632–1644

Harja M, Barbuta M, Rusu L., (2009), Obtaining and characterization of the polymer concrete with fly ash, *Journal Applied Science*, **9**, 88–96.

Hodul J., Hodná J., Drochytka R., Vyhnánková M., (2016), Utilization of waste glass in polymer concrete, *Materials Science Forum*, **865**,171-177.

John P., (2006), Solid surface composites, USA Patent No. *20060112646*.

Kaya A. Kar F, (2016), Properties of concrete containing waste expanded polystyrene and natural resin, *Construction and Building Materials*, **102**, 572–578.

Lipovsky K., (2006), *Overcoming Vitrification of Polyester Solid Surface Resin for Kitchen Environment Using Postcure*, In*: Composites Convention and Trade Show American Composites Manufactures Association*, St. Louis, USA.

Lokuge W. Aravinthan T., (2013), Effect of fly ash on the behaviour of polymer concrete with different types of resin, *Materials and Design*, **51,** 175–181.

Pozzi P., Taurino R., Zanasi T., (2013), New composite materials based on glass waste, *Composites: Part B*, **45**, 497–503.

Pozzi P., Taurino R., (2015), *New Polyester Composites From Recycling Glass*, In: *Atti Ecomondo*, *2015*, Rimini (IT).

Saribiyik M., Piskin A., Saribiyik A., (2013), The effects of waste glass powder usage on polymer concrete properties, *Construction and Building Materials*, **47**, 840–844.

Shao Y., Lefort T., Moras S., Rodriguez D., (2000), Studies on concrete containing ground waste glass, *Cement Concrete Research*, **3**, 91–100.

Shi-Cong K., Chi-Sun P., (2013), A novel polymer concrete made with recycled glass aggregates, fly ash and metakaolin, *Construction and Building Materials*, **41**, 146–151.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2455-2463
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

CONTROL MEASURES FOR *Cyanobacteria* AND *Cyanotoxins* IN DRINKING WATER

Sabrina Sorlini[1]*, Maria Cristina Collivignarelli[2], Alessandro Abbà[1]

[1]*Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, via Branze 43, 25123, Brescia, Italy*
[2]*Department of Civil Engineering and Architecture, University of Pavia, via Ferrata 1, 27100 Pavia, Italy*

Abstract

Algal bloom can represent a serious consequence of the eutrophication of surface water. Some of these algae, called cyanobacteria, are of particular interest for their effect on human health due to their capacity to produce cyanotoxins. In many countries, in fact, there are important problems of poisoning attributed to toxic cyanobacteria and contamination of water sources (specially lakes) resulting in increased cyanobacterial growth. *Cyanobacteria* can become particularly harmful for humans when water is used for drinking consumption; in fact, they can generate many problems in drinking water treatment plants (increase of solids load, bacterial growth in sand and GAC filters, low efficiency of disinfection) and in the distribution system (growth in reservoir tanks and pipes). Moreover, algal toxins produced by cyanobacteria can be released during water treatment and can persist in water until final consumption. For these reasons, appropriate technologies should be used for water treatment in order to efficiently remove cyanobacteria cells, to reduce the risk of cyanotoxins release and to efficiently remove dissolved toxins. In this work, an overview on the main conventional and advanced processes for *Cyanobacteria* and *Cyanotoxins* removal from drinking water will be presented. Moreover, the main results of an experimental research on the removal of *Cyanobacteria* cells (coagulation/flocculation, sand filtration, GAC filtration, chlorine oxidation) and of cyanotoxins (activated carbon) will be discussed.

Key words: Cyanobacteria, Cyanotoxin, drinking water, microcystin-LR

Received: March, 2018; Revised final: September, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The use of lake water for drinking purpose can present some quality problems due to the presence of algae, turbidity, color and odorous compounds. *Cyanobacteria*, known as blue-green algae, are photosynthetic algae with dimension ranging from 1 µm to more than 100 µm.

They can be aggregated in colonies or filaments, and their growth and formation of blooms is influenced by a variety of physical and chemical factors like temperature, length of daylight, macronutrients (phosphorous and nitrogen) concentration, micronutrients (iron and molybdenum) concentration, alkalinity, pH and climatic conditions (Health Canada, 2002).

They are very common in lakes, artificial reservoirs, small natural reservoirs and rivers with weak flow; their proliferation is favored by the presence of light, high temperature, low turbulence, presence of nutrients. *Cyanobacteria* sanitary relevance is of concern for their capacity to produce algal toxins with toxic effects for human health.

Of the more than fifty known species, those most commonly associated with toxicity are *Microcystis, Planktothrix, Anabaena, Aphanizomenon*, *Nodularia*, *Schizotrix* capable of producing the following toxin classes:

* Author to whom all correspondence should be addressed: e-mail: sabrina.sorlini@unibs.it; Phone: +39 030 3711299

- Neurotoxins (toxic to the nervous system): *Anatoxin-a, Anatoxin-a (s), Homo-anatoxin-a, (Saxitoxin), Paralytic Shellfish Poisons*;
- Hepatotoxins (toxic to the liver): *Microcystina, Cylindrospermopsin*;
- Endotoxins (contact dermo-irritants): *Debromoaplysiatoxin, Lyngbyatoxin, Aplysiatoxin*.

The hepatotoxins (in particular the *Microcystin*) are the most frequent and can be released from the genera *Microcystis, Planktothrix, Anabaena, Aphanizomenon, Nodularia, Nostoc, Cylindrospermopsis* and *Umezakia*. Among the *Microcystins*, the most frequent and present in greater concentration is the *Microcystin-LR* (with toxic effect for humans), which is generally contained in the algal cell but can be easily released following cell lysis. *Microcystin-LR* is a potent inhibitor of eukaryotic protein serine/threonine phosphatases 1 and 2A; due to its toxic and carcinogenic effect for human health, a provisional guideline value of 0.001 mg/L (for total *Microcystin-LR*, free plus cell-bound) was indicate by WHO (WHO, 1999; WHO, 2006, WHO, 2011) and Funari et al. (2014).

Table 1 shows a correspondence between the cyanobacterial species and the toxins produced.

Table 1. Main cyanobacterial species and related toxins (WHO, 2004)

Cyanobacterial species	***Toxins***
Anabaena spp.	Anatoxin-a(S), anatoxin-a, microcystins, saxitoxins
Anabaenopsis millenii	Microcystins
Aphanizomenon spp.	Anatoxin-a, saxitoxins, cylindrospermopsin
Cylindrospermum spp.	Cylindrospermopsin, saxitoxins, anatoxin-a
Lyngbya spp.	Saxitoxins, lyngbyatoxins
Microcystis spp.	Microcystins, anatoxin-a (minor amount)
Nodularia spp.	Nodularins
Nostoc spp.	Microcystins
Oscillatoria spp.	Anatoxin-a, microcystins
Planktothrix spp.	Anatoxin-a, homoanatoxin-a, microcystins
Raphidiopsis curvata	Cylindrospermopsin
Umezakia natans	Cylindrospermopsin

Relevant concentrations of cyanotoxins in surface waters have been registered in many countries: China, Portugal, Australia, Finland, USA (WHO, 1999) and significant outbreaks in drinking water have been registered in Brazil, Zimbabwe, Cameroon, China, Austria and Australia (Health Canada, 2002). In Italy cyanobacterial blooms affect many regions and the main frequent genera are *Microcystis* (*M. aeruginosa* and *M. flos-aquae*), *Aphanizomenon* (*Ap. flos-aquae*) and *Anabaena* (*A. flos-aquae* and *A. planctonica*) and *Planktothrix rubescens* (Funari et al., 2006; Mattei et al., 2005).

In the most case, the cyanobacteria toxins naturally exist in intracellular form and are retained within the cells; so, when the cells die the toxins are released in water. This behavior can occur in the drinking water treatment plants after the application of some processes: in this case, the cyanobacteria toxins can increase.

The adoptable alternatives to reduce the risk of presence of cyanobacteria and cyanotoxins in water for human use are:

- an appropriate choice of source of supply, so as to avoid drinking water from contaminated sources;
- the reduction of nutrient supply (in particular phosphorus) to the source of supply;
- the use of adequate treatments for the removal of algae;
- the use of adequate treatments for the removal of algal toxins.

Below we will analyze the main treatments used in water treatment, paying particular attention to the effect they can have on the removal of cyanobacteria and cyanotoxins.

2. Technologies for cyanobacteria and cyanotoxins removal

Appropriate technologies for cyanobacteria control must reflect proper management of the watershed and reservoir to prevent algal growth, correct treatments for the removal of both cyanobacteria and their toxins and an appropriate monitoring program. In the following paragraphs, an overview on the treatment processes for their removal in drinking water treatment plants will be presented and discussed.

2.1. Pre-treatments

Micro sieving (mesh 20 - 40 μm) represents a valid technique for the physical separation of algal cells, with very variable yields depending on the cyanobacterial species (algal size), the cell aggregation (single cell, aggregates, filaments, etc.) and the presence of solids in water. Fine screens can cause cell lysis, and consequent release of toxins, which could occur because of cell rupture during filtration (WHO, 1999). Another effective pre-treatment is aeration, especially for the removal of volatile and gaseous compounds, such as carbon dioxide, hydrogen sulfide and volatile organic compounds associated with algal decomposition (WHO, 1999).

2.2. Chemical oxidation

Chemical oxidation is a widely used treatment in water purification and can be applied as pre-oxidation, intermediate oxidation or final disinfection. The specific effect may be that of cellular inactivation of algae with their subsequent immobilization in the flocs or inside the filters. Moreover, pre-oxidation can be considered one of the main methods of improving the subsequent coagulation and filtration processes, since it is able to reduce both the organic coating that forms on colloidal particles and the stabilizing effect that algae can have on colloids and compromising their removal (Edzwald, 1993; Gibbs, 1983).

It is therefore evident that the practice of pre-oxidation (or oxidation along the treatment line) is a very controversial choice and must be carefully assessed based on the content of algal cells that can favor the formation of oxidation by-products and the release of cyanotoxins. Therefore, the application of oxidative treatments is optimal after having carried out a physical separation of algal cells and is mainly addressed to the removal of cyanotoxins.

The most commonly used oxidizing agents, based on their cost and the possibilities of their use, are chlorine or hypochlorite, chlorine dioxide, ozone, potassium permanganate. Tsuji et al. (1997) observed that microcystin-LR (MC-LR) removal after 60 minutes contact time was about 36% with a chlorine dose of 0.7 mg/L and 100% at a dose of 2.8 mg/L. Although these results seem to encourage the use of chlorine for toxin removal, pre-oxidation of the cells must be avoided, because it increases the risk of toxin release from algae and produce trihalomethanes during water treatment. Acero et al. (2005) found that chlorination could be applied in pre-oxidation and disinfection processes for cyanobacterial toxin control if the pH is kept below 8. Merel et al. (2010) found that chlorination is very effective on microcystins and its efficiency depends on pH, chlorine dose and oxidant nature.

As concerns chlorine dioxide, Kull et al. (2004) found that ClO_2 is not a suitable oxidant for the degradation of microcystins in drinking water treatment processes; moreover ClO_2 is rapidly consumed by fulvic and humic acids, leaving less ClO_2 residual to oxidise MC-LR and the generated oxidation products resulted to be nontoxic (Kull et al. 2006).

Montiel and Weltè (1998) have shown that ozone can represent a preliminary treatment able to improve the removal performance of algae from 75 to 95% with subsequent flotation treatments, rapid filtration on biolith or slow filtration on sand. The same conclusion was reached by Bauer et al. (1998) in the study of water treatment of the Thames, by analyzing the effects on multilayer pre-oxidation filtration with ozone and in-line filtration (dosing of coagulant inlet to filtration) with iron sulphate individually and combined: algae removal increased from about 50% without chemical additions to 90% with ozone and iron. Ozone pre-oxidation has proved particularly effective in the destruction of some classes of toxins, although many researchers agree that dosages and contact time depend on the quality of the water and the nature of the substance to be oxidized (Croll and Hart, 1996; Rositano, 1996).

A good removal of dissolved toxins was observed, with yields of 95% on MC-LR at a dose of 1 mg/L of potassium permanganate for 30–minutes contact time; however, the effect was decidedly negligible on intracellular toxins inside the algal cells, whose release, however, could be promoted during treatment (Lam et al., 1995). A kinetic database has been compiled by Rodrìguez et al. (2007a, b) for different oxidants and the results showed that permanganate can effectively oxidize *anatoxin-a* and MC-LR, while chlorine can oxidize *cylindrospermopsin* and MC-LR and ozone is capable of oxidizing all three toxins with the highest rate.

2.3. Coagulation/flocculation/sedimentation

The effectiveness of this treatment in algae removal is greatly influenced by the typical characteristics of algal cells such as the high motility and the elongated and filamentous geometry that can compromise the entrapment in the flakes. Bernhardt and Clasen (1991) have shown that there is a direct proportionality between the total surface area of the algae particle / cell, then the cell concentration, and the coagulant dosage required for the flocculation process, as long as the cell is more or less spherical and smooth. Hoeger et al. (2004) observed a removal of cyanobacteria cells of 99% with coagulation, flocculation and sedimentation. The removal with coagulation and flocculation of small and spherical algal cells is better than filamentous cells like *Planktotrix rubescens* (Bernhardt and Clasen, 1991). Coagulation/flocculation has a negligible effect on extracellular toxins removal. Rositano and Nicholson (1994) found no toxins removal by comparing ferric sulphate, alum and polyaluminium chloride.

The effectiveness of sedimentation is generally not satisfactory, not only because of the inevitable escape of the smaller flocs, but also because in the relatively long retention times of the water in the basin it is easier for the algae with greater motility to "free themselves" from the trap of the floc. However, as generally the algal flocs are very slow to settle, it is good to apply sedimentation with relatively low flow rates to facilitate the process (Edzwald, 1993). However, in the same basin, "new" algae can grow due to light and long retention time.

2.4. Dissolved air flotation

Although sedimentation is still the most widespread system for primary water clarification, flotation is indicated for the separation of naturally dense particles (such as algae). Hargesheimer and Watson (1996) confirm that flotation can obtain removals included in the range 29 - 85% against sedimentation that reaches a maximum of 49%. With floatation tests performed on waters rich in algae (>50,000 cells/L, 50% of which are blue-green algae), the removal percentages obtained are between 95% and 99%. Also, in the case of Dissolved Air Flotation (DAF), the efficiency of the treatment often depends on the type of algae, as well as on its concentration with removals between 57 and 100% (WHO, 1999).

2.5. Rapid sand filtration

Rapid sand filtration can remove up to 75% of cyanobacteria but its efficiency is very variable; if this treatment is combined with a coagulation/flocculation or ozone oxidation, algae removal increases up to 90%. Algae with high motility (*Cryptomaonas*, *Rhodomonas*, etc.) are very resistant to filtration and the removal is generally lower than 50% (Petrusevski et al., 1995). Direct filtration seems to be more effective than rapid sand filtration (Bauer et al., 1998) on cyanobacteria removal. Otherwise, low sand filtration (hydraulic load of 0.5 - 1 m/h) is very efficient for cyanobacteria removal (WHO, 1999).

Some limits of the filtration treatment are the low yield of removal in the case of algae with high motility, the possibility of algal proliferation on the filtering support and the effect of cell lysis induced by the filter.

2.6. Activated carbon adsorption

Among the conventional processes, activated carbon adsorption, which is commonly adopted in drinking water treatment plants, appears to be one of the most effective option. The activated carbons derived from wood showed very interesting results, due to their high mesopore volume: Drikas (1994) showed that the use of 25 mg/L of wood-based PAC (with a contact time of 30 minutes) reduce the concentration of microcystin-LR from 50 μg/L to a value lower than 1 μg/L. MC-LR adsorption was improved with activated carbon with higher mesopore and macropore volume while Natural Organic Matter (NOM) caused a reduction in the capacity of carbon for MC-LR (Huang et al., 2007). Wang et al. (2009) observed that GAC filtration has shown to be promising as it is not only an efficient adsorbent, but also can support biodegradation of microcystins, extending the lifetime of this application. Up to 70% removal of microcystin-LR was still observed after 6 months of operation of the sterile GAC column, indicating that adsorption still played a vital role in the removal of this toxin.

The adsorption efficiency of the PAC for both MC-LR and MC-LA was affected by the amount of DOC in the water with lower adsorption for both compounds with higher DOC concentration (Cook and Newcombe, 2008). Pendleton et al. (2001) observed that both the adsorbent surface chemistry and the primary micropores volume have virtually no influence on the amount of MC-LR adsorbed and an adjustment of the solution pH conditions, to low pH, results in an enhanced adsorption of MC-LR. Craig and Bailey (1995) showed a significant breakthrough of MC after 5 months of operation of a GAC filter using an Empty Bed Contact Time (EBCT) of 15 minutes. In addition, they showed that an EBCT of 6 minutes resulted in a significant microcystin breakthrough after 1 month of operation. Moreover, Bernezeau (1994), using pilot scale tests on water with microcystins at 30-50 μg/L, showed microcystins removal higher than 90%, until 7,000-10,000 Bed Volumes (BV). After these values, the efficiency dropped to less than 63% due to the GAC saturation with dissolved organic carbon (DOC). The removal of MC-LR in a real treatment plant was evaluated by Lambert et al. (1996) that found that the conventional treatment processes combined with activated carbon generally removed more than 80% of MCs from raw water, with a residual concentration of 0.1 - 0.5 mg/L for both GAC and PAC treatment facilities. Sorlini and Collivignarelli (2011) observed a higher removal of MC-LR with mineral than vegetal activated carbon and limit concentration for MC-LR was reached after about 4,000 BV during column tests.

2.7. Combined treatments

The chemical oxidation processes are generally effective in cyanobacteria inactivation but they can cause toxin release due to the cells die and break open. The advantage is that algal cells, after inactivation, are immobilized and can be more easily removed by means flocculation or granular filtration. Among the chemical oxidation processes, ozonation is the most effective in cyanobacteria inactivation. Montiel e Weltè (1998) observed that ozone applied before flotation, rapid or slow sand filtration, increases algal cells removal from 75% to 95%. A treatment work including pre-oxidation, coagulation, flotation and filtration removes an average 96% of influent cells, while rapid gravity filters alone removes 63-75% (Henderson et al., 2008).

2.8. Advanced oxidation processes (AOPs)

AOPs are oxidation processes obtained by combining simultaneously different oxidants mainly H_2O_2, UV and O_3. Some researchers observed that H_2O_2 and UV radiation alone determine a negligible destruction of MC-LR (Tsuji et al., 1994). Similar results were observed studying the oxidation of MC-LR (10 mg/L) with variable-intensity UV radiation (up to 12 μE/(cm^2 s)) for a maximum exposure time of 60 minutes, showing no significant toxin reduction (Gajdek et al., 2004). Other researchers studied the effect of combining different UV radiation and H_2O_2 doses as well as different pH on MC-LR oxidation (0.15 mg/L). The authors found that H_2O_2 is ineffective, UV radiation ensures 85% oxidation yield after 90 minutes contact time (UV dose = 153 μW/cm^2 and pH = 7.2), while H_2O_2/UV process show a 95% oxidation yield after 32 minutes contact time (UV dose = 153 μW/cm^2, pH = 7.2 and H_2O_2 concentration of 2 mmol/L). Moreover, MC-LR degradation yields decrease with increasing pH (Li et al., 2009).

2.9. Membrane filtration

As concerns membrane processes, Chow et al. (1997) reported yields of removal of Microcystis aeruginosa over 98% by ultrafiltration with flat-sheet membranes. In the same study, experiments with different reverse osmosis membranes, however, showed removal yields for MC-LR of 96%. A study from Campinas and Rosa (2010) demonstrated that ultrafiltration with a hollow fiber cellulose acetate membrane was an effective barrier against cyanobacteria, producing water free of M. aeruginosa and with a turbidity below 0.1 NTU, while it was ineffective against *Microcystin*.

The removal of intra and extra-cellular toxins by means of ultrafiltration and nanofiltration was studied by Gijsbertsen-Abrahamse et al. (2006). The ultrafiltration treatment was very effective in removing intracellular toxins, with a removal efficiency higher than 98%, while nanofiltration was effective in the removal of extracellular toxins, with a removal efficiency ranging between 96 and 99% depending on the type of toxin considered. Teixeira and Rosa (2006) confirmed the high removal efficiency of dissolved MC-LR and *anatoxin-a* by nanofiltration. Dixon et al. (2011) studied the removal of intra and extra-cellular cyanotoxins using a multi-barrier treatment consisting of coagulation, powdered activated carbon (PAC) adsorption and ultrafiltration. The system was able to reduce 90% of *saxitoxin* and 92% of intracellular *microcystin*. Other authors (Sorlini et al., 2013) observed that the removal rates of cyanobacteria and total algae content, with the use of microfiltration, are greater than 98% and between 98% and 99%, respectively.

2.10. Comparison among treatments

Treatment effective for the removal of cyanobacteria includes filtration to remove intact cells. Treatment effective against free *microcystins* in water (as well as most other free cyanotoxins) includes oxidation through ozone or chlorine at sufficient concentrations and contact times, as well as GAC and PAC applications (WHO, 2015). Table 2 reports an overview on the treatment performance for cyanobacterial cells and cyanotoxins removal (WHO, 2015).

A more detailed comparison among the performance of the treatment processes for the removal of cyanobacterial cells, intra- and extracellular cyanotoxins is reported in WHO (2015), as listed in Table 3.

3. Case study: lab-scale tests on conventional processes for cyanobacterial cells removal

The case study presented in this paper concerns some experimental tests carried out at lab-scale in order to optimize the functionality of conventional treatment processes applied in a full-scale drinking water treatment plant. Many utilities apply conventional treatments in their plants and the presence of a new pollutant often requires the optimization of conventional treatments already present in the plant rather than the use of advanced technologies and new plants. In particular, the tests, such as those described in this case study, are a useful support for assessing the performance of the treatment processes, already existing or of future implementation for upgrading a drinking water treatment plant. Therefore, these tests can guide the water company in choosing the best solutions to ensure a good performance in removing specific pollutants.

In this case study, experimental tests were performed in order to evaluate the efficiency of cyanobacterial cells removal with the following conventional treatments: micro screen, coagulation/flocculation, flotation, sand filtration, granular activated carbon (GAC) filtration and chlorine oxidation.

Table 2. Treatment performance for cyanobacterial cells and cyanotoxins for which guideline values have been established (WHO, 2015)

	Chlorination	***Ozonation***	***Coagulation***	***Activated carbon***	***Advanced oxidation***	***Membranes***	***Biological treatment***
Cyanobacterial cells			+++			+++	
Cyanotoxins	+++	+++		+++	+++		+++

+++ = 80% or more removal.

Table 3. Treatment performance for cyanobacterial cells and cyanotoxins (WHO, 2015)

	Cyanobacterial cells, intracellular cyanotoxins, geosmin and 2-methylisoborneol	***Extracellular free cyanotoxins***	***Extracellular (free) geosmin and 2-methylisoborneol***
Coa~~u~~gulation/sedimentation	+	-	-
Riverbank and slow sand filtration	+	+	+
Membrane filtration	+	-[a]	-[a]
Dissolved air flotation	+	-	-
Activated carbon	-	+	+
Ozonation[b]	-	+	+
Chlorination (free chlorine)[c]	-	+	-
Chloramination and Chlorine dioxide	-	-	-
Pre-oxidation	-	-	-

+ = 80% or more removal; - = not so effective; [a]Depends on the size of membrane (nanofiltration is effective); [b]Ozonation may release cyanotoxins and is not effective for saxitoxins; [c]Chlorination may release cyanotoxins and is not effective for anatoxin-a

All the experiments were performed directly on the raw water; however, it should be considered that these are complementary processes and therefore need to be evaluated according to a logic that reflects their combination in the real treatment plant.

3.1. Raw water quality

Raw water characteristics show that the main critical parameters are the microbiological contaminants and algae as shown in Table 4. These data were analyzed once a month during 10 month-period, during which the lab-scale tests for water treatment were also performed.

Table 4. Raw water quality (average quality of 11 samples)

Parameter		***Value (min-max)***
pH	pH unit	7.8-8.3
Color	mg/L Pt/Co	<1
Odor	-	<1
Turbidity	NTU	<1
Temperature	°C	10.8-12.7
TOC	mg/L	<1
Ammonia	$mgNH_4^+/L$	<0.05
Nitrate	$mgNO_3^-/L$	<2
Nitrite	$mgNO_2^-/L$	<0.03
Total colony count 22°C	CFU/1 mL	144->300
Total colony count 36 °C	CFU/1 mL	86- >300
Coliforms 37 °C	CFU/100 mL	<1-40
Escherichia coli	CFU/100 mL	<1-40
Enterococci	CFU/100 mL	<1-9
Clostridium perfringens	CFU/100 mL	<1-7
Algae	N/100 mL	230-1,800

3.2. Coagulation/flocculation

Several series of jar tests have been carried out (Fig. 1) in order to identify yields, operating conditions and characteristics of the sludge produced through the use of different coagulants ($FeCl_3$, PAC and $Al_2(SO_3)_4$) and flocculants for the removal of cyanobacteria by means of coagulation/flocculation/sedimentation.

Fig. 1. Jar test apparatus

It emerged that the aluminum sulphate has been excluded because, while showing a good efficiency in algal removal (50% -100%), it shows considerable difficulties in flocculation and sedimentation of the produced flakes. Ferric chloride presents the advantage of forming more stable flakes and producing less sludge than the PAC (15-40 mg/L SST of $FeCl_3$ versus 40-140 mg/L for PAC); the advantage of removing toxic algae in a variable percentage up to 100% and releasing high Fe residues in the supernatant.

The aluminum polychloride (PAC) proved to be the most effective (Fig. 2) both from the point of view of the removal of the algal load (with yields of 100%) and of the characteristics of sedimentation of the sludge and of the metal residue in the supernatant.

The only weak point is the high production of sludge, especially in view of a filtration by subsequent contact. The high-negatively charged organic polyelectrolyte is the only flocculant that is able to improve the yield of ferric chloride and to decrease its metal residues in the supernatant.

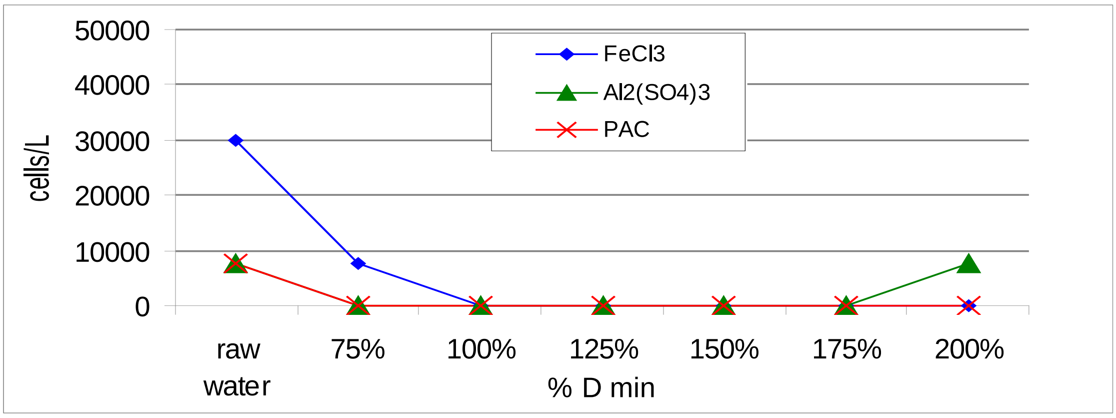


Fig. 2. Cyanobacteria cells concentration versus coagulant dose (indicated as percentage of the minimum dose) in the jar tests

3.3. Rapid multimedia filtration

Rapid multilayer filtration (sand/anthracite) shows that the simple filtration, in conditions of low algal load, proves sufficient for the total removal of algal content and for a good removal of suspended solids (22-92%). Although, in conditions of high algal load, reaches algae removal of 99.6%, however, reveals the need to be combined with other treatments for better control of cyanobacteria. The contact filtration shows a total removal of algae with both ferric chloride and aluminum polychloride. Filtration is more effective in removing ferric chloride residues rather than those of aluminum polychloride, in fact in the first case the Fe remains < 5μg/L as the value in the raw water, while in the second case the Al increases up to 27 μg/L.

3.4. Activated carbon

Filtration on activated carbon can be a good support for simple filtration in case of high algal content, in fact it offers a yield reduction of algal cells of 99.5%. It represents the best way to remove the toxins most frequently produced by cyanobacteria present in the lake (*Planktothrix* and *Microcystis*).

3.5. Disinfection with sodium hypochlorite

Disinfection with sodium hypochlorite has no effect on algal killing in high cell load conditions. The tested assays did not result in the formation of by-products such as trihalomethanes (THMs) in significant concentrations. In particular, at the chlorine concentrations applied (0.5-1.5 mg/L), the increased presence of algae did not show any increase in the formation of THMs as shown in Table 5.

3.6. Combined treatments

The results (Table 6) show that flotation alone can remove *Planktothrix* (*Oscillatoria*), that was the only cyanobacteria species detected in these tests, with an efficiency of about 90% (test FL1). This result can be improved if the flotation process is combined with a coagulation or polyelectrolyte and no differences were observed between the use of a coagulant (iron chloride or PAC; tests FL2 and FL3) or a polyelectrolyte (test FL4).

Better results were obtained with the addition of both a coagulant and a polyelectrolyte (FL5-6) followed by flotation.

The micro screen alone is an effective process for algae removal (test M1) but its efficiency can be significantly improved if it is followed by coagulation/flocculation and flotation (tests M2-3), where the yield improves up to 99.4%. The use of a sedimentation process after micro screen and coagulation/flocculation (test S1-2) instead of flotation (tests M2-3) decreases the total yield from more than 99% to 93%.

4. Conclusions

The experimental tests show that coagulation/flocculation was very efficient for algae removal. When this process was followed by DAF instead of sedimentation better results were obtained.

Table 5. Algae removal and trihalomethanes formation during the oxidation with sodium hypochlorite

Parameter	***Raw lake water***				***Lake water after storage***			
	Chlorine concentration (mgCl₂/L)				***Chlorine concentration (mgCl₂/L)***			
	0	***0.5***	***1***	***1.5***	***0***	***0.5***	***1***	***1.5***
Algae (cells/L)	375,000	255,000	240,000	230,000	1,500,000	1,500,000	1,350,000	1,575,000
Chlorophyll-a (mg/L)	1.5	1.2	1.2	1.5	10.4	10.8	2.3	8.6
Trihalomethanes (mg/L)	<5	<5	<5	<5	<5	<5	<5	<5

Table 6. Concentration and yield of *Planktothrix* removal with the combination of different processes

Sample	***Algae concentration (cells/L)***	***Yield of algae removal (%)***
RW	4,309,800	-
FL1	420,100	90,2
FL2	342,400	92.1
FL3	300,500	93.0
FL4	375,600	91.3
FL5	120,300	97.2
FL6	49,800	98.8
M1	218,000	94.9
M2	29,000	99.3
M3	27,000	99.4
S1	141,100	96.7
S2	286,400	93.4

RW = raw water; FL1: flotation; FL2: coagulation (iron chloride)+flotation; FL3: coagulation (PAC)+flotation; FL4: polyelectrolyte+flotation; FL5: coagulation (iron chloride)+polyelectrolyte+flotation; FL6: coagulation (PAC)+polyelectrolyte+flotation; M1: micro screen; M2: micro screen+coagulation (iron chloride)+flotation; M3: micro screen+coagulation (PAC)+flotation; S1: micro screen+coagulation (iron chloride)+sedimentation; M3: micro screen+coagulation (PAC)+sedimentation.

When the suspended solid flocs were removed by means of a flotation process the results were not influenced by the coagulant type (iron chloride and PAC) while better results were obtained with the addition of a polyelectrolyte. Otherwise, when the coagulation/flocculation was followed by a sedimentation process, iron chloride was better as it produced more stable flocs, a more easily settleable sludge and a lower sludge amount than PAC.

The sand filtration further improved the removal of cyanobacterial cells after their aggregation in the flocculation process. The micro screen could be applied as water pre-treatment as it could offer significant algae removal. The use of sodium hypochlorite for algae inactivation did not show promising results and the algae content did not seem to influence THMs formation.

Acknowledgements
The authors thank Gardauno S.p.a. for supporting this research; the Sanitary Local Agency (ASL) of Brescia for the analytical support; Maria de Laurentis and Massimiliano Manzini for their collaboration in conducting the experimental tests.

References

Acero J.L., Rodriguez E., Meriluoto J., (2005), Kinetics of reactions between chlorine and the cyanobacterial toxins microcysitins, *Water Research*, **39**, 1628-1638.

Bauer M.J., Bayley R., Chipps M.J., Eades A., Scriven R.J., (1998), Enhanced rapid gravity filtration and dissolved air flottation for pre-treattment of river Thames reservoir water, *Water Science and Technology*, **37**, 2.

Bernezeau F., (1994), Can microcystins enter drinking water distribution systems, *Toxic Cyanobacteria, Current Status of Research and Management*, Proc. of an Int. Workshop, Adelaide, Australia, 115-118.

Bernhardt H., Clasen, J., (1991), Flocculation of micro-organisms, *Journal of Water Supply: Research and Technology - AQUA*, **40**, 76-87.

Campinas M., Rosa M.J., (2010), Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, *Separation and Purification Technology*, **70**, 345–353.

Chow C.W.K., Panglisch S., House J., Drikas M., Burch M.D., Gimbel R., (1997), A study of membrane filtration for the removal of cyanobacterial cells, *Journal of Water Supply: Research and Technology - AQUA*, **46**, 324-334.

Cook D., Newcombe G., (2008), Comparison and modelling of the adsorption of two microcystin analogous onto powdered activated carbon, *Environmental Toxicology*, **29**, 525-534.

Craig K., Bailey D., (1995), *Cyanobacterial Toxin Microcystin-Lr Removal using Activated Carbon. Hunter Water Corporation Experience*, Proc. 16th Federal AWWA Convention, Sydney, 579-586.

Croll B., Hart J., (1996), *Algal Toxins Customers*, Proc. UKWIR-AWWARF Technology Transfer Conference, Philadelphia.

Dixon M.B., Richard Y., Ho L., Chow C.W.K., O'Neill B.K., Newcombe G., (2011), A coagulation-powdered activated carbon-ultrafiltration — multiple barrier approach for removing toxins from two Australian cyanobacterial blooms, *Journal of Hazardous Materials*, **186**, 1553–1559.

Drikas M., (1994), *Removal of Cyanobacterial Toxins by Water Treatment Processes*, Proc. of Toxic cyanobacteria - A global perspective, Adelaide, 30-44.

Edzwald J.K., (1993), Coagulation in drinking water treatment: particles, organics and coagulants, *Water Science and Technology*, **27**, 21-35

Funari E., Scardala S., Testai E., (2006), *Potentially toxic cyanobacteria: ecological, and methodological aspects and risk assessment - ISTISAN Report 08/6*, National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ/cont/08-6%20web.1208243077.pdf.

Funari E., Scardala S., Testai E. (2014), *Cyanobacteria: guidelines for managing blooms in bathing waters - ISTISAN Report 14/20* (in Italian), National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ/cont/14_20_web.pdf.

Gajdek P., Bober B., Mej E., Bialczyk J., (2004), Sensitised decomposition of microcystin-LR using UV radiation, *Journal of Photochemistry and Photobiology* B*: Biology*, **76**, 103-106.

Gibbs R.J., (1983), Effects of natural organic coating on the coagulation of particles, *Environmental Science and Technology*, **17**, 237–240.

Gijsbertsen-Abrahamse A.J., Schmidt W., Chorus I., Heijman S.G.J., (2006), Removal of cyanotoxins by ultrafiltration and nanofiltration, *Journal of Membrane Science*, **276**, 252–259.

Hargesheimer E.E., Watson S.B., (1996), Drinking water treatment options for taste and odor control, *Water Research*, **30**, 1423-1430.

Health Canada, (2002), Guidelines for Canadian Drinking Water Quality: Supporting Documentation, Cyanobacterial Toxins – Microcystin-LR, On line at: http://hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/water-eau/cyanobacterial_toxins/cyanobacterial_toxins-eng.pdf.

Henderson R., Parsons S.A., Jefferson B., (2008). The impact of algal properties and pre-oxidation on solid-liquid separation of algae, *Water Research*, **42**, 1827-1845.

Hoeger S.J., Shaw G., Hitzfeld B.C., Dietrich D.R., (2004), Occurrence and elimination of cyanobacterial toxins in two Australian drinking water treatment plants, *Toxicon*, **43**, 639–649.

Huang W.-J., Cheng B.-L., Cheng Y.-L., (2007), Adsorption of microcystin-LR by three types of activated carbon, *Journal of Hazardous Materials*, **141**, 115–122.

Kull T.P., Backlund P.H., Karlsson K.M., Meriluoto J.A., (2004), Oxidation of the cyanobacterial hepatotoxin microcystin-LR by chlorine dioxide: reaction kinetics, characterization, and toxicity of reaction products, *Environmental Science and Technology*, **38**, 6025-6031.

Kull T.P., Sjövall O.T., Tammenkoski M.K., Backlund P.H., Meriluoto J.A., (2006), Oxidation of the cyanobacterial hepatotoxin microcystin-LR by chlorine dioxide: influence of natural organic matter, *Environmental Science and Technology*, **40**, 1504-1510.

Lam A., Prepas E., Spink D., Hrudey S.E., (1995), Control of hepatotoxic phytoplankton blooms; implications for human health, *Water Research*, **29**, 1845-1854.

Lambert T.W., Holmes C.F.B., Hrudey S.E., (1996), Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment, *Water Research*, **30**, 1411-1422.

Li L., Gao N-y., Deng Y., Yao J.-j., Zhang K.-j., Li H.-j., Yin D.-d., Ou H.-s., Guo J.-w., *(*2009*)*, Experimental and model comparisons of H_2O_2 assisted UV photodegradation of Microcystin-LR in simulated drinking water, *Journal of Zhejiang University SCIENCE A*, **10**, 1660-1669.

Mattei D., Melchiorre S., Messineo V., Bruno M., (2005), Toxic algal blooms in Italy: risk assessment and epidemiology - *ISTISAN Report 05/29*, National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ2/cont/05-29.1140181875.pdf.

Merel S., Clement M., Thomas O., (2010) State of the art on cyanotoxins in water and their behaviour towards chlorine, *Toxicon*, **55**, 677-691.

Montiel A., Weltè B., (1998), Preozonation couplet with flotation filtration: successedful removal of algae, *Water Science and Technology*, **37**, 65-73.

Pendleton P., Schumann R., Wong S.H., (2001), Microcystin-LR Adsorption by Activated Carbon, *Journal of Colloid and Interface Science*, **240**, 1–8.

Petrusevski B., Van Breemen A.N., Alaerts G.J., (1995), Optimisation of coagulation conditions for direct filtration of impounded surface water, *Journal of Water Supply: Research and Technology - AQUA*, **44**, 93-102.

Rodrìguez E., Onstadb F.D., Kull T.P.J., Metcalf J.S., Acero J.L., von Gunten U., (2007a), Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate, *Water Research*, **41**, 3381–3393.

Rodrìguez E., Majado M.E., Meriluoto J., Acero J.L., (2007b), Oxidation of microcystins by permanganate: Reaction kinetics and implications for water treatment, *Water Research*, **41**, 102–110.

Rositano J., Nicholson B.C., (1994), *Water Treatment Techniques for Removal of Cyanobacterial Toxins from Water*, Australian Centre for Water Quality Research, Salisbury, Australia.

Rositano J., (1996), *The Destruction of Cyanobacterial Peptide Toxins by Oxidants used in Water Treatment*, Urban Water Research Association of Australia, Melbourne, Australia.

Sorlini S., Collivignarelli C., (2011), Microcystin-LR removal from drinking water supplies by chemical oxidation and activated carbon adsorption, *Journal of Water Supply: Research and Technology - AQUA*, **60**, 403-411.

Sorlini S., Gialdini F., Collivignarelli C., (2013), Removal of cyanobacterial cells and Microcystin-LR from drinking water using a hollow fiber microfiltration pilot plant, *Desalination*, **309**,106-112

Teixeira M.R., Rosa M.J., (2006), Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration, *Water Research*, **40**, 2837–2846.

Tsuji K., Nalto S., Naohlsa K., Watanabe M.F., Suzuki M., Harada K., (1994), Stability of microcystins from Cyanobacteria. Effect of light on decomposition and isomeration, *Environmental Science and Technology*, **28**, 173-177.

Tsuji K., Watanuki T., Kondo F., Watanabe M.F., Nakazawa H., Suzuki M., (1997), Stability of microcystins from Cyanobacteria. IV. Effect of chlorination on decomposition, *Toxicon*, **35**, 1033-1041.

Wang H., Lewis D., Newcombe G., Brookes J., Ho L., (2009), Separated adsorption and bacterial degradation of microcystins in GAC filtration, *International Journal of Environment and Waste Management*, **3**, 236-243.

WHO, (1999), Toxic Cyanobacteria in Water. A guide to their public health consequences, monitoring and management, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/42827/0419239308_eng.pdf?sequence=1&isAllowed=y

WHO (2004), Guidelines for drinking water quality - Volume 1 - Reccomandations, World Health Organization, Geneva, Switzerland, On line at: http://who.int/water_sanitation_health/dwq/GDWQ2004web.pdf

WHO, (2006), Guidelines for drinking water quality - Volume 1 – Reccomandations: addendum, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/43242/9241546743_eng.pdf?sequence=1

WHO, (2011), Guidelines for drinking water quality, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf?sequence=1

WHO, (2015), Management of cyanobacteria in drinking water supplies: Information for regulators and water suppliers. Technical Brief, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/153970/WHO_FWC_WSH_15.03_eng.pdf?sequence=1

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2465-2471
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

SUSTAINABLE REMEDIATION TECHNOLOGIES FOR CONTAMINATED MARINE SEDIMENTS: PRELIMINARY RESULTS OF AN EXPERIMENTAL INVESTIGATION

Francesco Todaro*, Sabino De Gisi, Michele Notarnicola

Department of Civil, Environmental, Land, Building Engineering and Chemistry, Polytechnic University of Bari, Via E. Orabona n. 4, 70125 Bari, Italy

Abstract

This paper deals with the relevant environmental issues concerning marine sediments contamination, for which there is the need for further development of sustainable remediation technologies. Among the in-situ remediation options, the reactive capping turns out to be an interesting approach. On the other hand, when the sediments must be dredged, the stabilization and solidification (S/S) treatments can represent an efficient and sustainable solution for the recovery of the materials, in the spirit of the circular economy. In the present paper, the first results of an on-going experimental investigation on remediation of the contaminated marine sediments from the Gulf of Taranto are presented. The research activities aim at assessing the effectiveness of both solutions as remediation options for marine sediments contaminated by heavy metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

Key words: contaminated sediments, reactive capping, solidification/stabilization

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Aquatic sediments are identified as an ultimate receptor for many hazardous pollutants produced by the human activities (Zhang et al., 2016).

Sediment-bound pollutants pose major concerns for human health and the environment because these contaminants can re-enter the overlying water and become available to benthic organisms and subsequently pass into aquatic food chains. Thus, sediments act as both carriers and long-term secondary sources of contaminants for aquatic ecosystems.

Contaminated sediments remediation strategies may consist of in situ (i.e., treatments operating where the contamination is present with no sediments dredging) and ex situ options (i.e., treatments including sediments dredging or resuspension phenomena to some extent).

In situ remedial alternatives generally involve (i) Monitored Natural Recovery (MNR), which is essentially based on a deep knowledge of the system and its resilience capacity to reduce the risk over time through natural processes (De Gisi et al., 2017), (ii) in situ containment and treatment, in which either contaminated sediments are physically and chemically isolated from aquatic ecosystems or the contaminants in sediments are sequestered and degraded (Lofrano et al., 2017).

Ex situ remedial alternatives typically need several component technologies to dredging or excavation, transport, pre-treat, treat, and/or dispose sediments and treatment residues. The pollutants are extracted from the sediments or degraded through a series of chemical, physical, biological or thermal methods in specially designed reactors. Most ex situ remediation technologies developed for soil or waste

* Author to whom all correspondence should be addressed: e-mail: francesco.todaro@poliba.it; Phone: +390994733203; Fax: +39 3397787542

can be used for dredged sediments (De Gisi and Notarnicola, 2016a).

Among the remediation options, In Situ Capping (ISC) can become, in some cases, one of the most sustainable options, i.e. in terms of efficacy, durability and economy. It consists in placing a layer of clean materials over the sediments to isolate the contaminant from the overlying water column and biota, to reduce contaminant flux into the biologically active part of the sediment, and to create new habitats for aquatic organisms (Reible, 2017). Conventional (passive) caps consist of a layer of clean neutral materials and they rely on containment, rather than treatment, of contaminated sediments. The cap may also include: geotextiles to enhance the layer separation or improve geotechnical stability, amendments (that are made up of chemically reactive materials, i.e. Active/Reactive Cap solutions) to boost the treatment efficacy, or additional layers to armour and keep the cap integrity or to help the development or restoration of the habitat characteristics. The use of chemically reactive materials allows the sequestration and/or degradation of the sediment contamination, reducing its mobility, toxicity, and bioavailability, thus performing both containment and treatment of the contaminated sediments. A variety of materials are proven to achieve the goals of cap; however, limited proved options exist for enhancing contaminant adsorption and degradation processes. Several laboratory experiments and recent field studies demonstrated that a layer of activated carbon, thick some centimetres, can effectively decrease contaminant flux from sediments to the overlying water (Abel and Akkanen, 2018; Gilmour et al., 2018; Hua et al., 2017).

Reactive capping is usually applied either for slightly polluted sediments or when there is the need to accelerate the lowering of contamination to get a faster risk mitigation. However, for heavily polluted sediments, or if dredging is compulsory to reach a desired bathymetric level, ex situ technologies for sediments remediation become the most appropriate choices. In these cases, the “beneficial reuse” of dredged materials is highly encouraged, e.g. Italian Ministerial Decree No. 173/2016 (MD, 2016). Therefore, treatments for decreasing pollutant concentration have become part of the sediments management process (Todaro et al., 2016).

Stabilization/solidification (S/S) of contaminated sediments seems to be an appealing technology for both the chemical and mechanical improvement (i.e. heavy metal immobilization, compressibility reduction and strength improvement). The S/S techniques can be different and vary depending on the target to be reached for the sediment reuse. They are based on adding chemical compounds to dredged material to achieve (i) the chemical immobilization of the contaminants, and (ii) the improvement of mechanically characteristics for reuse of the stabilize material as new construction material. S/S treatments generally do not remove the contaminants from the dredged material since the pollutants are transformed into a less mobile and harmful species.

This study reports the first results of an experimental laboratory investigation, carried out on marine sediments contaminated by heavy metals, PAHs and PCB, to explore the sustainability of the following remediation technologies: in situ reactive capping and ex situ stabilization/solidification. In detail, the following issues have been investigated: (1) chemical characterization of contaminated marine sediments of Gulf of Taranto (South of Italy), (2) effect of Reactive Permeable Mats (RPM) with organoclay (OC) or activated carbon (AC) on the contaminant migration and (3) leaching of ex situ S/S treated sediments with several additives (i.e. Portland cement, lime, active carbon and organoclay).

2. Material and methods

2.1. Contaminated marine sediments

The sediments were sampled in the Gulf of Taranto, one of most polluted marine areas in Europe, declared Site of National Interest (SIN) (Italian Law, 1998) also because of serious contamination of marine sediments (Vitone et al., 2016).

The samples were taken up to depths of about 1.5 m from the seafloor, that is about the depth of interest in view of any mitigation solution. These were passed through a 2-cm sieve, homogenized by mixing and stored at 4 °C until use.

The standard protocols of ISPRA (the Italian Institute for the Environmental Protection and Research) was used for determining grain-size, moisture content and organic matter of sediments (ICRAM, 2001). The concentrations of heavy metals were obtained by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) in accordance to the EPA method 200.8 (EPA, 1994). For the determination of the total PAHs and PCBs concentrations, as well as of each compound or homologue group, Gas Chromatography - Mass Spectrometry (GC-MS) EPA method 8275A (EPA, 1996) was used.

2.2. In situ option: laboratory experiments with reactive permeable mats

Reactive permeable mats with organoclay or active carbon were used. RPM represent an innovative remediation technique, consisting of a reactive layer (“mat”) containing one or more materials that are confined between two permeable geotextiles (Fig. 1a). The use of reactive mats for active ISC solutions can be useful to increase their adsorption capacity compared with that of the traditional caps (commonly made up of clean neutral materials: sand, silt, clay, and crushed rock debris), through the minimisation of cap thickness. Moreover, it has been verified that the same amendment is generally more effective when used in a cap than when placed directly into sediments (ITRC, 2014). The layers of synthetic geotextiles provide a bioturbation barrier that prevents the mixing of amendments with the underlying sediments, allowing their uniform application, and reducing the effect of erosion processes (Olsta et al., 2006). However, their durability is conditioned by the site use; if anthropic activities are foreseen to be conducted in the site, a protecting layer of sand cannot be avoided (Fig. 1b). When possible, a new habitat layer can be directly overlapped on the mat (Fig. 1c).

A RPM 0.6 cm thick and a quantity of either Organoclay (OC) or Activated Carbon (AC) equal to 3 kg/m^2 have been used. OC is a modified clay that shows a specific adsorption behaviour towards PAH, free oil and grease (FOGs) and chlorinated hydrocarbons. It has been also verified that OC can have good potential for remediating different heavy metals under real environmental conditions (Meric et al., 2014). AC, which derives from thermal decomposition of various carbonaceous materials followed by an activation process, is probably the most widely used material among active substances (De Gisi et al., 2016b). Various laboratory studies showed that active sediment mixing with AC can significantly reduce the aqueous concentrations, bioavailability, and bioaccumulation of PCBs, PAHs and several heavy metals (Choi, 2018; Gustafsson et al., 2017).

The experimental set-up (Fig. 2) was designed and assembled to test the efficacy of the reactive capping at lab-scale level. The set-up is intended to be an accurate physical model of the subaqueous site with contaminated sediment, reactive mat and water column in place. The columns used are 15 cm in diameter and 150 cm in length. They are made up of two sections of different length (50 cm and 100 cm) to facilitate handling and cleaning.

A porous plate at the base of the columns has been fixed to allow for water injections into the column through a 6.35 mm opening. Various sampling ports are present at different heights along the columns for chemical sampling of the effluent to be taken during the test. After every 20 days the water of each column has been sampled and analysed. The settlement of the top sediments has been recorded over time to follow the development of the consolidation process.

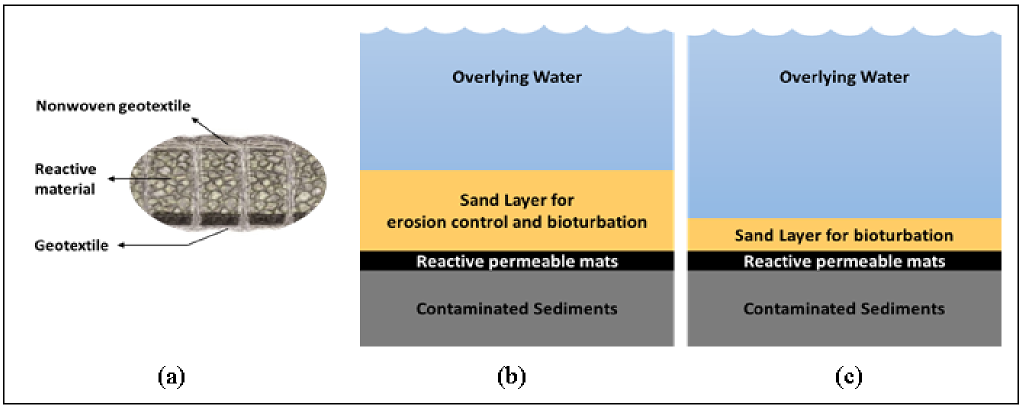


Fig. 1. (a) Reactive permeable mats (Zhang et al., 2016, modified), (b) active cap with sand protecting layer, (c) active cap with sand habitat layer

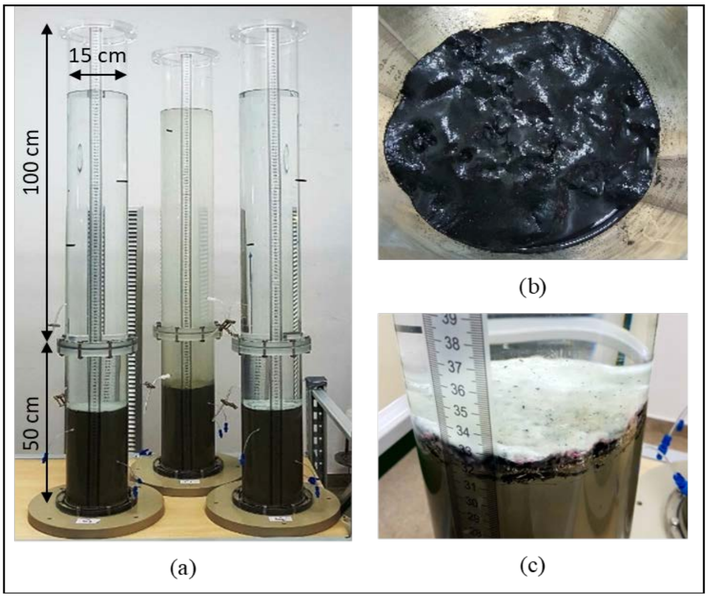


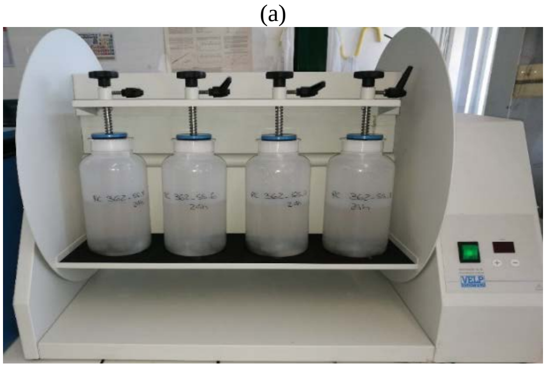
Fig. 2. Experimental set-up: (a) columns, (b) sediments, (c) reactive permeable mats

The mixtures were prepared by using different contents of several additives, namely CEM I 42.5 R Portland cement (C), lime (L), activated carbon (AC) and organoclay (OC). An 0.8 water/dry matter ratio (w) was used for all experiments; the value was based on the results of preliminary tests as well as the high clay content in sediment (Table 1). All the materials were initially mixed for 5 min with a standard mixer and, then, a steel trowel to ensure a homogeneous paste was used. In the casting phase, the prepared mixture was introduced into different plastic moulds with hemispherical shape. The samples, in the curing phase, were kept at 20 ± 5 °C and 80% humidity (Fig. 3a). In Italy, as in some other EU countries, the reuse options of treated sediments are evaluated with leaching tests (UNI EN, 2004). To this aim, for each sample a 40-g portion was sampled and transferred to a polyethylene bottle.

Distiller water was added with a solid-liquid ratio of 1:10 by weight and the bottle was kept in rotation at 12 rpm for 24 hours using Rotax 6.8-Velp Scientifica (Fig. 3b).

To end of the 24 hours, a short retention time was given to the extraction vessels for the settlement of suspended coarse solids; then, the leachate was filtered for the removal of suspended solids. The soluble concentrations of heavy metals of interest (As, Co, Cr, Ni, V and Zn) were analysed using ICP-OES.

(a)



(b)

Fig. 3. Samples (a) and leaching test (b)

Table 1. Mix design for recycling sediments by S/S treatment

Mixture	***Additive***	***Reagent***	***A+R content***	***Water/dry matter***
MIX_1	Cement	-	10%	0.8
MIX_2	Cement	Activated Carbon	15%	0.8
MIX_3	Cement	Organoclay	15%	0.8
MIX_4	Lime	-	10%	0.8
MIX_5	Lime	Activated Carbon	15%	0.8
MIX_6	Lime	Organoclay	15%	0.8

Table 2. Physical-chemical properties of the sediments used for the tests

Parameter	***Unit***	***Value***	***St. Dev.***
pH	u. pH	8.8	0.05
Eh	mV	-100.9	0.28
Conductivity	mS/cm	4.1	0.95
Moisture content	%	44.8	0.23
Ashes at 600°C	%	87.3	2.50
Organic matter content	%	12.3	2.50
Sand fraction	%	19.4	-
Silt fraction	%	43.2	-
Clay fraction	%	37.4	-
PAHs	μg/kg	5389	300
PCBs	μg/kg	1669	100
As	mg/kg	12.3	0.4
Co	mg/kg	7.1	0.03
Cr	mg/kg	54.0	3.4
Ni	mg/kg	38.2	0.6
Pb	mg/kg	87.4	4.1
V	mg/kg	53.3	4.0
Cu	mg/kg	69.6	10.5
Zn	mg/kg	189.2	16.6

3. Results and discussion

The sediments used for the tests were characterised; particle size distribution and physical-chemical properties are reported in Table 2. According to the marine sediment management guideline in Taranto SNI (ICRAM, 2004), the sediments are to be considered contaminated because the contaminants concentrations exceeded the site-specific thresholds, even if below Italian national limit values (LD, 2006).

Column tests were carried out to assess the effectiveness of reactive capping materials in the sequestration of various heavy metals and organic contaminants in saltwater. Column water quality monitoring was performed for 20 days from the reactive permeable mat placement. The water samples were analysed for 8 heavy metals, PCBs and PAHs.

Heavy metals were detected in water samples (all close to 1 µg/l), but these values were statistically equal to those measured for pre-cap conditions. This show that the metals are strongly bound on sediments and that the presence of reactive agents (i.e. AC and OC) not increased the rate of diffusion. The release of Cd, the most mobile metal and hard to stabilization with apatite, active carbon or other capping materials (Dixon and Knox, 2012; Kang et al., 2016), was effectively controlled by RPM.

PCB (29 congeners) concentrations in water samples were not detectable (MDL is approx. 0.001 µg/l). The hydraulic condition applied for the columns (no pore-water flow) found a minor short-term desorption of PCBs compared to laboratory tests conducted with continuously mixed reactors (Choi et al., 2014), suggesting that the contaminant transport depends on flow of porewater. Also, the low permeability of the fine-grained sediments used (Vitone et al., 2016) could have hindered the desorption of contaminants. PAHs were detected in water inside the reactor, both for cap and no-cap conditions. Fig. 4 shows the PAH concentrations at 20 days after the start of test conditions. The results show that PAH concentrations in water decreased from initial 0.1 µg/l to near 0.04-0.06 µg/l for column apparatus with cap. It is also observed that PAHs in water increased to 0.17 µg/l without the cap (Fig. 4). Therefore, after 20 days from the placing, RPM provided a reduction of the 60% (RPM with AC) and 40% (RPM with OC) of the original PAH contamination.

The results confirm that reactive amendments (such as organoclay and active carbon) sequester the organic contaminants and control their mobility to the water column (Knox et al., 2012). However, several studies also report concerns about the durability of the effectiveness of the active/reactive cap solutions (Lofrano et al., 2017; Zhang et al., 2016).

Regarding S/S treatment, the results of leaching tests showed that organic contaminants were not present in the eluates, while heavy metals were released with concentrations varying with the reagents percentages. Fig. 5 shows a comparison of the leaching of heavy metals for the several mix designs used for S/S treatments. The ratio between the 28 days heavy metals concentration (C_{28}) and the law limit (C_{LAW}) is reported for the six mixing solutions. Only for the samples named MIX_2 (Cement + AC) and MIX_3 (Cement + OC) all heavy metals concentrations are lower than the law limit (i.e. C_{28}/C_{LAW} is always lower than 1). The leached copper amount reached values more than the law limit (0.05 mg/l) in samples with lime (MIX_4, MIX_5 and MIX_6). Moreover, in the samples without reagents (MIX_1 and MIX 4) the leached nickel amount reached values more than the law limit (0.01 mg/l).

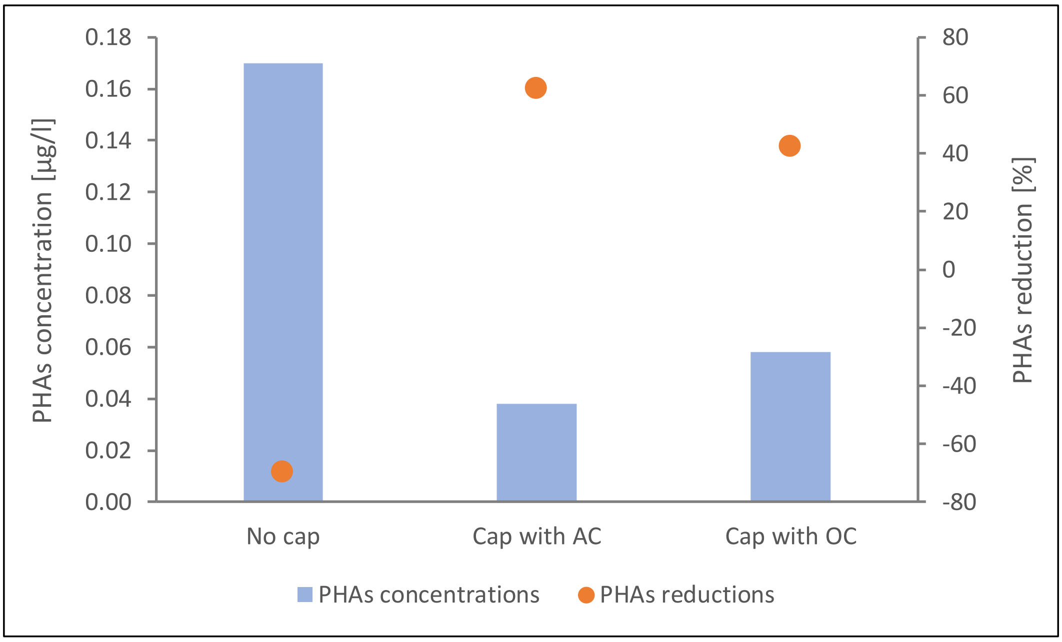


Fig. 4. PAHs concentrations in water after 20 days of capping test

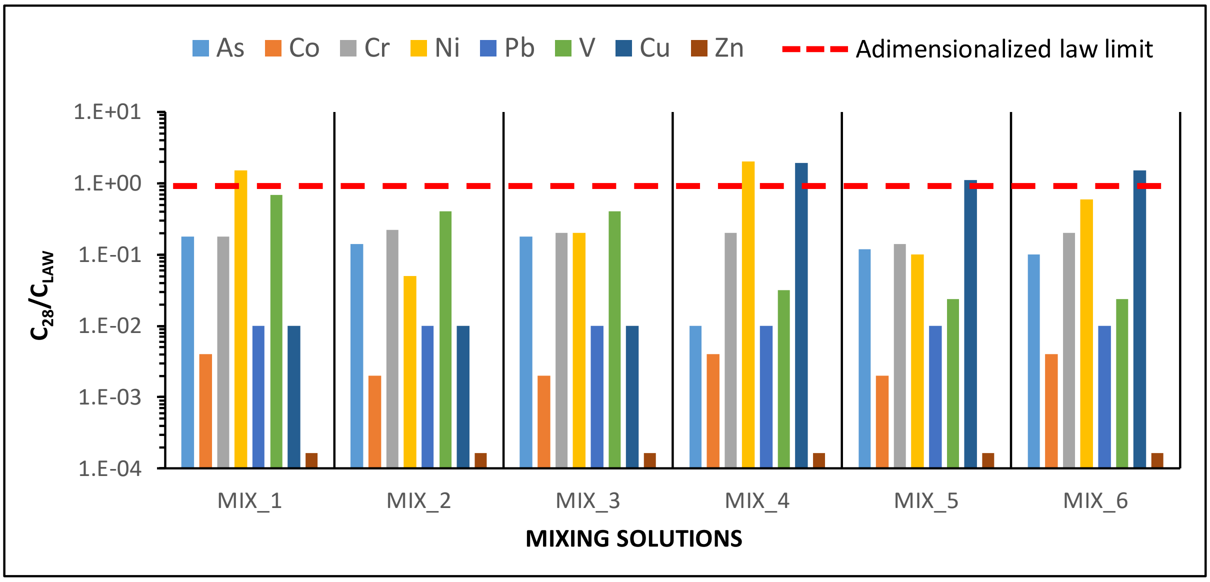


Fig. 5. Leaching at 28 days for each mix design and each heavy metal compared to law limit

The simplest form of treatment was obtained by the addition of either Portland cement or lime. The additives were used for the optimisation of performances, because the organic contaminants can interfere with the chemistry of binders, compromising the effectiveness of both the chemical and mechanical stabilization (Wang et al., 2013).

Therefore, for the mixtures with cement and OC or AC, the absence of leaching allows the beneficial reuse of contaminated sediments after S/S treatment.

The treated sediments can be recycled as aggregates for road construction (Pinto et al., 2011; Wang et al., 2012), cemented mortars (Couvidat et al., 2016), fill material and blocks (Tang et al., 2015; Wang et al., 2015) or raw material in brick production (Todaro et al., 2016; Cappuyns et al., 2015).

4. Conclusions

The results of column tests have shown that the reactive capping could represent an interesting option in situ remediation technology for contaminated sediments. In particular, after 20 days from the placing of capping there is a reduction of the 60% (RPM with AC) and 40% (RPM with OC) of the original PAHs contamination; metals and PCBs are not released in water. However, the research needs to be further developed with special reference to the long-term effectiveness of the amendments.

This study also explored the possibility of re-using dredged contaminated sediments as resource via S/S treatment. After 28 days from preparation, only the sediments mixtures with cement and adsorbent materials (MIX_2 and MIX_3) have complied with the acceptance criteria for reuse in terms of leachability. In fact, the leached concentrations of copper, for the mixtures with lime, and the nickel, for the mixtures without adsorbents, have reached values more than the law limits. For the mixtures with cement, the results show that the use of OC and AC has optimized the chemical stabilization.

However, to investigate the actual recovery potential of the S/S treated sediments, a mechanical testing program aimed at deepening the effectiveness of the treatments also in terms of sediment strength and compressibility needs to be carried out.

References

Abel S., Akkanen J., (2018), A combined field and laboratory study on activated carbon-based thin layer capping in a PCB-contaminated Boreal Lake, *Environmental Science and Technology*, **52**, 4702-4710.

Cappuyns V., Deweirt V., Rousseau S., (2015), Dredged sediments as a resource for brick production: Possibilities and barriers from a consumers' perspective, *Waste Management*, **8**, 372-380.

Choi Y., Cho Y., Luthe R. C., (2014), In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 1. Column studies, *Environmental Science and Technology*, **48**, 1835-1842.

Choi H., (2018), Treatment characteristics of various sediment components spiked with 2-chlorobiphenyl using reactive activated carbon, *Journal of Hazardous Materials*, **347**, 1-7.

Couvidat J., Benzaazoua M., Chatain V., Bouamrane A., Bouzahzah H., (2016), Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars, *Construction and Building Materials*, **112**, 892-902.

De Gisi S., Minetto D., Todaro F., Lanzolla A.M.L., Notarnicola M., (2017), *Monitored Natural Recovery of Contaminated Marine Sediments. Proposal of a Monitoring Plan for in situ Continuous Testing and Sensing*, Proc. 2th Int. Symp. on Instrumentation and Measurement Technology, Turin, vol. 1, 529-534.

De Gisi S., Notarnicola M., (2016a), Waste minimization in the remediation of contaminated sites: using the oil belt skimmer technology for the removal of heavy hydrocarbons from groundwater, *Environmental Science and Pollution Research*, **23**, 24092-24106.

De Gisi S., Lofrano G., Grassi M., Notarnicola M., (2016b), Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review, S*ustainable Materials and Technologies*, **9**, 10-40.

Dixon K.L., Knox A.S., (2012), Sequestration of metals in active cap materials: a laboratory and numerical evaluation, *Remediation*, **22,** 81-91.

EPA, (1994), Method 200.8: Determination of trace elements in waters and wastes by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), U.S. Environmental Protection Agency, Washington, D.C., On line at: https://www.epa.gov/sites/production/files/2015-06/documents/epa-200.8.pdf.

EPA, (1996), Method 8275A: Semivolatile Organic Compounds (PAHs and PCBs) in soils/sludges and solid wastes using Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS), U.S. Environmental Protection Agency, Washington, D.C., On line at: https://www.epa.gov/sites/production/files/2015-12/documents/8275a.pdf.

Gilmour C., Bell T., Soren A., Riedel G., Riedel G., Kopec D., Bodaly D., Ghoshc U., (2018), Activated carbon thin-layer placement as an *in situ* mercury remediation tool in a Penobscot River salt marsh, *Science of The Total Environment*, **621**, 839-848.

Gustafsson A., Hale S., Cornelissen G., Sjöholm E., Gunnarsson G., (2017), Activated carbon from kraft lignin: A sorbent for in situ remediation of contaminated sediments, *Environmental Technology & Innovation*, **7**, 160-168.

Hua S., Gong J., Zeng G., Yao F., Guo M., Ou X., (2017), Remediation of organochlorine pesticides contaminated lake sediment using activated carbon and carbon nanotubes, *Chemosphere*, **177**, 65-76.

ICRAM, (2004), Values of intervention for sediments of areas strongly anthropized with reference to the site of reclamation of national interest in Taranto (in Italian), Central Institute for Scientific and Technological Research applied to the Sea, Rome, Italy.

ICRAM, (2001), Reference analytical methodologies of the reference program for the control of the coastal marine environment (2001-2003) (in Italian), Central Institute for Scientific and Technological Research applied to the Sea, Rome, Italy.

Italian Law, (1998), Italian Law No. 426/1998, regarding new interventions in the environmental field, (in Italian), *Italian Official Journal*, No. 291 from 14th of December, 1998.

ITRC, (2014), Contaminated sediments remediation. Remedy selection for contaminated sediments, Interstate Technology and Regulatory Council, Washington, D.C., On line at: https://clu-in.org/download/contaminantfocus/sediments/Sediment-ITRC-CS-2.pdf.

Kang K., Lee C., Choi J., Kim Y., Park S., (2016), Evaluation of the use of sea sand, crushed concrete, and bentonite to stabilize trace metals and to interrupt their release from contaminated marine sediments, *Water, Air & Soil Pollution*, 227-308.

Knox A.S., Paller M.H., Roberts J., (2012), Active capping technology. New approaches for in situ remediation of contaminated sediments, *Remediation Journal*, **22**, 93-117.

LD, (2006), Legislative Decree No. 152/2006, regarding the environmental, (in Italian), *Italian Official Journal*, No. 88, 04.04.2006.

Lofrano G., Libralato G., Minetto D., De Gisi S., Conte B., Todaro F., Calabrò D., Notarnicola M., (2017), In situ remediation of contaminated marine sediment: an overview, *Environmental Science and Pollution Research*, **24**, 5189-5206.

Meric D., Alshawabkeh A. N., Shine J. P., Sheahan T. C., (2014), Bioavailability of hydrophobic organic compounds in thin-layered capped sediments, *Chemosphere*, **103**, 281-289.

MD, (2016), Ministerial Decree No. 173/2016, regarding the technical procedures and criteria for the authorization of seabed excavation materials at sea, (in Italian), *Italian Official Journal*, No. 208 from 6th of September, 2016.

Olsta J., Hornaday C., Darlington J., (2006), Reactive material options for in situ capping, *Journal of ASTM International*, **3**, 1-6.

Pinto P.X., Al-Abed S.R., Barth E., Loftspring C., Voit J., Clark P., Ioannides A. M., (2011), Environmental impact of the use of contaminated sediments as partial replacement of the aggregate used in road construction, *Journal of Hazardous Materials*, **189**, 546-555.

Reible D.D., (2017), *Processes, Assessment and Remediation of Contaminated Sediments*, Springer, New York.

Tang I.Y., Yan D., Lo I., Liu T., (2015), Pulverized fuel ash solidification /stabilization of waste: comparison between beneficial reuse of contaminated marine mud and sediment, *Journal of Environmental Engineering and Landscape Management*, **23**, 202-210.

Todaro F., De Gisi S., Notarnicola M. (2016), Contaminated marine sediments: waste or resource? An overview of treatment technologies, *Procedia Environmental Science, Engineering and Management*, **3**, 157-164.

UNI EN, (2004), Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction), Italian National Unification, UNI EN 12457-2:2002.

Vitone C., Federico A., Puzrin A. M., Ploetze M., Carrassi E., Todaro F., (2016), On the geotechnical characterization of the polluted submarine sediments from Taranto, *Environmental Science and Pollution Research*, **23**, 12535-12553.

Wang D., Abriak N. E., Zentar R., Chen W., (2013), Effect of lime treatment on geotechnical properties of Dunkirk sediments in France, *Road Materials and Pavement Design*, **14**, 485-503.

Wang D.X., Abriak N.E., Zentar R., Xu W., (2012), Solidification/stabilization of dredged marine sediments for road construction, *Environmental Technology*, **33**, 95-101.

Wang L., Kwok J.S.H., Tsang D.C.W., Poon C., (2015), Mixture design and treatment methods for recycling contaminated sediment, *Journal of Hazardous Materials*, **283**, 623-632.

Zhang C., Zhu M., Zeng G., Yu Z., Cui F., Yang Z., Shen L., (2016), Active capping technology: a new environmental remediation of contaminated sediment, *Environmental Science and Pollution Research*, **23**, 4370-4386.

Environmental Engineering and Management Journal October 2017, Vol.17, No. 10, 2473-2484
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

SEPARATE COLLECTION OF ORGANIC WASTE AND CARDBOARD: ASSESSING THE IMPACT OF A DEVELOPMENT COOPERATION PROJECT IN TULKAREM, WEST BANK

Francesca Villa[1], Mentore Vaccari[1*], Silvia Gibellini[1]

CeTAmb LAB, Research Laboratory on Appropriate Technologies for Environmental Management in resource-limited Countries, University of Brescia, via Branze 43, 25123, Brescia, Italy

Abstract

This research aimed to analyze the impact of the introduction of a separate collection system for organic waste and cardboard in the Governorate of Tulkarem, West Bank (Occupied Palestinian Territories). The amount of waste diverted from the final disposal at the landfill of Zahret Al-Finjan was quantified and the quality of separate materials was evaluated. An economic and environmental analysis was performed to quantify the impact of separate collection in terms of greenhouse gas emissions and the costs for the local waste management authority. Different methods for data collection were used, such as meetings, field visits and database analysis, allowing the construction of a scientific-based and coherent descriptive framework for the local solid waste management system. The results of the study demonstrate that the separate collection of organic waste and cardboard is a sustainable solution under the environmental point of view, while criticality has been identified in terms of economic sustainability. The proposed method has led to a proper assessment, allowing the identification of the material collection as the most expensive stage and creating the basis for further intervention on the waste management system.

Key words: composting, lower-middle-income countries, material recovery, municipal solid waste

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The importance of solid waste management has received more and more acknowledgement in the time due to its nexus with both environment pollution and public health (Wilson et al., 2015). Also Sustainable Development Goals deal with this topic, as a healthy and environmentally sounded waste management system has a direct impact on at least three goals: Clean water and sanitation, Sustainable cities and communities and Responsible consumption and production (UN General Assembly, 2015).

Waste management can affect human population and environment in all its stages, from the collection to the final disposal (Vaccari and Perteghella, 2016). In particular, the final disposal of the waste represents a big issue especially in low- and lower-middle-income countries, where waste is mostly disposed in uncontrolled dumpsites (Caniato et al., 2015; Hoornweg and Bhada-Tata, 2012; Vaccari et al., 2012; Wilson et al., 2015). Uncontrolled dumpsites have environmental and social impacts (Crowley et al., 2003; Damgaard et al., 2011; Di Bella and Vaccari, 2014) on the local (soil, water and air pollution; breeding place for disease vectors; etc.) and on the global level, with reference to greenhouse gases emissions, but they remain a common way to face the problem, above all if waste regulation is lacking (Caniato and Vaccari, 2014).

Waste management has consequently become the object of many projects of development cooperation. Apart from the establishment of sanitary

* Author to whom all correspondence should be addressed: e-mail: mentore.vaccari@unibs.it; Phone: +39 030 3711300

landfills, implemented strategies consider also the preferential order of waste treatment options described by the waste hierarchy (Hultman and Corvellec, 2012; Lee et al., 2016), proposing reuse, recycling or recovery alternatives. In some of these projects, attention has been given to the collection stage as well. In fact, between waste management stages, the collection one (from the initial storage at producers' place to the final destination of the waste, whether a treatment plant or a disposal site) has the biggest impact on public budgets and urban living (Coffey and Coad, 2010; Collivignarelli et al., 2011). Moreover, an effort toward separate collection can lead to environmental and economic benefits (Vaccari et al., 2013), and the value of separated waste fractions can be enhanced because source separation leads to a higher level of pureness. Composting requires a pure segregated organic fraction (Perteghella and Vaccari, 2017; Zhao et al., 2016), and so do other organic waste treatments (Lohri et al., 2017); recovered cardboard and paper need a high quality in the collection to be achieved, as well (Miranda et al., 2010; Scott, 2011).

In this framework, it is worth to understand the impact of a development cooperation project targeting waste management, as achieved results influence its sustainability. The importance of a proper assessment for a clear comprehension of points of strength and weakness of the system is recognized (Wilson et al., 2015; Zurbrügg et al., 2014).

In a cooperation project, the assessment should normally be concluded in a short time, while continuous changes occur, making difficult to understand properly the importance of each issue. This study proposes strategies for the assessment of a waste management cooperation project, pointing out some criticality in data collection and case description.

This study has been performed within the "Green Tulkarem Project", implemented by the Italian NGO CESVI and funded by the Italian Agency for Development Cooperation. The project was based in the Governorate of Tulkarem, located in the North of the West Bank (Occupied Palestinian Territories) (Fig. 1) and characterized by a population of 185,314 inhabitants, most living in towns (124,551 inhabitants) (PCBS, 2017). With a GDP (Gross Domestic Product) per capita of 2700 EUR (about 3000 US$), West Bank is considered a lower-middle-income economy (World Bank, 2017). Concerning solid waste management, despite the low generation rate and the high collection service, major issues are related to the widespread waste disposal at landfills, the scarce compliance with the 3Rs principle of waste management (reduce, reuse and recycle), an improper allocation of budgets for solid waste management need and lack of public awareness (Al-Khatib et al., 2007; Al-Khateeb, 2017). Some issues are also related to the political situation of the country and the lack of space for waste treatment and disposal. In fact, West Bank is divided into three areas, namely areas "A", "B" and "C", depending on whom is responsible for the administration and the military control, whether the State of Israel or the Palestinian National Authority (PNA). Even if the Israeli-Palestinian Interim Agreement (also known as OSLO II), in 1995, transferred environmental powers and responsibilities to the PNA in areas defined as areas "A" and "B", the most of facilities need to be located in areas "C" (under the administrative and military control of Israel), with significant administrative delays in their construction (SWEEP-Net, 2014).

Fig. 1. Geographic location of Tulkarem in West Bank (Occupied Palestinian Territories)

2. Material and methods

2.1. Background: MSW management in the Governorate of Tulkarem and the "Green Tulkarem Project"

According to the Environmental Law, the solid waste management system in West Bank is established within the framework of the "National Strategy for Solid Waste Management in the Palestinian Territory 2010-2014" (PNA, 2010), which sets two main actors in charge of waste management: the Municipalities and the Join Service Councils for Solid Waste Management (JSCs-SWM). Those authorities are responsible for the 90.6% of collected waste in the North of the West Bank (PCBS, 2015). In the Governorate of Tulkarem, the collection of Municipal Solid Waste (MSW) is performed by the JSC Wadi Shaer (hereafter indicated simply as JSC), autonomously (e.g. in the case of the village of Deir Al Ghousun) or in collaboration with the Municipalities (e.g in Tulkarem and Anabta). The collected MSW is hauled to the Transfer Station (TS) of Wadi Shaer, managed by the JSC, and then transported and disposed of into the landfill of Zahret Al.Finjan, managed by the JSC Jenin.

The landfill of Zahret Al-Finjan was opened in 2009 and it is 2.9 million m^2 extended. It was designed to receive waste from Jenin and Tubas, but it is receiving also solid waste from Tulkarem, Nablus, Ramallah and Al-Bireh Governorates (El-Kelani et al., 2017). The landfill represents a pollution source because it is not provided with any system of biogas and leachate collection and treatment.

The "Green Tulkarem Project", which was active between April 2014 and March 2017, introduced the Separate Collection (SC) of organic waste and cardboard beside the existing MSW collection. Collected organic waste was destined to an agricultural cooperative (Thinnabeh), where it was composted in aerated turned windrows. Cardboard was collected by the JSC on the behalf of a private enterprise, which covered collection costs; after the storage at the TS, cardboard was sold to a paper factory by the enterprise itself.

A proper understanding of the impact of the project is given by taking into account differences between target subjects and areas involved in the collection of the three different streams of waste (MSW, Organic waste, Cardboard). In fact, MSW collection addressed the whole population through street containers, while cardboard collection focused more on big producers, even if through street containers (steel containers cages), and organic waste collection addressed just big producers (markets, vegetable shops), which were identified and provided with containers of different sizes.

Furthermore, the project went through different stages. In a first phase (Stage 0), several small areas were identified on a morphological basis (i.e. central urban areas; suburbs; rural areas), in order to choose a proper collection model for each of them. In August 2015, the collection was covering the whole city of Tulkarem (Stage 1). The design extension (Tulkarem, 'Attil, Deir Al Ghousun, Qaffin, 'Illar, Al Sharquiywa, Iktaba, Anabta, Kafr Al Labad, Beit Lid and Bal'a) was reached from March to September 2016 (Stage 2). Subsequently, the area of interest was reduced, because covering the farer villages was too expensive. The final area included the city of Tulkarem, Nur Shams Camp and the villages of Deir Al Ghousun and Anabta (Stage 3), with a total population of 86,038 people (PCBS, 2017). The following discussion will not consider the Stage 0, which was characterized by daily changes due to a "trial-and-error" approach, but it will focus on the other three stages.

2.2. Data collection

In order to assess the impact of actions introduced by the "Green Tulkarem Project" both on the local and on the global level, this study is divided into two sections, according to following research questions: (a) Evaluation of the project: which has been the local impact of the project in the area of the Governorate of Tulkarem in terms of quantity and quality of recovered materials? (b) Environmental and economic analyses: which are the environmental and economic consequences of the introduction of SC of organic waste and cardboard, in terms of greenhouses gases emissions and costs?

Data were collected during field visits by:

- meetings with officials and employees of the JSC;
- acquisition, analysis and processing of data included in the database of the JSC (Database JSC-SWM), which included daily logs for waste entering or leaving the TS in the period 01/01/2014 – 13/02/2017 as well as other useful information (e.g. fuel expenses, maintenance costs, distances traveled by the vehicles);
- GPS tracking: routes for organic fraction and cardboard collection were tracked by GPS and analyzed with the software QuantumGIS, together with a mapping of collection points;
- Organic waste composition characterization.

2.3. Evaluation of the project

The implementation of the "Green Tulkarem Project" caused changes in the interested area. It influenced the organization of the SWM system in the Governorate, with the establishment of new collection routes and the involvement of new actors. One of goals of the project was the diminishing of the amount of waste landfilled in Zahret Al-Finjan, together with a different distribution of expenses within the system. This aspect has been analyzed, taking into account the step-by-step development of the new system. Qualitative results of SC were also assessed.

2.3.1. Quantity of waste collected, materials recovered and waste landfilled

The total amount of MSW collected was estimated for the whole Governorate and for the area covered by the project, considering changes occurred during the project. Data on total amounts of MSW were extracted from the Database JSC-SWM or estimated on previously collected aggregated data, when the collection was performed from actors different from the JSC and detailed data were not available. The total amount of collected organic fraction and cardboard was calculated from the Database JSC-SWM, as well. This leads to the evaluation of the impact of the waste diversion from landfill disposal to recycling and composting on the whole waste production in the Governorate.

Potential amounts of the separated fraction in the area were calculated considering the MSW composition in the Governorate of Tulkarem (Hamada, 2011), in order to evaluate the performances of the project. In the starting year of the project (2014), a survey to producers (markets, vegetable shops) within the design area was done to understand the amount of organic waste and cardboard produced by commercial activities targeted by the project. These estimates are resumed in Table 1.

Table 1. MSW daily production in Tulkarem divided for each fraction (2014)

MSW daily production for the Governorate of Tulkarem (2014) (1)			***139.07 t/d***
MSW daily production for the Municipality of Tulkarem (2014) (1)			***64.11 t/d***
Fraction	***Estimated daily production for each fraction (t/d)***		
	MSW (2)		***Commercial activities (3)***
	Governorate of Tulkarem	***Municipality of Tulkarem***	
Organic	63.97	29.49	4.74
Plastic	16.27	7.50	
Cardboard	15.30	7.05	3.5
Paper	5.56	2.56	
Wood	6.12	2.82	
Glass	5.98	2.76	
Metals	7.65	3.53	
Textile	12.52	5.77	
(1) Estimate (Database JSC-SWM, 2017; Filippini, 2014)			
(2) Estimate based on waste composition (Hamada, 2011)			
(3) Survey performed in 2014 (Vitali, 2014)			

2.3.2. Quality of the collected organic waste

The quality of the collected organic waste was assessed through the characterization of the organic fraction, performed at the composting plant. The waste was sorted manually according to the following categories:

1. organic fraction, subdivided in: vegetable waste from markets, greengrocers and vegetable plants;
2. undesired materials, subdivided in: glass, metal, tissue, cardboard, paper, aluminum, plastic, WEEE (Waste Electrical and Electronic Equipment), construction and demolition waste, health care waste, others.

The whole amount of the organic waste was analyzed during four different days (four samples), which were chosen in order to address possible changes during the time span of a week. The total weight of the organic waste was measured in the Transfer Station by a truck scale (sensitivity = ±10kg), while undesired materials were measured through a digital scale (maximum load = 30 kg; sensitivity = ±0.002 kg).

2.4. Environmental and economic analyses

The environmental and economic analyses were based on the comparison between the previous system (unseparated waste collection and landfilling) and the introduction of SC of organic fraction and cardboard. Environmental impacts and economic costs were calculated with reference to one tonne of material (MSW or separated organic waste or cardboard) (w/w wet weight) because it allows a comparison between different systems (Coffey and Coad, 2010).

Table 2 resumes the management phases of each material collected (i.e. MSW, Organic waste, Cardboard). In order to calculate emissions and costs, fuel consumptions for transport stages (Collection; Transfer to Zahret Al-Finjan) and energy consumptions for treatments were assessed. In particular, concerning fuel consumptions, data came from the Database JSC-SWM. The database was divided into two sections: the first one contained information related to the amount and the origin of the material for each load entering (Collection stage) or leaving (Final disposal stage) the Transfer Station; the second one contained fuel consumptions (L) and costs (EUR-Average change for 2017: 1 EUR = 4.06 NIS (New Israeli Shekel)) and covered kilometers for each vehicle owned by the JSC. Other information available for each vehicle were the plate number and the dimension, but not the model or the car brand. Nonetheless, it was mentioned the kind of fuel (Diesel).

Table 2. Management phases of each material collected

Stream	***Management phases***
MSW	Collection by the Municipality or the JSC; Primary storage at the TS; Transfer and final disposal at Zahret Al-Finjan landfill.
Organic waste	Collection by the JSC; Weighing at the TS; Primary storage at the Thinnabeh cooperative; Treatment (shredding; composting); Sale.
Cardboard	Collection by the JSC; Primary storage at the TS; Treatment (pulper; compacting); Sale.

The two Tables were associated as a function of dates and vehicles identifier. Average characteristics of the collection trip for each stream were calculated from the whole Database JSC-SWM, while it was possible to measure distances covered during organic waste and cardboard collection through GPS Tracking of collection trucks (Table 3). Fuel Consumption for tonne of material collected was calculated using the Eq. (1) ($i = 1,\ldots., N$) where N is the number of recorded trips):

$$Fuel\ Consumption\ \ for\ Tonne\ of\ Waste(L/t) = \tag{2}$$

$$= \frac{1}{N}\sum_{i=1}^{N}\frac{Trip\ Length_i(km) * Fuel\ Consumption_i(L/km)}{Load\ Weight_i(t)} \tag{1}$$

Table 3. Average characteristics of the collection trip for each stream (MSW, Organic, Cardboard)

	Collection stage			Final disposal at the landfill of Zahret Al-Finjan
Average characteristics	***MSW***	***Organic fraction***	***Cardboard***	
Length of the collection trip (km)	58.96	49.9 *	36.9 *	67.30
Load weight of waste (t)	5.45	1.02	1.42	28.84
Length of the trip per load weight of waste (km/t)	10.81	48.92	25.99	2.33
Fuel consumption (L/km)			1.33	1.77
Cost of fuel (EUR/L)			1.38	1.39

** Measured values*

Energy consumptions were also calculated. The organic fraction was treated with a shredding machine before being composted in turned windrows: the shredding machine for organic waste was composed by two engines with a nominal power of 5.3 kW for conveyor belts and one engine with a nominal power of 22 kW for the shredder and it treated 2 tonnes of organic waste per hour. Cardboard was processed in the TS by a compactor (nominal power of 11.2 kW, 1.75 tonnes for hour) before selling.

2.4.1. Greenhouse gases emissions

A comparison between MSW, organic waste and cardboard management procedures (Table 2), concerning greenhouse gases emission, has been done. Greenhouse gases emission in terms of carbon dioxide equivalent (CO_2eq) considering a time span of 100 years has been calculated using simplified mass balances, resumed as follows:

- Fuel consumption - Collection and transfer to the landfill implicate fuel consumption for operating trucks. Fuel consumption (diesel, with a density of 0.832 kg/L) for collecting and transferring one tonnes of waste was calculated for each stream (MSW, organic waste, cardboard). The stoichiometric equation Eq. (2) was used for combustion in order to calculate the pure CO_2 emissions:

The contribution of CH_4 and N_2O (then transformed in CO_2 equivalent) was calculated using the emission factors provided by EPA (2018). More precisely, we used an average value between "Diesel Light duty vehicles" and "Diesel medium and heavy-duty vehicles" values for collection stages (0.01616 gCH_4/km; 0.00196 gN_2O/km) and the "Diesel medium and heavy-duty vehicles" values for transport from TS to landfill stage (0.03169 gCH_4/km; 0.00298 gN_2O/km).

Power consumption for electromechanical equipments - Nominal power for the shredding machine and the compactor was known, and operating hours were calculated considering the load capacity of each of equipments. CO_2eq emissions for electric kWh depend on the energy mix: for the Middle East this value is assumed to be 205.76 gCO_2/kWh (IEA, 2017);

Composting - CH_4 and N_2O emissions from the biological treatment of 1 kg of wet waste were assumed to be 4 g CH_4/kg and 0.24 g N_2O/kg (IPCC, 2006). GWP100 (Global Warming Potential over 100 years) used for the conversion to CO_2eq emissions is 25 for methane and 298 for nitrous oxide;

Landfill disposal - The volume production of biogas per tonne of waste was calculated from literature values (Sirini et al., 2010): 0.75 m^3/kg_{VS} (VS = Volatile Solids), considering that for MSW from households, VS constitute the 52% w/w of the waste. It has been assumed that 100% of the biogas produced is emitted into the atmosphere (since there is no biogas collection system in the Zahret Al-Finjan landfill). In order to calculate, from the volume of the produced biogas, the mass of CH_4 and CO_2 emitted, it was considered that biogas is composed of 50% CH_4 (density 0.7168 kg / m^3) and 50% CO_2 (density 1.9768 kg / m^3) (De Feo et al., 2012). Finally, through the GWP100 methane index, everything has been transformed into terms of CO_2eq.

2.4.2. Economic analysis

Operational costs for each management procedure (Table 2) was assessed considering personnel costs, fuel and energy consumptions, maintenance costs, administrative expenses and disposal fees (only for MSW). While fuel consumptions were estimated using daily logs from the Database JSC-SWM, other data were obtained from meetings. Check lists were compiled together with local partners, leading to the construction of the economic framework. In fact, personnel costs were calculated on the basis of data provided by the JSC. The JSC provided also its budget for the year 2015 (the last one available), on which maintenance (4.5 EUR/t) and administration costs (7.4% of total collection costs) were deduced. Concerning treatment costs, the average energy cost for the shredding machine (19.7 EUR/month) was provided by the director of the compost station, while no data were available about the operation of the compactor machine for cardboard.

3. Results and discussion

3.1 Evaluation of the project

3.1.1 Quantity of waste collected, materials recovered and waste landfilled

The impact of the "Green Tulkarem Project" on the SWM system of the Governorate of Tulkarem was calculated with respect to three different levels.

First, the impact of SC on the total amount of MSW collected in the whole Governorate was calculated. As shown in Table 4, the percentage of organic waste and cardboard diverted from the landfill reached 2.58% of MSW collected during the first period of 2017.

Subsequently, the impact of SC was calculated with respect to the area actually interested by the project (hereafter mentioned as "real area"). Concerning the organic waste, the involved area went through the three stages explained in Materials and methods. On the other hand, cardboard SC started in September 2016, covering Tulkarem, Deir Al Ghousun, Anabta and Kafr Al Labad. Fig. 2 shows the amount of MSW, organic waste and cardboard collected in the "real area" on a monthly basis (t/month) in comparison with the amount of collected MSW in the "design area". In Table 5 performances of the SC are shown as a percentage of the daily amount of collected waste in the "real area" (average on monthly basis), giving the magnitude of the amount of material which needs to be managed daily.

Continuous changes in the set-up of the project affected its performances and made difficult the analysis. For example, variations of the project area were supposed to influence the amount of organic waste collected. Nonetheless, the Stage 2, coinciding with the widest area covered by the project, did not correspond to larger amounts of collected organic waste (Fig. 2), and was also characterized by the lowest efficiency with reference to MSW collected in the project area (Table 5). Even after the resizing of the area (Stage 3), the efficiency did not reach the level reached during Stage 1. It is not clear whether the efficiency would have been influenced by other variables, such as the seasonal variability, the organization of the collection or the level of involvement of organic waste producers. A possible reason can be found in the drop out of the project of some merchants, which were not satisfied with the timing of the collection, or were disappointed because during the transition period the collection service was not guaranteed. Anyway, this information was collected during informal dialogues and not cross-checked in a systematic way. On the contrary, performances of the SC of cardboard, started in September 2016, were increasing during all the period of study.

Finally, the performances of the project were evaluated comparing collected amounts to the expected production of each fraction in the target area or population. As previously mentioned (Section 2.3.1), the survey to producers involved in the project resulted in 4.74 t/d of organic waste, of which 1.85 t/d of animal origin (bones, meat, chicken skin) which could not be composted due to safety reasons (De Nardo, 2017). An unknown amount of organic waste was destined to direct animal feed as well.

Cardboard was collected through street collection, so an estimate of 15.75 t/d for January 2017 was calculated on the whole MSW production, assuming an incidence of cardboard of 15% (Hamada, 2011). With reference to these values, the project reached in January 2017 about 45% (1.31 t/d) of the amount of organic waste produced by target users, and about 21% (3.36 t/d) of the amount of cardboard produced in the target area.

Table 4. MSW collected in the Governorate of Tulkarem (t/year): 2014-2017

Year	***2014***	***2015***	***2016***	***2017 (3)***
MSW managed by the JSC through the Transfer Station (1)	41,400	42,553	43,969	5,531
* MSW destined for disposal in landfill (collected by the JSC)	13,634	13,179	12,680	2,116
* MSW destined for disposal in landfill (collected by Municipalities)	27,766	29,285	30,937	3,232
* SC of organic waste	0	89	306	45
* SC of cardboard	0	0	46	138
MSW managed by other actors	9,360	11,552	12,760	1,575
* Villages in the project (Attil, Illar, Baqa Al Sharqiywa, Qaffin) (2)	9,360	11,552	12,760	1,575
* Other villages	n.a.	n.a.	n.a.	n.a.
Total	50,760	54,104	56,729	7,106
* Rate of SC of organic waste on MSW collected in the Governorate of Tulkarem	-	0.16%	0.54%	0.63%
* Rate of SC of cardboard on MSW collected in the Governorate of Tulkarem	-	-	0.08%	1.94%
* Rate of SC on MSW collected in the Governorate of Tulkarem	-	0.16%	0.62%	2.58%

(1) Database JSC-SWM
(2) Estimation on 2014 values (Filippini, 2014)
(3) Period: 1st January - 12th February 2017 (not annualized)

Table 5. Performances of SC of organic waste and cardboard (%)

Stage	*Month*	*MSW (t/d)*	*SC on MSW Collected in the real area (%)*		
			Cardboard	*Organic waste*	*Separate Collection (SC)*
1	2015-08	71	-	0.74	0.74
	2015-09	63	-	0.65	0.65
	2015-10	64	-	0.75	0.75
	2015-11	69	-	1.32	1.32
	2015-12	65	-	1.94	1.94
	2016-01	67	-	1.73	1.73
	2016-02	65	-	1.71	1.71
2	2016-03	142	-	0.86	0.86
	2016-04	139	-	0.80	0.80
	2016-05	155	-	0.58	0.58
	2016-06	155	-	0.41	0.41
	2016-07	154	-	0.63	0.63
	2016-08	147	-	0.69	0.69
	2016-09	137	1.35	0.77	2.12
3	2016-10	101	1.23	1.14	2.37
	2016-11	97	1.79	1.33	3.12
	2016-12	107	1.84	1.27	3.11
	2017-01	105	3.20	1.25	4.44

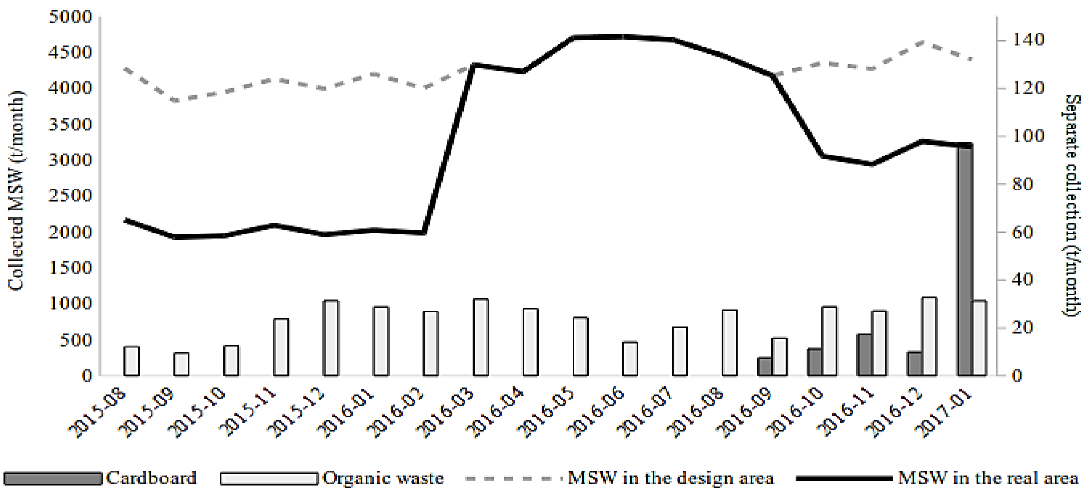


Fig. 2. Comparison between SC of organic waste and cardboard with MSW Collection in the design area and in the real area (t/month)

3.1.2 Quality of the collected organic waste

The characterization of the collected organic waste resulted in an average percentage of contaminants of 0.223 ± 0.001 % out of four samples analyzed. The organic fraction (99.777 ± 0.001 %) was composed mainly of discarded vegetables, with a considerable amount of wood coming from a canning industry working with banana fruits. Even if wet cardboard and tissues could be composted, they were considered as undesired materials because these fractions are supposed to be collected separately. Plastic is the most relevant fraction among undesired materials (ranging from 30% to 73% w/w); it includes several types of polymers, which were separately weighted: MDPE (films) was predominant, followed by HDPE (hard containers), polypropylene (wires), PET (soft plastic bottles), polylaminate (snack packaging) and latex (gloves) (Fig. 3). Other undesired materials were mostly glass bottles (0-18% w/w) and aluminum cans (0-2% w/w), while the presence of other objects (toys, nappies, medicine packs) occurred randomly.

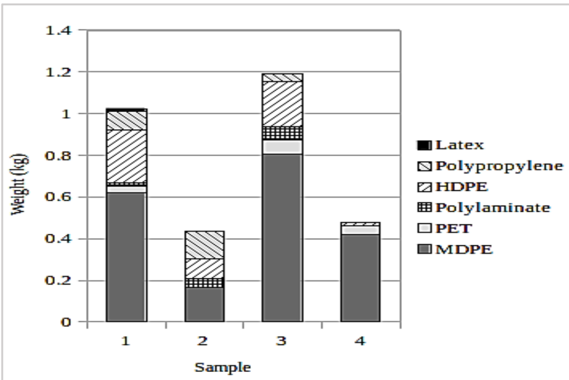


Fig. 3. Amount and kind of plastic present in the organic waste collected

3.2. Environmental and economic analysis

3.2.1 Greenhouse gases emissions

Analyzing the Database JSC-SWM, the average fuel consumption for tonne of waste was calculated: for the collection stage it resulted in 7.20 L/t for MSW, 36.52 L/t for organic waste, 22.46 L/t for cardboard; for the transport of MSW from the TS to the landfill it resulted in 2.58 L/t. Greenhouse gases emissions in terms of carbon dioxide equivalent (CO_2eq) were calculated: they account for 3,905,569 g CO_2eq/t for MSW, 270,747 gCO_2eq/t for organic waste, 60,760 g CO_2eq/t for cardboard. Detailed results are resumed in Table 6.

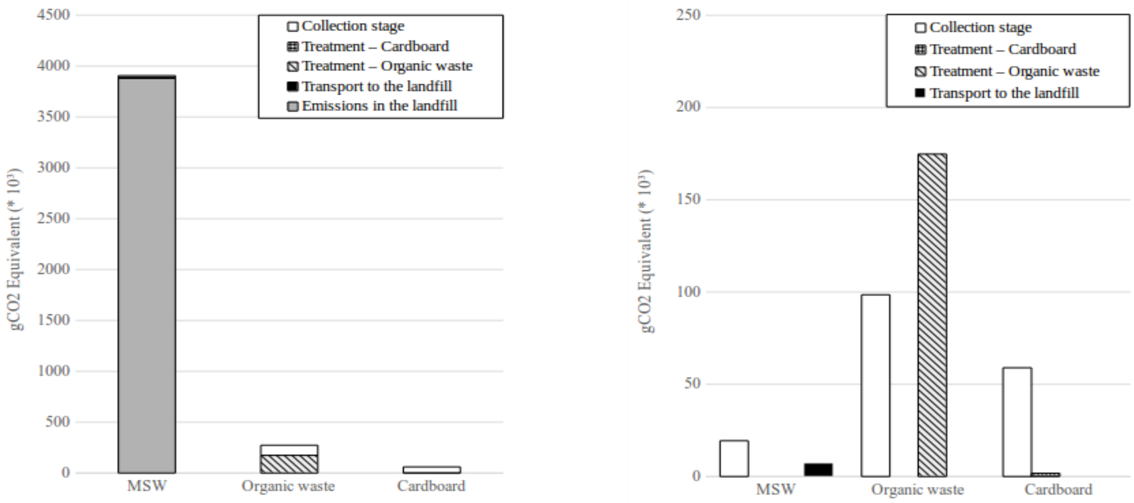
In terms of carbon dioxide equivalent, emissions from the landfill have a magnitude higher than other considered emissions (Fig. 4a). In order to allow the comparison between other emissions, results are shown in Fig. 4b without taking into account emissions generated by waste landfilling. Comparing emissions in the collection stage, the transport of one tonne of organic waste leads to more emissions than transport of both cardboard and MSW. This is because a collection trip for organic waste is longer than other collection trips, and the amount of transported waste is lower on average, not exploiting the entire load capacity of the truck.

Comparing emissions of SC of organic waste and cardboard, therefore taking into account the whole procedure, the management of organic waste results as the most impacting, due also to emissions in the composting process. It has to be pointed out that the lack of information related to the treatment and subsequent transport of the cardboard is likely to lead to an underestimate of emissions. At the same time, the lack of information about the location of the paper plant and production processes did not consent to calculate the amount of avoided emissions due to the use of recycled cardboard in substitution to the primary raw material. This aspect would have influenced the balance in positive terms, diminishing the amount of estimated emissions.

Finally, it is worth to mention that the contribution of CH_4 and N_2O from the fuel combustion, which was calculated on the basis of the length of the trip, may be eventually neglected in a more semplified approach as it accounts for less than 1% on total GHG emissions.

Table 6. Greenhouse gases emission in terms of gCO_2eq for tonne of waste calculated for each waste stream (MSW, organic waste, cardboard)

Stream: MSW	***GHG emissions (g CO_2eq/ t)***
Collection stage (fuel consumption)	18,915
Primary storage at the Transfer Station	neglected
Transfer from the TS to the landfill (fuel consumption)	6,778
Final disposal (emissions from the landfill)	3,879,876
Total emissions	3,905,569
Stream: Organic waste	***GHG emissions (g CO_2eq/ t)***
Collection stage (fuel consumption)	95,935
Treatment:	
Shredder (energy consumption)	2,263
Conveyor belts (energy consumption)	1,029
Composting process (emissions)	171,520
Transfer to the final user (fuel consumption)	N.A.
Total emissions	270,747
Stream: Cardboard	***GHG emissions (g CO_2eq/ t)***
Collection stage (fuel consumption)	58,997
Treatment:	
Compactor (energy consumption)	1,764
Transfer from the TS to the paper mill	N.A.
Avoided emissions due to the use of secondary raw material in the production of cardboard and paper	N.A.
Total emissions	60,760



(a) (b)

Fig. 4. Greenhouse gases emission in terms of gCO_2 for tonne of waste calculated for each waste stream

(MSW, organic waste, cardboard) with (a) or without (b) emissions generate by waste landfilling

3.2.2 Economic analysis

Average costs for managing one tonne of MSW (collected and transferred to Zahret Al-Finjan – CT; simply transferred - T), organic waste or cardboard have been calculated. Concerning transport stage (collection and transfer to the landfill), daily logs contained in the Database JSC-SWM allowed the calculation of costs referred the collection of one single tonne of waste. Management costs covered by the JSC and its partners (Thinnabeh and the private enterprise charged with the cardboard collection) are included in the calculation. Collection costs for MSW collected by Municipalities and transferred to the landfill by the JSC (MSW-T) are not available. Nonetheless, the total cost for MSW-T has been calculated considering the storage in the TS and final disposal costs. These costs are in fact covered by the JSC and they are necessary to calculate the total cost of the SWM system. The results are shown in Table 7.

Total management costs for cardboard (54.17 EUR/t) and organic waste (79.54 EUR/t) are higher than total MSW management costs (45.89 EUR/t). Total MSW management costs are comparable with literature data for the West Bank: for the city of Qalqilia the estimate ranged from 46 to 63 EUR/t (Hinde, 2010), for the city of Nablus costs were estimate in 47 EUR/t in 2005 (Al-Khatib et al., 2010), while for the Governorate of Jenin they were calculated in 25 EUR/t (Sweep-Net, 2014). In a study of UN-Habitat on twenty cities in the world, total MSW management costs ranges from 10 to 128 EUR/t (UN-HABITAT, 2010).

In this study, collection results as the most expensive phase, with costs influenced by collection duration, distance covered by trucks and waste collected amount.

Concerning organic waste, collection costs are higher because the compactor truck covers a higher distance to collect less waste if compared with MSW and cardboard routes. Possible solutions to minimize organic waste collection costs can include the selection of a smaller and more efficient truck, the increment of the number of user involved in the collection (maintaining the same area), or a further resizing of the collection area. On the contrary, collection costs for cardboard are covered almost entirely by the private enterprise. This represents a saving of 14 EUR/t (MSW-T) to 43 EUR/t (MSW-CT) for the JSC, which should have otherwise paid these collection costs. Earnings of the private enterprise from the sale of cardboard to the paper factory are not known. Treatment costs, with reference to the organic waste and to cardboard, have a little influence on total costs. Transfer and disposal costs of MSW affect only MSW management and can be consequently considered as "avoided costs" for both organic waste and cardboard. Annual costs for waste management calculated on the amount of waste managed by the JSC are resumed in Table 8, including costs covered by the private enterprise and not those covered by Municipalities. Table 8 shows an economic impact of organic waste SC of about 2% of the annual budget.

The results of both environmental and economic analysis are resumed in Fig. 5. For each type of waste stream (MSW, organic waste or cardboard) every phase is described, with corresponding management costs in EUR/t and greenhouse gases emissions in kg CO_2eq/t.

Table 7. Waste management costs (EUR/t) covered by the JSC and other partners

	Organic waste (EUR/t)	***Cardboard (EUR/t)***	***MSW-CT (EUR/t)***	***MSW-T (EUR/t)***
Management costs, of which	79.54	54.17	45.89	17.00
- covered by the JSC	78.77	2.96	45.89	17.00
- covered by other partners	0.77	51.22	-	-
Collection	72.93	47.43	26.76	n.a.
* Personnel (drivers, workers)	18.04 (1)	11.92 (1)	12.29 (1)	n.a.
* Fuel	50.36 (2)	30.97 (2)	9.94 (2)	n.a.
* Maintenance	4.53 (1)	4.53 (1)	4.53 (1)	n.a.
Administrative expenses	5.83	3.79	2.14 (1)	n.a.
Storage in the Transfer Station (cardboard, MSW)	-	2.96 (1)	2.96 (1)	2.96 (1)
Treatment (organic waste, cardboard)	0.77	n.a.	-	-
* Energy consumption (shredding machine for organic waste)	0.77 (1)	-	-	-
* Energy consumption (pulper for cardboard)	-	n.a	-	-
* Energy consumption (compactor for cardboard)	-	n.a	-	-
* Management costs for Thinnabeh (organic waste)	n.a.	-	-	-
Transfer to Zahret Al-Finjan (MSW)	-	-	14.04	14.04
* Fuel (MSW)	-	-	3.58 (3)	3.58 (3)
* Truck maintenance and driver (MSW)	-	-	2.33 (1)	2.33 (1)
* Disposal fee (MSW)	-	-	8.13 (1)	8.13 (1)

(1) Based on interview results
(2) Based on Database JSC-SWM (average fuel price: 1.38 NIS/L)
(3) Based on Database JSC-SWM (average fuel price: 1.39 NIS/L)

Table 8. Annual costs for waste management (EUR/year)

	2014	*2015*	*2016*	*2017 (1)*
Collection and transfer (MSW-CT)	625,647	604,761	581,898	97,123
Transfer (MSW-T)	471,848	497,656	525,728	54,922
Organic waste	0	7,101	24,333	3,575
Cardboard (of which covered by JSC)	0	0	2,477 (135)	7,482 (408)
Total	**1,097,494**	**1,109,518**	**1,134,436**	**163,102**
(1) Period: 1st January - 12th February 2017 (not annualized)				

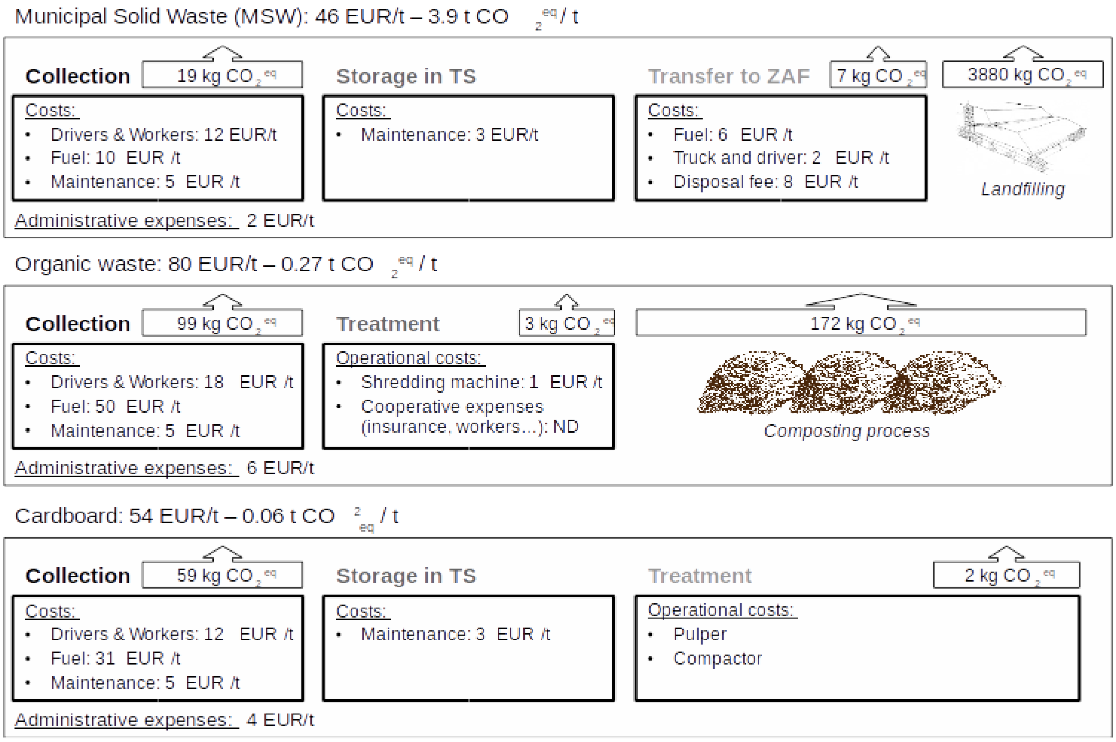


Fig. 5. Overview of the waste management system: stages, processes, greenhouse gases emissions and management costs

4. Conclusions

This study has the purpose of assessing the environmental and economic impact of the SC system introduced by a development project in a city of the West Bank.

In the target area, the introduction of the SC has led to the separation of a satisfactory amount of the expected production of the organic waste (45%) and cardboard (21%), characterized by a high levels of quality. These results were due to the awareness activities addressing shop keepers and merchants and the engagement of collection workers, which actively contribute to a good collection. Considering the whole Governorate of Tulkarem, a small impact on the whole SWM was reached as well, with the 2.58% of waste diverted from the landfill.

On the side of the environmental assessment, the SC has led to lower GHG emissions in comparison with the previous system: in fact, the complete management of one tonne of organic waste (0.27 tCO_2eq) and cardboard (0.06 tCO_2eq) is far less impactful of the disposal of one tonne of MSW in the landfill (3.9 tCO_2eq), even considering the impact of the collection phase.

From the economic point of view, higher costs for SC have been observed, balanced out by revenues only in the case of the cardboard. The relevance of the collection stage in this sense has been confirmed, as it accounts for 92% (organic waste stream), 88% (cardboard stream) and 58% (MSW stream) of waste management costs.

These results confirm the feasibility of the SC of organic waste and cardboard with reference to attitudes of the population but point out a criticality on the economic side. In fact, the lack of economic sustainability led to the suspension of the SC of organic waste at the end of the project, when the international funding finished.

From the methodological point of view, the analysis was affected by the lack of data, which is common in developing context (*inter alia*) (Di Bella et al., 2012; Domini et al., 2017). Moreover, the several changes which occurs within the project prevent analysis to be done on a long term period characterized by stable boundary conditions. Those obstacles have been tackled with the adoption of simplified models for both environmental and economic assessment. This choice has revealed itself suitable for the context, leading to representative results.

Overall, the "Green Tulkarem Project" should be considered as the first tentative to establish SC in the area. It did not reach a final efficient set up, but the cost of organic waste SC in this phase was not exceeding the 2% of the annual budget of the JSC for SWM, and it could have been eventually balanced out by savings originated by cardboard SC. Consequently, such a project can have a positive impact, whether considered as a first step of warming-up toward a more efficient management system.

Furthermore, an improvement of the system may arise from the use of available data, which were collected by the JSC but roughly analyzed. In fact, more detailed analysis can support the choice of cheaper solutions, intervening on the collection stage and maintaining the separation at source, which is known to be a pre-requisite for sustainable recycling of cardboard (Miranda et al., 2013) and valorization of the organic waste. Solutions to minimize the cost of SC should be identified, for example through the optimization of transports or the local and decentralized treatment of organic waste. A final aspect which should be targeted in further studies is the existence of local practices, such as the direct animal feed, often overlooked. Located at the apex of the food waste hierarchy (Papargyropoulou et al, 2014), such a practice might lead to positive impact whether considered in the whole waste management system.

Acknowledgements

The authors are grateful to Cesvi NGO for its logistical and financial support and to the local staff (above all Marco Caniato, Maddalena Caddeo and Saad Zabadi) and authorities for their support on site. This study was carried out in the project "Miglioramento delle condizioni sanitario-ambientali nel Governatorato di Tulkarem attraverso il supporto alla raccolta e il riciclaggio dei rifiuti e la riabilitazione di discariche abusive", funded by Italian Ministry of Foreign Affairs. Mentore Vaccari set and supervised the research activity; Francesca Villa collected data and, with the co-authors, performed their elaboration. Silvia Gibellini estimated the greenhouse gas emissions. The authors want to thank their colleagues Francesco Vitali, Fabiola Zambetti and Federico De Nardo, which followed the previous stage of the project during their doctoral studies.

References

Al-Khateeb A.J., Al-Sari M.I., Al-Khatib I.A., (2017), Factors affecting the sustainability of solid waste management system - the case of Palestine, *Environmental Monitoring and Assessment*, **189**, 93.

Al-Khatib I.A., Arafat H.A., Basheer T., Shawahneh H., Salahat A., Eid J., Ali W., (2007) Trends and problems of solid waste management in developing countries: A case study in seven Palestinian districts, *Waste Management*, **27**, 1910-1919.

Al-Khatib I.A, Monou M., Abu Zahra A.S.F., Shaheen H.Q., Kassinos D., (2010), Solid waste characterization, quantification and management practices in developing countries. A case study: Nablus district – Palestine, *Journal of Environmental Management*, **91**, 1131-1138.

Caniato M., Vaccari M., (2014), How to assess solid waste management in armed conflicts? A new methodology applied to the Gaza Strip, Palestine, *Waste Management & Research*, **32**, 908-917.

Caniato M., Tudor T., Vaccari M., (2015), Understanding the perceptions, roles and interactions of stakeholders networks managing health-care waste: A case study of the Gaza Strip, *Waste Management*, **35**, 255-264.

Coffey M., Coad A., (2010), *Collection of Municipal Solid Waste in Developing Countries*, Un-Habitat Press, Nairobi, Kenya.

Collivignarelli C., Vaccari M., Di Bella V., Giardina D., (2011), Techno-economic evaluation for the improvement of MSW collection in Somaliland and Puntland, *Waste Management & Research*, **29**, 521–531.

Crowley D., Staines A., Collins C., Bracken J., Bruen M., Fry J., Hrymak V., Malone D., Magette B., Ryan M., Thunhurst C., (2003), Health and Environmental Effects of Landfilling and Incineration of Waste - A Literature Review, Dublin Institute of Technology, On line at: http://arrow.dit.ie/schfsehrep.

Damgaard A., Manfredi S., Merril H., Stens S., Christensen T.H., (2011), LCA and economic evaluation of landfill leachate and gas technologies, *Waste Management*, **31**, 1532-1541.

De Feo G., De Gisi S., Galasso M., (2012), *Solid waste. Design and management of treatment and disposal plants*, (in Italian), Dario Flaccovio Press, Palermo, Italy.

De Nardo F., (2017), *Strategies to improve organic waste recovery in Palestine using participatory approaches and value chain analysis*, PhD Thesis, Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, Italy.

Di Bella V., Ali M., Vaccari M., (2012), Constraints to healthcare waste treatment in low-income countries – a case study from Somaliland, *Waste Management & Research*, **30**, 572-575.

Di Bella V., Vaccari M., (2014), Constraints for solid waste management in Somaliland, *Proceedings of Institution of Civil Engineers: Waste and Resource Management*, **167**, 62-71.

Domini M., Gibellini S., Villa F., Vidoni A., Difrancesco L., Sorlini S., Vaccari M., (2017), *The Challenge of Sharing Data in Cooperation Projects: Cause for Reflection*, Congress Coordination University Development Cooperation, Milano, Italy, 14-15 Settembre 2017.

EPA, (2018), Emission Factors for Greenhouse Gas Inventories, On line at: https://www.epa.gov/sites/production/files/2018-03/documents/emission-factors_mar_2018_0.pdf

El-Kelani R., Shadeed S., Hasan A.F., Ghodieh A., Burqan M., (2017), Geospatial Implications Assessment of Zahrat Al Finjan Solid Waste Landfill, North of West Bank, Palestine, *IUG Journal of Natural Studies*, **25**, 1-9.

Filippini G.C., (2014), *Technical Supervisor final report on "Green Tulkarem" project* (in Italian), Italian Agency for Development Cooperation.

Hamada S.R., 2011, *Comparative Analysis of Separation Versus Direct Transport of Solid Waste from Tulkarem District to Zahret Al-Finjan*, MSc Thesis, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

Hinde I.M., (2010), *Cost Analysis of Solid Waste Management for the City of Qalqilia*, MSc Thesis, Faculty of Graduated Studies, An-Najah National University, Nablus, Palestine.

Hoornweg D., Bhada-Tata P., (2012), What A Waste - A Global Review of Solid Waste Management, World Bank, On line at: https://openknowledge.worldbank.org/handle/10986/17388.

Hultman J., Corvellec H., (2012) The European Waste Hierarchy: from the sociomateriality of waste to a politics of consumption, *Environment and Planning A*, **44**, 2413-2427.

IEA, (2016), CO2 Emissions from Fuel Combustion - 2016 Highlights, International Energy Agency, On-line at: https://webstore.iea.org/co2-emissions-from-fuel-combustion.

IPCC, (2006), IPCC Guidelines for National Greenhouse Gas Inventories, Institute for Global Environmental Strategies (IGES), Hayama, Japan, On line at: https://www.ipcc-nggip.iges.or.jp/public/2006gl.

Lee S., Vaccari M., Tudor T., (2016), Considerations for choosing appropriate healthcare waste management treatment technologies: A case study from an East Midlands NHS Trust, in England *Journal of Cleaner Production*, **135**, 139-147.

Lohri C.R., Diener S., Zabaleta I., Mertenat A., Zurbrügg C., (2017), Treatment technologies for urban solid biowaste to create value products: a review with focus on low- and middle-income settings, *Reviews in Environmental Science and Biotechnology*, **16**, 81-130.

Miranda R., Bobu E., Grossmann H., Stawicki B., Blanco A., (2010), Factors influencing a higher use of recovered paper in the European paper industry, *Cellulose Chemistry and Technology*, **44**, 419-430.

Miranda R., Concepcion Monte M., Blanco A., (2013), Analysis of the quality of the recovered paper from commingled collection systems, *Resources, Conservation and Recycling*, **72**, 60-66.

Papargyropoulou E., Lozano R., Steinberger J.K., Wright N., Ujang Z., (2014), The food waste hierarchy as a framework for the management of food surplus and food waste, *Journal of Cleaner Production*, **76**, 106-115.

PCBS, (2015), Percentage Distribution of Households in Palestine by the Solid Waste Disposal Doer and Region, 2015, Palestinian Central Bureau of Statistics, On line at: http://www.pcbs.gov.ps/Portals/_Rainbow/Documents/HHE%202015%20e%204.htm.

PCBS, (2017), Localities in Tulkarm Governorate by Type of Locality and Population Estimates, 2007-2016, Palestinian Central Bureau of Statistics, On line at: http://www.pcbs.gov.ps/Portals/_Rainbow/Documents/tulkrm.htm.

Perteghella A., Vaccari M. (2017), Organic waste valorization through composting process: a full-scale case study in Maxixe, Mozambique, *Environmental Engineering and Management Journal*, **16**, 1819-1826.

PNA, (2010), National Strategy for Solid Waste Management in the Palestinian Territory 2010-2014, Palestinian National Authority, On line at: http://www.molg.pna.ps/studies/TheSolidWasteManagementStrategy2010-2014.pdf.

Scott G.M., (2011), *Chapter 10 - Recovered Paper*, In: *Waste*, Letcher T.M., Vallero D.A. (Eds.), Academic Press, 137-149.

Sirini P., Tchobanoglous G., La Diega R.C.N., (2010), *Handbook of Solid Waste Management* (in Italian), McGraw-Hill, Milan.

SWEEP-Net, (2014), Country report on the solid waste management in Occupied Palestinian Territories, The Regional Solid Waste Exchange of Information and Expertise network in Mashreq and Maghreb countries, On line at: www.environment.pna.ps.

UN General Assembly, (2015), Transforming our world: the 2030 Agenda for Sustainable Development, A/RES/70/1, On line at: https://documents-dds-ny.un.org/doc/UNDOC/GEN/N15/291/89/PDF/N1529189.pdf?OpenElement.

UN-HABITAT, (2010), Solid waste management in the World's cities, United Nations Human Settlements Programme, Washington, USA, On line at: https://unhabitat.org/books/solid-waste-management-in-the-worlds-cities-water-and-sanitation-in-the-worlds-cities-2010-2/.

Vaccari M., Torretta V., Collivignarelli C., (2012), Effect of improving environmental sustainability in developing countries by upgrading solid waste management techniques: A case study, *Sustainability*, **4**, 2852–2861.

Vaccari M., Bella V.D., Vitali F., Collivignarelli C, (2013), From mixed to separate collection of solid waste: Benefits for the town of Zavidovići (Bosnia and Herzegovina), *Waste Management*, **33**, 277-286.

Vaccari M., Perteghella A. (2016), Resource recovery from waste by Roma in the Balkans: a case study from Zavidovici (BiH), *Waste Management & Research*, **34**, 866–874.

Wilson D.C., Rodic L., Cowing M.J., Velis C.A., Whiteman A.D., Scheinberg A., Vilches R., Masterson D., Stretz J., Oelz B., (2015), "Wasteaware" Benchmark Indicators for Integrated Sustainable Waste Management in Cities, *Waste Management*, **35**, 329-342.

World Bank, (2017), World Development Indicator for West Bank and Gaza, On line at: http://databank.worldbank.org/data/reports.aspx?source=2&country=LMC,PSE.

Zhao C.Y., Wan H.F., Wei Y.S., Han S.H., Ge Z., Zheng B.F., Li H.M., (2016), Effects of addition of red mud on emission of greenhouse gases and ammonia from full-scale swine manure windrow composting, *Environmental Engineering and Management Journal*, **15**, 2245-2252.

Zurbrügg C., Caniato M., Vaccari M., (2014), How assessment methods can support solid waste management in developing countries-a critical review, *Sustainability*, **6**, 545-570.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2485-2496
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

GASIFICATION OF BIOMASS FROM RIVER MAINTENANCE AND CHAR APPLICATION IN BUILDING MATERIALS PRODUCTION

Vittorio Vezzali*, Fernanda Andreola, Luisa Barbieri, Isabella Lancellotti, Paolo Pozzi, Giulio Allesina, Simone Pedrazzi, Paolo Tartarini

Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Vivarelli, 10/1 – 41125 Modena, Italy

Abstract

This paper exposes the research activities regarding REBAF (Energetic Recover of River Biomasses) project, focused on the maintenance operations self-sustainability of the Secchia river (Italy). Poplar was found as the most abundant and representative wood plant of Secchia riverbanks, with a good behavior during gasification process: from 1 hectare of maintenance every three year, it was possible to produce 23 MWh of electrical power and 31 MWh of thermal power. The biochar obtained was characterized and mixed with local red clay to create both lightweight aggregates (LWAs) for green roofs applications and bricks. Ashes coming from the gasifier cyclone were characterized and used to create bricks. The aims are the saving of raw materials and the obtaining of weight-lightened products with high porosity. Biochar and ashes were found to be suitable for this purpose given their organic carbonaceous nature, according to X-ray diffractometry, Loss on Ignition (LOI) and TG-DTA results. Application on LWAs by substituting 15%wt of the clay with biochar leads to a weight-lightening of the material. To optimize LWAs pH, spent coffee grounds (SCG) were added with proportion of 85% clay-15% biochar/SCG. A greater decrease in weight and pH values in the neutrality range were observed. Adding 20%wt biochar or ashes on bricks led to a significant reduction of materials bulk density (from 2 to 1.5 g/cm^3) and the achievement of 40-45% porosity. With higher additions (until 40%wt) bulk density gets lower (1.2 g/cm^3–1.3 g/cm^3), but the material results weaker with a worst mechanical strength.

Key words: bio-char, biomass, brick, gasification, lightweight-aggregate

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

Biomass from river maintenance is not widely used for bioenergy production. In fact, the high moisture, the high ash content and the variable size distribution decrease the quality of these feedstock which it is less exploitable into power plants compared to wood chips or wood pellets (IEA, 2012). However, the wide availability of biomass per hectare of riverbed justifies the cost of power plants optimized for these kinds of feedstocks, in fact wetland crops like *A. Donax* produce up to 42 Mg ha^{-1} year^{-1} in Italy (Ceotto et al, 2013; Spinelli, 2005). Over the energy convenience of the conversion processes, river maintenance is a vital operation to ensure the safety of banks and to prevent ruinous floods. The vegetation on the river bed reduces the velocity of the water waves, thus increasing their height and the pressure-related stress on the river banks. Flood waves can pull out the vegetation together with part of the bank, this fact further erodes the soil of the banks (Silingardi, 2007). In this paper, we summarized the first activities and results regarding the project of the REBAF project of the Emilia Romagna region. During several field surveys near the Secchia riverbanks, we found out that the dominant arboreal species are poplar, willow, alder and elm. About the grass biomass, the most abundant species are Typha L., *Phragmites*, rushes and sedges, *Rumex L.* and *Equisetum*. There are also some species such as reeds and panic with characteristic in between

* Author to whom all correspondence should be addressed: e-mail: vittorio.vezzali@unimore.it; Phone: +39 0592056221; Fax: +390592056243

wood and grass biomasses. About wood biomasses suitable for gasification, poplar is the most abundant plant which can be collected from river maintenance (Spinelli, 2005). The cut of poplar is made regularly every 3 years. For this reason, in the REBAF project we consider that the composition of the biomass can be assimilated to that of poplar. In addition, willow and poplar woods have similar composition and higher heating value (ECN, 2018). Literature suggests that about 50-70 ton/ha of biomass is obtainable from maintenance of rivers located in Northern Italy every 3 years (Spinelli, 2005). The initial moisture of this biomass is very high. Basu (2010). suggests about 40-50% of moisture for freshly cut wood chips. This work investigates the problem in the worst case: amount of 50 ton/ha only of poplar wood chips with moisture content up to 50% and the cut is made every 3 years. Experimental gasification tests of wood chips from river maintenance were done in a commercial gasification power plant All Power Labs PP20 (All Power Labs, 20187).

The by-product of this process is biochar: a fine-grained vegetable carbon extracted from the bottom of the gasifier. If added to the soil it can improve its chemical-physical properties thanks to the strongly stable nature of organic C, which is not subject to degradation and mineralization, either because it is a very porous material with a high reaction surface, which increases water retention for example of sandy soils. Further, the improvement is related to the increasing soil fertility and crop yield because of it is often used as soil improver. A further advantage of the storage of biochar in the ground is the reduction of CO_2 emissions into the atmosphere (Glaser et al., 2002; Lehmann, 2007; Van Zwieten et al., 2008; Yamato et al., 2006),) thanks to the carbon sink process where carbon dioxide is subtracted from the cycle of carbon.

If the use of biochar as soil or substrate improver has been studied a lot in the last 15 years, the application of this substance in building materials or other composites is starting to gain more attention recently. Indeed, in addition to the great advantage of carbon sequestration, the use of biochar can reduce the energy associated with the production process of such materials, by decreasing firing temperature, as well as the consumption of raw materials. Furthermore, in many applications, for example cement or other materials, an improvement of various physical properties is found when biochar is added. A growing interest can be seen in cement composites application: Gupta et al. (2017), for example demonstrated the feasibility of using biochar in cementitious materials, focusing on carbon sequestration. Choi et al. (2012), after testing mixture with 5, 10, 15 and 20% of biochar, reported that introduction of 5% biochar in cement mortar increased 28-day compressive strength with no significant decrease in flowability. All the specimens prepared with biochar had less moisture evaporation and better water retention, so biochar seems to act like a self-curing agent for cement material. Addition of 1% of hazelnut and peanut shell biochar in cement paste was found to increase flexural toughness because biochar particles act as obstacle to cracks propagating, increasing its tortuosity, with the corresponding increase in toughness and fracture energy (Khushnood et al.,2016). Ahmad et al. (2015) also found an increase in compressive strength by 30% when 0.20% of bamboo biochar when added to cement mortar. Other recent uses of biochar in the building sector can be identified in the field of composite materials and asphalts. Wood-polypropylene composites, which belong to the first typology, are materials widely used in automotive and building sector. DeVallance et al. (2015) added hardwood biochar at 5, 15, 25 and 40wt% instead of wood flour in these materials, with a substantial increase in flexural strength, tensile strength and tensile elasticity. For the second typology, Zhao et al. (2014) mixed 10wt% of switchgrass biochar with asphalt components and compared its properties to carbon black and carbon fiber additions. The results indicate that biochar reduces the temperature susceptibility in asphalt binders and induces a higher rutting resistance.

Considering the introduction of a waste, such as biochar, into a production process, we can see that the building materials industry has interesting receptive features as can absorb a wide range of waste even in large quantities. In particular ceramics as bricks, cement materials and polymers, thanks to their own matrix structure, are the best building materials not only for receiving but also for inertising several types of residues. Building materials industry has also large margins of improvement from an environmental and economic point of view: the consumption of natural resources such as sand, rocks or water is so high that the only construction industry consumes more raw materials than any other activity.

In this work two types of waste were characterized: biochar (with grain size under 4 mm) coming from the gasification reactor and ashes coming from the soot collection vessel of the cyclone. Original feedstock consists in woodsy biomass from river maintenance. Chemical, thermal and physical analyses were made to fully characterize the materials and understand their nature and behaviour. The previously characterized biochar and cyclone ashes were then applied in various building materials such as bricks and LWAs (lightweight aggregates) for green roofs. SCG (spent coffee grounds) were also used in the preparation of LWAs. SCG are the majority of coffee residues and they are obtained from the brewing process or from soluble coffee industry (Cruz et al., 2012).

2. Material and methods

2.1. Gasification facility

The small gasification power plant used in this work is depicted in Fig. 1. It is a commercial All Power Labs PP20 gasifier. The reactor architecture consists in an air-blown Imbert type downdraft gasifier, typical of mall scale reactors (Vakalis and

Baratieri, 2015). Wood chips are loaded in the hopper that has a volume of about 300 liters. The chips are moved to the gasification reactor by an auger and they are converted in producer gas and biochar. About 5% in mass of the inlet biomass is converted into biochar and extracted from the bottom of the reactor through an auger connected to a vessel. The producer gas is filtered in a cyclone, cooled down and purified in the final char candle filter. After the filtration, the producer gas is mixed with air and it is burned into the engine that drags an alternator to produce electrical power. The engine is equipped with a heat exchanger that extracts about 20 kW of thermal power form the engine coolant when the electrical generator produces 15 kW of electrical power. System specification are summarized in Table 1. The temperature within the reactor reaches its maximum at the throat. In this point, the air blasted through the nozzles creates a combustion stage with peak temperatures around 880-950°C. In the part of the reactor below the throat, char reduction takes place. This endothermic process makes the temperature to drop from 950 to 650°C approximately.

Fig. 1. All Power Labs PP20 gasifier (All Power Labs, 2018).

Table 1. Specification of the All Power Labs PP20 with CHP auxiliary subsystem

Characteristic	***Value***
Continuous electrical power rating	15 kW_{el} @50 Hz
Continuous thermal power rating	20 kW_{th} at 15 kW_{el}
Biomass P16 W10 consumption	1.2 kg/ kWh_{el}
Biomass moisture content	5-30% dry basis
Electrical efficiency with P16 W10	18.5 %
Thermal efficiency with P16 W10	24.6 %
Installed foot print	1.36 x 1.36 m
Run time with hopper fill	3 hours at 15 kW_{el}

2.2. Chemical characterization

Riverbanks and red spruce biochars and cyclone ashes samples (one specimen for each type) were examined by scanning electron microscope (SEM) “ESEM-Quanta 200 FEI”, to evaluate particle structure and surface morphology of the materials. Energy Dispersive Spectroscopy (EDS), coupled with SEM, was also carried out to identify the atomic elements in these materials and their relative proportions (%). With EDS total carbon content was evaluated also for different biochar. The content of C, H, N, S in gasification biochar and ashes was measured on an elemental analyser “CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112”. The test refers to a sample of biochar and ashes coming from red spruce and was made in order to confirm the results given by EDS analyser. The materials were grounded prior to this analysis. For pH measurements of the biochar, an "XS Instruments, pH 6" pH meter was used. Biochar samples and cyclone ashes (10 g) were immersed in deionized water at a ratio of 1:5 and 1:10 by weight and 1:5 by volume and kept for 1 hour under magnetic stirring prior to the pH measurement following UNI EN 13037 (2012). The pH meter was previously calibrated with standard buffers at pH 4, 7 and 10. The measurement of specific electrical conductivity is directly linked to the presence of salts in solution, the dissociation of which generates positive and negative ions. The analyses were conducted on the same eluates analysed with pH meter with reference to the UNI EN 13038 (2012). The measurement was carried out with the “Oakton CON 6/TDS 6” model conductivity meter. The determination of major crystalline phases present in the biochar and ashes was achieved by using an X-ray diffractometer “Phillips PANalyticalPW3710” on grounded and dried material. Carbonates analysis was made using a “Dietrich-Fruhling” calcimeter. The material was grounded and dried prior to the analysis.

2.3. Thermal characterization

Moisture content was determined following UNI EN 13040 (2008) standard in a stove at 105°C for 24h. The loss of mass and thermal behavior with increasing temperature were determined by Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA), using a “Netzsch STA 409” analyser. The temperature range was set between 20°C and 1300°C, with a heating rate of 10°C/min. The mass of biochar and ashes in the platinum crucible ranged from 5 to 20 mg. Three different Loss on Ignition (LOI) tests at 700°C, 900°C and 1100ºC were also performed on biochar samples (three measurements for each temperature using 10g sample) to compare the results achieved in TG-DTA. The material was weighed and placed in ceramic crucibles. After each two-hours-heating test in a muffle furnace, the biochar was allowed to cool completely in the oven before weighing. The data reported are an average value of the three obtained.

2.4. Physical characterization

The particle size distribution of the biochar and ashes was determined using a stainless-steel sieve set (mesh 2, 1, 0.5, 0.25, 0.125 mm) placed in a vibration sieve shaker for 15 minutes. The materials were analysed as received, without pre-treatments. Another analysis was also carried out with a laser granulometer "Malvern mastersizer 2000" in the range of 0.1-2000 µm, after an ultrasound treatment, to better understand the behavior of the finer fraction of the two materials. Specific surface area was determined by the Brunauer-Emmett-Teller (BET) method by nitrogen gas sorption with a "Gemini V" analyser; the biochar was outgassed for 24 h at 105°C prior to the measure. Particle density was measured by helium pycnometer "AccuPyc II 1340, Micromeritics" with precision on standard deviation and on mean of 0.0001 g/cm^3. Bulk density of the two materials was evaluated experimentally by adding a known amount of specimen mass into a graduated cylinder to measure the volume. Before both measurements, the samples were dried in an oven at 105°C. Porosity ε (Eq. 1) was evaluated with the following formula (Brady and Weil, 1996; Flint and Flint, 2002):

$$\varepsilon = 1 - (\rho_b / \rho_p) \quad (1)$$

where: ε [ad] is the char porosity, ρ_b [kg/dm^3] is the char bulk density and ρ_p [kg/dm^3] is the char particle density. Multiplying the result obtained by 100 it was possible to obtain the value expressed in %.

2.5. LWA samples production

For the production of LWAs, two distinct types of preparations were made. The first, aimed at demonstrating the feasibility of inserting the biochar in these materials, involved the preparation of aggregates with biochar (with a particle size of less than 250 µm) and two different types of local red clay (with a particle size of less than 1 mm): clays were named a and b. Both samples were prepared with 85wt% clay (a or b)-15wt% biochar and were named BCa (85wt% red clay a, 15wt% biochar) and BCb (85wt% red clay b, 15wt% biochar). These two specimens were compared with control samples named ROa (100% red clay a) and ROb (100% red clay b).

The second, aimed at optimizing aggregates with biochar, saw the inclusion of a second waste in substitution of biochar, spent coffee grounds (SCG) collected from some local commercial activities, dried and sieved under 250 µm, in order to obtain an improvement in terms of pH of the finished product. The ratio in this case was 85% clay b-15% biochar/SCG and the sample was named CBCb. All the raw materials used were previously dried in an oven at 105°C to remove all traces of free water. The homogeneous mixing between the clays and residues was carried out inside a ceramic container; then, distilled water was added to the powders to obtain a workable paste. Once the homogeneous mixture was obtained, LWAs were manually made, trying to make the samples similar in weight and shape to the most known commercial LWAs (0.6-0.8 cm diameter); from each mixture a variable number of spheres was obtained (between 35 and 60 elements). All the obtained aggregates were dried at 105°C for about 24 hours to remove excess free water used in the preparation process. The aggregates were than subjected to a firing treatment in a static oven at 1000°C for 1h. Finally, some important parameters were assessed for the use of aggregates in green roofs:

- weight loss during drying and firing were obtained by difference between the weight before and after drying stage and firing stage using a "Bel Engineering M124A" analytical balance, with 120g scale and accuracy of 0.0001g;
- pH value, according to UNI EN 13037 (2011) standard, was measured using a pHmeter "XS Instruments, pH 6";
- specific electrical conductivity (EC), according to UNI EN 13038 (2011) standard, was measured using an "Oakton CON 6 / TDS 6" conductivity meter;
- static absorption in water over 24h was evaluated by difference between the weight before and after the residence time in water;
- surface microstructure of the materials was evaluated by a scanning electron microscope (SEM) "ESEM-Quanta 200 FEI".

2.6. Bricks samples production

Before the specimen preparation, TG-DTA ("Netzsch STA 409") tests were performed on three types of mixtures to test the behaviour of the biochar and cyclone ashes during firing. R100 (100% red clay) as standard composition, B70 (70wt% red clay – 30wt% biochar) and A70 (70wt% red clay – 30wt% cyclone ashes) were prepared and tested from 20°C to 1300°C, with a heating rate of 10°C/min. Later, several cylindrical specimens (40mm Ø x 4mm) with biochar and cyclone ashes ratios from 5 to 40% and a red local clay were created by pressing at 22bar after a 7% humidification of the mixtures. Materials used were previously dried in an oven at 105°C to remove all traces of free water.

Biochar and cyclone ashes were sieved under 250 µm and clay under 1 mm. All the obtained samples were dried at 105°C for about 24 hours and then were subjected to a firing treatment in a static oven at 950°C for 30 minutes. Weight loss in drying and firing was evaluated by difference between the weight before and after drying and firing stage using a "Bel Engineering M124A" analytical balance, with 120g scale and accuracy of 0.0001g. Drying and firing shrinkage were evaluated by difference between the specimen diameter before and after drying and firing stage using a digital caliper. Bulk density of the fired samples was evaluated by measuring their volume and weight.

3. Results and discussion

3.1. Wood chips from river maintenance gasification tests

Three gasification tests with a total duration of 15 hours using about 250 kg of wood chips from river maintenace were performed and the specific consumption and the power delivery was found in line with the manufacturer data. However, a biomass drying to 10% is required in order to not afflict the performance and to not increase O&M costs. This drying can be done using the heat from the engine heat exchanger or the sensible heat of the exhaust of the engine thar are currently discarged at about 300°C. Considering a biomass drying to 10% of moisture, from one heactare of rivernbanks maintenance made every 3 years it is possible to obtain about 27.8 tons of wood chips that can be used to produce about 23 MWh of electrical power and 31 MWh of thermal power. In addition, considering a biochar of 5% in weight, about 1.4 tons of biochar is disposed from the char vessel of the plant.

3.2. Chemical characterization results

Three different methods to measure pH, as shown in Table 2, were performed to verify the alkalinity of the materials, widely documented in literature studies. pH values are generally lower for biochar produced at lower pyrolysis temperatures. A substantial increase in pH usually occurs at higher temperatures due to the increase in the relative concentration of inorganic elements such as Ca and Mg of the original raw materials that have not been pyrolyzed and of the formation of surface oxides. pH changes depending on the maximum process temperature and residence time (Novak et al., 2009; Rehrah et al., 2014).

Table 2. Results of pH, specific electrical conductivity and $CaCO_3$ analysis

Chemical analysis	***Units***	***Materials***	
pH and specific electrical conductivity		***Biochar***	***Cyclone Ashes***
pH (deionized water) 1:5 w/w 1h (UNI EN 13037, 2012)	pH unity	11.8	12.2
pH (deionized water) 1:10 w/w 1h	pH unity	12.1	12.4
pH (deionized water) 1:5 v/v 1h	pH unity	10.7	11.0
EC (deionized water) 1:5 w/w 1h (UNI EN 13038,2012)	mS/cm	5.7	8.6
EC (deionized water) 1:5 v/v 1h	mS/cm	5.3	8.3
$CaCO_3$	%	7.1	8.1

Observing Table 2, it’s possible to note in all the measurements that biochar and ashes are strongly alkaline; indeed, the high temperatures reached during the gasification process strongly influence the pH of the final products, causing alkalinity. This parameter is important because a very alkaline pH could influence the final material in the application that will be chosen, altering its acceptability in a certain range of values, as following reported. The values of biochar specific electrical conductivity are in the range 5-6 mS/cm and they are consistent with values found in literature studies. Li for example (Li et al., 2013), finds an increasing variability for rice straw biochar from 4.09 to 7.72 mS/cm by changing the charring temperature from 100 to 800°C. The analysis with a calcimeter shows a significant presence of calcium carbonates, later confirmed by the EDS and XRD analyses data. Yuan et al. (2011) found a linear correlation between alkalinity and carbonate content, although also carboxyl and hydroxyl groups may contribute to the pH of biochars.

The EDS chemical analysis, coupled with SEM, was carried out on different samples of biochar and ashes (coming from both river biomass and red spruce) with a focus on different areas of the single sample. The average content of element was the average content of all the dots and areas for a sample analysed. The result shows a wide range of values that well represents the high variability of the material analysed compared to the starting biomass. As we can see from Table 3, the total carbon content in different biochars and ashes (coming from different biomass) can change from 45% to 85%. These values are in agreement with literature studies on various types of biochars from different feedstocks and different processes: Al-Wabel for example found a C content of 82.93% for conocarpus biochar obtained at 600°C, Li found a C content of 77.24% for rice straw biochar obtained at 600°C (Al-wabel et al., 2013; Kim et al., 2012; Li et al., 2013; Xie et al., 2014). The values obtained from elemental analysis, referred to the red spruce biochar and ashes, fall within the ranges identified by EDS analysis.

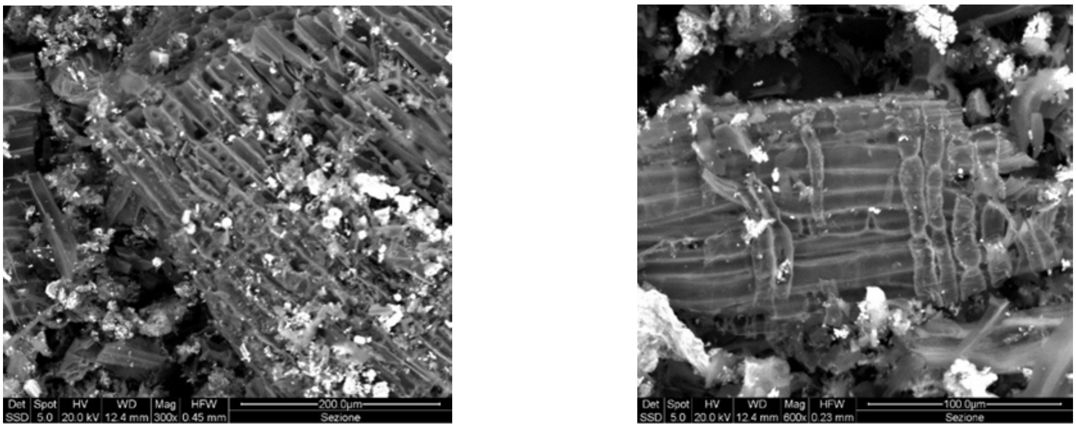
Table 3. Results of EDS and elemental analysis

Chemical analysis	***Units***	***Material***	
EDS chemical analysis *(range values from both river biomass and red spruce)*		***Biochar***	***Cyclone Ashes***
C	%	45-85	55-70
O	%	10-21	15-18
Ca	%	4.5-9	7.5-10
K	%	2-3	2-3
Si	%	0.5-1.4	0.5-3.5
Fe	%	\	1
Elemental analysis (from red spruce)			
C	%	53.90	67.54
H	%	1.00	1.26
N	%	0.33	0.26
S	%	0.00	0.00

According to Zhao et al. (2013), biochars derived from woody materials (like those analyzed in this study) has a low ash content (often less than 3%) and a medium-high content of C. This content of C is to be referred to unburnt coal, organic compounds of different complexity and carbonates, as confirmed by the thermal analysis. Figs. 2a-b show the SEM images of biomass riverbanks biochar particles at 300x and 600x magnifications. The pores created in the biochar during the gasification process are visible on the surface of the material and are attributable both to the nature of the original feedstock and to the release of volatile and organic substances during the thermal process. Wood, indeed, is a material made of fibers, where we can find gas and water transport channels creating walls; the size of these channels determines the following size of the pores in the biochar (Warnock et al., 2007). The pores created during the gasification of the original biomass can be subdivided into micropores (<2 nm), meso-pores (2 nm-50 nm) and macro-pores (50 nm). Structures attributable to the original biomass with an evident macro-porosity can be seen in the two figures at different magnifications. Figs. 3a-b show the SEM image of biomass riverbanks cyclone ashes particles at 300x and 600x magnifications.

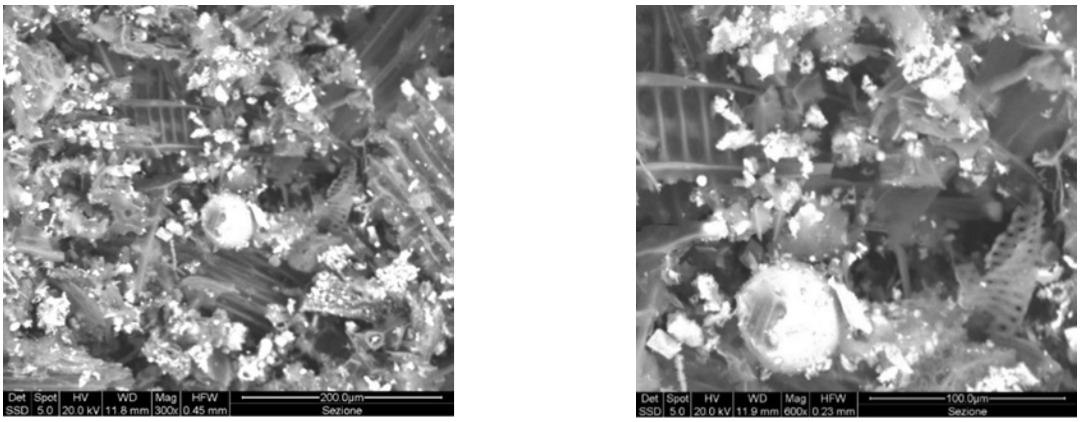
From these it can be visualized an inhomogeneous structure. Some structures attributable to the nature of original feedstock, similar to biochar sample. Additionally, there is a greater presence, compared to biochar, of mainly inorganic spherical structures, with diameters from 10 to 30 µm, probably due to a faster cooling of the material. These spheres show by EDS analysis compositions rich in Si (around 17%), K (13%) and Al (7%).

The X-ray diffractometry patterns are visible in Fig. 4. At high process temperatures, as 900 °C in our case, the biochar and cyclone ashes obtained show a predominantly amorphous nature. Indeed, the peak attributable to cellulose disappears when 400°C of process are reached, with a consequent weight loss of around 300 and 400°C (Wang, Cao and Wang, 2009). In this case, the only crystalline phases present can be identified mainly as calcite ($CaCO_3$), with traces of quartz (SiO_2). The presence of calcium carbonate, according to EDS and carbonates analysis, is confirmed by the peak at $2\theta = 29{,}4°$, and can also be found in other literature studies (Devi and Saroha, 2013).



(a) (b)

Fig. 2. Biochar particle structures at: 300x (a) and 600x (b) magnifications



(a) (b)

Fig. 3. Cyclone ashes particle structures at: 300x (a) and 600x (b) magnifications

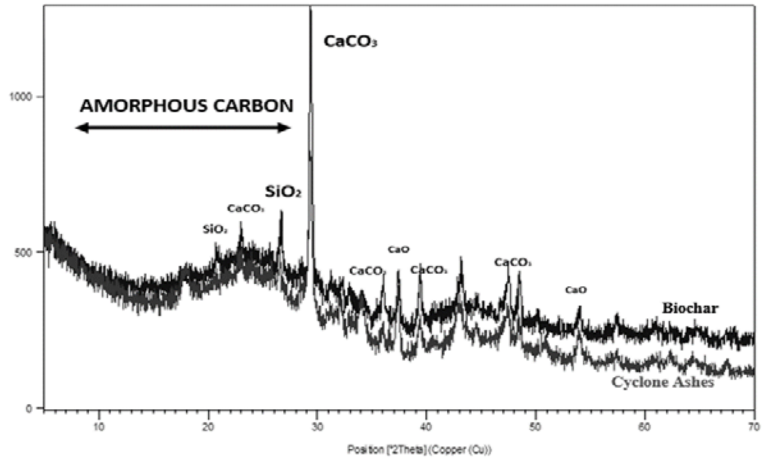


Fig. 4. X-ray diffractometry patterns of biochar and cyclone ashes

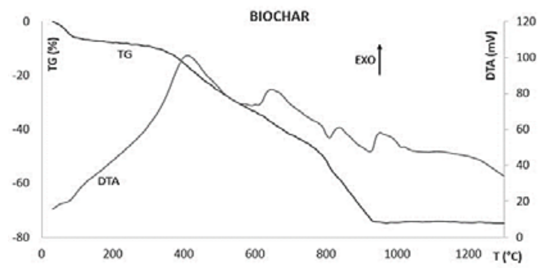
3.3. Thermal characterization results

During the drying time at 105°C the sample achieved zero weight loss and a "oven-dried" biochar was obtained. The amount of water present in the biochar can vary greatly, depending on how it was produced and if it has accumulated moisture during the next storage. In this case the values (1.5% for biochar and 3.1% for cyclone ashes) are similar to average values found in literature (1-15%) (Brown, 2009) but it's important to underline that the humidity removed at 105°C is only part of the actual humidity contained in a sample of biochar. In fact, the strong hygroscopicity and the high absorption capacity for water vapor of this material, require a more intense drying, at 200°C, to remove all the absorbed water and thus determine a biochar base "without humidity".

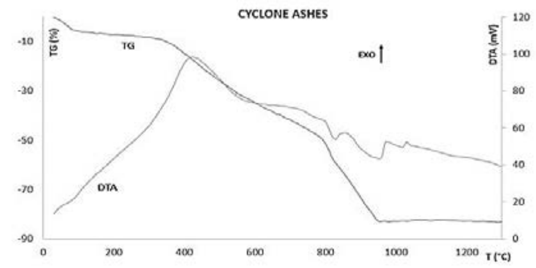
In Fig. 5a-b we can see the TG-DTA curves related to biochar and cyclone ashes respectively. The trends of both the TG and DTA curves are very similar in the two materials. The first slight weight loss is from room temperature up to about 200°C and corresponds to the loss of moisture and highly volatile organic compounds. Subsequently a loss of organic matter is visible corresponding to an exo-peak around 400°C followed by a decarbonation at higher temperatures (800/950°C) that was expected considering the previous analyses. The final loss is about 82% and occurs within 950°C, a temperature above which there is no longer any weight decrease.

3.4. Physical characterization results

In the context of a characterization concerning the physical properties of the materials, a sieve analysis was made on both wastes "as received". Knowledge of biochar particle size is important for determining the predisposition or not for each chosen application. Particle size distribution is mainly influenced by the biochar original feedstock (biochar from crop residues have generally a finer structure than biochar from woody biomass) and by the conditions in which thermal process occurs (particle size decreases with increasing temperature) (Cetin et al., 2004; Downie et al., 2009). The results obtained by a sieve analysis are displayed in Fig. 6a-b. Looking at the biochar (a), we can notice a fairly uniform subdivision of particle sizes between the various bands, each one ranging from 10 to 20% of the total. 43% of the analysed material remains over 1 mm Ø sieve. The cyclone ashes (b), on the other hand, have a finer composition. Only 9% of the material analysed does not pass below 1 mm Ø sieve and a large percentage, about 40%, has a grain diameter of less than 100 µm. Both materials, excluding the fraction above 2 mm Ø, were than subjected to analysis with a laser granulometer. The results, in Table 5, show how, after an ultrasound treatment, the granulometric classes of the two materials looks very similar. The biochar has a slightly finer particle size than the cyclone ashes (80.7% of the material passes under <0.045 mm Ø against 72.2% of the ashes). This result could be due to the fact that biochar "as received" occurs in a state of aggregation of granules greater than cyclone ashes.



(a)

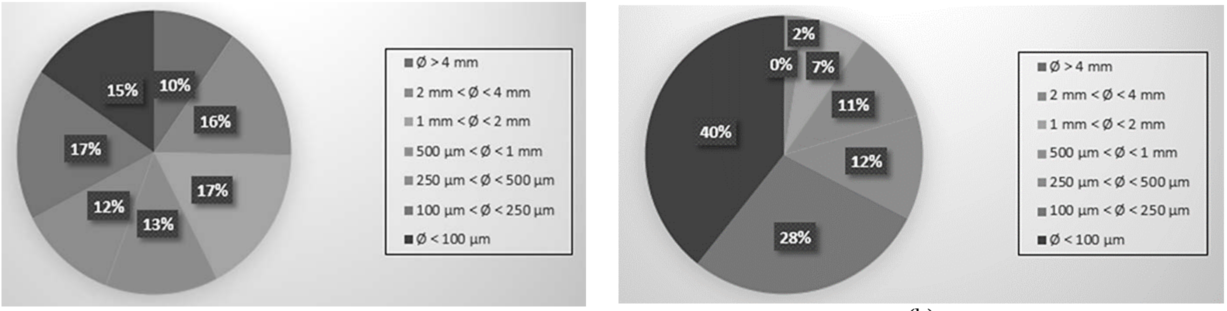


(b)

Fig. 5. TG-DTA curves related to biochar (a) and cyclone ashes (b)

Table 4 LOI and EDS analysis results on biochar samples

Biochar	***LOI (wt%)***	***C (%)***	***O (%)***	***Ca (%)***	***K (%)***	***Fe (%)***	***Si (%)***
700°C	34.78	66	19.6	6.9	2.7	1.4	0.6
900°C	50.90	53	20.7	17.4	3.4	1.3	0.6
1100°C	70.97	39.5	28.5	20.5	2.4	3.2	1.5



(a) (b)

Fig. 6. Results of sieve analysis on biochar as received (a) and cyclone ashes as received (b)

BET analysis, performed on the dried material, shows the physical adsorption of gas molecules on the biochar and cyclone ashes solid surface with the aim to quantify the specific surface area of the materials. As can be seen in Table 5., the biochar has a larger specific surface than the cyclone ashes, in accordance with the previous granulometric analysis. The value of surface area (210.50 ± 5.94 m^2/g) is on average if compared to other literature studies (Bedussi, 2015; Brewer et al, 2014) although much lower than a commercial activated carbon (500-3000 m^2/g). The increase in the maximum process temperature and residence time in the pyrolyser/gasifier can lead to an increase in the porosity of the char and thus influences the surface area value (Brewer et al., 2014). Biochars coming from high temperature treatments generally have higher surface area values (Giorcelli et al, 2016). Biochar bulk density can vary with feedstock and process.

Table 5. BET, Particle size distribution, bulk and particle density and total porosity results on biochar and cyclone ashes

	Unity	***Biochar***	***Cyclone Ashes***
BET Surface area	m^2/g	210.50 ± 5,94	157.18 ± 3.56
Particle Size Distribution			
<0.045mm	%	80.7	72.2
0.045mm-0.125mm	%	18.5	26.8
>0.125mm	%	0.8	1.0
Bulk Density	g/cm^3	0.16	0.19
Particle Density	g/cm^3	2.23 ± 0.004	2.15 ± 0.004
Total Porosity	%	92.8	91.2

The biochar values of 0.16 g/cm^3 is very low, but comparable to other literature results where, for example, a 90% spruce - 10% hardwood biochar it's found to be 0.18 g/cm^3 or a maple biochar it's 0.26 g/cm^3 (Allaire et al., 2015). Particle density is higher than the bulk density for a given solid since pore volume is no longer included. The values found in this study (Table 5) are higher than common values that can be found in literature (Brewer et al, 2014). This is because the analysed biochar comes from a high temperature gasification process and not pyrolysis. Indeed, it's verified that biochar particle density increases with pyrolysis temperature (Brewer et al, 2014). This because, as the temperature rises, solid carbon condenses into a more compact aromatic rings structure with an increasing degree of graphitization, approaching the particle density value of solid graphite (2.25 g/cm^3). The total porosity calculated by Eq. 1, is 92.8% for the biochar. A high value, according to the BET analysis, which is similar to other literature works (Bedussi, 2015).

3.5. Lightweight aggregates

All the samples of LWA prepared were characterised by a good feasibility in processing and showed a good level of final aggregation. No samples showed any breakage during the firing process. The biochar gives a darker colour to the aggregates but, after the firing process, this is lost with a final standard red colour. In Table 6 we can see the results of the characterization tests conducted on all types of samples prepared both with clay a and b and with the addition of SCG.

The addition of 15% of biochar inside the materials leads, with both clays (BCa and BCb), to an increase in weight loss during firing and a consequent weight-lightening of the material (8.32% of the BCa compared to 4.41% of the ROa and 13.64% of the BCb compared to 9.08% of the ROb). Clay b has a higher weight loss in firing; this is probably due to the higher presence of carbonates.

Table 6. Characterization results on LWAs samples

	ROa	***BCa***	***ROb***	***BCb***	***CBCb***
W.L. (%) 105°C 24h	19.8	25.7	22.9	27.1	26.2
W.L. (%) 1000°C 1h	4.4	8.3	9.1	13.6	17.8
pH	6.4	11.9	6.7	9.3	7.9
Specific electrical conductivity (mS/cm)	0.26	3.17	0.32	0.90	0.41
Static water absorption (%) 24h	11.5	18.5	4.7	13.6	12.5

However, the generated porosity does not mean greater water absorption. This is indeed less for clay b, with or without biochar, compared to a. The alkaline pH of the biochar gives at the final product, with both clays, a value beyond the optimal range of plant comfort (6-8). The value of EC is less than 2 mS/cm (optimal range of plant growth) only using clay b. Considering these results, it was decided to continue the study using clay b, which has better pH and EC values. To optimize these parameters, aggregates were created with SCG. The addition involves, as expected, a greater loss in firing and therefore a further weight-lightening. This is because this type of waste is organic, has a LOI of about 98% and has a high theoretical high calorific value. The low pH value of the coffee that remains in the aggregates after firing, gives encouraging results that fall within the optimum values of pH and conductivity.

Fig. 7, at 800x magnification, shows the difference in microstructure between the BCb and CBCb sample. Small pores (even 1-2 μm) in a better-sintered matrix, present in the CBCb aggregate, could be a consequence of SCG combustion.

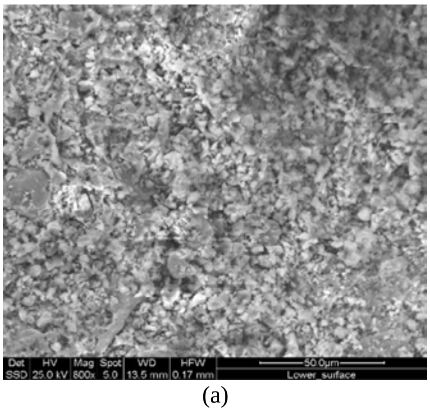
3.6. Bricks

The TG analysis (Fig. 8a) of the two mixtures prepared with a fixed percentage (30%) of pore forming agent, confirms theoretically the weight-lightening effect of the biochar and shows a very similar trend for the cyclone ashes. Indeed, both the mixtures with wastes show values of weight loss far greater than the mixture with only red clay. At about 950°C, ceramic bricks firing temperature, R100 shows a weight decrease of about 4%, while A70 and B70 reach a decrease of about 11%.

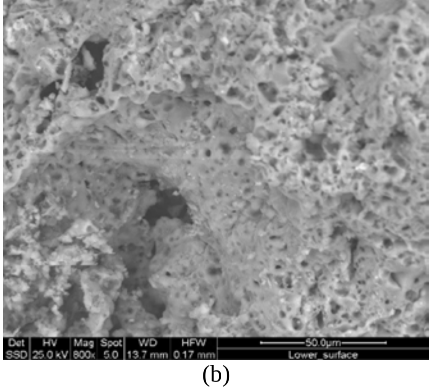
The DTA graph (Fig. 8b) shows a marked exo-peak and therefore a release of substances, associated with the presence of biochar and ashes in the mixture, around 400-500°C. These temperatures are higher than those found in systems where other types of weight-lightening waste in bricks are used. In these plants materials such as sawdust release various types of volatile pollutants at around 250-300°C, with relevant problems in fume disposal systems. Further emission studies will be needed on the specimens with biochar and ashes, to verify the negligible impact of these substances on the emissive framework of the furnace.

The samples with only clay and with various percentages from 5 to 40 of biochar and cyclone ashes, were then subsequently prepared as previously described and the measurements made are shown in Table 7. An increase in black color was observed when the amount of biochar or ashes introduced was increased. However, after the firing process all the specimens had the same red-clay-color, typical of ceramic bricks. The BC40 sample with 40% of biochar had some problems immediately following the pressing phase, crumbling at the touch. It is considered necessary a greater quantity of water added to the initial mixture, even if after the drying phase the same problem could be found again, due to the low plasticity of the mixture (only 60% of clay). Considering all the other samples, no particular problems (like for example “black heart” defect) have been found and the post-pressing and drying specimens appear to have good consistency and stability.

Table 7. shows that weight loss after firing confirms the results obtained from the TG analyses on the mixtures. The values are very similar as weight loss of 11%, which was related to the introduction of a 30% of biochar/ashes, falls here in the interval between 9.13 (20%) and 15.36 (40%) for the ashes.

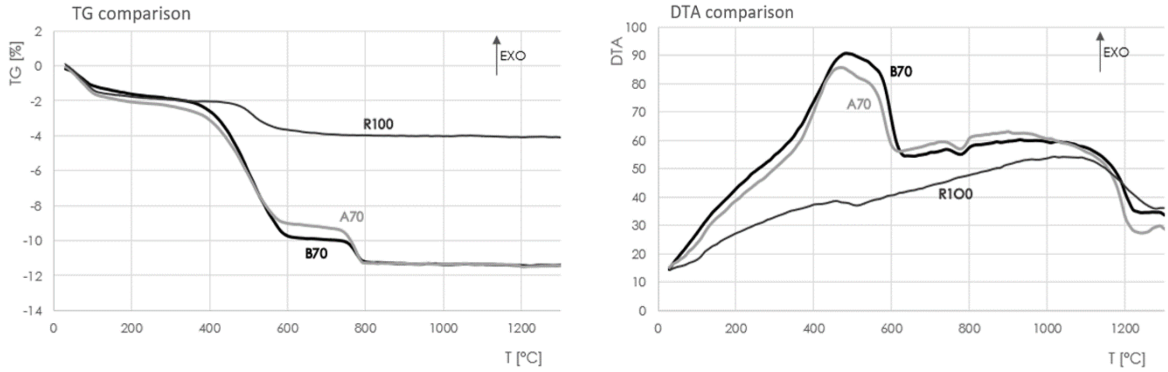


(a)



(b)

Fig. 7. Microstructure of BCb sample (a) and CBCb sample (b)



(a) (b)

Fig. 8. TG (a) and DTA (b) analysis of the two mixtures prepared with a fixed percentage (30%) of pore forming agent, compared to R100, the mixture with only clay

The material is effectively lightened. The shrinkage of the samples both during the drying phase and the firing phase, remains below 1%. This value can be considered negligible and in line with values relating to industrial processes.

Table 7. Characterization results on brick samples

	% W.L. (%) 950°C 30 min	*Drying shrinkage (%)*	*Firing shrinkage (%)*	*Bulk density (g/cm^3)*
RO	3.34	0.10	0.62	1.99
BC5	4.82	0.03	0.07	1.85
BC10	6.58	0.05	0.32	1.75
BC20	10.25	0.00	0.57	1.47
BC40	\	\	\	\
AS5	4.93	0.02	0.05	1.88
AS10	6.06	0.05	0.37	1.78
AS20	9.13	0.00	0.37	1.58
AS40	15.36	0.10	0.49	1.23

Considering the bulk density measured on the samples, it can be seen how the introduction of biochar/ashes makes possible to reach values around 1.5 g/cm^3, starting from about 2 g/cm^3 of the clay alone. Minor densities of 1.2 g/cm^3 – 1.3 g/cm^3, which can be considered very interesting for the market and a future industrial use, are achieved only by adding 40% of biochar/cyclone ashes in the samples. This, however, weakens the material, which crumbles quite easily to the touch and does not exhibit good mechanical strength. Subsequent thermal conductivity studies will be needed to verify the impact of the biochar/cyclone ashes on this property.

The shape of the alveolus has an important impact on the thermal resistance of the product (Krcmar, 2001) so that even a higher density, due to the introduction of percentages lower than 40%, could however lead to good results. Assuming an average particle density of clay materials of 2.65 g/cm^3 (Blake et al., 2008) and considering the bulk density values shown in Table 7, it is possible to obtain a roughly porosity value of the samples (Eq. 1). For the specimen with only red clay, the total porosity is about 25% but with the introduction of 20% biochar and ashes this value rises to 44.5% and 40.4% respectively.

4. Conclusions

REBAF project activities suggest the possibility to do maintenance on the Secchia River in a sustainable way. Afterwards field survey, the most abundant and representative wood plant is poplar. This wood behaves good in gasification to produce electricity and thermal power. Results suggests that from 1 hectare of riverbanks maintenance every three year, it is possible to produce 23 MWh of electrical power and 31 MWh of thermal power. The biochar and the cyclone ashes produced during the gasification tests was characterized from the chemical, thermal and physical point of view. In particular, by considering an application as weight-lightening agents in clay-based materials, analysis of thermal properties is important. Loss on Ignition (LOI) and TG-DTA curves showed similar trends with loss of moisture, organic matter and decarbonation respectively at 200,400 and 800-950°C. TG final weight loss is about 82% (950°C), a high value indicating the organic carbonaceous nature of the material.

Application on lightweight aggregates for green roofs by substituting 15%wt of the raw clay leads to an increase in weight loss during firing and a consequent weight-lightening of the material. The alkaline pH of the biochar gives the final product a value beyond the optimal range of plant comfort (6-8) and, to optimize this parameter, aggregates were created with addition of spent coffee grounds. This involves, as expected, a greater loss in firing and therefore a further weight-lightening, because this type of waste is organic and has a high calorific value. The low pH value of the coffee that remains in the aggregates after firing, gives encouraging results that fall within the optimum values of pH and conductivity. Application on bricks leads to a weight-lightening effect as well, with a significant reduction in the bulk density of the materials. The insertion of biochar and cyclone ashes is feasible up to a percentage of 20/25%wt, with the achievement of 40-45% porosity.

The positive results about biochar/cyclone ashes reusing can make more sustainable the gasification process by extending its use in different application fields.

Acknowledgements

The authors thank "Regione Emilia Romagna" that it co-funds the REBAF project and also the company Boschiva F.lli Valentini s.r.l. that it provided the wood chips from river maintenance.

References

Ahmad S., Khushnood R.A., Jagdale P., Tulliani J.-M., Ferro G.A., (2015), High performance self-consolidating cementitious composites by using micro carbonized bamboo particles, *Materials & Design*, **76**, 223–229.

All Power Labs, (2018), Power Pallet PP20 datasheet, On line at: http://www.allpowerlabs.com/wp-content/uploads/2015/10/PP20GeneratorOneSheet10_25_15Small.pdf

Al-wabel M.I., Al-Omran A., El-Naggar A.H., Nadeem M., Usman A.R.A., (2013), Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes, *Bioresource Technology*, **131**, 374–379.

Allaire S.E., Lange S.F., Auclair I.K., Quinche M., Greffard L. (The Char Team), (2015), Report: Analyses of biochar properties, CRMR-2015-SA-5, Centre de Recherche sur les Matériaux Renouvelables, Université Laval, Québec, Canada, 1-59, On line at: http://www.biochar-international.org/sites/default/files/Analyse_comparative-biochar-ENG.pdf (accessed 16.11.2017).

Basu P., (2010), *Biomass Gasification and Pyrolysis*, Academic Press Elsevier, Burlington USA.

Bedussi F., (2015), *Evaluation of the potential of biochar as a component of cultivation substrates*, PhD Thesis, Department of Agricultural and Environmental Sciences, University of Milan, Italy.

Blake G.R., Steinhardt G.C., Pontevedra Pombal X., Nóvoa Muñoz J.C., Martínez Cortizas A., Arnold R.W., Schaetzl R.J. (2008), *Pedoturbation*, In: *Encyclopedia of Soil Science*, *Encyclopedia of Earth Sciences Series*, Chesworth W. (Eds), Springer, Dordrecht.

Brady N.C., Weil R.R., (1996), *The Nature and Properties of Soils*, Prentice Hall Inc., New Jersey.

Brewer C.E., Schmidt-Rohr K., Satrio J.A., Brown R.C., (2014), Characterization of biochar from fast pyrolysis and gasification systems, *Environmental Progress & Sustainable Energy*, **28**, 386-396.

Brown R., (2009), *Biochar Production Technology*, In: *Biochar for Environmental Management: Science and Technology*, Lehmann J., Joseph S. (Eds), Earthscan, London.

Ceotto E., Di Candilo M., Castelli F., Badeck F.-W., Rizza F., Soave C., Volta A., Villani G., Marletto V., (2013), Comparing solar radiation interception and use efficiency for the energy crops giant reed (Arundo donax L.) and sweet sorghum (Sorghum bicolor L. Moench), *Field Crops Research*, **149**, 159-166.

Cetin E., Moghtaderi B., Gupta R., Wall T.F., (2004), Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars, *Fuel*, **83**, 2139–2150.

Choi W.C., Yun H.D., Lee J.Y., (2012), Mechanical properties of mortar containing biochar from pyrolysis, *Journal of the Korea institute for structural maintenance and inspection*, **16**, 67–74.

Cruz R., Baptista P., Cunha S., Pereira J.A., Casal S., (2012), Carotenoids of Lettuce (Lactuca sativa L.) Grown on Soil Enriched with Spent Coffee Grounds, *Molecules*, **17**, 1535–1547.

DeVallance D.B., Oporto G.S., Quigley P., (2015), Investigation of hardwood biochar as a replacement for wood flour in wood–polypropylene composites, *Journal of Elastomers and Plastics*, **48**, 1–13.

Devi P., Saroha A.K., (2013), Effect Of Temperature On Biochar Properties During Paper Mill Sludge Pyrolysis, *International Journal of ChemTech Research*, **5**, 682–687.

Downie A., Crosky A., Munroe P., (2009), *Physical Properties of Biochar*, In: *Biochar for Environmental Management: Science and Technology*, Lehmann J., Joseph S. (Eds.), Earthscan, London, 13-32.

ECN, (2018), Phyllis 2 - Database for biomass and waste, Willow #345; On line at: https://www.ecn.nl/phyllis2/Browse/Standard/ECN-Phyllis#willow

Flint A.L., Flint L.E., (2002), *The solid Phase: Particle Density*, In: *Methods of Soil Analysis*, Part 4 Physical Methods, Soil Science Society of America, Madison, 229-240.

Giorcelli M., Khan A.A., Tagliaferro A., Savi P., Berruti F., (2016), *Microwave Characterization of Polymer Composite Based on Biochar: A Comparison of Composite Behaviour for Biochar and MWCNTs*, 7th IEEE Int. Nano Electronics Conference (INEC), Chengdu, China.

Glaser B., Lehmann J., Zech W., (2002), Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review, *Biology and Fertility of Soils*, **35**, 219-230.

Gupta S., Kua H.W., (2017), Factors determining the potential of biochar as a carbon capturing and sequestering construction material: a critical review, *Journal of Materials in Civil Engineering*, **29**.

IEA, (2012), Technology Roadmap - Bioenergy for Heat and Power. Technical report, On line at: https://webstore.iea.org/technology-roadmap-bioenergy-for-heat-and-power

Khushnood R.A., Ahmad S., Restuccia L., Spoto C., Jagdale P., Tulliani J.-M., Ferro G.A., (2016), Carbonized nano/microparticles for enhanced mechanical properties and electromagnetic interference shielding of cementitious materials, *Frontiers of Structural and Civil Engineering*, **10**, 209–213.

Kim K.H., Kim J.-Y., Cho T.-S., Choi J.-W., (2012), Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida), *Bioresource Technology*, **118**, 158–162.

Krčmar W., (2001), Development of a high thermal insulating plane-ground brick with a thermal conductivity coefficient of $\lambda = 0.12$ W/mK by reduction of the ceramic body thermal conductivity and optimization of the perforation pattern geometry, *Ziegelindustrie International (Brick and Tile Industry International)*, 67-87.

Lehmann J., (2007), Bio-energy in the black, *Frontiers in Ecology and the Environment*, **5**, 381–387.

Li X., Shen Q., Zhang D., Mei X., Ran W., Xu Y., Yu G., (2013), Functional Groups Determine Biochar Properties (pH and EC) as Studied by Two-Dimensional ^{13}C NMR Correlation Spectroscopy, *PLoS ONE*, 8, e65949, On line at:

http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0065949
Novak J.M., Lima I., Xing B., Gaskin J.-W., Steiner C., Das K.C., Ahmedna M., Rehrah D., Watts D.W., Busscher W.J., Schomberg H., (2009), Characterization of designer biochar produced at different temperatures and their effects on a loamy sand, *Annals of Environmental Science***, 3**, 195–206.
Rehrah D., Reddy M.R., Novak J.M., Bansode R.R., K.A. Schimmel K.A., Yuc J., Watts D.W., Ahmedna M., (2014), Production and characterization of biochars from agricultural by-products for use in soil quality enhancement, *Journal of Analytical and Applied Pyrolysis*, **108**, 301–309.
Silingardi M., (2007), *Indice di funzionalità fluviale IFF 2007*, Report APAT, Lineagrafica Bertelli Editori snc, Trento, On line at: http:/www.appa.provincia.tn.it/pubblicazioni/
Spinelli R., (2005), Biomassa legnosa e manutenzione degli alvei fluviali., *Alberi e Territorio*, **6**, 18-22.
UNI EN 13037, (2012), European Standard, Soil improvers and growing media - Determination of pH, On line at: https://www.en-standard.eu/din-en-13037-soil-improvers-and-growing-media-determination-of-ph/?gclid=CjwKCAiA_ZTfBRBjEiwAN6YG4deaJcZjSA-1qMC03z71q2wUGl2-w60A0ASFQV0P-7P9MPZUql-00BoC0GIQAvD_BwE.
UNI EN 13038, (2012), European Standard, Soil improvers and growing media - Determination of electrical conductivity, On line at: https://www.en-standard.eu/din-en-13038-soil-improvers-and-growing-media-determination-of-electrical-conductivity/?gclid=CjwKCAiA_ZTfBRBjEiwAN6YG4eav_BxWMA7bAbPn4lyhgyvxRGZ9f6-G-EbtdokXdSyscm2sCpFbcBoCLQcQAvD_BwE.
UNI EN 13040, (2008), Eurpean standard, Soil improvers and growing media - Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density, On line at: https://www.en-standard.eu/din-en-13040-soil-improvers-and-growing-media-sample-preparation-for-chemical-and-physical-tests-determination-of-dry-matter-content-moisture-content-and-laboratory-compacted-bulk-density/?gclid=CjwKCAiA_ZTfBRBjEiwAN6YG4frSRtjx5sfdl4kU_RqTYSx0FqquxTXkBhUIFkHPoWE4QMWvrIce4RoC_UwQAvD_BwE.
Vakalis S., Baratieri M., (2015), State-of-the-Art of Small Scale Biomass Gasifiers in the Region of South Tyrol, *Waste and Biomass Valorization*, **6**, 817-829.
Van Zwieten L., Kimber S., Sinclair K., Chan K.Y., Downie A., (2008), *Biochar: Potential for climate change mitigation, improved yield and soil health*, Proc. of the 23rd Annual Conf. of the Grassland Society of NSW, 152.
Wang Z., Cao J., Wang J., (2009), Pyrolytic characteristics of pine wood in a slowly heating and gas sweeping fixed-bed reactor, *Journal of Analytical and Applied Pyrolysis*, **84**, 179–184.
Warnock D.D., Lehmann J., Kuyper T.W., Rillig M.C., (2007), Mycorrhizal responses to biochar in soil – concepts and mechanisms, *Plant Soil*, **300**, 9–20.
Xie T., Reddy K.R., Wang C., Yargicoglu E., Spokas K., (2014), Characteristics and applications of biochar for environmental remediation: A review, *Environmental Science and Technology*, **45**, 939–969.
Yamato M., Okimori Y., Wibowo IF., Anshori S., Ogawa M., (2006), Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia., *Soil Science and Plant Nutrition*, **52**, 489-495.
Yuan J., Xu R. and Zhang H., (2011), The forms of alkalis in the biochar produced from crop residues at different temperatures, *Bioresource Technology*. Elsevier Ltd, **102**, 3488–3497.
Zhao L., Cao X., Masek O., Zimmerman A., (2013), Heterogeneity of biochar properties as a function of feedstock sources and production temperatures, *Journal of Hazardous Materials*, 256–257, 1–9.
Zhao S., Huang B., Shu X., Ye P., (2014), Laboratory investigation of biochar-modified asphalt mixture, *Transportation Research Record: Journal of the Transportation Research Board*, **2445**, 56–63.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2497-2505
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

INTEGRATED APPROACH FOR INNOVATIVE MONITORING STRATEGIES OF RESERVOIRS AND LAKES

Wiebke Warner[1*], Karsten Nödler[2], Alessandro Farinelli[3], Jason Blum[3], Tobias Licha[1]

[1]*Department of Applied Geology, Geoscience Centre, University of Goettingen, Goldschmidtstr. 3, 37077 Goettingen, Germany*
[2]*Water Technology Center Karlsruhe (TZW), Karlsruher Straße 84, 76139 Karlsruhe, Germany*
[3]*Computer Science Department, University of Verona, Verona CAP 37134, Italy*

Abstract

An innovative strategy significantly increasing data density by introducing a flexible, problem-orientated, and cost-effective water quality monitoring approach is presented. Most current monitoring strategies produce water quality data based on fixed stations conducted on fixed dates throughout a defined period of time and, thus, often give a biased and insufficient picture of the water quality. Establishing a refined picture of water quality while not increasing monitoring costs clearly needs a change in monitoring strategy. The complexity of social-economic needs, environmental aspects and evolving legislative guideline values makes the design of a suitable innovative strategy challenging. The combination of investigative and risk-based monitoring with real-time monitoring of proxies (e. g., electrical conductivity (EC)) is a vital asset within this here proposed innovative strategy. For the former, organic micropollutants (e. g., pesticides, pharmaceuticals) are suggested in this article to be a powerful tool for source apportionment as they allow to determine and quantify the cause and impact of water quality impairments. This strategy was tested in a field campaign in which an area of elevated EC was investigated at Lake Garda, Italy. A radio-controlled boat was used for EC mapping and sampling. As no chemical indicators for significant anthropogenic sources could be detected, the elevated EC could be assigned to natural sources.

Key words: water quality monitoring, innovative monitoring strategy, micropollutants, proxy mapping, indicator concept

Received: March, 2018; Revised final: June, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

According to the Water Framework Directive (WFD) (EC Directive 60, 2000) all member states of the European Union (EU) have to ensure a good chemical and ecological status of all surface water bodies by the year of 2027. Furthermore, within the precautionary principle article 7 (3) of the WFD states that "Member States shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water.". Besides the EU framework directive, the water safety plans derived by the World Health Organisation (WHO, 2005) give new directions towards water quality monitoring by compromising the management of drinking water "from catchment to consumer". As a novelty compared to previous and established monitoring strategies this includes a preventive risk elimination and recurrent quality control. State-of-the-art monitoring to date stands for a water quality assessment based on data derived from *fixed* station on *fixed* dates with regular *frequencies* for *fixed* parameters. On account of modern analytical techniques, however, the number of detected anthropogenic micropollutants in the water cycle steadily increases (Amare, 2017; Brumovský et al., 2017; Petrie et al., 2014; Reemtsma et al., 2016; Scheurer et al., 2017; Yang et al., 2018).This bears

* Author to whom all correspondence should be addressed: e-mail: wiebke.warner@geo.uni-goettingen.de

substantial drawbacks to the current monitoring strategies as no information on system's dynamics nor compound diversity is given and, hence, this insufficiently reflects the real status of the water quality on catchment scale. This strategy is highly susceptible to discontinuous and/or unpredictable hazardous events, such as direct discharge of sewage, combined sewer overflows or surface run-off from agricultural areas into drinking water resources or water bodies used for recreational purposes. Such events occur occasionally and are usually not reflected by *fixed* date measurements and the results of those investigations are often rather poor in terms of data density, predictive power, and, thus, for deriving effective countermeasures. This points out the great importance of an improved monitoring strategy leading to more reliable datasets and, hence, allowing the prediction of water quality on catchment scale as well as paving the way to water quality improvements (Voulvoulis et al., 2017). In the view of the current water quality monitoring strategy at many sites the demand for more reliable data would require a larger number of sampling points with significantly higher sampling frequencies in order to gain temporally and spatially better resolved data. This is remarkably time and cost intensive, not feasible and often leads to the so called "data-rich but information-poor" syndrome (Ward et al., 1986). Thus, an innovative monitoring strategy will be a shift from mainly static sampling to dynamic real-time monitoring, which leads to an *optimum* water quality monitoring frequency for individual water bodies and, hence, an increase in information density without increasing costs, especially caused by non-focused sampling. Nearly three decades ago, scientist and stakeholders already called for more reliable and meaningful data by a strategic change in water quality monitoring and a more holistic approach by including the catchment information into monitoring strategies (Ward, 1997; Ward et al., 1986). Especially with the implementation of the WFD and recent developments of new monitoring tools such as remote sensing, automated sampling devices and effect-based tools, new strategies for water quality monitoring are needed (Behmel et al., 2016). But most tools are either too general or too site-specific and there is unfortunately no "one-size-fits-all" solution serving every catchment (Behmel et al., 2016). Newly developed mathematical models are more generic and enable to predict meaningful sampling points within a catchment: Thus, the implementation of decision support systems (DSS) can help decision makers to establish a monitoring network with optimum information density (Alilou et al., 2018; Behmel et al., 2016). Additionally to surveillance (long-term changes) and operational monitoring (asses success measures), especially investigative water quality monitoring is needed, because accidental pollution or areas with unknown problems in water quality are often overseen and can significantly harm water safety (Milano et al., 2018; Premazzi et al., 2003; Radu et al., 2016).

This publication aims to present a highly promising and target-oriented approach into investigative water quality monitoring leading into long-term real-time water quality monitoring using proxies. The first application of the investigative aspect of this innovative strategy from an exemplarily short field campaign on Lake Garda in autumn 2017 using a platypus boat equipped with an electrical conductivity (EC) probe for real-time mapping and an automatic sampling device is presented.

2. Aspects of an innovative monitoring strategy

The variety of climatic, topographical, geomorphological, hydrological, physical and cultural factors influencing water quality (Hu, 1999) creates numerous factors influencing water quality and makes finding a suitable strategy for water quality monitoring on catchment scale highly complex. Improving data quality and density without increasing the monetary effort in these complex systems therefore needs a shift into innovative information driven monitoring strategies. Considering the whole catchment in water quality management concepts allows identifying substantial sources for water quality deterioration as well as detecting hot spots and areas of higher risks than others. At these locations, highly spatially and/or temporally resolved or even real-time data can significantly better describe a potential risk, while at points of low potential risk monitoring efforts and, thus, costs can be minimised. Another important key element is investigative monitoring and, thus, assigning the appropriate best fit and problem oriented long-term monitoring strategy based on the area's vulnerability. This can be best achieved by using source and process specific indicator compounds (e. g., organic micropollutants) to identify the cause of water quality deterioration, differentiate between multiple sources or even quantify their impact accordingly. The idea of considering the whole catchment in water quality management strategies was developed in the early 1990s but to the authors' knowledge there is only one successful case study in Australia published (Bennett and Lawrence, 2002; Mitchell and Hollick, 1993) and a further publication on the transfer of the Australian study to China (Hu, 1999). All these publications mainly focus on the sociological and organisational aspects between stakeholders and citizens but not on a strategic technical approach as this publication aims to deliver.

An innovative monitoring strategy must include the reliable identification of the water quality status and must allow the detection of pollution sources and their impact. It should further allow the monitoring of the effect of management measures taken in the catchment in order to improve water quality selectively (e. g., elimination of misconnections, improvement of combined sewer overflows (CSO)). At the same time, it needs to be capable to capture single pollution events such as accidents or spillages, the release of combined sewage overflows (CSO) or wash off during rain events.

Furthermore, it must allow the prioritization of catchment measures based on their efficiencies in improving water quality on catchment scale. Finally, it is important that the strategy is flexible and applicable to a large variety of different water bodies and catchments across Europe and the entire world. Recently, a shift from the static state-of-the-art water quality monitoring into a dynamic risk-based strategy found application in a draft for a novel drinking water act in Germany, based on changes in the annexes of the European drinking water guideline 98/83/EG (EU: 31998L0083), which emphasizes the need for novel strategies also for surface water bodies.

First step: *Composing existing data and defining problems and needs for water quality*

A crucial point in setting up an innovative monitoring strategy for a catchment is to re-analyse existing data and to re-evaluate the current monitoring program. This includes the evaluation of the number and locations of existing observation points and monitoring parameters, the frequency of data collection and the water quality development on the basis of historic datasets. This will give a first impression on water quality issues and allows to judge on the meaningfulness and significance of the existing strategy. Initially, a catchment assessment which includes morphological information (e. g., estimation of run-off flow direction), land uses to identify possible pollution sources and especially locations which are very vulnerable to hazardous events (e. g., areas used for drinking water production) needs to be carried out. Additional information can be gathered from historical data, local stakeholders (e. g., farmers), and from citizens. Within this context existing numerical models can be used and, if required, extended. If the existing data base is not sufficient in its resolution, more information needs to be gathered and individual initial monitoring campaigns with focus on investigative monitoring might be useful to close these gaps. A further crucial factor is that the requirements on the water quality together with standards are clearly defined. Initially, legislative guideline values (in agreement with WFD, national guidelines or bathing water guidelines) should be identified. Then, socio-economic needs, such as the apparent water quality (e. g., odour, colour or turbidity), the requirements for fishing, bathing and tourism must be considered. These water quality demands can be diverse and strongly dependent on the individual requirements of the end users.

Second step: *Investigative real-time water quality mapping, sampling and identification of an appropriate set of source and process specific indicators*

A key element of the presented strategy is the investigative real-time mapping of areas with either real or suspected water quality issues by using universal sensors prior to collecting samples for laboratory analysis. As EC is a general parameter which comprises the simultaneous detection of numerous ionic substances it can be used to identify water quality changes or issues easily. Using such a probe in tracking contamination from, e. g., wastewater is well established. Bonvin et al. 2011 demonstrated the linear correlation of elevated EC with elevated source specific micropollutants, especially benzotriazoles (corrosion inhibitors) and paracetamol (analgesic). They could assign this water quality impairment to the effluent of a wastewater treatment plant discharging 30 m below the water table of Lake Geneva. Besides natural sources (e. g., caused by geological processes) EC can also be correlated to nitrate contaminations (Hu et al., 2005), pesticides (Castilho et al., 2000) and even to mining activities (Olías et al., 2004). Covering the most common pollution sources known for aquatic systems EC is a powerful parameter to detect any hot spots within the system. In combination with temperature (T) it may even be a more powerful tool within investigative monitoring strategies for water quality impairment detection. Mapping can be conducted manually (if accessible) by simple field measurements with handheld probes or via automated robotic systems, such as boats or drones equipped with a sensor and a positioning system. Manual samples should only be taken wherever anomalies in form of a deviation from the mean background (baseline) value of the system are detected. At these locations water quality impairments are very likely.

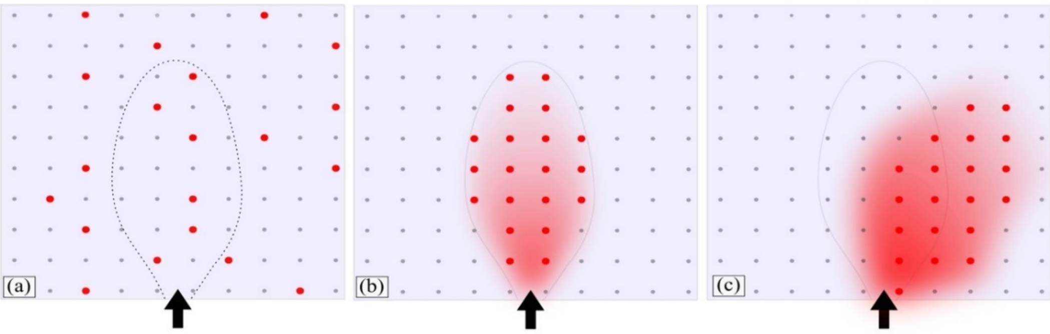


Fig. 1. All three figures show a potential plume (dotted line) originating from a hypothetic point source. The fixed number of twenty samples are marked as red dots. The proxy map (e. g., EC) is marked in red. By allocating all samples according to the mapped plume the information density increases remarkably and becomes independent from plume dynamics. In (a) all are samples distributed equally over the water body, in (b) they are distributed within the plume and (c) they are distributed accordingly to the drifted plume

As shown in Fig. 1, mapping can increase data density significantly: In Fig. 1a all hypothetic samples are distributed equally over the water body and randomly six out of twenty samples were collected within the actual plume (dotted line). After mapping (red coloured) all sampling points were located in the area of the plume and information density increases from 30 % to 100 % without increasing the total number of samples (Fig. 1b) and thus, cost. If the plume drifts (Fig. 1c), for example due to changing weather conditions, real-time mapping is able to visualise this change and sampling locations can be reallocated accordingly without any information loss and avoids non-focused sampling. Water bodies are highly dynamic systems. Contamination plumes, flow directions or the impact of water quality impairing sources are highly variable. Initial mapping reduces cost for sampling and laboratory analysis because only meaningful samples are taken. In order to assign the observed anomaly (e. g., increased EC) to the induced causes in an investigative monitoring strategy samples are then screened for a variety of chemical source and process indicators with a cost-effective multi-residue analytical method. Here, micropollutants such as life-style products, pharmaceuticals, personal care products or pesticides and their respective transformation products are well established (Barbosa et al., 2016; Glassmeyer and Meyer, 2005; Jekel et al., 2013; Lapworth et al., 2012; Lim et al., 2017). According to their negligible natural background and often unique transformation products, they are highly selective compared to classical inorganic tracers, which allows them to be very source specific (Khazaei and Milne-Home, 2017). Their wide range of physicochemical properties let them interact in numerous ways with the environment (e. g., during transport processes) and thus can help to estimate residence times or flow paths (Clara et al., 2004; Gasser et al., 2010; Warner et al., 2016).

Some prominent and established examples are briefly given in Table 1. For most catchments, a standard set of indicators is already established and can be easily adapted to specific catchment requirements (Jekel et al., 2015; Lim et al., 2017; Seitz and Winzenbacher, 2017; Zirlewagen et al., 2016). Chemical analysis for these indicators is often conducted using modern techniques such as liquid-chromatography coupled with tandem mass spectrometry (LC-MS/MS). A strategy for method development can, for example, be found in Nödler et al. 2010; Wode et al. 2015; Reemtsma et al. 2016; or Gago-Ferrero et al. 2015. Recent analytical developments allow simplified methods with small sample volumes, direct injections of water samples, and short analysis and processing times, which significantly decreases costs (Oliveira et al., 2015). The high sensitivity of modern analytical instruments also simplified the sampling procedure and logistics, as sample volumes <50 mL are rather the rule than the exception. Once contamination sources, their impact, location and point of discharge are identified by the aforementioned indicators, the overall number of analytes can be limited to a few meaningful and problem-orientated key indicators to even further reduce laboratory costs in future investigative monitoring strategies.

Table 1. Examples of typical indicators used in the last decades

Source	***Indicator***	***Reference***
Untreated effluent	Caffeine and its human metabolites	Seiler et al. (1999) Hillebrand et al. (2012)
	Cyclamate (artificial sweetener)	Zirlewagen et al. (2016)
Treated effluent	Valsartan Acid	Nödler et al. (2016)
Agriculture	Selected pesticides	(e.g., Nödler et al. 2013)
	Selected veterinary antibiotics (livestock)	e.g., Kay et al. (2005)
Tourism	Selected UV blocker	e.g., Gago-Ferrero et al. (2013)

Building a correlation function between a real-time parameter collected by a sensor such as temperature or EC and the source of deterioration, e.g., wastewater, using the chemical indicators will now allow the continuous and cost-efficient quantification of the individual amount of discharge and to reflect the dynamics of the impact. For mainly site-specific problems individual specific problem oriented tools, e.g., nitrate sensors or even biosensors (Proll et al., 2005) are possible options. Some established proxies are potassium as a proxy to quantify the impact of effluents from wastewater treatment plants (Nödler et al., 2011) and turbidity as a proxy for *E. coli* and for CSO overflow (Nnane et al., 2011; Viviano et al., 2017). Another well-established proxy for eutrophication is chlorophyll-α, which can be easily detected by remote sensing techniques (Barrett and Frazier, 2016; Duan et al., 2007).

Third step: *Real-time monitoring by using proxies*

Once the proxy-source-relationship is established and a suitable proxy sensor type or sensor array is selected, the amount and source(s) of the water quality impairment become quantifiable by the proxy(ies) in real-time. The proxies can serve in long-term, cost-efficient monitoring programs generating real-time monitoring data and contribute to the understanding of water quality on catchment scale. Thus, they are important within a risk-based monitoring strategy. Within this context threshold values need to be defined for indicating a potential risk for water quality deterioration. These should not be mistaken with legislative guideline values. When just a single source for water quality impairment was detected during the investigative strategy it may be sufficient to solely monitor one proxy parameter and directly associate it to that specific source. If there are multiple sources such as leakage from waste-water pipes and run-off from agriculture causing water quality deterioration in the same catchment, more proxies are needed. Possible powerful ways are building ratios of proxies to differentiate between sources, e.g., temperature and EC or using combination of them as sampling or monitoring criterion. If only one proxy is available because of limited probe availability, this general proxy is still useful in investigative and long-term monitoring to give a warning signal and for triggering meaningful manual sampling. These samples must later be screened for the specific key indicators as defined in step two. After screening, all sources and their impact can be differentiated with greater confidence and the appropriate and most efficient catchment management measures even preventative ones can be implemented. A crucial point is to regularly verify the proxy-source-relationship as catchments are dynamic systems in space and time. When demands, water/land uses within the catchment or sources and their impact change new proxies or indicators might need to be included or need to be changed to reflect the sources and their impact and, thus, to ensure a safe monitoring strategy.

By using this innovative monitoring concept samples are limited to source identification and apportionment or within the validation of the proxy-water-quality-impairment relationship. This significantly saves resources and costs. A graphical summary can be found in form of a flowchart in Fig. 2. In order to demonstrate the applicability of the investigative aspect of the presented monitoring strategy under field conditions data from a test site at Lake Garda, Italy, is presented in the following.

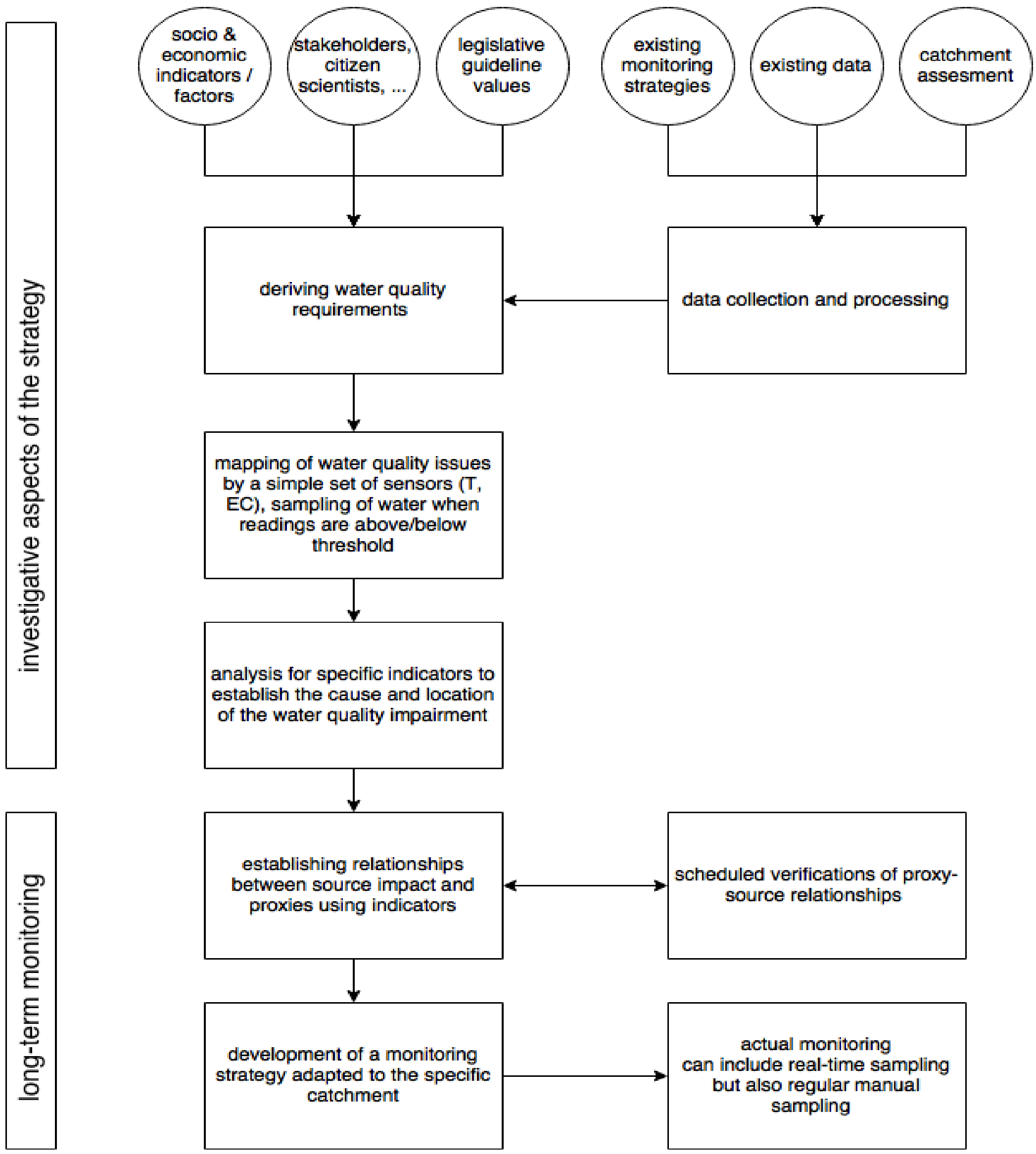


Fig. 2. Graphical overview over the different steps of the described innovative monitoring strategy

3. Application of the investigative monitoring aspects within the innovative monitoring strategy

3.1 Field site

With a total surface area of 368 km^2 and a catchment area of 2,350 km^2 Lake Garda is the largest lake in Italy. The main tributary of Lake Garda is the River Sarca (North) but it is also served by smaller streams. The northern part of the lake catchment is dominated by woodlands, mountains and agriculture, while the southern part functions as popular touristic area with amusement parks, campsites, hotels and marinas. As Lake Garda is dominated by tourisms it has a summer population estimated to be more than 400,000 and in contrast less than 80,000 people during winter months. A circular pipeline collects wastewater from all municipalities around the lake and serves a centralised WWTP (330,000 PE) in Peschiera del Garda, which discharges into the River Mincio.

Routine water quality monitoring at Lake Garda is accordingly to the WFD and comprises four samples per year to define the ecological status and twelve samples to evaluate the chemical status of the water body. For bathing water quality 65 sampling points on the Eastern shore are tested monthly from May to September for the detection of two microbiological parameters (*E. coli* and intestinal Enterococci). Further, the lake water serves as raw water resource for 6 % of the population. Therefore, four locations around the lake are tested according to national guideline values. Key challenges for the catchment of Lake Garda include ensuring a good bathing water quality and evaluating the impact of combined sewage overflows (CSO).

During a short field campaign in autumn 2016 at Lake Garda near the village Ronchi (20 km West of Verona, Italy) significantly elevated EC values of up to 1,348 µS/cm were observed in a small tributary of Lake Garda. This elevated EC (five times higher than the background value of lake Garda, 250 µS/cm) can be caused by either natural or anthropogenic sources. Possible causes for elevated EC include misconnections in the sewage system of the amusement park nearby or the stream might be connected to saline hot springs in Colà, a small town a few kilometers upstream. Additionally, nearby sampling points for bathing water quality occasionally show impairments in the microbiological parameter. As this area is used for recreational activities and is a natural reserve for birds a contamination by wastewater would be a significant impairment despite the low flow rate of the tributary.

3.2. Materials and methods

Initial EC-mapping was conducted by a robotic in-water propeller boat produced by Platypus engineered for the INTCATCH project (EU, Horizon 2020). This boat is equipped with an automated sampling system for four water samples and an EC/T-probe. Automated sampling was triggered by an exceeded EC value three times higher (800 µS/cm) than the background EC value of Lake Garda (250 µS/cm). Samples were carefully transferred into glass storage vials for transport and stored under cool and dark conditions until analysis via LC-MS/MS (Sciex Qtrap 6500+ equipped with a Shimadzu Nexera X2 liquid chromatography system) by direct injection. In total 76 organic contaminants as indicators were analysed.

Additionally to analytes in Nödler et al., 2010 samples were screened for 4-nitro-sulfamethoxazole, acesulfame, atenolol acid, bentazone, benzenesulfonic acid, benzimidazole, benzocaine, fluorescent brightener 28, chloridazon, desphenyl-chloridazon, desphenyl-methyl-chloridazon, ethyl sulfate, famotidine, furosemide, gabapentin, haloperidol, irbesartan, losartan, melamine, metaldehyd, primidone, propranolol, ritalinic acid, sulfamic acid, valsartan and valsartan acid. Method quantitation limits varied between 0.3 ng L^{-1} (isoproturon) and 34.5 ng L^{-1} (fluorescent brightener 28).

3.3. Results

An additional field campaign in October 2017 with the aim of testing the proposed monitoring strategy was conducted. On both days, a distinct plume of elevated EC around the area where the tributary meets the lake was observed. As can be seen in Fig. 3 the location and extend of the plume significantly changed between both days. This clearly points out how dynamic surface water bodies may be and, hence, the importance of real-time-mapping supported sampling.

No micropollutants which would indicate a possible anthropogenic influence of, e.g., domestic wastewater was detected. Besides, constantly increasing EC values of up to 1,410 µS/cm and temperatures of up to 25.9°C near Colà (hot springs) were observed by manual measurements upstream using a handheld probe. Beyond the area of hot springs, decreasing EC values and lower temperatures were observed. As a result, it can be concluded that the elevated EC values are predominately caused by a natural source most likely from hot springs upstream. Based on this, no immediate catchment measures need to be taken, because the risk that pathogens are connected to natural hot springs is assumed to be low. Further investigative monitoring can rule out anthropogenic influences completely. Moreover, in this area of Lake Garda EC can serve as a proxy for compounds introduced by tributaries. This information can be implemented within emergency plans: In case of substantial contamination within a tributary (e.g., accidents, spillages etc.) the application of the here proposed monitoring strategy will allow for straightforward and focused determination of the distribution of associated pollutants.

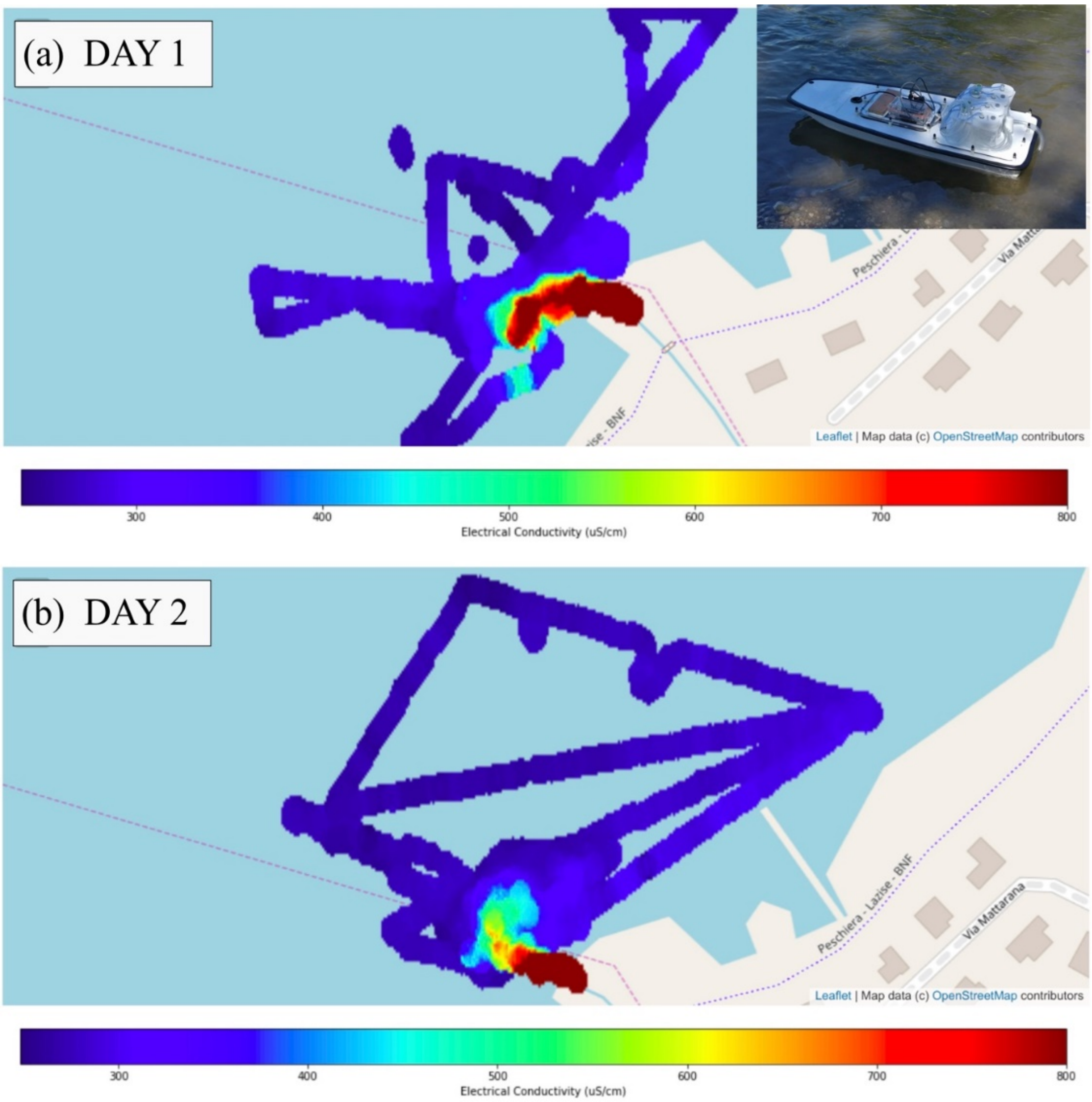


Fig. 3. Picture of a proxy mapping campaign by using an automated boat during a mapping and sampling campaign in October 2017 in Italy / Lake Garda near Ronchi. As can be seen in: (a) on the first day the plume drifts southwards, while (b) one day later the plume changed directions

4. Conclusions

The field campaign at Lake Garda clearly demonstrated the superiority of the suggested water monitoring strategy over state-of-the-art approaches. Mapping by using general parameters, such as EC and T, before actual sampling increases information density significantly and greatly reduces costs. Especially for highly dynamic systems, such as plumes, this approach is highly effective. Source and process specific chemical indicators allow to differentiate between different sources, such as anthropogenic and natural sources and enable to derive most efficient catchment management measures.

A promising micropollutant-based indicator set for the described test site is caffeine to detect untreated wastewater, valsartan acid for treated wastewater, a dermal UV blocker for tourism and a corrosion inhibitor, e.g. tolyltriazol, for industry or facilities from the amusement park nearby. As a proxy for long-term monitoring at Lake Garda we suggest EC to cover all possible sources of water quality impairments even though this is supportive rather than directive.

Finding a suitable relationship between a proxy and the source makes even real-time monitoring affordable and informative, which can significantly reduce potential risks in highly vulnerable areas. This demonstrated the effectiveness of the investigative aspects of the here suggested innovative monitoring strategy. Even with a small budget and little time it was possible to differentiate between the two potential sources with completely different risk potentials. How transferable this monitoring strategy is to river systems may depend on flow velocity, river size and morphology.

Acknowledgments
This study was funded by the European Commission

(contract number 689341), INTCATCH, “Development and application of Novel, Integrated Tools for monitoring and managing Catchments”. The catchment information for Lake Garda has been kindly provided by Instituto Di Santia (ISS) and Azienda Gardesana Servizi Spa (AGS).

References

Alilou H., Moghaddam Nia A., Keshtkar H., Han D., Bray M., (2018), A cost-effective and efficient framework to determine water quality monitoring network locations. *Science of the Total Environment*, **624**, 283–293.

Amare E., (2017), Wastewater Confronting Realities for Sustainable Livelihood in Developing Countries: Case Study Mekelle University, Ethiopia, *Water Conservation Science and Engineering*, 21–30.

Barbosa M., Moreira N., Ribeiro A., Pereira M., Silva A., (2016), Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495, *Water Research*, **94**, 257–279.

Barrett D., Frazier A., (2016), Automated Method for Monitoring Water Quality Using Landsat Imagery, *Water*, **8**, 257.

Behmel S., Damour M., Ludwig R., Rodriguez M.J., (2016), Water quality monitoring strategies — A review and future perspectives, *Science of the Total Environment*, **571**, 1312–1329.

Bennett J., Lawrence P., (2002), *Adaptive Management Framework for Catchment and Coastal Management and Decision Making*, Coastal CRC conference, 24–27.

Bonvin F., Rutler R., Chavre N., Halder J., Kohn T., (2011), Spatial and temporal presence of a wastewater-derived micropollutant plume in Lake Geneva, *Environmental Science and Technology*, **45**, 4702–4709.

Brumovský M., Bečanová J., Kohoutek J., Borghini M., Nizzetto L., (2017), Contaminants of emerging concern in the open sea waters of the Western Mediterranean. *Environmental Pollution*, **229**, 976–983.

Castilho J.A.A., Fenzl N., Guillen S.M., Nascimento F.S., (2000), Organochlorine and organophosphorus pesticide residues in the Atoya river basin, Chinandega, Nicaragua, *Environmental Pollution*, **110**, 523–533.

Clara M., Strenn B., Kreuzinger N., (2004), Carbamazepine as a possible anthropogenic marker in the aquatic environment: Investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration, *Water Research*, **38**, 947–954.

Duan H., Zhang Y., Zhang B., Song K., Wang Z., (2007), Assessment of chlorophyll-a concentration and trophic state for lake Chagan using Landsat TM and field spectral data, *Environmental Monitoring and Assessment*, **129**, 295–308.

EC Directive 60, (2000), Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32000L0060.

Gago-Ferrero P., Díaz-Cruz M., Barceló D., (2013), Liquid chromatography-tandem mass spectrometry for the multi-residue analysis of organic UV filters and their transformation products in the aquatic environment. *Rapid Communications in Mass Spectrometry: RCM*, **5**, 722–30.

Gago-Ferrero P., Schymanski E., Bletsou A., Aalizadeh R., Hollender J., Thomaidis N., (2015), Extended suspect and non-target strategies to characterize emerging polar organic contaminants in raw wastewater with LC-HRMS/MS, *Environmental Science and Technology*, **49**, 12333–12341.

Gasser G., Rona M., Voloshenko A., Shelkov R., Tal N., Pankratov I., Elhanany S., Lev O., (2010), Quantitative evaluation of tracers for quantification of wastewater contamination of potable water sources, *Environmental Science and Technology*, **44**, 3919–3925.

Glassmeyer S., Meyer M., (2005), Transport of chemical and microbial compounds from known wastewater discharges: potential for use as indicators of human fecal contamination, *Environmental Science and Technology*, **39**, 5157–5169.

Hillebrand O., Nödler K., Licha T., Sauter M., Geyer T., (2012), Identification of the attenuation potential of a karst aquifer by an artificial dualtracer experiment with caffeine, *Water Research*, **46**, 5381–5388.

Hu K., Huang Y., Li H., Li B., Chen D., White R.E., (2005), Spatial variability of shallow groundwater level, electrical conductivity and nitrate concentration, and risk assessment of nitrate contamination in North China Plain, *Environment International*, **31**, 896–903.

Hu X., (1999), Integrated catchment management in china: Application of the Australian experience, *Water International*, **24**, 323–328.

Jekel M., Ruhl A., Meinel F., Zietzschmann F., Lima S., Baur N., Wenzel M., Gnirß R., Sperlich A., Dünnbier U., Böckelmann U., Hummelt D., Van Baar P., Wode F., Petersohn D., Grummt T., Eckhardt A., Schulz W., Heermann A., Reemtsma T., Seiwert B., Schlittenbauer L., Lesjean B., (2013), Anthropogenic organic micro-pollutants and pathogens in the urban water cycle : assessment, barriers and risk communication (ASKURIS), *Environmental Science Europe*, **25**, 20, https://doi.org/10.1186/2190-4715-25-20

Jekel M., Dott W., Bergmann A., Dünnbier U., Gnirß R., Haist-Gulde B., Hamscher G., Letzel M., Licha T., Lyko S., Miehe U., Sacher F., Scheurer M., Schmidt C., Reemtsma T., Ruhl A., (2015), Selection of organic process and source indicator substances for the anthropogenically influenced water cycle. *Chemosphere*, **125**, 155–167.

Kay P., Blackwell P., Boxall A.B., (2005), Column studies to investigate the fate of veterinary antibiotics in clay soils following slurry application to agricultural land, *Chemosphere*, **60**, 497–507.

Khazaei E., Milne-Home W., (2017), Applicability of geochemical techniques and artificial sweeteners in discriminating the anthropogenic sources of chloride in shallow groundwater north of Toronto, Canada, *Environmental Monitoring and Assessment*, **189,** 218. doi: 10.1007/s10661-017-5927-1.

Lapworth D.J., Baran N., Stuart M.E., Ward R.S., (2012), Emerging organic contaminants in groundwater: A review of sources, fate and occurrence, *Environmental Pollution*, **163**, 287–303.

Lim F., Ong S., Hu J., (2017), Recent advances in the use of chemical markers for tracing wastewater contamination in aquatic environment: a review, *Water*, **9**, 143, doi:10.3390/w9020143.

Milano M., Chèvre N., Reynard E., (2018), Assessing watercourse quality: challenges in implementing European and Swiss legal frameworks, *Environmental Science and Pollution Research*, **25**, 805–823.

Mitchell B., Hollick M., (1993), Integrated catchment management in Western Australia: Transition from concept to implementation, *Environmental Management*, **17**, 735–743.

Nnane D.E., Ebdon J.E., Taylor H.D., (2011), Integrated analysis of water quality parameters for cost-effective faecal pollution management in river catchments, *Water Research*, **45**, 2235–2246.

Nödler K., Licha T., Bester K., Sauter M., (2010), Development of a multi-residue analytical method, based on liquid chromatography-tandem mass spectrometry, for the simultaneous determination of 46 micro-contaminants in aqueous samples, *Journal of Chromatography A*, **1217**, 6511–6521.

Nödler K., Licha T., Fischer S., Wagner B., Sauter M., (2011), A case study on the correlation of micro-contaminants and potassium in the Leine River (Germany), *Applied Geochemistry*, **26**, 2172–2180.

Nödler K., Licha T., Voutsa D., (2013), Twenty years later - Atrazine concentrations in selected coastal waters of the Mediterranean and the Baltic Sea, *Marine Pollution Bulletin*, **70**, 112–118.

Nödler K., Tsakiri M., Aloupi M., Gatidou G., Stasinakis A., Licha T., (2016), Evaluation of polar organic micropollutants as indicators for wastewater-related coastal water quality impairment, *Environmental Pollution*, **211**, 282–290.

Olías M., Nieto J.M., Sarmiento A.M., Cerón J.C., Cánovas C.R., (2004), Seasonal water quality variations in a river affected by acid mine drainage: The Odiel River (South West Spain), *Science of the Total Environment*, **333**, 267–281.

Oliveira T.S., Murphy M., Mendola N., Wong V., Carlson D., Waring L., (2015), Characterization of Pharmaceuticals and Personal Care products in hospital effluent and waste water influent/effluent by direct-injection LC-MS-MS, *Science of the Total Environment*, **518**–**519**, 459–478.

Petrie B., Barden R., Kasprzyk-Hordern B., (2014), A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring, *Water Research*, **72**, 3–27.

Premazzi G., Dalmiglio A., Cardoso A.C., Chiaudani G., (2003), Lake management in Italy: The implications of the water framework directive, *Lakes and Reservoirs: Research and Management*, **8**, 41–59.

Proll G., Tschmelak J., Gauglitz G., (2005), Fully automated biosensors for water analysis, *Analytical and Bioanalytical Chemistry*, **381**, 61–63.

Radu V.M., Ivanov A.A., Ionescu P., Deak G., Tudor M., (2016), Development of a multiparametric quality index for water quality monitoring, *Environmental Engineering and Management Journal*, **15**, 1069-1074.

Reemtsma T., Berger U., Arp H., Gallard H., Knepper T., Neumann M., Quintana J., Voogt P., (2016), Mind the Gap: Persistent and mobile organic compounds - Water contaminants that slip through, *Environmental Science and Technology*, **50**, 10308–10315.

Scheurer M., Noedler K., Freeling F., Janda J., Happel O., Riegel M., Mueller U., Storck F.R., Fleig M., Lange F.T., Brunsch A., Brauch,H.-J., (2017), Small, mobile, persistent: Trifluoroacetate in the water cycle – Overlooked sources, pathways, and consequences for drinking water supply, *Water Research*, **126**, 460–471.

Seiler R., Zaugg S., Thomas J., Howcroft D., (1999), Caffeine and pharmaceuticals as indicators of waste water contamination in wells, *Ground Water*, **37**, 405–410.

Seitz W., Winzenbacher R., (2017), A survey on trace organic chemicals in a German water protection area and the proposal of relevant indicators for anthropogenic influences, *Environmental Monitoring and Assessment*, **189**, 244.

Viviano G., Valsecchi S., Polesello S., Capodaglio A., Tartari G., Salerno F., (2017), Combined Use of Caffeine and Turbidity to Evaluate the Impact of CSOs on River Water Quality, *Water, Air, & Soil Pollution*, **228**, 330.

Voulvoulis N., Arpon K.D., Giakoumis T., (2017), The EU Water Framework Directive: From great expectations to problems with implementation, *Science of the Total Environment*, **575**, 358–366.

Ward R.C., (1997), WATER QUALITY MONITORING: WHERE' S THE BEEF?' nation' s water quality is in terrible condition and the resulting data, in many ways, are comparable Current, and popular, efforts to curtail public monitoring programs will be unable to document grou, *Water Resources Bulletin*, **32**.

Ward R.C., Loftis J.C., McBride G.B., (1986), The "data-rich but information-poor" syndrome in water quality monitoring, *Environmental Management*, **10**, 291–297.

Warner W., Ruppert H., Licha T., (2016), Application of PAH concentration profiles in lake sediments as indicators for smelting activity, *Science of the Total Environment*, **563**–**564**, 587–592.

WHO (2004), Guidelines for drinking water quality - Volume 1 - Reccomandations, World Health Organization, Geneva, Switzerland. On line at: http://who.int/water_sanitation_health/dwq/GDWQ2004web.pdf

Wode F., van Baar P., Dünnbier U., Hecht F., Taute T., Jekel M., Reemtsma T., (2015), Search for over 2000 current and legacy micropollutants on a wastewater infiltration site with a UPLC-high resolution MS target screening method, *Water Research*, **69**, 274–283.

Yang Y.-Y., Zhao J.-L., Liu Y.-S., Liu W.-R., Zhang Q.-Q., Yao L., Hu L.-X., Zhang J.-N., Jiang Y.-X., Ying G.-G., (2018), Pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs) in surface and ground waters and their application as indication of wastewater contamination, *Science of The Total Environment*, **616**–**617**, 816–823.

Zirlewagen J., Licha T., Schiperski F., Nödler K., Scheytt T., (2016), Use of two artificial sweeteners, cyclamate and acesulfame, to identify and quantify wastewater contributions in a karst spring, *Science of the Total Environment*, **547**, 356–365.

Environmental Engineering and Management Journal October 2018, Vol.17, No. 10, 2507-2514
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

INNOVATIVE USE OF SCRAP AND WASTE DERIVING FROM THE STONE AND THE CONSTRUCTION SECTOR FOR THE MANUFACTURING OF BRICKS. REVIEW OF THE INTERNATIONAL SCENARIO AND ANALYSIS OF AN ITALIAN CASE STUDY

Marco Migliore[1]*, Mauro Carpinella[2], Giancarlo Paganin[3], Franco Paolieri[2], Cinzia Talamo[1]

[1]*Department of Architecture, Building Environment and Construction Engineering (ABC), Politecnico di Milano, via Ponzio 31, 20133 Milano, Italy*
[2]*Catalyst srl, Borgo Santa Croce 6, 50122 Firenze, Italia*
[3]*Department of Architecture and Urban Studies (DASTU), Politecnico di Milano, via Bonardi 3, 20133 Milano, Italy*

Abstract

The construction sector has evolved a lot over the last few years promoting the design and manufacturing of innovative and environmentally sustainable materials and products. In accordance with European and national guidelines, with a growing awareness of environmental issues several experiences are showing the interest of companies to qualify their products as green and environmentally sustainable. In the European context many directives have been introduced which, among their themes, speak of circular economy, reduction of the use of resources, better efficiency of production, etc. At the same time, initiatives related to the GPP were activated in the Italian context, that foresee an increase of the recycled content in building materials. Especially the brick manufacturing industry is very sensitive to the issue of the waste recovery and many experiences show that is possible to obtain optimum products with weighted material mixes (virgin raw materials and secondary raw materials). This procedure also contributes to a gradual recovery of waste otherwise disposed of in landfills. In the international scenario there are many studies about the reuse of waste and scraps in the bricks material mixes; the studies mainly derive from heterogeneous sectors as, for example: fly ash from coal plants, scraps and waste from the natural stone extraction, ceramic production residue, aggregates from demolition, waste oil, slag from steel mills, sawmill sludge and dust, glass powdered, recycled plastic, textile fibers, etc. The analysis of many experiences highlighted two key issues: the importance of cross-sectorial exchanges as a condition for enabling strategies of circular economy and the high intrinsic value of the material scrap. Particular attention has been paid to the Catalyst case study, a company that has developed different types of bricks, produced almost entirely with secondary raw material.

Key words: bricks, circular economy, reuse, scraps, sustainable production, waste

Received: March, 2018; Revised final: July, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The construction sector represents a very impactful industry, both from the point of view of energy consumption and use of natural resources. Therefore, every innovation developed within the construction sector (production of materials and/or semi-finished products with recycled content, rather than design solutions with environmental attention) represents a good outcome from the point of view of sustainability. The need to promote sustainable lifestyles is therefore representing an ethical and social choice no longer postponed (EC Communications, 2011a; 2014; 2015; SPREAD, 2012).

* Author to whom all correspondence should be addressed: e-mail: marco.migliore@polimi.it; Phone: +39 02.2399.5172

In this regard the report Signals 2017 (EEA, 2017) of the European Environment Agency shows that energy efficiency and the use of natural resources are the only viable perspective to accelerate process of shared sustainability. The improvement of natural resource efficiency is also at the heart of the UNEP International resource panel, the UN Program for the environment, indeed in the report *Resource Efficiency: Potential and Economic Implications* (UNEP, 2017) two fundamental aspects emerge: the first is that the efficient use of resources can contribute to economic growth and job creation; the second aspect is that it can offset the costs that the GDP of the world should support to hold the global warming within the limit of +2 (UNEP, 2017) respecting the limits set by the Paris agreement.

The importance of intervening to improve the use of natural resources is annually remembered by Global Footprint Network. In the report on Earth Overshoot day (Global Footprint Network, 2017) is underlined the day of the year in which the world's population runs out of their resources. In this year, the Earth Overshoot day coincided with the August 2nd, in a significant advance of the day reported in 2016 and in 2015 and forecasts say that in 2030 this day could fall at the end of June.

Compared to these premises it is clear that it is essential to promote initiatives aimed at the enhancement of waste recovery (both pre-consumer and post-consumer) especially in heterogeneous contexts and in cross-sectorial reality (Migliore et al., 2015). This type of approach presupposes a revision of manufacturing processes capable of overcoming the "linear" vision of the process in favor of a "systemic" logics (Cutaia et al., 2015). Waste cannot be seen only as the output of a process, this would represent a reductive view, rather we should try to see in waste, resources to be exploited (Mihajlov and Stevanovic-Carapina, 2015).

In accordance with these principles, many studies have been conducted and some were translated into real productive cases with marketing of sustainable products with recycled content. The paper will consider some experiences that intended to convey towards the manufacturing of bricks, different types of scraps and/or waste (to add and/or replace the typical mixture of materials), with the aim of highlight potential and good practices replicable in other contexts. Finally, a case study concerning the company Catalyst of Carrara, which has developed highly innovative patented products, will be analyzed. These products have been designed with the objective of contributing systematically both to the reduction of waste disposed on the territory and enhancing scrap/waste.

2. Innovative bricks production

2.1. Scraps and waste concerning the building sector

In 2014, according to Eurostat statistics, the total waste production by the economic activities and domestic waste in the EU-28 accounted for 2.503 billion tons.

This quantity represents the highest amount registered in the EU-28 over the period 2004-2014. A large part of the total waste generated is related to demographic and economic dimension of the EU, but it appears that the construction sector accounted for 34.7% of the total in the 2014, followed by mining (28.2%), manufacturing activities (10.2%), water and waste services (9.1%) and household activities (8.3%); the remaining 9.5% of waste was generated by other economic activities (Eurostat, 2014). It is a fact that cannot be overlooked because it highlights the potential derived from strategic interventions for environmental improvement in the supply chain in general.

The European Commission has estimated that if in the construction sector were applied systematically environmental improvements and new management procedures, we could have a positive impact on 42% of final energy consumption, on 35% of our emissions of greenhouse gases and on over 50% of mined materials, it would also save up to 30% water (EC Communication, 2011b).

The EEA (European Environmental Agency), within its report (EEA, 2012), reported that adding the impacts due to building products, in their whole lifetime, to those generated during the use of residential buildings, buildings are responsible for 31% of the contribution to global warming, the 20% of the causes of acidification, 21% is their contribution to tropospheric ozone precursors emissions and, 22% is their part of the consumption of material resources. On the basis of all these considerations this research work aims to highlight what it can be obtained by giving value to scrap materials, referring mainly to the production of brick.

2.2. The use of waste and scraps as secondary raw materials in the bricks production

The experiences carried out nationally and internationally on the recovery of waste as secondary raw material for the production of bricks for the building industry, are numerous and heterogeneous.

Considering the types of scrap/wastes that are already used it is possible to list the following: scraps from quarries (kaolin, basalt, etc), blast furnace slag, sawmill sludge, dust and waste glass, cotton waste, paper production scraps, etc.; each retrieval of material give origin to products/materials that have higher performances and/or that are environmentally more sustainable (considerable materials are many more, but the study has focused the attention to those that have led to the production of materials that are also innovative, from the point of view of the performance, of the production process and of application system, compared to traditional production).

A study (El-Mahllawy, 2008) on the ability to reuse scraps of kaolin quarries, blast furnace slag and scraps from basalt quarries, pointed out that not only this scrap could entirely replace the virgin raw materials, but it can improve the resistance in acidic environment of bricks products. In this case it was particularly interesting the aspect related to the renewed and enhanced product: the scrap/waste recovered not only contributed to an environmental improvement (impact avoided disposal in landfill and the reduced consumption of virgin raw materials), but it has also fostered a remarkable process of up-cycling. The scraps arising from the stone industry has been proved as useful in the mixtures for the manufacturing of bricks in other circumstances.

In one study it has been showed the ability to retrieve both the sawmill sludge (from stone industry) and the glass dust and waste, in sizes ranging from 25 to 75% of the original mixture (Turgut, 2008) for the production of bricks. Another study underlined the possibility to recover the quarries dusts mixed with waste from the working of aluminum and generic ash (Shakir Alaa et al., 2013). Referring the attention to the stone sector in the Italian context, emerges an interesting research (Corcione et al., 2018) project that integrates the use of waste deriving from the Lecce stone extraction/processing and the use of 3D printing of building components. In this case the waste is used to produce slabs for buildings facades. Other studies (Van Wijk et al., 2015) were conducted on this theme and these shows how many possible developments are possible, and above all how these can foster environmental improvement and the development of forms of circular economy. In other cases, the waste from C&D was recovered as secondary raw material with excellent results, a study (Seco et al., 2018) conducted in Spain established that concrete waste could be used to substitute up to 50% of the clay whereas ceramic wastes could only substitute a maximum of 30% of the clay.

The waste that can be used for the production of bricks, as shown, comes from different production sectors, a study conducted in Belgium (Nabil et al. 2018) showed that the waste foundry sand from Belgaum foundry industry is useful as secondary raw material in the percentage up to 50% in clay bodies to produce bricks. Even the waste of cotton processing and the waste from the paper mill can be reused to produce bricks (Rajput et al., 2012) and it has been shown that this type of wastes can be used to replace the 90% of the quantity of material brick making (the remaining 10% is compensated with the use of cement).

Even the agriculture sector can provide useful waste for the production of bricks mixture: rice straw (Kung-Yuh et al., 2009) can be used in the production of bricks helping to reduce the thermal conductivity of brick. Other studies have highlighted possible mixtures to be obtained by adding expanded polystyrene (Ling and Teo, 2011) or sand (Lertsatitthanakorn et al., 2009). Similarly, to the above-described experiences, it is possible to trace significant proposals within projects financed at Community level from the Life programme. A study conducted in Spain (LIFE, 2005) showed that the sludge from wastewater treatment can become a good component for mixture of bricks and quantifies the percentage between 1 and 2.5% of the total weight. The proposed production system also promotes a significant reduction of energy consumption, because, the sludge does not require treatments, the combustion for the firing of bricks, frees them from all organic substances that could cause problems. Another very interesting project Life (LIFE, 2008) that is working on the reduction of energy consumption in manufacturing phase has been developed in Germany. In this case the waste types treated as secondary raw material are the sawmill sludge from stone sector, which allow a reduction in firing temperature and therefore a considerable gain in terms of energy consumption and emissions.

Reported cases give the idea of the multiplicity of initiatives that can be activated within the supply chain of brick manufacturing, and it is possible to point out how scrap materials and waste - coming from areas completely unrelated to the supply chain of brick and more generally to the construction sector - can become valuable resources for the production of excellent quality products (this study is part of a research developed in the context of the valorization of pre-consumer waste financed by the Fondazione Fratelli Confalonieri di Milano). All these falls within the Community directives on environmental sustainability and represents an evolution of the productions toward increasingly sustainable production systems.

3. Case studies

3.1. Catalyst case study

Based on the assumptions made, a case study has been selected that has been able to tackle different environmental aspects, leading to production of different types of bricks. The bricks have the added value of being produced almost entirely with secondary raw material and they are manufactured using a production system with a reduced environmental impact.

The case study of this company has been selected because it has received several mentions, including that of the European Union in the framework of eco-innovation proposals suitable for the Horizon2020 projects and that of the 2016 SAIE (an important Italian event related to the construction sector) that reward the processes that leads to the zero impact.

The Catalyst company has developed two types of bricks very innovative for their characteristics, the first type is the "Carrara-block ®" the second one is the "Ri-block ®". The first type of brick, "Carrara-block ®" is very interesting because it combines and solves two very important environmental issues: the first one is linked to the large quantity of waste deriving from the extraction of marble throughout the territory (the Catalyst company works in the Apuan district, a territory characterized by the presence of the marble quarries and the enormous environmental impact caused by the chain that goes from the extraction to the processing of stone); the second one is connected to significant reduction in energy consumption (compared to traditional bricks manufacturing) because this type of bricks is obtained by pressing and not by firing. The production system (Fig. 1) starts from taking the scraps from the marble producers (the scraps currently are stored in permanent landfills, and although some quantities are retrieved, it's never an up-cycling processes); scraps are transported in machining centers where they are crushed, screened and chemically tested; than they are mixed with binder elements (white cement and water in very small quantities) and finally are compacted with high compression presses. After a period of curing, the product is ready to use.

From an environmental perspective the benefits associated with this type of bricks are:

- *Control of the use of natural resources*. The brick is made using almost completely recycled material (75% recycled deriving from the waste of local companies related to the extraction/processing of stone and 25% cement binder).
- *Reduction of impacts generated by the waste deriving from stone sector.* With a production and a systematic use of this brick, Apuan territory may benefit from the decrease of waste production (the waste became secondary raw material) and especially could reduce the growth of landfills. If we refer to the quantities of material extracted (over 3 million tons according to Massa-Carrara ISR data) and to the quantity of waste material (variable percentage from 35 to 75%), it evident that at present the environmental impact linked to the lithic sector is decidedly too high. The marble, the main product of the stone sector, increases its ecological footprint by almost three times, because it assume in its global cost what is necessary to manage and/or dispose waste (Table 1).
- *Reduction of emissions.* The production of “Carrara-block®” doesn't include combustion or firing, so in terms of issue, it impacts less in percentage than the traditional brick manufacturing.
- *Improved performance.* The brick product, not being subject to shrink, can be laid with a reduced use of adhesives and mortars (reducing the consumption of raw materials), also less use of bedding mortar provides greater resistance of masonry.
- *Recyclability.* At the end of the lifecycle of the building, “Carrara-block®” is 100% recyclable, because it can be crushed and re-manufactured again.

The second type of product is the "Ri-block®", that is produced from construction and demolition waste and is able to manage two environmental issues: the first one is related to the management of C&D waste (discussed in section 2.1) and the second, as in the case of "Carrara-block®", is connected to the avoidance of significant energy consumption required for traditional bricks firing, because this type of brick is obtained by pressing and not by firing. The manufacturing system (Fig. 2) proceeds by taking the C&D waste from yards and/or construction and demolition waste storage sites, carries it in machining centers where it is crushed, screened and chemical tested, then is mixed with binder elements (cement and water in very small quantities) and finally is compacted with high compression presses.

An interesting aspect of this brick is that its manufacturing can be realized directly on site, because the presses (Fig. 3) are transportable. This aspect makes the material very interesting because it can contribute to the almost total decrease of the impacts related to transportation (raw materials first and finished products at the end). This production system can be extremely efficient even to deal with emergencies related to natural disasters such as earthquakes.

Referring the attention to one of the latest earthquakes that occurred in Italy, it can be estimated that for each 100 tons (about half the quantity of material that may constitute an apartment) disposed of into the nearest storage site, it is released into the atmosphere 1 ton of CO_{2eq}, it should be noted that government sources affirm that the total rubbles are almost 2,500 million tons.

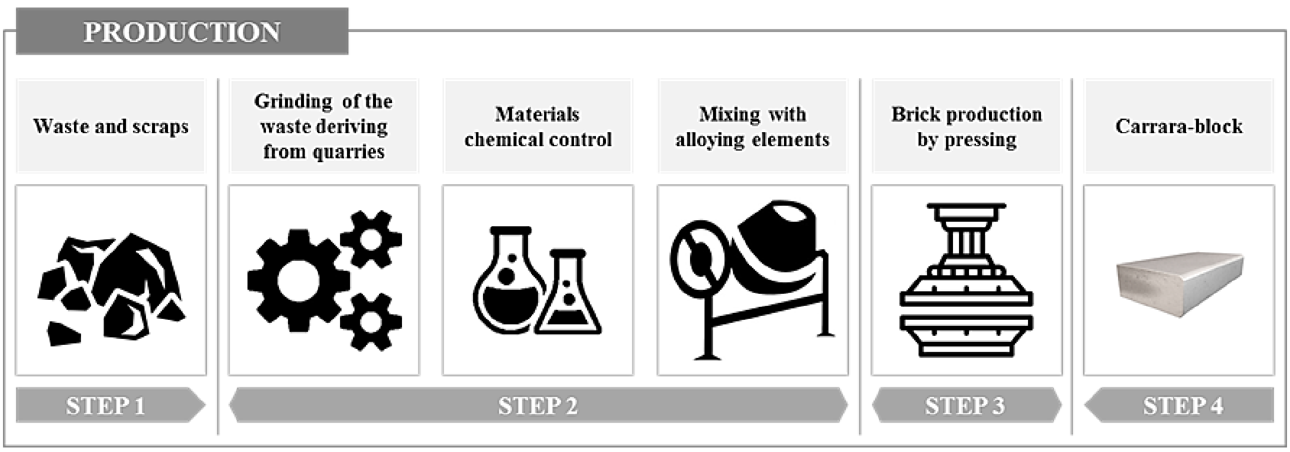


Fig. 1. Production of the “Carrara-block®”

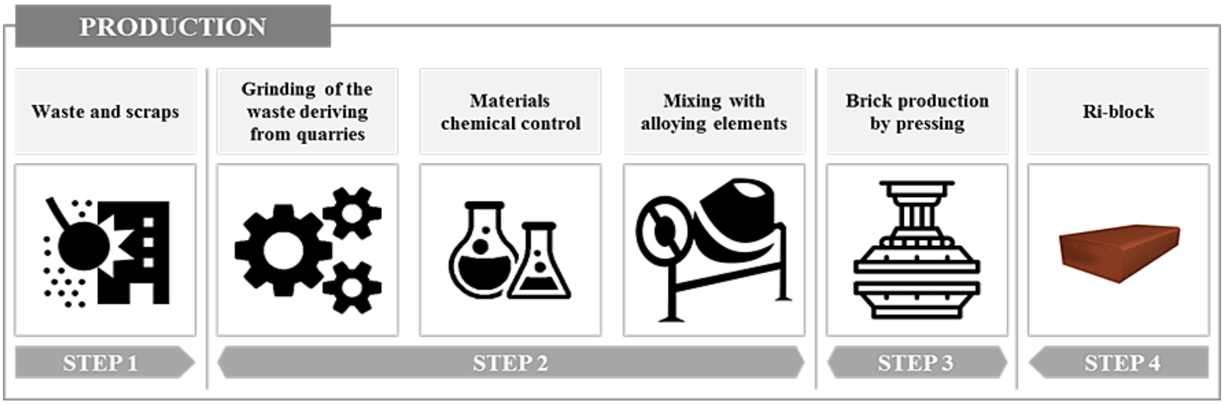


Fig. 2. Production of the "Ri-block®"

Table 1. Comparison between impact generated from transport and disposal of waste and forecast scenarios (Data from Sima Pro 8.3 and Ecoinvent 3.3)

	[u.m]	*[f.u.] 1ton*	*Impact allocation (forecast scenarios)*					
			*0% recycled **		*30% recycled ***		*50% recycled ****	
TRANSPORT	$kgCO_{2\ eq}$	0.158	0.158 $kgCO_{2\ eq}$	0%	0.110 $kgCO_{2\ eq}$	-30%	0.079 $kgCO_{2\ eq}$	-50%
	MJ_{eq}	0.027	0.027 MJ_{eq}	0%	0.018 MJ_{eq}	-30%	0.013 MJ_{eq}	-50%
LANDFILL	$kgCO_{2\ eq}$	5.073	5.073 $kgCO_{2\ eq}$	0%	3.551 $kgCO_{2\ eq}$	-30%	2.536 $kgCO_{2\ eq}$	-50%
	MJ_{eq}	0.166	0.166 MJ_{eq}	0%	0.116 MJ_{eq}	-30%	0.083 MJ_{eq}	-50%

*Note: * this scenario describes the current situation in which 100% of the impacts are allocated to the only product; ** this scenario describes the possibility to recycle 30% of waste and to be able to relocate with mass criterion the impacts generated by transport and landfill on a bigger quantity of products;*** this scenario describes the possibility to recycle 50% of waste and to be able to relocate with mass criterion the impacts generated by transport and landfill on a bigger quantity of products.*

From an environmental perspective the benefits associated with this type of bricks manufacturing are:

- *Control of the use of natural resources.* The brick is made using almost entirely waste material deriving from construction and demolition and can be produced and used directly on site. An interesting aspect that emerges is the ability to use the press directly in areas affected by the earthquake, avoiding the high costs of disposal of rubble and the cost and the impacts deriving from the transport (Table 2).
- *Reduce of the impacts generated by the construction sector.* With a production and a systematic use of "Ri-block®", the incidence of generated impacts by construction and demolition waste would decline significantly. The entire construction sector would benefit and landfills would be resized.
- *Reduction of emissions.* The production of "Ri-block®" doesn't include combustion or firing, so in terms of issue, it impacts less than the traditional brick manufacturing.
- *Improved performance.* The brick product, not being subject to shrink can be laid with a reduced use of adhesives and mortars (less raw materials), also reduced use of bedding mortar provides greater resistance of masonry.
- *Recyclability.* At the end of the lifecycle of the building, "Ri-block®" is 100% recyclable, because can be crushed and re-product again.

The last three characteristics are identical for the two products, because they have the same production process. Another aspect that should not be overlooked is that both bricks examined in this study, despite the presence of recycled and the type of production process, can be considered of excellent quality from the performance point of view. Table 3 shows the values related to the specific performance of Catalyst bricks compared with bricks with similar characteristics and emerged that in no case the bricks with recycled content is lower.

3.2. Building product and CAM (minimum environmental criteria) in Italy

The bricks produced by Catalyst are just one of the initiatives undertaken at EU and globally level to promote virtuous cycles and examples of circular economy, also because it agrees with what is expressed within the CAM (Environmental Minimum Criteria) launched by the Italian Government (Ministry of the Environment, 2017). The CAM's are environmental requirements defined for the various phases of the purchasing process in the general framework of GPP "Green Public Procurement", in order to identify the best products, design solutions or services from an environmental point of view along the life cycle, taking into account the availability of market.

The CAM's are defined in the scope of the provisions of the Plan for Sustainability in consumption in the field of public administration and shall be adopted by Decree of the Minister of the Environment, Land and Sea Protection.

Fig. 3. High compression press used for the production of the “Ri-block®”

Table 2. Impact generated from transport and disposal of C&D waste that can be avoided with a system of recycling like the one proposed by the Catalyst

	[u.m]	*[f.u.] 1 ton*	*Quantity [ton]*	*Distance [km]*	*Total impact 0% recycled **
TRANSPORT	$KgCO_{2\ eq}$	0.158	2.500.000 t	30 km	11.850.000 $KgCO_{2\ eq}$
	MJ_{eq}	0.027	2.500.000 t	30 km	2.025.000,00 MJ_{eq}
LANDFILL	$KgCO_{2\ eq}$	5.073	2.500.000 t	-	12.682.500 $KgCO_{2\ eq}$
	MJ_{eq}	0.166	2.500.000 t	-	415.000 MJ_{eq}

*Note: * this scenario describes the current situation*

Table 3. Comparison between typical bricks and bricks made with recycled material

		 *medium bricks*	 *Carrara-block®*	 *Ri-block®*
STRUCTURAL CHARACTERISTICS		*	**	**
Average Compressive Strength	N/mm^2	46.80	48.76	52.10
Water absorption	%	8.5	3.3	6.6
THERMAL CHARACTERISTICS				
Thermal resistance	m^2K/W	0.32	0.072	0.081
Thermal conductivity	W/mK	0.72	0.76	0.62

*Note: * data from comparison with similar products; ** data from Laboratorio Sigma s.r.l. (RINA Iso 9001/2008)*

Their systematic and uniform application, allows to disseminate environmental technologies and environmentally preferable products, and produces a leverage effect on the market, causing virtuous economic operators to adapt to the new requirements of public administration. In Italy, the effectiveness of CAM’s was secured thanks to art. 18 of l. 221/2015 and, later, in art. 34 on “Energy and Environmental Sustainability Criteria” of Legislative Decree 56 (2016) (in Italian).

This requirement ensures that national public procurement policy is effective not only with the aim of reducing environmental impacts, but with the objective of promoting more sustainable and circular models of production and consumption and in spreading the "green" jobs. In addition to the enhancement of environmental quality and respect for social policy, the application of the Minimum Environmental Criteria also responds to the need of the public administration to rationalize their consumption and reduce, where possible, the expenses.

Referring to the attention to the construction industry for Public Administrations (as featured in the "National Action Plans on Green Public Procurement (PANGPP)" released in November 2017) is required the use of products with recycled content of at least 30% of the total of its weight; it also provides that waste (non-hazardous) resulting from construction and demolition waste must recycled or reused for at least 70% by 2020 (Ministry of the Environment, 2017). This is an important signal intended to sensitize companies to innovate in a sustainable manner and to take into account the value of scraps/waste as secondary raw material.

4. Conclusions

The aim of the paper was to highlight the actual weaknesses of sustainability management practices within the construction industry which could be improved by starting with small initiatives that, if conducted in a systematic manner and on a global scale, could lead to radical changes. As reported by several sources the construction sector is responsible for 37% of the whole of the waste produced in the Europe Community and efforts to reduce these impacts would lead to perceptible improvements, both at the local scale (production of waste landfills, etc.) and at the global scale (emissions etc.).

The presented experiences want to give an idea of what is now ongoing to face the environmental issues with the objective to highlight that the waste cannot be seen only as a problem but we should look at these as to new resources to compensate the fact that natural resources are declining at a planetary scale. The selected case study is fully in line with the theme of sustainability, because is able to address several aspects that can promote environmental improvements (reduction of waste and their enhancement, product and process innovation, etc.); but especially wants to demonstrate that also and especially in a small scale, it is possible to activate virtuous processes that, if well managed can lead to excellent results (the data deriving from the environmental assessments on the induced impacts demonstrate what has just been said).

Specifically, considered the Apuan industrial district, the inclusion of the Catalyst, in the stone sector supply chain, brings benefits not only to the territory (other destination of waste and consequent valorization), but also to the stone sector that could become more environmentally sustainable if all waste products would be classified as by-products of processing and therefore not as a problem but as an additional resource.

References

Corcione C., Palumbo E., Masciullo A., Montagna F., Torricelli M., (2018), Fused Deposition Modeling (FDM): An innovative technique aimed at reusing Lecce stone waste for industrial design and building applications, *Construction and Building Materials*, **158**, 276-284.

Cutaia L., Luciano A., Barberio G., Sbaffoni S., Mancuso E., Scagliarino C., La Monica M., (2015), The experience of the first industrial symbiosis platform in Italy, *Environmental Engineering and Management Journal*, **7**, 1521-1533.

EC Communication, (2011a), COM (2011) 21 final - Communication from the Commission to the European Parliament, the Council and the Committee of the Regions: A resource-efficient Europe - Flagship initiative under the Europe 2020 Strategy, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52011DC0021.

EC Communication, (2011b), COM (2011) 571 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Roadmap to a Resource Efficient Europe, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52011DC0571.

EC Communication, (2014), COM (2014) 398 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Towards a circular economy: A zero waste programme for Europe, On line at: https://eur-lex.europa.eu/resource.html?uri=cellar:aa88c66d-4553-11e4-a0cb-01aa75ed71a1.0022.03/DOC_1&format=PDF.

EC Communication, (2015), COM (2015) 614 - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Closing the loop - An EU action plan for the Circular Economy, On line at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A52015DC0614.

EEA, (2012), SOER 2015 — The European environment— State and Outlook 2015, European Environmental Agency, Publication, Copenhagen, On line at: https://www.eea.europa.eu/soer.

EEA, (2017), Shaping the future of energy in Europe: Clean, smart and renewable, European Environmental Agency, Publication, Copenhagen, On line at: https://www.eea.europa.eu/signals/signals-2017/articles/shaping-the-future-of-energy.

El-Mahllawy M., (2008), Characteristics of acid resisting bricks made from quarry residues and waste steel slag, *Construction and Building Materials*, **22**, 1887-1896.

Eurostat, (2014), Waste generation by economic activities and households, EU-28. On line at http://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics.

Global Footprint Network, (2017), Annual report on the Earth overshoot day, On line at: http// http://www.footprintnetwork.org/content/uploads/2017/07/GFN_AR_2016_final_lo.pdf.

Kung-Yuh C., Ping-Huai C., Ching-Rou H., Kuang-Li C., Chris C., (2009), Lightweight bricks manufactured from water treatment sludge and rise husks, *Journal of Hazardous Material*, **171**, 76-82.

Legislative Decree 56, (2017), Supplementary and corrective provisions to the legislative decree 18 April 2016, n. 50, (in Italian), On line at: http://www.bosettiegatti.eu/info/norme/statali/2017_0056.htm.

Lertsatitthanakorn C., Atthajariyakul S., Soponronnarit S. (2009), Techno-economical evaluation of a rice husk ash (RHA) based sand-cement block for reducing solar conduction heat gain to a building, *Construction and Building Material*, **23**, 364-369.

LIFE, (2005), LIFE05 ENV/E/000301 -EcoCeramics - Ecological ceramics optimization. Alternative to sludge disposal, On line at: http://ec.europa.eu/environment/life/project/Projects/index.cfm

LIFE, (2008), LIFE08 ENV/D/000029 - EcoBrick - Manufacturing Sand-Limestone Bricks, Recycling Energy and Organics from Sewage Sludge, On line at:

http://ec.europa.eu/environment/life/project/Projects/index.cfm

Ling I.H., Teo D.C.L., (2011), Properties of EPS RHA lightweight concrete bricks under different curing conditions, *Construction and Building Material*, **25**, 3648-3655.

Migliore M., Campioli A., Lavagna M., Oberti I., Paganin G., Talamo C., (2015), Intersectorial resue of waste and scraps for the production of building products: strategies and valorization of waste, *Environmental Engineering and Management Journal*, **14**, 1675-1681.

Mihajlov A., Stevanovic-Carapina H., (2015), Rethinking waste management within the resource-efficient concept, *Environmental Engineering and Management Journal*, **14**, 2973-2978.

Ministry of the Environment, (2017), National Action Plan on Green Public Procurement (PAN GPP). Minimum environmental criteria for the awarding of design and construction services for the new construction, renovation and maintenance of public buildings, (in Italian, On line at: http://www.minambiente.it/sites/default/files/archivio/allegati/GPP/all.to_19_PAN_GPP_definitivo__21_12_2007.pdf

Nabil H., Das P., Mohan M.K., George J., (2018), In-plant production of bricks containing waste foundry sand. A study with Belgaum foundry industry, *Case Studies in Construction Materials*, **9**, 1-13.

Rajput D., Bhagade S.S., Raut S.P., Ralegaonkar R.V., Mandavgane Sachin A., (2012), Reuse of cotton and recycle paper mill waste as building material, *Construction and Building Materials*, **34**, 470-475.

Seco A., Omer J., Marcelino S., Espuelas S., Prieto E., (2018), Sustainable unfired bricks manufacturing from construction and demolition wastes, *Construction and Building Materials,* **167**, 154-165.

Shakir Alaa A., Naganathan S., Nasharuddin Mustapha K., (2013), Properties of bricks made using fly ash, quarry dust and billet scale, *Construction and Building Materials*, **41**, 131-138.

SPREAD, (2012), Final Report Summary - SPREAD (Social Platform identifying Research and Policy needs for Sustainable Lifestyles), On line at: https://cordis.europa.eu/result/rcn/59298_en.html.

Turgut P., (2008), Properties of masonry blocks produced with waste limestone sawdust and glass powder, *Construction and Building Materials*, **22**, 1422-1427.

UNEP, (2017), Resource efficiency: Potential and Economic Implications. A report of the International Resources Panel, On line at: http://www.resourcepanel.org/sites/default/files/documents/document/media/resource_efficiency_report_march_2017_web_res.pdf

Van Wijk A.J.M., Van Wijk I., (2015), *3D Printing with Biomaterials: Towards a Sustainable and Circular Economy*, IOS Press, The Netherlands.

Environmental Engineering and Management Journal

"Gheorghe Asachi" Technical University of Iasi, Romania

73 Mangeron Blvd., 700050, Iasi, Romania
Tel./Fax. +40-232-271759, PO 10, BOX 2111,
URL: *http://omicron.ch.tuiasi.ro/EEMJ/*
e-mail: *eemjournal@yahoo.com*, *eemj.office@gmail.com*

INSTRUCTIONS FOR AUTHORS

1. Introduction

Environmental Engineering and Management Journal (EEMJ) is an international medium for publication of Original Papers, Reviews, Case Studies, Book Reviews on the fundamentals, applications in environmental engineering and technologies, applied environmental sciences, environmental health, management, sustainable development, education for sustainability. Advertising is also accepted with contractual payment forms.

Submission of a manuscript implies that the work described has not been published before (except in the form of an abstract or as part of a published lecture, or thesis); that it is not under consideration for publication elsewhere; that its publication has been approved by all coauthors, if any, as well.
Papers, books for review, offers to review, suggestions and commercials (advertising) should be submitted to the *Editor-in-Chief* All papers will be published in English. Non-English speaking authors should seek the advice of a professional language expert or an English speaker to help translate the paper.

2. Legal requirements

The author(s) guarantee(s) that the manuscript is/will not be published elsewhere in any language without the consent of the copyright holders, that the rights of third parties will not be violated, and that the publisher will not be held legally responsible should there be any claims for compensation.
Authors wishing to include figures or text passages that have already been published elsewhere are required to obtain permission from the copyright holder(s) and to include evidence that such permission has been granted when submitting their papers. Any material received without such evidence will be assumed to originate from the authors.
The author(s) are encouraged to transfer the copyright of the article to the publisher upon acceptance of an article by the journal, using the Authors' Warranty and Assignment of Copyright agreement. This transfer enables the Editor to protect the copyrighted material for the authors, but does not relinquish the author's proprietary rights. The publication of an article is conditioned by the signature of the author to whom correspondence should be addressed on this Authors' Warranty and Assignment of Copyright that is provided by the Editor.

Ethics in Publishing

For information on ethics in publishing for journal publication see http://omicron.ch.tuiasi.ro/EEMJ/plagiarism.htm

Conflict of interest

All authors are requested to disclose any actual or potential conflict of interest such as any financial, personal or other relationships with other people or organizations concerning the submitted work that could inappropriately influence, or be perceived to influence, their work.

3. Editorial procedure

For original papers, an upper limit of 7000 words is recommended (including Abstract, Keywords, References, Figures and Tables), processed with MS editing facilities.

For review papers (critical evaluation of existing data, defined topics or emerging fields of investigation, critical issues of public concern), an upper limit of 15000 words is recommended (including Abstract, Keywords, References, Figures and Tables).

Manuscripts should be written in English (American or British usage is accepted, but not a mixture of these) and submitted **electronically**, in .doc format (please do not use .docx) to the *Editor-in-Chief*, at one (and only one) of the following e-mail addresses: **eemjournal at yahoo dot com**; **eem_journal at yahoo dot com**; **eemjeditor at yahoo dot com**; **eemj_editor at yahoo dot com**; **eemjournal at gmail dot com**; **eemjeditor at gmail dot com; eemjoffice at gmail dot com.**
Please be sure to include your full affiliation and e-mail address (see Sample manuscript).

When submitting the manuscript, it is mandatory to include a cover letter to the editor. The cover letter must state:

- that all authors mutually agree that the manuscript can be submitted to EEMJ;
- that the manuscript contains the original work of the authors;

- the novelty in results/findings, or significance of results;
- that the manuscript has not already been published, or is not under consideration for publication elsewhere.

Manuscripts are evaluated first in the Editorial Office (as a preliminary condition for acceptance) in terms of meeting the requirements of the journal, including attempts of plagiarism. The authors are responsible for the accuracy of the whole paper and references. Authors will be notified about the registration of their contribution. Only those contributions, which conform to the following instructions, can be considered for the peer-review process. Otherwise, the manuscripts are returned to the authors, with observations, comments and annotations.

The peer review process is decisive for paper acceptance. It could be done in several stages, depending on the revision quality of the manuscript in accordance with the requirements of paper evaluators.

Please do not transmit electronic data or requirements to the publisher until your manuscript has been reviewed and accepted for publication. Please follow the instructions below.

A minimum of four suitable *potential reviewers* should be provided by the authors. Please provide their name, email addresses, and institutional affiliation. When compiling this list of potential reviewers please consider the following important criteria: they must be knowledgeable about the manuscript subject area of the manuscript; they must not be from the authors' own institution or country; they should not have recent (less than five years) joint publications with any of the authors. However, the final choice of reviewers is at the editors' discretion.

4. Manuscript preparation

General:
Authors must follow the Instructions for authors strictly, failing which the manuscripts would be rejected without review. Editors reserve the right to adjust the formatting style to conform to the standards of the journal.

Manuscripts should be concise, in 1.5 line spacing, and should have 2 cm all over margins. The font should be Times New Roman of size 12 points. The numbering of chapters should be in decimal form. Ensure that each new paragraph is clearly indicated, using TAB at 1.25 pts.

The text layout should be in single-column format. Keep the layout of the text as simple as possible. Most formatting codes will be removed and replaced on processing the manuscript. However, do use bold face, italics, subscripts, superscripts etc. Add line numbering and page numbers. To avoid unnecessary errors it is strongly advised to use the 'spell-check' and 'grammar-check' functions of your word processor.

Title page will contain:

- A concise and informative title (Times New Roman bold, all caps of size 14 points); the maximum length of the title should be maximum 100 letters and spaces; The full name(s) of the author(s) (first name, then last name, with Times New Roman bold 12 points) should be written below the title. The affiliation(s) and complete postal address(es) of the author(s) will be provided immediately after the full name of the authors and will be written with Times New Roman 12 points. When the paper has more than one author, their name will be followed by a mark (Arabic numeral) as superscript; for the corresponding author, an asterix will be added using *Word_Insert_Reference_Footnote_Symbol* sequence. Also, the full and e-mail addresses, telephone and fax numbers of the corresponding author will be provided in the footer of the first page, as: Author to whom all correspondence should be addressed: email….., Phone…….., Fax…………
- **Abstract:** each paper must be preceded by an abstract presenting the most important results and conclusions in no more than 250 words. Do not include citations in the Abstract.
- **Keywords:** three to five keywords should be supplied after the Abstract for indexing purposes, separated by comma, **ordered alphabetically,** using American spelling and avoiding general and plural terms and multiple concepts (avoid, for example, "and", "of"). Be sparing with abbreviations: only abbreviations firmly established in the field may be eligible.
- The text of the paper should be divided into **Introduction, Materials and methods (**or **Experimental), Results and discussion, Conclusions, References** (for papers dealing with environmental management, policy, education etc., the Experimental part can be replaced by case-studies presentation).

1. Introduction
State the objectives of the work and provide an adequate background, avoiding a detailed literature survey or a summary of the results.

2. Material and methods (or 2. Experimental)
Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

3. Results and discussion
Results should be clear and concise. Discussion should explore the significance of the results of the work, not repeat them. Avoid extensive citations and discussion of published literature.

4. Conclusions
The main conclusions drawn from results should be presented in a short Conclusions section. Do not include citations in this section.

Formulae, symbols and abbreviations:
Formulae will be typeset in Italics (preferable with the Equation Editor of Microsoft Office 2003) and should be written or marked as such in the manuscript, unless they require a different styling. The formulae should be numbered on the right side, between brackets:

$$a^3 = 3M / 4N \quad (1)$$

Always refer in the text to Equations as (Eq. 1), Eqs. (1-4) etc.
The more complex Chemical Formulae should be presented as Figures.
Abbreviations should be defined when first mentioned in the abstract and again in the main body of the text and used consistently thereafter.

SI units must be used throughout.

Footnotes should be avoided.

References:
The list of References should only include works that are cited in the text and that have been published. References should be cited in the text in brackets ***(Harvard style)*** as in the following examples:

(Chisti, 1989), (Gavrilescu and Roman, 1996), (Moo-Young et al., 1999).
References should be alphabetically listed at the end of paper, with complete details, as follows:

Books: Names and initials of authors, year (between brackets), chapter title, title of the book (italic), editors, edition, volume number, publisher, place, page number:
Mauch K., Vaseghi S., Reuss M., (2000), *Quantitative Analysis of Metabolic and Signaling Pathways in Saccharomyces cerevisiae*, In: *Bioreaction Engineering*, Schügerl K., Bellgardt K.H. (Eds.), Springer, Berlin Heidelberg New York, 435-477.
Faber K., (2000), *Biotransformations in Organic Chemistry – A Textbook*, vol. VIII, 4th Edition, Springer, Berlin-Heidelberg-New York.
Handbook, (1951), *Handbook of Chemical Engineer*, vol. II, (in Romanian), Technical Press, Bucharest, Romania.

Symposia volumes: Names and initials of authors, year (between brackets), paper title, symposium name, volume number, place, date, page numbers:
Clark T.A., Steward D., (1991), *Wood and Environment*, Proc. 6th Int. Symp. on Wood and Pulping Chemistry, Melbourne, vol. 1, 493-498.

Journal papers: Names and initials of authors, year (between brackets), full title of the paper, full name of the journal (italic), volume number (bold), first and last page numbers:
Tanabe S., Iwata H., Tatsukawa R., (1994), Global contamination by persistent organochlorines and their ecotoxicologcial impact on marine mammals, *Science of the Total Environment*, **154**, 163-177.

Patents: Names and initials of authors, year (between brackets), patent title, country, patent number (italic):
Grant P., (1989), Device for Elementary Analyses. USA Patent, No. *123456*.

Dissertations: Names and initials of authors, year (between brackets), title, specification (PhD Thesis, MSc Thesis), institution, place:
Aelenei N., (1982), *Thermodynamic study of polymer solutions*, PhD Thesis, Institute of Macromolecular Chemistry Petru Poni, Iasi, Romania.
Star K., (2008), *Environmental risk assessment generated by natural hazards*, MSc Thesis, Institute of Hazard Research, Town, Country.

Legal regulations and laws, organizations: Abbreviated name, year (between brackets), full name of the referred text, document type, author, URL address:
ESC, (2007), Improving access to modern energy services for all fundamental challenge, Economic and Social Council, ENV/DEV/927, On line at: http://www.un.org/News/Press/docs/2007/envdev927.doc.htm.
EPA, (2007), Biomass Conversion: Emerging Technologies, Feedstocks, and Products, Sustainability Program, Office of Research and Development, EPA/600/R-07/144, U.S. Environmental Protection Agency, Washington, D.C., On line at: http://www.epa.gov/Sustainability/pdfs/Biomass%20Conversion.pdf.
EC Directive, (2000), Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000, on the incineration of waste, Annex V, *Official Journal of the European Communities*, L 332/91, 28.12.2000, Brussels.
GD, (2004), Governmental Decision No. 1076/2004 surnamed SEA Governmental Decision, regarding the procedure for strategic environmental impact assessment for plans or programs, *Romanian Official Monitor*, Part I, No. 707 from 5th of August, 2004.

Web references
The full URL should be given in text as a citation, if no other data are known. If the authors, year, title of the documents are known and the reference is taken from a website, the URL address has to be mentioned after these data:
Burja C., Burja V., (2008), Adapting the Romanian rural economy to the European agricultural policy from the perspective of sustainable development, MPRA, Munich Personal RePEc Archive, On line at: http://mpra.ub.uni-muenchen.de/7989/1/MPRA_paper_7989.pdf

Web references must not be listed separately, after the reference list.

All references must be provided in English with a specification of original language in round brackets.

Citation in text
Please ensure that every reference cited in the text is also present in the reference list (and vice versa). Do not cite references in the abstract and conclusions.
Unpublished results, personal communications as well as URL addresses are not recommended in the references list..
Citation of a reference as "in press" implies that the item has been accepted for publication.

Papers which have been accepted for publication should be included in the list of references with the name of the journal and the specification "in press".

References style

Text: All citations in the text may be made directly (or parenthetically) and should refer to:

- *single author:* the author's name (without initials, unless there is ambiguity) and the year of publication: "as previously demonstrated (Smith, 2007)"; "as Smith (2007) demonstrated"
- *two authors:* both authors' names and the year of publication: (Arnold and Sebastian, 2008; Smith and Hansel, 2006; Stern and Lars, 2009)
- *three or more authors:* first author's name followed by "et al." and the year of publication: "As has recently been shown (Werner et al., 2005)…", "Kramer et al. (2000) have recently shown ...."

Citations of groups of references should be listed first alphabetically, then chronologically.

Examples: "…..as demonstrated (Aden, 1996a, 1996b, 1999; Allan and Jones, 1995; Han et al., 2007; Weiss and Schmidt, 1988)".

Abbreviations

Define all abbreviations at their first mention in the text. Ensure consistency of abbreviations throughout the article.

Acknowledgements

Include acknowledgements in a separate section at the end of the article before the references and do not, therefore, include them on the title page, as a footnote to the title or otherwise. List here those individuals who provided help during the research (e.g., providing language help, writing assistance or proof reading the article, funding supports etc.).

Footnotes

Footnotes must be avoided. Do not include footnotes in the Reference list.

Table footnotes

Indicate each footnote in a table with a superscript lowercase letter.

Tables

Draw the Tables in grid format using a basic, solid line style without shadows.

Ensure that the data presented in Tables do not duplicate results described in Figures or elsewhere in the paper.

Figures

Number Figures consecutively in accordance with their appearance in the text. All illustrations should be provided in camera-ready form, suitable for reproduction, which may include reduction without retouching. Photographs, charts and diagrams are all to be referred to as Figure(s) and should be numbered consecutively, in the order to which they are referred.

Figures may be inserted preferably as black line drawings. They should be pasted on, rather than taped, since the latter results in unclear edges upon reproduction.

Ensure that each illustration has a caption, placed below the Figure. Supply also captions separately, not attached to the figure. A maximum limit of 8 Figures are allowed per manuscript.

A caption should comprise a brief title (**not** on the Figure itself) and a description of the illustration. Keep text in the illustrations themselves to a minimum but explain all symbols and abbreviations used. Multiple Figures can be expressed as one Figure (for e.g. 1a, 1b, 1c etc...), while retaining the maximum limit of 6.

ALL Figures must be submitted in either .jpg or .tiff format with a very good resolution (but do not submit graphics that are disproportionately large for the content).

Figures and Tables must be embedded in the text.

Proofs

Proofs will be sent to the corresponding author (by e-mail) and should be returned within 72 hours of receipt. Corrections should be restricted to typesetting errors; any other changes may be charged to the authors.

Paper in Electronic Format:

Authors are asked to submit their final and accepted manuscript as an attachment to one of the above-mentioned e-mail addresses. Use the **.doc** format (not .docx !).

5. Page charge

There is no charge per printed page for regular papers.

6. Reprints

The corresponding author will be provided with a .pdf file of the paper via e-mail, free of charge. A hard copy Of the issue containing the paper can be provided on request, for a fee. This request will be formulated when the final form of the manuscript (the electronic one) is provided.

7. Additional procedures for the editorial management of *Environmental Engineering and Management Journal*

Starting with volume 13/2014, the members of the Scientific Advisory Board and the Corresponding authors will receive each issue of the journal in electronic .pdf format. Printed copies can be delivered on request.

An author cannot appear on more than two papers per regular issue. An author cannot appear on more than three papers in a Guest Editor/ Conference issue.

The evaluation/peer-review process of manuscripts submitted for Guest Editor / Conference issues published according to journal *Editorial Procedure and Policy* will be handled and evaluated as with regular manuscripts, so that only consistent papers will be published. The manuscripts must be sent at least six months before the presumed data of publication. Those manuscripts which do not fulfill the journal requirements will be rejected. This is to discourage superficiality in the development of the manuscript, from formal and scientific points of view. No amount of money will be refunded following the rejection of manuscripts.

No more than 160 pages and no more than 20 papers are acceptable for regular issues. No more than 180 pages and no more than 25 papers are opportune for special issues. The number of pages is based on the published version of an article, not on the submitted version (for instance, when page breaks are changed and when images are enlarged for easier viewing).

An issue can include, as an exception, a number of 25-30 papers as a maximum. This situation could appear when the authors of an already accepted paper need and ask for early publication, from the position in the list of accepted papers. In this circumstance, a yearly submission to our journal (500 Euro) will be asked for each already accepted paper, for its publication in advance.

A newly-received manuscript can be evaluated by priority, when a deposit of 200 Euro shall be paid by authors in advance. If the manuscript is deemed unsuitable for publication, the authors will not be eligible for a refund.

Failure to pay mandatory charges may result in the paper being withheld from early publication.

In all cases, the corresponding author will sign an agreement with the *Editor-in-Chief*, and the *Director* of the *EcoZone* Publishing House according to journal *Editorial Procedure and Policy.*

Automated software is used for checking against plagiarism. In order to avoid false results, the generated reports are cautiously checked and confirmed by journal staff. We do not send plagiarism reports to authors. Any manuscripts which do not prove to be at least 90% original will be rejected. The rejection for plagiarism may arise at any phase of the editorial / review process, even if the manuscript was accepted for publication. The authors are solely responsible for the originality of their submission. Therefore, any manuscript should be carefully checked for such inconsistencies before submitting to EEMJ.

The authors are required to follow academic publishing rules, to adhere to the principles of scientific ethics and to sign the Authors' warranty and Copyright transfer.

Detailed information concerning these issues may be found of the EEMJ website, under *Editorial Procedure and Policy.*

October 2018 Vol.17 No.10 ISSN 1582-9596

Environmental Engineering and Management Journal is edited by the
ECOZONE Publishing House of the
Academic Organization for Environmental Engineering and Sustainable Development (OAIMDD)
within the ***Department of Environmental Engineering and Management***
Faculty of Chemical Engineering and Environmental Protection
under the aegis of "Gheorghe Asachi" Technical University of Iasi
73 Prof.Dr.docent Dimitrie Mangeron Street, 700050-Iasi, Romania

"Gheorghe Asachi" Technical University of Iasi

Printed in Romania by *POLITEHNIUM* Iasi