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Edited by Nicola Pirrone

CONFERENCE PROCEEDINGS OF THE CNR-INSTITUTE OF ATMOSPHERIC POLLUTION RESEARCH

9-10 MAY 2018
Montelibretti (Rome), Italy

CNR-IIA

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FOREWORD

The initial remit of the Institute, like many national research institutes around the world, was to address environmental problems that had been identified locally and over time been recognised to be occurring in a number of cities or regions, in our case the impact of atmospheric pollution. Over the years the international scientific and health communities realised that local phenomena were influenced by the surrounding regions, other countries further afield and eventually by atmospheric transport at hemispheric and global scales. This progress in understanding is mirrored in the expansion of the scope of regulatory and policy responses to pollution, which grew from local and regional, to national, to in our case European, and as can be seen today global.

The last ten years have seen very significant advances in our understanding of the Earth System due to a huge increase in our capacity to observe and then process the data obtained. The Institute has responded to this by becoming, more than ever before, a truly interdisciplinary research facility, where seemingly disparate (even geographically) component parts, mesh to address the new faces of those same original problems, for the local, regional and global community.

A part of the reason that our capacity to more closely observe the Earth System has increased so much has been the advances in miniaturisation of the instrumentation used to monitor environmental parameters. This has lead to cheaper, lighter and thus more satellites, producing more regular coverage of the planet. It has also led to the possibility of air quality monitoring devices which rather than requiring a fixed monitoring sites, may now be positioned on citizen's balconies or roofs, on bus or taxi fleets, or even clipped to a cyclists backpack, giving a spatio-temporal level of detail which would have been unimaginable only a few years ago. This produces, of course, a lot of data, from a wide range of instruments, in a large number of places. Making sense of data, and even being aware that a certain dataset exists has become incredibly complex. Understanding whether comparing two data sets is valid requires knowledge of how those datasets were obtained and processed after collection. The Institute over the last decade has recognised the need to embrace the challenges of miniaturisation and the combination of satellite with in-situ observations and their links to the concepts of big data and interoperability. For this reason the Institute now finds itself remarkably well positioned within a number of European and international programmes and initiatives that are defining the next generations of Earth System observation methodologies and protocols.

The abstracts in this volume give an idea of how the Institute has evolved to meet the current challenges in atmospheric pollution research, the range of activities in which the Institute is involved, and demonstrate how these activities combine to produce research and innovation which is pertinent to current scientific questions, policy decisions and eventually the wellbeing of both the environment and society.

The Institute's increasing involvement over the last ten years in European and International research programmes, its increasing role as a source of information and know-how to inform and advise on policy nationally and internationally is a testament to the relevance of the Institute as a whole, and the quality and stature of the individuals whose daily efforts make it what it is.

Rome, June 4, 2018

Yours sincerely,
Nicola Pirrone
nicola.pirrone@iia.cnr.it

CNR–IIA

Conferenza dell'Istituto sull'Inquinamento Atmosferico
del Consiglio Nazionale delle Ricerche

Agenda

9-10 maggio 2018 Aula convegni
Area della ricerca Roma1
Montelibretti (RM)

9 Maggio 2018

08.15 – 09.00 Registrazione

09.00 – 10.00 Saluti di benvenuto

- Antonello Provenzale, Direttore sostituto del DTA, CNR
- Mariano Grillo, Direttore Generale, Ministero dell'Ambiente
- Gianni Silvestrini, Direttore Scientifico, Kyoto Club
- Gunther Landgraf, Head of Ground Segment Infrastructure Engineering Section, European Space Agency

10.00 – 10.45 L'Istituto nel contesto nazionale e internazionale

Nicola Pirrone

10.45 – 11.15 *Coffee break*

11.15 – 13.00 Highlight di storie di successo

(co-Chairs: Francesca Sprovieri e Angelo Cecinato)

- Dai dati alla conoscenza: il laboratorio virtuale
  ***S. Nativi**, P. Mazzetti, M. Santoro*
- Dati multi-sorgente di Osservazione della Terra (OT) per il monitoraggio degli ecosistemi (naturali, incluse le aree polari, ed urbane)
  ***P. Blonda**, R. Salvatori*
- Sviluppo di sensori low-cost ed eco-sostenibili per il monitoraggio della qualità dell'aria
  ***A. Macagnano**, J. Avossa, E. Zampetti, A. Bearzotti, P. Papa, A. Capocecera, F. De Cesare*
- Trasferimento di conoscenze tecnico-scientifiche per la produzione e l'attuazione della normativa ambientale
  A. Fardelli
- Aree industriali e salute: il progetto Centro Internazionale di Studi Avanzati Ambiente, Ecosistema e Salute Umana (CISAS)
  ***C. Perrino**, A. Budonaro, S. Canepari, M. Catrambone, M. Cerasa, S. Mosca, A. Pietrodangelo, S. Dalla Torre, G. Esposito, M. Giusto, S. Pareti, E. Rantica, T. Sargolini*
- Il Progetto ABC "Biocarburanti per aviazione"
  ***M. Rotatori**, C. Balducci, A. Budonaro, A. Cecinato, M. Cerasa, G. Esposito, M. Giusto, E. Guerriero, M. Montagnoli, S. Mosca, M. Perilli*
- Energie rinnovabili e biocombustibili: il CNR-IIA a supporto della transizione energetica
  ***F. Petracchini**, V. Paolini, L. Tomassetti*

13.00 – 14.30 Pausa pranzo

14.30 – 16.00 Sessione 1: Progetti e Programmi Europei e Internazionali

(co-Chairs: Daniela Pasella e Paolo Mazzetti)

- **The European network for observing our changing planet (ERA-PLANET):**
  - **SMart URBan Solutions for air quality, disasters and city growth (SMURBS)**
    Migranti in città intelligenti: il contributo dei dati di Osservazione della Terra
    ***P. Blonda**, G. Quattrone, C. Bassani, C. Tarantino, P. Adamo, P. Mazzetti, M. Santoro, S. Nativi, S. Di Franco, R. Salvatori*
  - **Essential Variables workflows for resource efficiency and environmental management (GEO Essential)**
    Variabili essenziali per la gestione efficace dell'ambiente e delle risorse
    ***M. Santoro**, P. Mazzetti*
  - **Integrated Global Observing Systems for Persistent Pollutants (iGOSP)**
    Sistemi di osservazione globale a supporto delle convenzioni internazionali
    ***I. M. Hedgecock**, and all the iGOSP participants*
  - **Integrative and Comprehensive Understanding on Polar Environments (iCUPE)**
    Conoscenza integrata degli ambienti polari
    ***R. Salvatori**, R. Salzano*
  - **ERA-PLANET management: Aspetti economico-gestionali**
    ***L. Ragazzi**, A. Fino, S. Cinnirella, M. Gensini, N. Pirrone*
- **Improving future ecosystem benefits through earth observations (ECOPOTENTIAL)**
  Sistema integrato per lo studio multi-scala delle funzioni e dei servizi degli ecosistemi in aree protette mediante dati OT in supporto a GEOSS
  ***S. Vicario**, M. Adamo, C. Tarantino, B. Biagi, F. M. Rana, S. Nativi, P. Mazzetti, M. Santoro, C. Bassani, P. Blonda*

16.00 – 16.30 Coffee break

16.30 – 18.15 Sessione 1 (*Cont'd*)

- **Discovery Access Broker for Edge (DAB4EDGE)**
  ***P. Mazzetti**, S. Nativi, M. Santoro*
- **Services for the European Open Science Cloud (EOSC-Hub)**
  ***S. Nativi**, P. Mazzetti, M. Santoro*
- **Global Mercury Observation System (GMOS) & UN Environment-GEF**
  ***F. Sprovieri**, M. Bencardino, S. Cinnirella, F. D'Amore, F. De Simone, I. M. Hedgecock, F. Carbone, V. Andreoli, A. Naccarato, A. Fino, A. Macagnano, E. Zampetti, A. Bearzotti, F. De Cesare, P. Papa, G. Esposito, N. Pirrone*
- **Global Observation System for Mercury (GOS4M)**: the GEO Flagship to support the Minamata Convention on Mercury
  ***S. Cinnirella**, F. D'Amore, M. Bencardino, F. Sprovieri, F. De Simone, I. M. Hedgecock, N. Pirrone*
- **European NEtwork for Redistributing Geospatial Information to user Communities** – Open Data (**ENERGIC-OD**)
  ***M. Liberti**, P. Mazzetti, S. Nativi*
- **Increasing Social Awarness and ACceptance of biogas and biomethane (ISAAC)**
  ***M. Segreto**, F. Petracchini, L. Tomassetti, V. Paolini, M. Torre, D. Borin*
- **Metrology for oxidised mercury (MercOx)**
  ***A. Naccarato**, I.M. Hedgecock, N. Pirrone*
- Esperienze conseguite e collaborazioni in corso con il **Programma Ambiente delle Nazioni Unite** (**UN Environment**) sull'inquinamento da mercurio
  ***A. Fino**, N. Pirrone*

10 Maggio 2018

09.00 – 09.20 Cambiamenti climatici recenti: dalle cause agli impatti su eventi estremi e qualità dell'aria.

__A. Pasini__, S. Amendola, M. M. Miglietta

09.20 – 09.40 Nuove sostanze e nuove prospettive nella valutazione del rischio sanitario ambientale.

__A. Cecinato__, C. Balducci, P. Romagnoli, M. Perilli

09.40 – 10.40 Sessione-2: Emissioni e qualità dell'aria
(co-Chairs: Cinzia Perrino e Mauro Rotatori)

- Caratterizzazione delle nanoparticelle in emissione da impianti del cemento
  __S. Mosca__, M. Catrambone, M. Giusto, M. Montagnoli, M. Perilli, E. Guerriero, M. Rotatori
- L'esperienza Nazionale nel rilascio delle Autorizzazioni Integrate Ambientali – le tecnologie per il miglioramento dell'efficienza energetica delle industrie energivore
  __C. Mazziotti__
- Caratterizzazione delle emissioni da una centrale termica alimentata a paglia
  __E. Guerriero__, A. Khalid, T. Mahmood, F. Gallicci, M. Carnevale, L. Longo, M. Cerasa, A. Budonaro, M. Perilli, E. Rantica, M. Frattoni, S. Mosca, S. Pareti, M. Catrambone, E. Paris, A. Del Giudice, M. Rotatori, M. Centritto
- Tecnologie per il biogas e il biometano
  __V. Paolini__, M. Segreto, L. Tomassetti, M. Torre, F. Petracchini

10.40 – 11.00 *Coffee break*

11.00 – 12.15 Sessione-2 (*Cont'd*)

- Mobilitaria: qualità dell'aria e politiche di mobilità in 14 grandi città italiane nel periodo 2006-2016
  __F. Petracchini__, L. Tomassetti, V. Paolini, M. Segreto, M. Torre
- Qualità dell'aria indoor in ambienti di studio e di lavoro: progetti Bando Ricerche in collaborazione (BRiC) 22 e 23
  __L. Tofful__, F. Marcovecchio, C. Perrino
- L'inquinamento indoor: risultati delle indagini condotte dall'IIA
  __C. Balducci__, P. Romagnoli, M. Perilli, A. Cecinato
- Creazione di un database nazionale in ambito della Società Italiana di Aerosol (IAS) sulla speciazione del particolato atmosferico
  __A. Pietrodangelo__, S. Becagli, A. Bigi, M.C. Bove, E. Brattich, R.Caggiano, G.Calzolai, D.Cappelletti, D. Cesari, C. Colombi, D. Contini, A. Donateo, L. Ferrero, V. Gianelle, S. Iacobellis, P. Ielpo, F. Lucarelli, M. Masiol, C. Perrino, M. G. Perrone, P. Prati, A. Riccio, L. Tositti, R. Udisti, E. Venturini, R. Vecchi
- Radon progeny in the Arctic region
  __R. Salzano__, A. Pasini, A. Ianniello, R. Traversi, R. Udisti

12.15 – 13.00 Sessione-3: Sistemi Osservativi e Tecnologie
(co-Chairs: Palma Blonda e Sergio Cinnirella)

- Tecniche data-driven e leggi di scala nell'analisi di serie storiche di dati ambientali
  __F. Carbone__, A. G. Bruno, F. De Simone, I. M. Hedgecock
- Dinamiche del mercurio su scala globale
  __F. De Simone__, F. Carbone, I. M. Hedgecock, S. Cinnirella, F. Sprovieri N. Pirrone
- Cambiamenti di uso del suolo da servizi Copernicus e Sentinel-2
  __C. Tarantino__, M. Adamo, P. Blonda

13.00 – 14.00 Pausa pranzo

14.00 – 15.00 Sessione-3 (*Cont'd*)

- Variabili essenziali da SAR: campi di vento
  M. Adamo
- Belharmony project: harmonization of time series on water target by various calibrations
  C. Bassani, *A. Fino, S. Sterckx*
- Recenti sviluppi nelle tecnologie per monitoraggio ambientale con sensori (chimici/fisici/ottici)
  A. Bearzotti, *E. Zampetti, P. Papa, J. Avossa, A. Capocecera, A. Macagnano*
- Un modello per le previsioni meteo stagionali a scala sub-regionale sull'Italia come strumento per la stima futura della qualità dell'aria
  S. Amendola, *A. Pasini*

15.00 – 16.30 Discussione inerente tre grandi tematiche

(Moderatore: Antonello Pasini)

- Aree urbane e industriali
- Sistemi e tecnologie di osservazione
- Dai Big Data alla conoscenza ambientale

16.30 – 17.00 Conclusioni

MAJOR ACHIEVEMENTS OF THE CNR INSTITUTE OF ATMOSPHERIC POLLUTION RESEARCH (CNR-IIA) DURING THE LAST DECADE (2008-2018)

N. Pirrone

CNR-IIA, Montelibretti, Italy
nicola.pirrone@iia.cnr.it

Since 2009 in light of the new priorities set out in European and national programs the mission of the Institute (www.iia.cnr.it) hhas been revised substantially and accordingly. Major emphasis was placed on the reinforcing the Institute's ability to develop multi- and inter-disciplinary research with particular focus on Earth Observation systems (in-situ and space-based) to support environmental science and policy development and implementation. This focus has led over the last ten years to the development of new and advanced monitoring technologies and methodologies for air quality and industrial emission assessment, the development of the global observing system for mercury to support the Minamata convention (www.gmos.eu) and the various EU projects (i.e., ERA-PLANET, EOSC-Hub, ENERGIC-OD, among many others) as part of the GEO programme (www.earthobservations.org), the characterization of emerging atmospheric pollutants, the design and testing of new technologies for producing bioenergy from waste, the design and operation of brokering systems to enhance the potential for discovery of environmental data and information, and ensure big data interoperability. Key to the Institute's activities over this period has been the determination to provide expertise and support to policy makers, the national Ministry of the Environment, and national and European institutions tasked with the preparation and implementation of environmental legislation. Hence the Institute's research has informed not only the wider scientific community, but also policy makers, and those bodies which implement and regulate policies, to the benefit of institutions, stakeholders and the public.

The Institute's success rate in competitive calls for proposals in the field of Environment and Climate Change of the European Commission framework programmes (namely FP7 and Horizon 2020) has been well above the CNR average, with 18 projects funded in FP7 (2008-2014) and 7 so far in the ongoing H2020 (2014-present), and it also coordinates large European programmes and flagships on Earth Observation and environmental research. Nationally, strong cooperation has been established with several public bodies and parts of the private sector in the field of environmental pollution control (i.e., of large industrial plants and urban settings), development of innovative technologies for environmental monitoring, and interoperable systems for big data discovery and analysis. A major effort has been made to transfer the research outcomes to policy makers which has led to ever increasing cooperation with the Italian Ministry of Environment, regional governments, and the European Commission. This cooperation occurs within the framework of national and international programmes, including UNEP, GEO, and the Belmont Forum, and conventions such as UNECE-LRTAP, and the Minamata and Stockholm conventions. The main focus of these collaborations has been to support national and European institutions in the preparation and implementation of new European and international environmental legislation and the assessment of the effectiveness of measures.

Today the Institute numbers roughly 150 employees, including research scientists and technologists, administrative staff and laboratory technicians.

During the last ten years research facilities have been built which include chemical and data science labs at three of its four divisions, new research atmospheric stations and air quality networks to support research programmes and the implementation and progress assessment of international conventions. The Institute is part of several international networks of excellence that focus on global change and environmental sustainability, and promote collaborative programmes with major policy-oriented environmental institutions and programmes worldwide (i.e., UNEP, GEO, OGC). The Institute's senior scientists contribute to PhD programmes around Italy (i.e., Univ. La Sapienza, Univ. of Calabria, Univ. of Perugia) with over 20 PhD students and post docs involved in its various research programmes. The Institute has a strong links and is involved in a large range of projects and initiatives with leading universities and research institutions worldwide.

Details of Institute's infrastructure, programmes and achievements can be found on the Institute web portal (www.iia.cnr.it), highlighted in the abstracts authored by our researchers, and in the overview presented at the Institute's conference reported in the annex to this brief abstract with reference to:

1. Research infrastructure and governance;
2. Human and financial resources;
3. Key on-going national and international projects and flagship programmes on Earth Observation, global observing systems, advanced sensors for environmental monitoring, brokering systems for big data science and interoperability, systems for producing bioenergy from waste, air quality studies in urban and industrial areas, industrial emissions and assessment of new monitoring technologies, capacity building and transfer of knowledge to policy makers and stakeholders, support to international, European and national bodies for environmental legislation preparation and implementation;
4. Concluding remarks.

ACKNOWLEDGEMENTS

I would like to acknowledge that the achievements of the Institute highlighted in this abstract is the result of the effort of scientists, technicians and administrative personnel that with dedication and passion have carried out high quality and innovative research in national and international contexts during the last decade.

L'Istituto nel Contesto Nazionale e Internazionale

Nicola Pirrone

Direttore
Istituto sull'Inquinamento Atmosferico del CNR

Conferenza dell'Istituto sull'Inquinamento Atmosferico del CNR
Area della Ricerca di Roma-1, Montelibretti (RM)
9-10 Maggio 2018

Mission

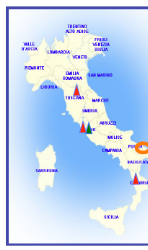
Ampliare la conoscenza dei molteplici meccanismi di emissione, trasformazione, trasporto e impatto degli inquinanti atmosferici coniugando competenze multidisciplinari nello sviluppo di nuove e innovative tecnologie e metodologie di indagine

Aree Tematiche

.... .dall'atto costitutivo del 15/04/2013

- **Inquinamento atmosferico in aree urbane e industriali.**
- **Sviluppo di metodologie e tecnologie analitiche da laboratorio e da piattaforma per la caratterizzazione della qualità e sostenibilità ambientale.**
- **Inquinamento industriale e ambienti ad elevato rischio ambientale.**
- **Cicli degli inquinanti atmosferici e influenza sui cambiamenti globali.**
- **Reti e sistemi osservativi per l'inquinamento atmosferico in supporto alle direttive europee e convenzioni internazionali.**
- **Sviluppo di sistemi e tecnologie per la condivisione delle informazioni geospaziali.**

Articolazione Territoriale



Personale:

- **> 140 unità di personale**
  - **70 T. Ind.** (*ca. 36 nel 2009*)
  - **50 T. Det.**
  - **24 (AdR, altro)**

Articolazione territoriale:

- **SEDE - AdR Roma1, MLIB (62)**
- **Sede Secondaria di Firenze (12)**
- **Sede Secondaria di Rende (24)**
- **Sede Secondaria di Roma c/o MATTM (36)**
- **UniBa – Gruppo (10)**

Infrastrutture

- **Laboratori di chimica ambientale (i.e. PM, POPs, PAH, HM)**
- **Laboratori per sviluppo sensori avanzati nanostrutturati**
- **Laboratori di microscopia**
- **Sei laboratori mobili (Qualità dell'Aria, Emissioni e TLR)**
- **Due stazioni fisse di osservazione in Italia (MLIB, Monte Curcio)**
- **Sistema Osservativo Globale per il Mercurio (GMOS) con oltre 40 siti in tutto il mondo con dati acquisiti in real-time presso UOS di Rende**
- **Laboratorio TLR (MIVIS + altra strumentazione)**
- **Centro Nazionale di Riferimento per il Mercurio (CNRM)**

Stazione Monte Curcio – 1850 m

Stazione "Liberti" – MLib

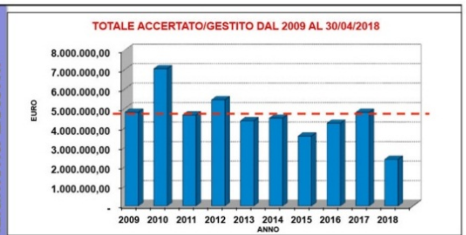
Rete Globale di Osservazione dell'Inquinamento da Mercurio

Finanziamenti Esterni

Progetti Europei, Internazionali e Nazionali (2010 - 2018)

- **H2020:** 7 progetti (2 come Coordinatori)
- **FP7:** 18 progetti (3 come Coordinatori)
- **Internazionali:** 4 progetti (*finanziati da:* NSF, GEF, USEPA, EPA Florida-Univ. Michigan)
- **Nazionali:** +30 progetti *(finanziati da:* MATTM, MIUR, MISE, Regioni Lazio, Basilicata, Calabria, INAIL, etc.)
- **Alta consulenza:** +20 progetti (*finanziati da:* HERA, Sipem, Eni, etc.)

Finanziamenti Esterni



Finanziamenti Esterni

TOTALE ACCERTATO/GESTITO DAL 2009 AL 2018 (al 30/04/2018)

ANNO	TOTALE ACC.TO/ GESTITO	INCIDENZA PERCENTUALE PER ORIGINE						TOTALI
		Ministeri	EPR	Enti Locali/Regioni	Privati	UE - Internaz.	Altro	
2009	4.811.226,28	66,13%	2,33%	3,33%	15,27%	10,68%	2,27%	100,00%
		3.181.455,00	112.308,00	160.000,00	734.577,20	513.660,00	109.226,00	4.811.226,28
2010	7.052.697,91	62,47%	0,68%	4,35%	22,62%	9,81%	0,08%	100,00%
		4.405.567,94	48.144,27	307.100,00	1.594.977,15	691.547,23	5.361,32	7.052.697,91
2011	4.672.258,57	63,29%	0,63%	0,83%	18,51%	16,66%	0,08%	100,00%
		2.956.870,00	29.525,00	39.000,00	864.990,43	778.326,99	3.546,15	4.672.258,57
2012	5.452.645,13	60,22%	0,28%	4,09%	22,49%	10,94%	1,98%	100,00%
		3.283.791,20	15.125,00	223.164,00	1.226.100,60	596.574,86	107.889,47	5.452.645,13
2013	4.373.670,60	55,33%	0,73%	2,29%	15,09%	26,46%	0,11%	100,00%
		2.420.169,87	31.803,18	100.000,00	659.948,90	1.157.107,59	4.641,06	4.373.670,60
2014	4.509.144,81	43,70%	0,85%	0,00%	32,26%	22,93%	0,26%	100,00%
		1.970.331,85	38.348,00	-	1.454.725,85	1.033.895,68	11.843,43	4.509.144,81
2015	3.591.121,09	40,63%	0,92%	14,31%	30,19%	13,86%	0,09%	100,00%
		1.459.116,14	33.100,00	513.792,16	1.084.255,48	497.630,75	3.226,56	3.591.121,09
2016	4.249.941,16	44,13%	0,34%	2,55%	24,53%	28,43%	0,02%	100,00%
		1.875.650,42	14.255,00	108.211,69	1.042.441,24	[illegible]	949,72	4.249.941,16
2017	4.806.086,75	34,71%	0,88%	7,35%	11,64%	45,30%	0,12%	100,00%
		[illegible]	42.500,00	353.238,40	559.612,15	[illegible]	5.716,66	4.806.086,75
2018	2.391.211,99	76,57%	0,00%	13,38%	3,58%	6,47%	0,00%	100,00%
		1.831.000,00		319.945,42	85.494,55	154.772,02		2.391.211,99
TOTALE	45.910.004,29	25.051.908,03	365.108,45	2.124.451,67	9.307.123,55	8.809.012,14	252.400,45	45.910.004,29

Framework Internazionale

- **Data Science & Interoperability** – from data to knowledge – contributi a GEO-GEOSS & UN 2030 Agenda on SD
- **Global Observing Systems** – cooperazione con UNEP & WHO a supporto della COP (e dei Paesi con economie in transizione) per lo sviluppo del Global Monitoring Plan (GMP) della Minamata
- **EuroGEOSS:** contributo Europeo a GEO per GEOSS attraverso i.e., ERA-PLANET e altri on-going EU projects (i.e., ECOPOTENTIAL, EOSC-Hub, …)
- **Attività in sede Europea e internazionale** a supporto della preparazione e attuazione della legislazione ambientale (Montreal, Basel, Paris, IPPC, NEC, ….)
- **Partecipazione a GdL in ambito CEN**

Framework Internazionale

Coordinamento di ERA-PLANET

ERA-PLANET

www.era-planet.eu

Coordinatori:

SMURBS: E. Gerasopoulos (NOA)

GEO Essential: A. Lehmann (UniGe)

iGOSP: N. Pirrone (CNR-IIA)

iCUPE: T. Petaja (FMI)

Partnership and Effort

ERA-PLANET

- **Coordinatore:** Nicola Pirrone
- **Periodo:** 2016-2021
- **34 Partners (15 countries)**

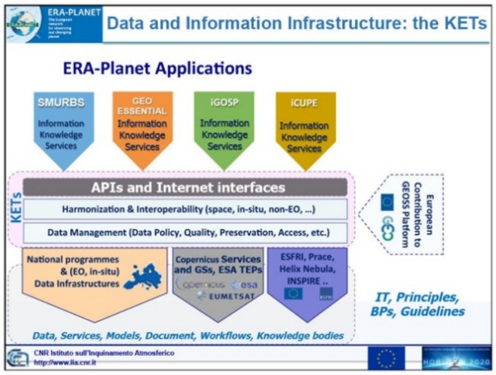
- **CNR:** IIA, IDPA, ISAC
- Università di Padova
- Università della Calabria
- ISPRA

- **Budget CNR:** 4.7 M€
- **Contributo MIUR:** 1.4 M€

MoU: CNR-IIA & ESA

Total Eligible Cost:
ca. 52 M€ → 33.6 M€

EU Contribution:
11 M€
+
Co-fund from Participating Countries
+
22.6 M€


ERA-PLANET
Data and Information Infrastructure: the KETs
ERA-Planet Applications
SMURBS Information Knowledge Services
GEO ESSENTIAL Information Knowledge Services
iGOSP Information Knowledge Services
iCUPE Information Knowledge Services
KETs
APIs and Internet interfaces
Harmonization & Interoperability (space, in-situ, non-EO, ...)
Data Management (Data Policy, Quality, Preservation, Access, etc.)
European Contribution to GEOSS Platform
National programmes & (EO, in-situ) Data Infrastructures
Copernicus Services and GSs, ESA TEPs
EUMETSAT
ESFRI, Prace, Helix Nebula, INSPIRE ..
IT, Principles, BPs, Guidelines
Data, Services, Models, Document, Workflows, Knowledge bodies
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ERA-PLANET
Supports the 2030 UN Agenda on SD
THE GLOBAL GOALS
For Sustainable Development
THE GLOBAL GOALS
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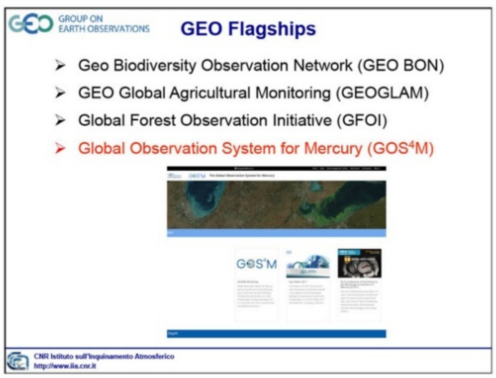
GEO GROUP ON EARTH OBSERVATIONS
GEO Flagships
Geo Biodiversity Observation Network (GEO BON)
GEO Global Agricultural Monitoring (GEOGLAM)
Global Forest Observation Initiative (GFOI)
Global Observation System for Mercury (GOS⁴M)
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GEO GROUP ON EARTH OBSERVATIONS
GMOS
http://www.gmos.eu
The Global Mercury Observation System (GMOS) is a five year project funded by the European Commission as part of the 7thFramework Programme
Worldwide Observation System
GMOS includes ground-based monitoring stations, ship-based measurements over the Pacific and Atlantic Oceans, European Seas, as well as aircraft-based measurements from the ground to the lower stratosphere
WP Leader: Francesca Sprovieri
Modelling
GMOS data are used to test regional and global scale atmospheric mercury models, which can then be used for determining mercury deposition to ecosystems and the current state of atmospheric mercury contamination.
WP Leader: Ian Hedgecock
The Interoperable System
GMOS developed an interoperable system to facilitate the sharing of information, including measurement databases and modelling results, with major stakeholders, policymakers and the public.
WP Leader: Sergio Cinnirella
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COP1, Sept. 2017, Geneva
Objectives:
To harmonize approaches for monitoring and to strengthen the capacity for mercury analyses, in humans and the environment.
Implementing partners of the GEF project are:
UN Environment, Chemical and Health Branch
The Italian National Research Council—Institute of Atmospheric Pollution Research (CNR-IIA); and
The World Health Organizations European Centre for Environment and Health (WHO);
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NANOTECNOLOGIE
Sviluppo di sensori avanzati per il monitoraggio della QA e ambientale utilizzando materiali nanostrutturati altamente performanti, robusti e non energivori.
iGOSP
ERA-PLANET
Nanocomposite sensor for Hg° monitoring in air
Sensors and Actuators B: Chemical
Procedia Engineering
Photocatalytically Decorated Au-nanoclusters TiO2 Nanofibres for Elemental Mercury Vapor Detection
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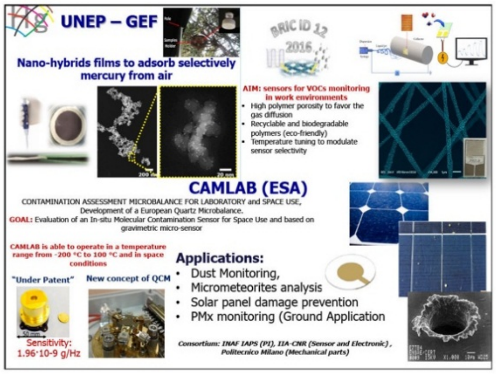
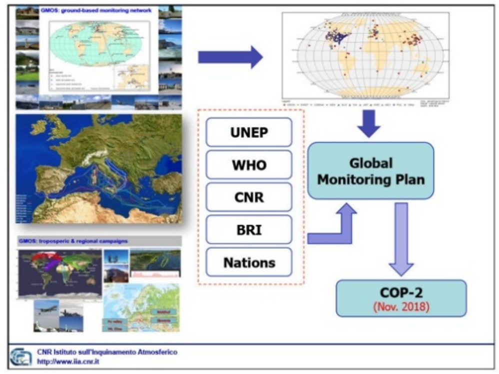




Global Monitoring Plan for Minamata Convention

Future steps:

- Proposal submitted a GEF a **Luglio 2018**
- **GEF propone a COP2** a **Settembre 2018**
- **COP2** si terrà a Ginevra a **Novembre 2018** - nella sua sessione plenaria esprimerà il parere sulla proposta
- Se il parere è favorevole GEF avrà il mandato a finanziare il progetto con **KO a Febbraio 2019**.
- **Total Budget = 28 M$**

GEO GROUP ON EARTH OBSERVATIONS

Il contributo a GEOSS

copernicus

- **Nell'ambito di progetti FP7 e H2020** l'Istituto ha fornito un contributo sostanziale nello sviluppo della **Piattaforma GEOSS –** la settimana scorsa **abbiamo co-organizzato** con ESA e GEO SEC il **workshop su "Data Providers"** avendo già organizzato il precedente a Firenze lo scorso anno.
- La solida **collaborazione con ESA** nello sviluppo della **piattaforma GEOSS** ha portato al progetto (**EDGE**) finalizzato a "*….improve the GEOSS Platform having in mind the "Needs" and "Contributions" of Users"*.
- **L'Istituto coordina GEO Italy** (www.geoitaly.org) che coinvolge molti istituto CNR, ISPRA, INGV, CMCC e Enti privati (i.e., Planetek, *e*-GEOS)
- L'Istituto **supporta molte GEO Initiatives e GEO Fundational Tasks**

GEO GROUP ON EARTH OBSERVATIONS

Il contributo a GEOSS

copernicus

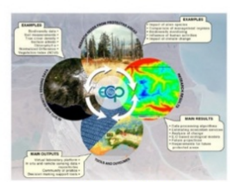
- **UN 2030 Agenda on** SD – *specifically through the participation to programs and initiatives that are strategic for GEO such as i.e., COP 21 Paris, DRR Sendai, Minamata Convention, UNECE just to cite a few.*
- come GEO Italy si supporta **EuroGEOSS** sin dall'inizio.
- **come GEO Italy** si contribuisce a "*…..foster data sharing and interoperability of models (including those related to Artificial Intelligence) that are needed to* ***support Policy Makers****. The great contribution of projects such as ECOPOTENTIAL, ERA-PLANET, EOSC-Hub are and example….*
- L'Istituto supporta molte **GEO Initiatives e GEO Fundational Tasks**

ECOPOTENTIAL

Funded by the European Union H2020 programme under grant agreement No 641762

- **Coordinator: Antonello Provenzale**
- 2015-2019 - 47 partners
- Focus on 25 targeted set of Protected Areas in Europe and beyond
- Mountain, arid and semiarid, coastal and marine ecosystems

✓ **Uses EO** data for understanding ecosystems structure
✓ **Delivers EO data products** to understand, model and monitor ecosystem changes and support the effective management of Protected Areas
✓ **Contributes to the GEOSS Platform** through a Virtual Laboratory Platform
✓ **Contributes to GEO ECO & GEO GNOME** - Builds a Community of Practice



www.ecopotential-project.eu

EOSC-hub

Services for the European Open Science Cloud (EOSC-hub)

Bring together multiple service providers to **create the Hub** which is **a single contact point for European researchers and innovators** to discover, access, use and reuse a broad spectrum of resources for advanced data-driven research

- **Start:** January 2018
- **End:** December 2020
- 100 partners from 53 countries
- 19 research communities
- 13 work packages
- 49 services ready for use

EOSC-hub

EOSC-hub Approach

- **Mobilize providers from the major European research infrastructures** (e.g. EGI Federation, EUDAT CDI, INDIGO-DataCloud) **to deliver a common catalogue of research data, services and software for research**
- On the top of the cloud, establish a set of scientific pillars to showcase: **CNR-IIA and GEO Sec are in charge of the GEO pillar**

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EUROGEOSS
TAILORING EARTH OBSERVATION SERVICES TO EUROPE'S NEEDS
Coordinate, combine and cooperate

EuroGEOSS is the European component of the Global Earth Observation System of Systems (GEOSS) with a focus on coordinating and scaling up user-driven applications being developed in Europe

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EUROGEOSS
TAILORING EARTH OBSERVATION SERVICES TO EUROPE'S NEEDS
Coordinate, combine and cooperate

- **Launched in October 2017** by the European GEO Caucus and driven jointly by DG RTD & DG GROW
- **From** "data-centric approach" to "**user-driven applications**"
- **Focus on SDGs and GEO SBAs** in a European context
- **Integrate scattered efforts**: Horizon 2020, Copernicus, ESA, national initiatives,…
- **Consolidation of** national GEO management structures → **GEO Italy (www.geoitaly.org)**

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EUROGEOSS
TAILORING EARTH OBSERVATION SERVICES TO EUROPE'S NEEDS
Coordinate, combine and cooperate

- Water Resources Management
- Sustainable Urban Development
- Infrastructure and Transport Management
- **Public Health Surveillance** *(Air Quality, Hg & POPs)*
- Food Security and Sustainable Agriculture
- Energy and Mineral Resources Management
- Disaster Resilience
- Biodiversity and Ecosystems Sustainability

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EUROGEOSS
TAILORING EARTH OBSERVATION SERVICES TO EUROPE'S NEEDS
Coordinate, combine and cooperate

- **Proposal:** EuroGEOSS Show-cases
- **CNR-IIA coordina** lo show-case on **Public Health Surveillance**
- **CNR-IIA coordina** la partnership CNR**:**
  IIA, IGG, IMAA, IREA, IDPA, IRPI

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Supporto al MATTM e PA

Attività in sede europea ed internazionale in materia di cambiamenti climatici e di sviluppo sostenibile

- **Trasferimento delle conoscenze tecnico scientifiche** nell'analisi e definizione di proposte negoziali internazionali e di documenti tecnici con particolare riferimento alla normativa in materia di cambiamenti climatici.
- **Partecipazione alle Conferenze delle Parti (COP)**, alle riunioni degli Organi sussidiari e dei Gruppi tecnici della Convenzione delle Nazione Unite sui cambiamenti climatici e della Convenzione di Vienna e il Protocollo di Montreal sulle sostanze che deteriorano lo strato di ozono.

Supporto al MATTM e PA

Attività in sede europea ed internazionale in materia di cambiamenti climatici e di sviluppo sostenibile

- **Trasferimento dei risultati della ricerca** alla definizione della **posizione italiana in sede di Commissione Europea** (Comitati e gruppi esperti) e del **Consiglio UE** (Gruppo Ambiente e Consiglio dei Ministri) e a livello internazionale in sede di **G7 e G20**;
- **Trasferimento dei risultati della ricerca** in materia di **riduzione delle emissioni climalteranti** del settore non ETS (Regolamento "Effort sharing" e Regolamento "LULUCF"), **emissioni di CO_2 dai trasporti su strada** (Regolamenti (UE) n. 443/2009 e n. 510/2011), ed in **materia di energia/clima** (Regolamento sulla Governance dell' Unione dell' Energia - Strategia Unione dell' Energia).

Programmi Internazionali

Tabella II – Partecipazione a programmi e convenzioni internazionali

Programma / Ente	WG / SB / TF	Ruolo svolto
UNECE-LRTAP	Steering Body EMEP	Capo Delegazione Italiana
UNECE-LRTAP	WG Effects	Membro del WG
UNECE-LRTAP	Task Force on Measurements and Modeling	Membro della TF
UNECE-LRTAP	Task Force on Hemispheric Transport of Air Pollutants	Coordinatore del WG
UNECE-LRTAP	WG on Strategies and Review	Membro del WG
UNECE-LRTAP	Task Force on POPs	Membro della TF
UNECE-LRTAP	Task Force on Heavy Metals	Membro della TF
Next Data / MIUR	Next Data System of Systems Infrastructure	Coordinatori
NSF – Earth Cube	A Broker Framework for Next Generation Geoscience - Brokering Building Blocks (B-Cubed)	Co-PI
GEO	GEO-DAB	Membro del IIB
UNEP	Global Partnership on Mercury Fate and Transport	Coordinatore
UNEP	Governing Council	Capo Delegazione Italiana
UNEP	Global Environmental Forum	Rappresentante Italiano
NSF & EC	Research Data Alliance	Responsabili del BIG
Science Europe	Data Access WG	Delegato CNR
European Geosciences Union (EGU)	ESSI	Presidente
American Geophysic Union (AGU)	WG on ESSI	Membro Executive Council
Open Geospatial Consortium (OGS)	WG on Earth System Science	• co-Chair del WG ESS • Membro di CF-netCDF • co-Chair del WG PubSub
INSPIRE	• Drafting Team per i Metadati • WG Atmospheric conditions and Meteorological Geographical Features	Membro
GEOSS	• WG on GCI Research – Phase 6 • Task HE-02 on Tracking Pollutants	• Membro • Coordinatore
GEO	• WP Health • European Standard & Operativity Forum	• Membro Executive Body • Leader
IEEE	Standards Working Group dell'IEEE Committee on Earth Observation (ISWG)	Membro
UNEP	Mercury Program - Partnership Advisory Group	Membro
EU	Union Commission for Data and Information"	National Contact Point

Attività in Ambito Nazionale

Accordi in essere tra CNR-IIA e MATTM

(con riferimento alla Lg. 241 del 7 Agosto 1990)

L'Istituto ha in essere **accordi con il MATTM**, ed in particolare con 4 delle 6 Direzioni Generali tecniche, ovvero con:

- DG per le Valutazioni e le Autorizzazioni Ambientali (**DVA**)
- DG per i Rifiuti e l'Inquinamento (**RIN**)
- DG per lo Sviluppo Sostenibile, per il danno ambientale e per i rapporti con l'Unione europea e gli organismi internazionali (**SVI**)
- DG per il Clima e l'Energia (**CLE**)

Attività in Ambito Nazionale

Trasferimento di Conoscenze Tecnico - Scientifiche per la Produzione e l'Attuazione della Normativa sull'Inquinamento Atmosferico e Ambientale

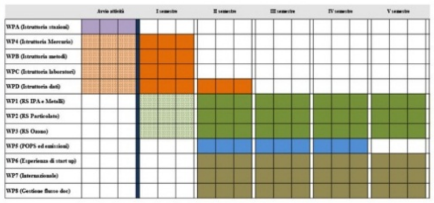
- Prevenzione e riduzione integrata dell'inquinamento (**AIA-IPPC**)
- **Qualità dell'aria ed emissioni** (anche combustibili ed emissioni dai natanti)
- Controllo dei pericoli di incidenti rilevanti (**Seveso**)
- Ciclo dei rifiuti (**sperimentazione per la produzione di Biogas / inertizzazione amianto**)
- **Piano d'azione** per la sostenibilità ambientale dei consumi PP.AA.- GPP
- **Regolamenti prodotti chimici** CLP e REACH
- **Agenti fisici** (inquinamento acustico ed elettromagnetico)

Reti Speciali per QA

ACCORDO DI COLLABORAZIONE PER L'AVVIO DELLE RETI SPECIALI DI CUI AL DECRETO LEGISLATIVO 155/2010

Il **D.Lgs. 155/2010**, attuazione alla Direttiva 2008/50/CE relativa alla qualità dell'aria ambiente e per un'aria più pulita, prevede all'art. 6 dei casi speciali di valutazione della qualità dell'aria ambiente ed in particolare dispone che **vengano individuati specifici siti fissi di misurazione del materiale particolato PM_{10} e $PM_{2,5}$, IPA e metalli pesanti** mediante l'emanazione di decreti del Ministro dell'ambiente, di concerto con il Ministro della salute e sentita la Conferenza unificata.

Reti Speciali per QA



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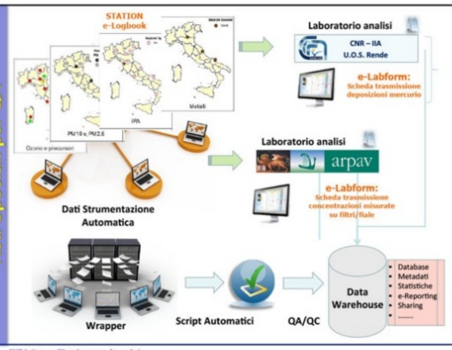
Reti Speciali per QA



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BioEnergie

- Realizzazione di **sistemi innovativi** per la produzione di energia da scarti urbani e agricoli
- Analisi delle tecnologie innovative sul mercato e supporto allo **sviluppo di nuovi sistemi** per l'utilizzo di biogas (upgrading a biometano) e riduzione delle emissioni in atmosfera
- **Supporto alla PA** su politiche energetiche e climatiche finalizzate a ridurre l'inquinamento atmosferico

Progettualità (Coordinate da: Francesco Petracchini):

- Progettazione congiunta con 10 Isole Minori di progetti di fattibilità per la riduzione delle emissioni da traffico e del consumo di energia (Smart Island) www.smartisland.it **(MIUR)**
- Progetti per la realizzazione di impianti per produzione di biogas/ biometano (**Regione Lazio e Regione Calabria**) www.micoprocess.it
- ISAAC (Social Awareness and ACceptance of biogas and biomethane) (www.isaac-project.it, **H2020**)
- Piani per l'utilizzo efficiente di fonti rinnovabili www.progettoselva.it **(Regione Lazio)**

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BioEnergie

Testing di nuove tecnologie per upgrading di biogas a biometano e produzione di energia da rifiuti solidi e liquidi

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BioEnergie

Titolo: Aerotrazione con BioCarburanti (ABC)

Produzione dei biocombustibili e loro utilizzo nel settore dell'aviazione

- **Accordo di cooperazione** tra MATTM e CNR, ENEA, Ministero Difesa (AM)
- **Periodo:** 2017-2018
- **Istituti CNR: IIA**, INO, IRC, IM
- **Resp. Sci. per IIA:** Mauro Rotatori
- **Obiettivi:** Analisi di biocarburanti per aerotrazione in termini di composizione, prestazioni ed inquinamento e definizione dei fattori di emissione

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Aree Industriali

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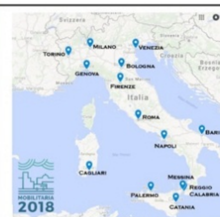
Siti Contaminati

MONITORAGGIO MICROINQUINANTI ORGANICI (PCDD/F, DL-PCB, IPA) IN ARIA AMBIENTE

Qualità dell'Aria in Italia



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Ambiente - Salute

Centro Internazionale di Studi Avanzati su ambiente, ecosistema e Salute umana (CISAS)

2016 – 2019

Coordinatore: Mario Sprovieri (IAMC)
Finanziato da: MIUR (fondi CIPE)
Budget: 6.5 M€

Studio dei meccanismi di trasferimento degli inquinanti dall'ambiente all'ecosistema e agli esseri umani.

- Inquinanti sia convenzionali che emergenti
- Tutte le matrici: atmosfera, suolo, mare, sedimenti, acque interne
- Altamente interdisciplinare
- Approccio non solo epidemiologico ma anche medico e sperimentale
- Focus sul cibo come via di introduzione degli inquinanti
- Attenzione alle donne in gravidanza e ai loro figli fino al compimento dei 3 anni
- Utilizzo della biomatematica per il trattamento dei dati

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Ambiente - Salute

WP2 - CONTAMINANTI NELL'AMBIENTE
WP Leader: Mario Sprovieri (IAMC)

Studio dei processi fisico-chimici che riguardano i principali inquinanti, convenzionali ed emergenti, identificati nelle diverse matrici ambientali ed all'interfaccia aria-acqua-suolo-sedimenti nei tre SIN di interesse

TASK 2.7 - CONTAMINANTI IN ATMOSFERA
Task Leader: Cinzia Perrino (IIA)

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Regione Basilicata

Accordi in essere tra CNR-IIA e Regione Basilicata

(con riferimento alla Lg. 241 del 7 Agosto 1990)

Accordo con la Regione Basilicata – Dipartimento Ambiente ed Energia – Ufficio Compatibilità Ambientale riguarda le seguenti tematiche:

VIA e AIA: relative alle attività di coltivazione dei giacimenti di idrocarburi presenti nel territorio della Val d'Agri (ENI s.p.a.) e Gorgoglione (Total)).

Qualità dell'Aria:

- problematiche e criticità relative agli stabilimenti presenti nel territorio della Val d'Agri;
- problematiche e criticità relative agli stabilimenti presenti nel territorio della Regione Basilicata;
- valutazione della rete regionale di monitoraggio della qualità dell'aria.

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Regione Basilicata

sito	denominaz. ARPAB	comune
A	Viggiano	Viggiano (Contrada Guard
B	Viggiano 1	Viggiano (Contrada Santa
C	Masseria de Blasiis,	Viggiano
D	Grumento 3	Grumento Nova (Contr. Carpineto M.)
F	Costa Molina Sud 1	Viggiano (Contrada Valloni)
PC	(Protezione Civile)	Viggiano

inquinante/azione	tecnica strumentale
PM_{10}	µ-bilancia
VOC	GC-MS, GC-FID
aldeidi e chetoni	HPLC-UV
n-alcani, IPA	GC-MS (GC-FID)
BTEX	GC-FID
NO_x, O_3, H_2S, SO_2	IC/Vis.
NO_2, O_3, SO_2	analizz. autom.
parametri meteo	monitor autom.
metalli ed elementi	ICP-MS/XRF
anioni e cationi	IC
EC/OC	Termo-ottico
analisi risultati	
valutaz. sorgenti	

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Considerazioni Conclusive

- ✓ L'Istituto ha raggiunto una importante collocazione e **leadership nelle reti di eccellenza** Europee e internazionali
- ✓ Ha **rafforzato la cooperazione** sia con le PA che con molte realtà regionali pubbliche e private
- ✓ **Diversificato** le fonti di finanziamento della ricerca **con incrementi significativi della componente EU e internazionale**
- ✓ **Arricchito le competenze** e la capacità di sviluppare ricerca multidisciplinare con l'apporto di nuovi ricercatori provenienti da altri istituti CNR
- ✓ Incrementato la **produzione scientifica**

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Considerazioni Conclusive

- ✓ **Potenziate le infrastrutture** di ricerca (lab. fissi e mobili, stazioni sperimentali)
- ✓ **La sfida futura** in ambito Europeo e internazionale è il prossimo FP (H2025) senza trascurare le grandi opportunità in ambito internazionale i.e., NSF, GEF
- ✓ Continuare a rafforzare la capacità di **trasferimento dei risultati della ricerca** alla PA e al settore privato.

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Grazie…

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FROM DATA TO KNOWLEDGE: THE VIRTUAL LABORATORY

S. Nativi[1], P. Mazzetti[1], M. Santoro[1]

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stefano.nativi@cnr.it

Keywords: modelling, information, knowledge, procedures, algorithms

Science is increasingly being called upon to support environmental policy makers by enabling an informed decision making process and by monitoring and assessing the progresses towards policy targets (e.g. UN Sustainable Development Goals or other international treaties). To this purpose, integrated modeling is an indispensable element. In fact, the complex and interrelated nature of real-world problems has led to a need of higher-order systems thinking and holistic solutions. Environmental models increase the level of understanding about natural systems and how they react to varying conditions (e.g. climate change). Despite the existence of many excellent models, their interoperability level is still limited. The complexity of Earth system requires breaking down research silos and bringing scientists from multiple disciplines together to collaborate with decision makers and other stakeholders to solve problems, all the while taking into consideration the social, economic, and environmental interdependency (Laniak *et al*., 2013). In the Earth system science domain, most current digital infrastructures are able to support data access rather than provide answers to complex questions – noticeably, supporting the ability to address the what-if questions posed by users. That is, there is the need to shift from the data sharing paradigm to the information/knowledge generation and sharing.
CNR-IIA is contributing to the advancement of this research area, in the context of the Global Earth Observation System of Systems (GEOSS) Model Web (Nativi *et al*., 2013) framework – specifically addressing the Science-to-Information Technology barrier (Santoro *et al*., 2016). In the context of the Group on Earth Observations (GEO) tasks and European projects (ECOPOTENTIAL, ERA-PLANET) CNR-IIA is developing a Virtual Laboratory, a cloud-based platform supporting the activity of environmental scientists in the: (i) generation of Essential Variables, Indicators and Indices from data and (ii) sharing of knowledge (ontologies), procedures (scientific business process), algorithms (source code) for reusability, reproducibility, etc.

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MULTISOURCE EARTH OBSERVATION (EO) DATA FOR ECOSYSTEMS MONITORING

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INTRODUCTION

Whether Earth Observation (EO) data comes from satellites, aircraft, unmanned aerial vehicles (UAV), in-situ measurements or other innovative platforms, artificial intelligence techniques and spatial analysis tools can be used to integrate such data with a range of other available records, including socio-economic information, in order to create value adding (downstream) services for different applications. Specifically, a major advantage of satellite EO data from optical and radar systems is that it can be made available for any region of the world - from local to continental spatial scales at different temporal resolution.

This abstract deals with the integration of multi-source data carried out within two recent European projects, namely FP7 (2010-2013) BIO_SOS (www.biosos.eu) and Horizon2020 (2015-2019) ECOPOTENTIAL (www.ecopotential-project.eu), focusing on habitat and ecosystem monitoring, respectively. Both Very High Resolution (VHR), (<3m), and High Resolution (HR), (3m - 30m), data have been used to monitor protected areas located in different bio-geographic regions.

Data integration was based on prior expert knowledge (i.e., from botanists, ecologists, remote sensing experts) and was carried out at both pixels and feature level (Zhang, 2010) for monitoring wetland habitats (FP7 BIO_SOS) as well as grassland ecosystems (HORIZON2020 ECOPOTENTIAL).

Due to the disproportionate loss of wetland habitats, their conservation is a major concern of the Coastal wetlands, European Union Biodiversity strategy for 2020. The importance of wetlands is profound, because they contribute approximately 40% of global environmental services, including water supplies, nutrient retention, flood mitigation, carbon sequestration, retention of nutrients and heavy metals, food production, wildlife habitat and areas for recreational use.

Despite this importance, almost 60% of wetlands in Europe have disappeared in recent decades due to drainage and Land Cover/Use (LC/LU) and habitat degradation (Zmihorski *et al*., 2016).

Although the use of EO data is well developed for the automatic production of Land Cover (LC) maps and their changes, related to habitat maps, LC are poorly related to biodiversity (Bunce *et al*., 2013). Thus, CNR_IIA research activities, within the two mentioned projects, focused on automatic LC-to-habitat translation based on incorporating ecological knowledge for habitat and ecosystem discrimination.

METHODOLOGY

A knowledge-based automatic system, named the Earth Observation Data for Habitat Monitoring (EODHaM), was developed for LC and habitat mapping from multi-temporal EO data, as well as change extraction (Lucas *et al*., 2015; Adamo *et al*., 2015). The EODHaM system, which implements the hierarchical classification scheme of the Food and Agricultural Organization Land Cover Classification (FAO_LCCS) taxonomy, has recently been further developed in the HORIZON2020 ECOPOTENTIAL project.

The new system, named Earth Observation Data for Ecosystem Monitoring (EODESM), can receive as input geophysical variables and use different classification techniques, both *knowledge and data driven*, to provide useful services for different end-users. Each service reliability depends on input data and technique used.

The FAO-LCCS offers a useful framework, based on life-forms, not only for LC map generation, but also for the integration of EO data with *in-situ* measurements and ancillary data. Such integration has been found appropriate to translate LC classes to

habitat classes, which can be labelled according to the Annex I of the European Habitats Directive (92/43 EEC Directive), Eunis habitat taxonomy (Tomaselli *et al*., 2013; Adamo *et al*., 2016) or General Habitat Categories (Bunce *et al*., 2012; Adamo *et al*., 2014).
Within FP7 BIO_SO project, multi-seasonal VHR optical images (i.e., WorlView2) and Light Detection And Ranging (LIDAR) data have been analyzed for LC mapping by using spectral and context-sensitive features. Then, phenological information and agricultural practices, as well as environmental attributes (e.g. water quality, lithology, soil surface aspect) have been introduced for subsequent translation of LC classes to-habitats (Tomaselli *et al*., 2013; Adamo *et al*. 2014). The environmental attributes help to solve, in most cases, the ambiguity of one-to-many relationships between LC and habitat classes.
However, environmental attributes can often be missing or else be not readily available or updated. These deficiencies affect mostly poorly studied regions located in the Mediterranean basin.
Some ambiguities still remain for habitats corresponding to the same input LC class and characterized by the same environmental attributes. Even for regions where environmental attributes are available, reliable translation from LC to habitats would require additional information. For instance, habitats 7210/D5.24 (Calcareous fens with Cladium mariscus and species of the Caricion davallianae) and X/A2.53C (Saline beds of Phragmites australis) correspond to the same LC class and are also characterized by the same LCCS environmental attributes (Tomaselli *et al*., 2013). Thus, in order to better discriminate the two habitats, spatial relations and phenological features (temporal relations) have been introduced (Tomaselli *et al*., 2016). Specifically, the spatial relations used include: *a)* topological relationships, such as adjacency and inclusion; *b)* non-topological relationships, related to distance and angle measurements (Arvor *et al*., 2013).
The spatial relations used are represent the pattern of zonation (i.e. topological rules) described by expert botanists familiar with two wetland sites. The temporal relations are associated with plant growth stages and vegetative cycles referring to single dominant species or entire plant communities (habitats) or, in the case of aquatic habitats, seasonal variations of the water regime (flooding and dry periods).
The assumption made is that natural habitats with similar morpho-structural characteristics can be differentiated by shifts in vegetative cycles or in the periodicity of flooding, which in turn correspond to different spectral signatures of EO images. In addition, LIDAR data have been used to extract vegetation structure as plant height measurements, useful for improving habitat discrimination.
The inclusion of such relations has provided better classification performances.

FINDINGS

The habitat mapping was applied to two wetland protected area in the Mediterranean, belonging to the Natural 2000 network. The expert rules considered for some habitats in Le Cesine site, is shown in Figure 1 (Adamo *et al*., 2016, Tomaselli *et al*. 2016.

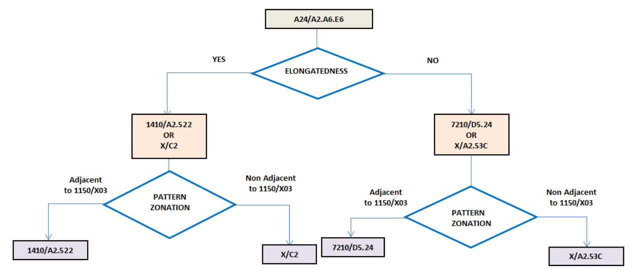

Figure 1. Graphical representation of the decision actions and conditions for discriminating the habitats associated to LCCS class A24/A2.A6.E6 (i.e. Natural Aquatic Vegetation/Herbaceous Graminoids Perennia) for Le Cesine wetland site. Credit: (Adamo *et al*., 2016)

When only expert rules and EO data are used, the final overall map accuracy, which is obtained by comparing reference ground truth patches to the ones depicted in the output map, is lower (75,1%) than the accuracy obtained using environmental attributes alone (97,0%) (Tomaselli *et al*., 2013). Some ambiguities that still remaining in habitat discrimination can be solved by integrating the use of LCCS environmental attributes (if available) with adjacency expert rules (96%) (Adamo *et al*., 2016).
The proposed methodology is considered novel, in the sense that it incorporates spatial and temporal (in terms of phenological analysis) reasoning that has recently become popular in ecological research (Chikalanov *et al*., 2012).
To date, in the framework of the Mapping and Assessment of Ecosystems and their Services (MAES), there has been little work done in automatic translation of LC to habitat classes based on the use of VHR EO data (fine scale) and expert knowledge (Maes *et al*., 2013). The methodology provides an automatic mapping technique useful for updating habitat maps without any need of in-field campaigns, as expert knowledge about the site features and

habitats can drive the classification process to solve ambiguities in the one-to-many LC to habitat mapping.

Reference ground truth data are only required for validation purposes, significantly reducing in-field campaign costs. LC maps can be frequently updated using satellite data (e.g., 5-10 days from new optical ESA Sentinel-2 imagery) and then translated into habitat maps.

CONCLUSIONS

The expert-knowledge based methodology is useful for relatively inaccessible sites (e.g. wetlands) as it does not require in-field campaigns (generally costly) but only the elicitation of ecological expert rules. This can support site (e.g. Natura 2000) managers in long-term operational automatic habitat as well as ecosystem mapping.

Changes in extent, fragmentation or status can be automatically detected by comparing map pairs, and trends can be quantified by analysing data time series. Such measurements can be used for evaluating conservation policies in force and elaborating habitat and ecosystem restoration actions and new policies. This can support Sustainable Development Goal 15 (sustainabledevelopment.un.org/sdg15) aimed at the sustainable use of terrestrial ecosystems and halt biodiversity loss. In addition, the measurements can be particularly useful to satisfy the commitments of the European Habitats Directive (92/43/EEC) which requires Member States to take measures to maintain, or restore to, favourable conservation status for those natural habitat types and species of community interest that are listed in the Annexes to the Habitats Directive.

Within CNR-IIA, the elicitation of expert rules through ontologies and semantic networks will be further exploited for ecosystem description.

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LOW-COST AND ECO-FRIENDLY SENSORS FOR AIR MONITORING

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Keywords: Electrospinning technology, nanocomposite materials, conductive and optical sensors, pollution monitoring

INTRODUCTION

Monitoring is one of the tools used to improve people understanding of air pollution patterns and trends and the long-term impacts on the several ecosystems and communities. In addition to the use of specialized equipment and analytical methods, in order to obtain more realistic and continuous results on the situation of pollutants distribution, EU projects guidelines report the need to involve also citizens in environmental monitoring, thus low-cost and easy-to-use technologies are required. To achieve this aim, novel sensors for environmental monitoring have been designed and developed to date to obtain consistent values comparable, to those provided by standard methods and technologies. At present, among nanotechnologies, electrospinning is considered as one of the most versatile and inexpensive manufacturing technologies to design and develop nanostructured sensors to detect gases and volatile organic compounds (VOCs) in the air (Macagnano *et al.* 2015, a). Some advantages in designing electrospun sensors are due to the unlimited choice of the raw molecules (polymers) and the ease of modifying (by blending, nanodoping, post processing, etc.). Sensors based on polymeric as well as metal-oxide fibers look extremely attractive for the low cost and great versatility of the raw materials that can be easily modulated, according to the transducer used and the application of interest, taking part to the resulting sensing features. The inclusion of variously working nanoparticles with different strategies of functionalization has allowed the sensors achieving excellent performances under various points of view, ranging from selectivity and sensitivity, response time, small size, low power, life-time, etc., let us suppose their actual application in air pollution monitoring. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics. Some successfully experiences will be here described.

1. TiO_2 nanofibers as suitable scaffold for Hg^0 monitoring

Exploiting the photocatalytic properties of the nanofibres of TiO_2, gold nanospheres were grown, under UV-light irradiation, on the electrospun titania nanofibres through the photocatalytic reduction of $HAuCl_4$ (tetrachloroauric acid). The sensing strategy was focused on the strong affinity of mercury to gold and the potentials of revealability of the sensing devices based on nanostructures. Sensor electrical properties (measured by Interdigitated Electrodes – IDEs), depending on shape, size and number of gold nanoparticles decorating the fibers, were easily tuned, showing the sensor was able to work at room temperature and highly sensitive to Hg^0 (tens of ppt) (Macagnano *et al* 2017, a, b; Macagnano *et al.* 2015, b).

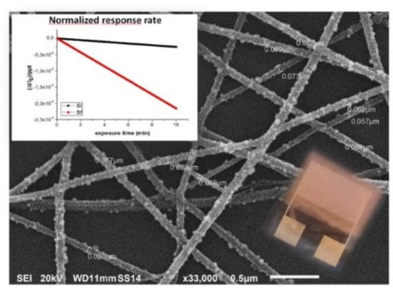

Figure 1. Fiber AuNPs decorated (SEM). Insets: a fibrous coating on IDEe current changes when Hg° was injected and flowed over the sensor

2. Eco-friendly hybrid fibers to detect selectively NO_2

Sensor working temperature has been used to tune both the sensitivity and the selectivity of a chemoresistor based on a nanostructured and nanocomposite polymer. Thus, exploiting the peculiarity of the deposition technique, through the usage of two incompatible polymers (polystyrene and polyhydroxybutyrate, recyclable and biodegradable polymers, respectively), a peculiar conductive nanopowder (mesoporous graphene), a proper mix of organic solvents and finally a surfactant salt, the resulting fibrous layer comprised a wide adsorption surface and a lot of interfaces. The high polymer porosity favored the gas diffusion such as the high available surface area of the porous graphene increased the chance to bind the analyte. When the sensor was subjected to increasing heating (40-80°C), a general decrease of sensitivity to VOCs and humidity was reported, despite the huge increasing sensitivity to NO_2. Such a result suggests that the sensor could be thermally driven in order to be more selective to NO_2 (LOD: 2 ppb) and that the role of the potential interferents in the environments could be significantly lowered.

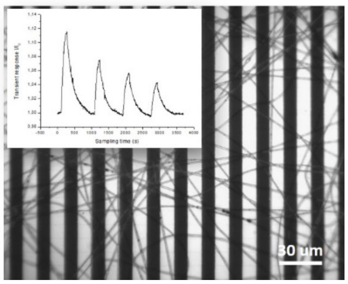

Figure 2. ptical micrograph of IDE electrodes coated by PHB-PS-Graphene fibers. Inset a plot showing transient responses to decreasing concentration of NO_2

3. Fluorescent nanocomposite fibers to detect selectively gas and VOCs

Optical sensors are generally preferred for their high sensitivity, fast response time and low power consumption

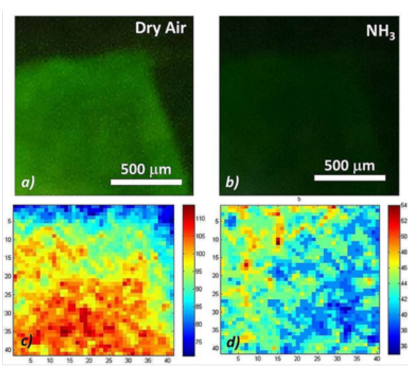

Figure 3. luorescent fibers UV-LED irradiated before (a) and after exposure to a few ppm of NH_3 for 20 min (b); image analysis of the GREEN matrix of pixels (among RGB matrices) before (c) and after gas exposure (d)

Therefore, TiO_2 nanofibrous layers have been decorated with fluorescent core/shell nanoparticles (CdSe/ZnS) and investigated as potential optical sensors for detecting toxic gases in air. The fibrous sample, housed and then shot in a very compact device, designed and fabricated by a 3D-printer in IIA-CNR, was irradiated by a low power LED (390 nm, 5 mW). Using an image analysis programme (MATLAB) the average luminance has been calculated and related to several gas and VOCs concentrations. Both the quenching and the enhancement of the fibers luminance were related to multiple and complex mechanisms, as long-range electronic-to-vibrational energy transfer from the QD to the gas-vibration molecules, non-radiative photoexcitation energy losses, electron-transfer and formation of OH radicals in surface due to the photocatalytic activity of TiO_2. Due to different processes occurring, the composite system resulted highly sensitive and selective to a series of selected gas pollutants.

CONCLUSIONS

The combination of some nanodoped 3D-nanoframeworks with microelectronics has allowed designing some novel, amazing and low cost sensors capable of operating, sometimes, with so high sensing performances to be comparable to more sophisticated and expensive equipment.

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COAL FIRED POWER PLANTS IN ITALY FROM PAST TO FUTURE

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***Keywords*:** large combustion plants, industrial emissions, IPPC permit, best available techniques, energy efficiency

INTRODUCTION

A relevant source of global emissions of CO_2 from human activities is due to the industrial processes. The burning of fossil fuels to generate energy, in particular the combustion of coal, is considered one of the largest responsible for the industrial emissions of greenhouse gases into the atmosphere.
The coal power plants are regulated by the EU legislation on Industrial Emissions Directive - integrated pollution prevention and control (IPPC-IED).
According to such a piece of legislation, IPPC permits should be based on best available techniques (BAT) in order to reach an adequate level of environmental protection (Evrad *et al*., 2016; Cafaro *et al*., 2015) and should establish all the necessary measures including operating conditions, emission limit values for relevant polluting substances as well as monitoring requirements.
Possible emissions to water, air, soil as well as energy efficiency, waste production, use of raw materials as well as recovering and recycling, prevention of accidents and restoration of the site upon closure are taken into account in IPPC permits.
The present paper provides a rapid glimpse into the operation conditions of coal fired power plant as presented in Cafaro *et al*., 2018.
Moreover, in Italy the reviews of the permits for such installations shall match to the decarbonisation scenarios, as identified by the Italian policy strategy "Strategia Energetica Nazionale (2017)", adopted by decree of 10 November 2017.
Such a strategy foresees a time horizon for the coal phase out at 2025 and, at the same time, a continuous support for renewables and energy efficiency. The goal will be achieved by means of management and technical actions on the infrastructures facilities and on the electrical grid to guarantee a safe national system and an adequate production of energy increasing renewable sources and gas.
As a matter of fact such this set of specific measures also allows to achieve the sustainable and environmental objectives as agreed in Paris in 2015 during COP21 with regard to the commitment to move towards low-carbon and resource-efficient energy models.

REFERENCE LEGISLATION CONTEXT

The combustion plants with installed thermal power ≥ 50 megawatts (named LCP: Large Combustion Plant) are regulated by the European Directive 2010/75/EU on industrial emissions - integrated pollution prevention and control (IED Directive). Such a directive takes into account the management of the raw materials, the efficient use of energy, the improvement of the environmental performance of the installation, through the application of the best available techniques (BAT).
On July 31, 2017, the European Commission has adopted the implementing decision establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of tha Council, for large combustion plants.
This document contains the emission levels associated with the best available techniques for the different types of combustion plants and all other operating conditions.
The BAT Conclusions also includes the techniques to be applied to optimize combustion and to reduce atmospheric emissions of CO and of unburned substances (BAT 6), the techniques to improve the energy efficiency of combustion units (BAT 12) and the techniques addressed to coal fired units (BAT 19) with the related energy efficiency levels (Table 1).
The directive IED establish that within 4 years of publication of decisions of BAT conclusions all the permit conditions are reconsidered and, if necessary, updated to ensure compliance with the directive.
In Italy the directive IED was implemented with legislative decree 46/2014, modifying the legislative decree 152/2006, to harmonise national legislation with European regulations.
The Italian IPPC permit for the exercise of the industrial installations is named AIA (Autorizzazione Integrata Ambientale) and released by the Italian Ministry for the Environment, Land and Sea for the main national plants.

In particular in Italy there are about 120 combustion plants subject to the release of IPPC permit by the Ministry of the environment (those with installed thermal power > 300 megawatts).
Among them, the majority of LCPs employ natural gas, while the remaining installations are fed with solid fuels (coal) or other fuels, such as synthesis gaseous fuels of neighbouring refineries. In the next months, the IPPC permits for these plants will be review, to adapt the operation conditions of the installations to the BAT Conclusions.
For the coal plants the review of permits must also take into account what is indicated in the national energy strategy document.

Table 1. Techniques to improve energy efficiency of combustion units (BAT 12 e BAT 19 BAT Conclusions, 2017)

BAT	Techniques
BAT 12: Techniques to improve energy efficiency applying an appropriate combination of the techniques	a. Combustion optimisation
	b. Optimisation of the working medium conditions (gas or vapor)
	c. Optimisation of the steam cycle
	d. Minimisation of energy consumption
	e., f. e h. Preheating of combustion air // fuel // Feed-water
	g. Advanced control system
	i. Heat recovery by cogeneration (CHP)
	l. Heat accumulation
	...
BAT 19: to increase the energy efficiency of the combustion of coal and/or lignite	a. Dry bottom ash handling Dry hot bottom ash falls from the furnace onto a mechanical conveyor system and, after redirection to the furnace for reburning, is cooled down by ambient air. Useful energy is recovered from both the ash reburning and ash cooling.

FINDINGS

The European legislation on integrated pollution prevention and control, set, for the main existing industrial plants, emission limit values and operating conditions very strict, with significant consequences for Italian installations.
One of the types of plants that was most affected by the new European policies are coal fired power plants. For these installations the application of the emission levels associated with the best available techniques has involved a break point with the past, causing the closure of plants technically outdating and highly polluting.

On the other hand the new environmental performance required have led to the implementation of plants technologically advanced, that have addressed important economic investments for the improvement of plants according with the best available techniques.

Table 2. Emission limit values from AIA compared with BAT Conclusions and with emission data for 5 main coal Italian plants (data source: European commission 2017; MATTM - Portal AIA)

Plant	*Pollutant*	*Limit value from AIA (mg/Nm^3)*	*Limit value from BAT Conclusions (mg/Nm^3)*	*Emission value 2016* (mg/Nm^3)*
1	**NO_X**	80 (d.a.) 100 (h.a.)	<85-200 (d.a.) 65-150 (y.a.)	61,23
	SO_2	80 (d.a.) 100 (h.a.)	25-205 (d.a.) 10-130 (y.a.)	47,71
	Dust	8 (d.a.) 10 (h.a.)	3-14 (d.a.) 2-8 (y.a.)	3,21
2	**NO_X**	150 (m.a.) 130 (m.a. from /01/2019)	<85-200 (d.a.) 65-150 (y.a.)	120,36
	SO_2	150 (m.a.) 130 (m.a. from /01/2019)	25-205 (d.a.) 10-130 (y.a.)	80,56
	Dust	15 (m.a.) 10 (m.a. from /01/2019)	3-14 (d.a.) 2-8 (y.a.)	4,52
3	**NO_X**	180 (d.a.)	<85-200 (d.a.) 65-150 (y.a.)	96,6
	SO_2	200 (d.a.) 220 (48h.a.)	25-205 (d.a.) 10-130 (y.a.)	81,85
	Dust	20 (m.a.)	3-20 (d.a.) 2-12 (y.a.)	4,9
4	**NO_X**	200 (m.a.) 220 (48h a.)	<85-200 (d.a.) 65-150 (y.a.)	157,75
	SO_2	200 (m.a.) 220 (48h a.)	25-205 (d.a.) 10-130 (y.a.)	100
	Dust	20 (m.a.) 22 (48h. a.)	3-20 (d.a.) 2-12 (y.a.)	2,25
5	**NO_X**	200 (d.a.)	155-210 (d.a.) 100-180 (y.a.)	168,33
	SO_2	250 (d.a.)	135-220 (d.a.) 95-200 (y.a.)	140,67
	Dust	5 (d.a.)	4-25 (d.a.) 2-14 (y.a.)	0,58

h.a. = hourly average
d.a. = daily average
m.a. = monthly average
y.a. = yearly average
48 h a.= 48 hours average
* yearly average of the monthly average

Therefore, these plants already achieve environmental performance comparable with those foreseen by the recent BAT conclusions, that must be respected from 2021 (Table 2 and 3).
Although the excellent performance reached by some of the coal plants currently in exercise in Italy, the national energy policy foresees in a short time the complete elimination of this fuel considered highly polluting.
The recent national energy strategy document considers the decarbonisation of the energy sector one of the main objective to be achieved, indicating the 2025 deadline as term for the phase out of coal.
Therefore the review of the permits for coal fired power plants will have to combine the need to respect from 2021 the performance indicated on the BAT Conclusions document, with the closure from 2025 of all coal fired Italian plants.

Table 3 Electric efficiency of solid fuel-fired combustion plants (MATTM –AIA Portal, 2015 and 2018; European Commission, 2017; Cafaro *et al.*, 2018)

Type of plant	Co-generation of heat and power CHP	Solid fuel-fired installation
Thermal efficiency (%) (BATC, 2017)	-	45 – 46 (new installation ≥ 1 000 MW) 36,5 – 41,5 (new installation < 1 000 MW) 33,5 – 44 (existing installation ≥ 1 000 MW) 32,5 – 41,5 (existing installation < 1 000 MW)
Installation A (%)		38
Installation B (%)		36
Installation C (%)		36
Installation D (%)	90	

CONCLUSIONS

The BAT Conclusions regulate at European level the operation conditions of coal fired power plant, the national energy strategy document ratifies their closure; how can entry in this context the review of the permits for this types of power plants?
It is likely that the next IPPC permits for coal plants have to regulate more than the implementation of technical provisions in line with the environmental performance foreseen by the most recent European documents, the progressive shutdown of installation as in the above mentioned Italian policy strategy "Strategia Energetica Nazionale (2017)".
As a matter of fact, such a strategy aims to promote a sustainable growth with cleaner technologies and by promoting energy and resource efficiency in order to achieve low-carbon development. As a result such strategy would provide further employment opportunities as well as specific measures for the mitigation of climate change.
At the same time the use of ICT (Information and Communication Technologies) would promote a prudent and sustainable use of resources in complex installations such as it is emerging in large combustion sector.

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MAJOR-ACCIDENT HAZARDS INVOLVING DANGEROUS SUBSTANCES FOCUS MORE THAN 40 YEARS AFTER THE SEVESO ACCIDENT

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Keywords: major-accident hazards, dangerous substances, industrial risk

INTRODUCTION

In July 1976 the release of a cloud containing 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD), ethylene glycol and sodium hydroxide (caustic soda) from the plant for the production of 2,4,5-tricolorophenol (TCP) of the chemical industry ICMESA (Industrie Chimiche Meda Società Azionaria) located in the Municipality of Meda in Italy, caused heavy health problems in about 240 people, the contamination of about 108 hectares of land, and serious chronic damage in the medium and long term; about 6’000 people were affected by the consequences of dioxin contamination (Ziglioli, 2010). This accident known as the Seveso disaster from the name of the most affected Municipality, related with other similar events occurred in Europe in those years, led to take in high regard the issue of industrial accidents. The European Union set up specific regulations in which the hazard of an industrial accident is determinate by the seriousness of the consequences produced, and by the probability that an event can occur during the life of the installation.

Forty years after the Seveso accident much has been done to increase knowledge and awareness about the risks related to the possible occurrence of major accidents: on the one hand, applying regulatory instruments more and more revised and updated; on the other hand with the continuous improvement of specific skills in the operators involved, which allows to ménage with greater awareness the events that occurred.

REFERENCE LEGISLATION CONTEXT

The Seveso accident marks a new approach in addressing the risk of accidents associated with specific industrial activities. For the first time the concept of major accident is introduced, therefore are identified specific types of industrial installation in which is considered possible the occurrence of accidents with considerable consequences for people and the environment (Ceci *et al*., 2012, 2016, 2017). As a result the laws issued, both at European and national level, indicate the industrial activities considered dangerous, where are used substances or preparations toxic, flammable or explosive or where there are the deposit of substances or preparations above specific quantities (Table 1). In the annex of European directives and Italian decrees are listed the substances included in the regulations; for each substance there are two distinct thresholds that identified two different types of installation: installation considered at upper risk and installation considered at lower risk.

Table 1. Main European and Italian regulations on the major accidents hazard

European directives	*Italian decrees*
82/501/CEE - Seveso I and subsequent amendment	Presidential Decree 175/88 and subsequent amendment
96/82/CE - Seveso II and subsequent amendment	Legislative Decree 334/99 and subsequent amendments
2012/18/UE - Seveso III	Legislative Decree 105/2015

FINDINGS

The first Seveso Directive, and the national implementation, made possible to carry out an initial census of the number and the locations of the establishments that fall within the obligations of these regulations. This first inventory shows, at the end of validity of the Presidential Decree 175/88 and subsequent amendments (first semester of the 1999), that in Italy there were 1’222 establishments at major-accident hazards; in particular 313 at upper risk (the so-called notifications) and 909 at lower risk (the so-called declarations) (Ricchiuti *et al*., 2000).

At the end of the validity of Legislative Decree 334/99 and subsequent amendments (national implementation of the second Directive) from the official data of the national inventory of

establishments at major-accident hazards, published on the site of the Ministry for the Environment Land and Sea (end of the 2014), there were 556 establishments active at risk of major accident in the "high" category and 540 in the "low" category, 1'096 in all (http://www.minambiente.it/).
From the beginning of the application of the current law, Legislative Decree 105/2015, transposition of the last Directive (the third), until today, in Italy there are 524 establishments with a higher threshold (upper-tier establishments) and 492 with lower thresholds (lower-tier establishments) for a total of 938 establishments (Table 2).

Table 2. Italian establishments at major accidents hazard after the three principal Seveso regulations

Italian decree	*Upper tier risk*	*Lower tier risk*	*Total*
DPR 175/88 and subsequent amendment	313	909	1'222
DLgs 334/99 and subsequent amendment	556	540	1'096
DLgs 105/2015	524	492	938

From the comparison of the data relative to the application of the "Seveso" legislation in Italy, some important observations are highlighted. A first aspect is related to the allocation of the establishments between high and low risk. With the implementation of the first Directive, the number of upper tier risk establishments is very low compared to those at low risk: low risk establishments are almost three time the other. This difference disappears with the two subsequent Directives with which the number of high and low risk establishments becomes almost equal.
This result is a consequence of one of the main regulatory changes introduced by the second Directive, that is the extension and the modification of the scope of the directive; in particular an additional category of substances has been introduced, the substances dangerous for the environment, and a different distribution has been used for the dangerous substances. As a result, many establishments have moved from the lower to the upper tier hazard, while other establishments have entered or left the scope of the Directive, thus the data referred to high and low risk establishments shows a flattening for the two groups. This trend remains unaltered moving from the second Directive to the third, because in this case the modifications were mainly related to the introduction of the international classification system for substances; the "old" regulation has been replaced at European level by the REACH-CLP system deriving from the "new" international system, the *Globally Harmonized System* (GHS). Related to the ratio of the number of establishments mentioned above it also seems plausible to assert that the redraw of the Seveso Directive to implement the change of the regulatory on the classification of the substances confirm the field of application; obviously this is incorrect for some very particular substances.
Therefore, since the entry into force of Legislative Decree 334/99, which implemented the Directive Seveso II, until today the trend in the number of high hazard establishments compared to those at low hazard remained unchanged with a slight prevalence of the high hazard establishments confirmed in the years (Figure 1).

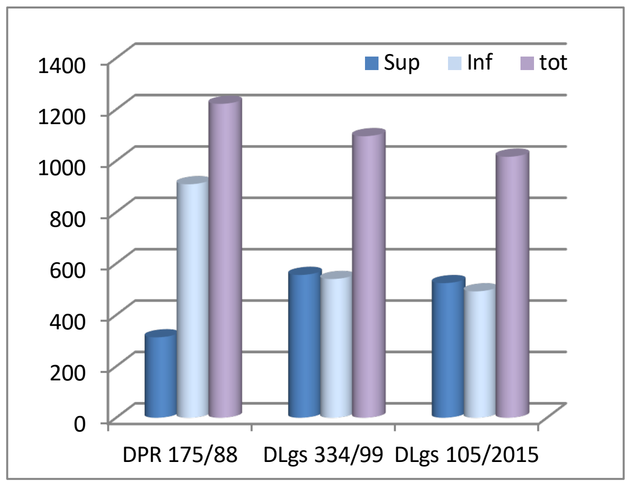

Figure 1. Trend of Italian establishment under the different main decrees

Another significant aspect that appears from the data reported in Table 2 is a constant decrease in the total number of the establishments over the years. This is an important element to highlight the general reduction in Italy in recent years of chemical and petrochemical industrial activities.
The table 3 shows that in the years in which the three directives were in force, there was a growing decrease of the number of the establishments at major-accident hazards. This reduction may be related both with the general decrease in the chemical and petrochemical industries, but also with a widespread diffusion and reorganization of the activities that led to a contraction of production, or to a specific specialization, bringing many factories or

to the downgrading or to the total exit from the scope of the Seveso Directive. This trend appears to be accentuated in the latter period, since the reduction of the Seveso plants in the last 3 years is 1,5 times higher than the previous 15 years, if this rate should be confirmed, to 2028 (after 15 years from the application of the decree 105/2015) a census of the Seveso establishments could be hypothesized just over 500.

Table 3. Trend of the reduction in Italy of the establishments from 1999 until today

Italian decree	*Year*	*Total number*	*% of reduction*	*Δ year*
DPR 175/88	1999	1’222	--	--
DLgs 334/99	2014	1’096	10%	15
DLgs 105/2015	today	938	14%	3

CONCLUSIONS

Based on the above commented data, it could be hypothesized that the inventory of establishments at major-accident hazards, arising from the application of the Seveso directive, can be used as a litmus test of the state of health of the Italian chemical and petrochemical industry. This aspect is also confirmed by analogous elaborations carried out on installations subject to the legislation on Integrated Pollution Prevention and Control (IPPC), for which a specific permit for the operation of the plants is released from Ministry for the Environment, Land and Sea (Cafaro *et al*., 2015); data from IPPC plants in Italy show a progressive reduction of about 30% of the number of installations over the last 8 years (CNR-IIA elaboration on MATTM-DVA data set).

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CLIMATE CHANGE, NATECH EVENTS AND REQUIRED ADAPTATION

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CHANGING OF METEOROLOGICAL EXTREME EVENTS FREQUENCY

Meteorological extreme events linked to climate change and global warming have already become a reality affecting our everyday life. There are no more doubts about the fatal connection between human activities and the global warming, especially if we have a look to the last thirty years.

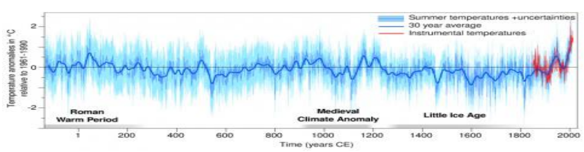

Figure 1. Reconstruction of summer temperature anomalies – source: JRC - European Commission [1]

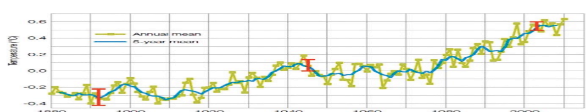

Figure 2. Land/ocean temperature index – source: NASA/FAO [2]

Damages and losses from disasters triggered by natural hazards are increasingly threatening the development gains of many communities in the whole world. During the year 2014, 87% of natural disasters were climate related (source: FAO's economic report 2015 [2])

Thanks to the study of the global climate changes, we could observe how most of the hit areas were located in poor and developing countries, the same countries marked by a very low level of pro capite emissions. The reality of this consideration was one of the reason for the introduction of some legal innovations during the last Conference of Parties of the Convention on Climate Change, settled in Paris during December 2015, as for example:

• the enforcement of the "loss & damage" principle, created to ensure some economic compensations to those countries, strongly hit by the consequences of climate change even without giving a significative contribution to greenhouse effect generation;

• the introduction of the "common and differentiated responsibility", in force of which, looking at their recent industrialization, developing countries, as China and India, could reduce their emissions in a longer timeframe and with an higher graduation.

European countries, anyway, are involved too. Looking at recorded temperatures in Europe, increasing values are observed during the last twenty years, with special peaks in 2003, 2010 and 2015. The 2014-2015 period will be remembered, in Europe, for the number of meteorological extreme events that took place.

With such a background, the development of national systems act to monitor, to report and to evaluate climate changes becomes extremely significant. Talking about "national systems" is appropriate, because climate change's events and consequences appear to be as different as the existing geographic areas of our continent are [3].

Italy, in the southern Europe, as well as the other countries of the Mediterranean area, is subject to meteorological events, caused by climate change, as: increasing temperature; decreasing number of raining days during the year; increasing number of extreme meteorological events; reduction of the river flow rate; desertification process and loss of biodiversity. If we take a look to the possible evolution of hazards coming from climate changes, southern Europe, as it's shown in the image below, is the European region with the highest risk for critical infrastructures and industries.

The outcome of the JRC report 2016, considering social, industry, energy and transport sectors, is a dramatic perspective of damages produced by climate change (3,4 billions € as baseline; 10,2 billions € in 2020s; 20,4 billions € in 2050s; 34 billions € in 2080s). Damages in South Europe are and will be heavier.

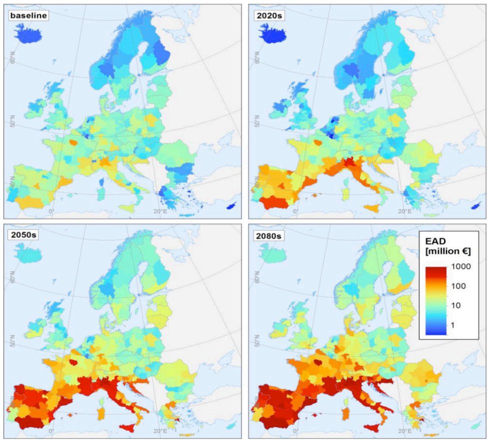

Figure 3. Evolution in time and space of expected annual multi-hazard impacts on critical infrastructures in the energy, transport, industry and social sectors. Damages are expressed as expected annual damage (EAD) in million € – source: JRC- "Resilience of large investments and critical infrastructures in Europe to climate change", 2016

As established by a European Council decision of 08/02/2013, European countries should invest at least the 20% of total budget put aside by EU for actions on adaptation to climate changes.

LEGAL IMPLICATIONS AND ECONOMIC EVALUATIONS

The explained situation reveals not only the need of international agreements for the reduction of industrial emissions (mitigation), but also the need of an immediate adoption of measures able to reduce the adverse impacts of climate change (adaptation). We can say, without any doubt, that the less efficient will be the measures to mitigate climate change (mitigation), the sharper and more determined should be the measures to reduce the adverse impacts of climate change (adaptation). These considerations should be treated during the development phase of the most important industrial and environmental laws.
Looking at the hazards connected to dangerous substances detained by industrial plants, the European Seveso legislation (dir. 2012/18/UE; D.lgs. 105/2015) should be the first to considerate and to impose appropriate adaptation policies. These policies should be oriented to minimize the adverse impacts caused by the so-called "NaTech events". We use to talk about a NaTech event when a technological disaster is triggered by a meteorological natural event.
With the last update of the legal regulation on the control of major-accident hazards involving dangerous substances ("Seveso III" directive n. 2012/18/EU), the European Union takes into account the risks descending by the increased frequency of meteorological extreme events. So, in the Italian national transposition law, we can find (Attachment C, point C.3, at D.lgs. 105/2015) an instruction to evaluate the chronology of meteorological extreme events during the preparation of safety reports by the operators. Instructions like these were also contemplated by the D.lgs. 334/99 (national transposition of "Seveso II" directive n. 96/82/CE), with the difference that now the same regulations are stronger, in consideration of the changes related to historical sequences that are at the basis of risk analysis [5]. The need of adaptation is considered by EU Seveso directive and therefore also in the Italian law for transposition (inspections, information on risk, emergency plan) moreover will be possible a further development of these topics during the national implementation phase, through the actions of actors involved in. However we expect something more as: a deep study about territorial vulnerability, a revision and an update of accidents scenario due to a varied frequency of extreme meteorological events, a significant number of structural interventions on installations to improve resistance.
In Italy, at least twenty "Natech events" were registered during the last twenty years. From the economic point of view, of both the operators and the national authorities, the impacts of these events could be really heavy, especially without the adoption of any prearranged adjustment policy. These impacts, in fact, look as inversely proportional to the plant security level and directly proportional to the land vulnerability.
With this simple consideration, just to follow the objective of a reduction of the adverse impacts of Natech events, we can identify two main roads to ride:

- land vulnerability analysis and consequent re-evaluation of accident scenario;
- realization of structural and technical interventions to improve the plant resilience.

In an economic way of thinking, while we are not in control of some specific data set to build a detailed case of study, we can approach with the S.W.O.T. analysis (Strengths; Weaknesses; Opportunities; Threats). This kind of analysis leads to the individuation of guidelines act to achieve an established goal. So, if we set our final goal as the reduction of industrial risks triggered by meteorological extreme events and if we approve, as said earlier, the land vulnerability analysis and the consequent realization of structural and technical interventions to improve resilience as the main roads to reach the final goal, we can carry out a S.W.O.T. analysis like the one below:

STRENGHTS	***WEAKNESSES***
- *reduction/zeroing of Natech event's impact* - *deeper knowledge of territory and land (localization of "sensible targets")* - *knowledge of hazards coming out in connection with the vulnerability land level* - *the vulnerability land study is based on owned skills and know-how* - *increasing resilience of installation enslaved to plants* - *technical works and interventions are based on owned common skills and know-how*	- *heavier job for operators and involved authorities* - *information responsibility for citizens and about the resulting coming out from the vulnerability land analysis* - *vulnerability land analysis cost* - *interventions on infrastructures costs(long term)* - *interventions and technical works on plants costs*
OPPORTUNITIES	***THREATS***
- *environment and civil recovery costs reduction/zeroing* - *environmental elements protection* - *industrial and civil future settlement right planning* - *possibility to replay tools and methods used for land analysis* - *possibility to replay used performances to lead technical works and interventions (considering one kind of event and one kind of plant)*	- *possible re-localization of plants requested by results coming out from the vulnerability land analysis.*

Figure 4. S.W.O.T. ANALYSIS - in red aspects related to vulnerability analysis; in blu aspects related to realization of structural and technical interventions to improve resilience; in black aspects related to both

The cartography related to the national distribution of "Seveso II" plants is reported in the image below, it could be very useful, especially in association with some cartographic representations of the historical repeating of relevant meteorological events in Italy, to identify hazards and risks of Natech events.

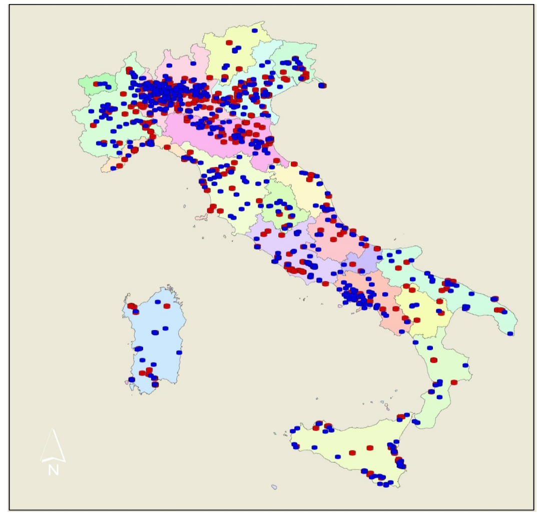

Figure 5. National distribution of "Seveso II" plants (source: MATTM-DVA)[6]

The underlined need to evaluate the plant resilience could be tested by the operator using an approach like the one reported in the framework below:

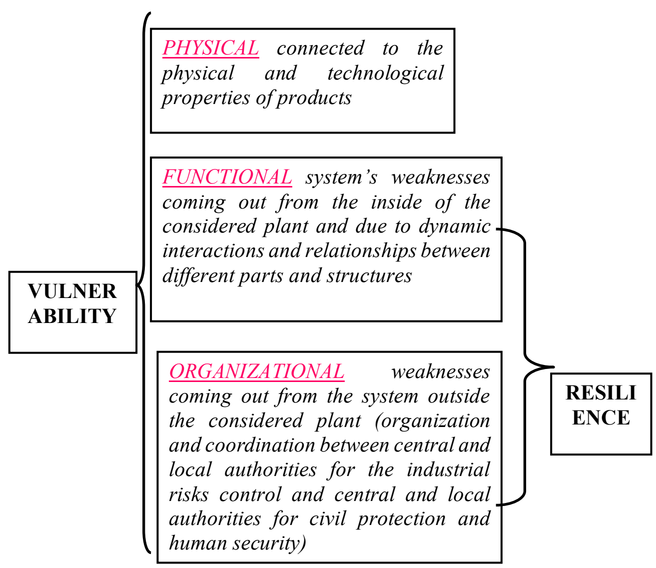

Figure 6. Possible approach to test the plant resilience (source: Department of Civil Protection)

CONCLUSIONS

Considering all the subjects treated in the present paper, it will be good to give a new push for the concrete realization of the "National Strategy for climate change adaptation".

In Italy the elaboration of a National Strategy [7] was launched in 2012, under the control of the Ministry of Environment. The formal adoption of the Strategy was realized by a ministerial decree (June 2015); a review is planned every five years. The paper contains principles, measures and guidelines to minimize the risks represented by climate change.

The orientation is focus on people and health protection, on environmental safety and on the improvement of resilience for natural, social and economic sources. The strategy identifies some action proposals, basically divided between long term actions (structural and infrastructural actions) and short term actions (non structural actions).
The time to turn a strategy into a "National Plan for climate change adaptation" has arrived. In fact, within the 31st of December 2016, the adopted national strategy should evolve in a real plan, that should be able to identify:

- rules and responsibilities for each action derived by the strategy;
- indications to create an appropriate climate scenario at local level;
- identification of adaptation options;
- evaluation of required resources (human and economic);
- individuations of markers to value the efficacy of the selected adaptation measures;
- the way to control and value the adaptation measures effects.

Moreover, a "national forum" to promote information for people and involved stakeholders will be soon established and, at the same time, "national observatory" for the identification of adaptation priorities will be formed by local authorities delegates.
The purpose of this article, once aware about the need of a strict relationship and a strong collaboration between the Civil Protection Department and the main national scientific research centres to adapt risk analysis methods and tools to the new challenge imposed by climate changes, is to involve every stakeholder in the next implementation of the National Plan of Action for the Climate Change Adaptation, that should take quite care of grown hazards caused by the existing Seveso plants and the observed vulnerability level of their localizations.
This route could pass by the reported adaptation phases, as follow:

EVENT: Climate changes could represent a huge risk for the operators and their activities and also for the other stakeholders (residents; national authorities; politicians; emergency operators) CHALLENGE for ADAPTATION: considering this during each risk management phase.

EVENT: Grown frequency of extreme natural events caused by climate change CHALLENGE for ADAPTATION: spread knowledge, among operators and national authorities.

EVENT: Climate change's consequences could be dangerous for national industrial and social development CHALLENGE for ADAPTATION: considering the possible effects on planned new industrial installations and infrastructures (paying a special attention to *Seveso* plants and their localization).

EVENT: Climate change's consequences could be dangerous for existing infrastructures and industrial plants CHALLENGE for ADAPTATION: vulnerability analysis to identify risk areas and priorities.

EVENT: Grown relevance of weather prediction CHALLENGE for ADAPTATION: development of updated scenarios and activation of advanced and appropriate meteorological equipment at local level

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ENVIRONMENTAL RISK ASSESSMENT FOR SOME ADDITIVES USED IN HYDROCARBON EXTRACTION ACTIVITIES INTO THE SEA

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Keywords: chemicals, environmental risk assessment, produced formation water, hydrocarbon extraction activities

INTRODUCTION

In relation to the oil and gas offshore platform activities, the Italian Ministry of the Environment, Land and Sea has the task to decide for the release/renewal of the authorisation to discharge the Produced Formation Water (PFW) into the sea. Before granting an authorisation, the Ministry conducts an assessment of the environmental impact of the offshore platform activities of discharge, by specific monitoring programmes. As reported in Maggi *et al*. (2007), the PFW discharge impact on marine ecosystems is highly dependent on its quality, its quantity, the characteristics of the receiving environment and dispersion processes. Also the additives used in the extraction activities have to be considered and the Ministry has recently decided to adopt a more comprehensive environmental risk assessment of these chemicals, starting from Diethylene glycol - DEG (CAS n. 111-46-6, EC 203-872-2). DEG is an organic substance registered according to Regulation (EC) n. 1907/2006 ("REACH Regulation"). Between 100.000 and 1.000.000 tons per year of DEG are produced in Europe; it has many application and it is also used in the dehydration of natural gas steams in the offshore platforms. As described in Maggi *et al.* (2015) during a glycol-based dehydration device, water vapor is removed from the gas stream in a DEG-absorber and the water-laden DEG is usually stripped of water in a stripping column. Because the dehydration efficiency is less than 100%, the DEG could be introduced in the marine environment through the production water, the main discharge originated from gas and oil platforms. In this study we evaluated the environmental risk assessment for DEG present in the Produced Formation Water released to the marine water, to set precautionary limits for the release of the production water in the environment.

METHODOLOGY

In order to assess the risk deriving from the Diethylene glycol used for the dehydration of natural gas steams, the methodology for environmental risk assessment in accordance with Annex I of REACH Regulation has been applied. This methodology is described in the "Guidance on Information Requirements and Chemical Safety Assessment" of the European Chemicals Agency (ECHA) (2017).

According to this methodology the actual or predicted environmental concentration (PEC) is compared to the Predicted No-Effect Concentration (PNEC) to determine if the risk of a substance is acceptable or not. If PEC/PNEC <1, namely the PEC<PNEC, the risk is acceptable. The PNEC is calculated on the basis of results coming from the ecotoxicological tests dividing the lowest value among the toxicity data for an assessment factor which differs on the basis of available data. The assessment factors decrease in magnitude from higher values, if only short-term acute studies are available, to lower values if also long term toxicity has been assessed. For long term studies the magnitude of the assessment factors also decreases as information on a wider range of species becomes available. Since the assessment relates to the marine environment, the assessment factor takes into account also the availability of additional studies on marine taxonomic groups.

FINDINGS

Regarding the evaluation of Diethylene glycol, we retrieved from the report made by ISPRA "*Programma di ricerca "GLICOL*" (2014) two long-term studies on two taxonomic groups representing two different trophic levels (algae, *P. tricornutum* and fish, *D. labrax*) and one additional marine long-term study on another taxonomic group (invertebrate, *T. philippinarum*).

In this case, based on table R.10-5 "Assessment factors proposed for deriving PNECwater for saltwater for different data sets" in Guidance on IR&CSA, chapter R.10 (2008), it is possible to apply an assessment factor of 50 to the long-term toxicity value related to the most sensible species (*T. philippinarum*, 28d NOEC: 365 mg/l). Therefore, PNEC for marine water is 365/50 mg/l = 7,3 mg/l. This PNEC value is related to a situation of constant/frequent release in marine environment. In case of intermittent release, defined in the Chapter R16 of the ECHA Guidance (2016) as occurring infrequently, i.e. less than once per month and for no more than 24 hours, we shall use the short-term studies results to derive the PNEC value. In this case, we applied an assessment factor of 100 to the lower value of acute toxicity between at least three short-term studies representing three trophic levels. The lowest toxicity data is related to the invertebrate *T. fulvus* (96 h EC50: 5900 mg/l).
Therefore, PNEC marine water for intermittent release is 5900/100 mg/l = 59 mg/l.
Regarding PEC derivation, usually the methodology is already agreed under the OSPAR Convention (2015), but this protocol foresees several parameters that have not been provided, therefore is possible to derive PEC from the evaluation of the local concentration in seawater during release ($Clocal_{seawater}$), according to equation R.16-35, paragraph A.16-3.3.5: *Calculation of PEClocal for the marine aquatic compartment* in the ECHA Guidance (2016):

$$Clocal_{seawater} = \frac{Clocal_{eff}}{(1 + Kp_{susp} \cdot SUSP_{water} \cdot 10^{-6}) \cdot DILUTION}$$

Where $Clocal_{seawater}$ is the local concentration in seawater during release episode (mg/l), $Clocal_{eff}$ is the concentration of the substance in the sewage treatment plant effluent (3500 mg/l), Kp_{susp} is the solids-water partitioning coefficient of suspended matter (≈ 0 l/kg), $SUSP_{water}$ is the concentration of suspended matter in the seawater (15 mg/l) and DILUTION is the dilution factor (assuming a realistic worst case of 100).
Assuming as negligible the contribution of concentration on a regional scale, PEC coincides with local concentration. Having access to a more detailed data, it will be possible to refine the value in a future assessment. Comparing the estimated exposure levels (PECs) with non-effect levels (PNEC), we obtain a Risk Characterization Ratio (RCR = PEC / PNEC) greater than 1 (RCR= 4.79) in the case of constant/frequent release and a RCR lower than 1 (RCR= 0.59) in the case of intermittent release. In the case of constant/frequent release, there is an unacceptable risk for marine water (Table 1).

Table 1 – Risk Characterization Ratio in case of constant/frequent and intermittent release of DEG in marine water

Type of release	*PEC (mg/l)*	*PNEC (mg/l)*	*PEC/PNEC*
constant/frequent	35	7.3	4.79
intermittent	35	59	0.59

To obtain an acceptable value that will not pose risks for the environment, PEC shall be less than PNEC. Therefore, the concentration limit value for offshore discharge of Diethylene glycol with constant/frequent release from platforms should be less than 730 mg/l.
With regard to intermittent release, the concentration limit value for Diethylene glycol at discharge into the sea should be less than 5900 mg/l.

CONCLUSIONS

The assessment of Dietylene glycol shows that the concentration below which the risk is considered adequately controlled is 730 mg/l for constant/frequent release (if PNEC=PEC therefore Clocaleff = PEC*Dilution factor = 7.3 *100) and 5900 mg/l for intermittent release (same reasoning). These limits have been included as a binding condition for granting the authorisaton to the platform manager to discharge the production water into the environment.
This approach is ongoing also for other additives aimed at having a safer use of these chemicals and a more complete overview of the impact of Produced Formation Water in the marine environment.

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AIR QUALITY ZONES IN ITALY

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***Keywords*: Zones, agglomerations, air quality assessment, classification**

INTRODUCTION

Directive 2008/50/EC on ambient air quality and cleaner air for Europe is the main legislative act regulating air quality assessment and management in Europe, integrated by directive 2004/107/EC relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air.

According to the mentioned directives, air quality assessment has to be done through the following steps:
• definition of zones and agglomerations;
• classification of zones and agglomerations;
• establishment of the monitoring network;
• annual air quality assessment;
• recognition of the specific areas where measures are necessary to improve air quality.

In Italy, all provisions included in European legislation have been transposed into the legislative decree n. 155 of the 13th August 2010, covering both directive 2008/50/EC and directive 2004/107/EC. Regarding criteria set for establishing zones and agglomerations, more stringent requirements are set in order to provide clear indications to local authorities for their definition over the national territory.
The present document summarises the process of defining and classifying the national air quality zones and agglomerations, which is described with more details in a previous work of Dirodi *et al*. (2015). The main focus is on the different results obtained after some changes in the procedure introduced by the legislative decree n . 155 of the 13th August 2010.

THE DEFINITION OF ZONES AND AGGLOMERATIONS - METHODOLOGY

Competences on environmental issues in Italy are distributed among different authorities. The State has the right to establish general rules related to the protection of the environment. Therefore also legislation on air pollution and ambient air quality is produced for the whole Country at national level.

Local Authorities, and mainly Regions and Autonomous Provinces, have specific competences related to air quality assessment and management; in particular, air quality zones are established with a legal act by each administration for its own territory. Such a distribution of competences lead in the past to different application of the legislative provisions in the different Regions and to an increase of the total number of zones.
When zoning the territory, agglomerations have to be identified firstly. Agglomerations are selected according to urban structure, population and population density, following the indications given in the definition. According to national legislation, the agglomeration is a “zone constituted by a urban area or a group of more urban areas at no more than few kilometers or a main urban area and some minor urban areas connected to the main one for several reasons (demography, services, people and goods mobility), and having a population in excess of 250,000 inhabitants or a population of less than 250,000 inhabitants with a population density per km^2 higher than 3,000 inhabitants”.
Afterwards, the remaining part of the territory has to be divided in zones. Zones are chosen on the basis of the characteristics of the territory and not evaluating the air quality regime, as it was in the past. Analyzing these characteristics, the aspects mainly affecting air quality are determined in the different areas and those which are similar for the dominant aspects are merged together in the same zone. In practice, the analysis has to be carried out in different ways depending on the nature of the pollutants. For primary pollutants (lead, carbon monoxide, sulphur oxides, benzene, benzo(a)pyrene and heavy metals) zoning is determined by the emission levels registered over the territory. For secondary pollutants such as particulate matter, nitrogen oxides and ozone, the analysis includes also orographic and meteo-climatic characteristics and the level of urbanization of the territory.
Zones can also be constituted by not neighbouring areas if they are homogeneous in terms of the dominant characteristics. For instance, all coastal

areas with high level of urbanization, where road transport is the main emission source, can be merged in the same zone, even if they are not all contiguous. Indications are also given for defining the same zones for nitrogen oxides and particulate matter, if feasible; as much as possible, zones are also to be selected respecting the administrative boarders in order to simplify air quality management. Finally, in order to facilitate any necessary action to reduce the atmospheric concentration of pollutants, whenever it is possible it is recommended to define zones in accordance to the local administrative borders.

FINDINGS: THE NUMBER OF ZONES AND AGGLOMERATIONS

In accordance with Italian legislation, Regions and Autonomous Provinces must submit projects with a preliminary zoning and classification of their territory to the Ministry for the Environment, Land and Sea for an evaluation before final adoption.

The information extracted from the mentioned regional projects and made available by the Ministry has been analyzed and results are shown in the present document.

Regions designated zones and agglomerations, where feasible, for all pollutants. With the implementation of decree 155/2010, Italy reduced the total number of zones from 143 to 83 (Figure 1). The number of agglomerations was reduced from 35 to 21 (Figure 2).

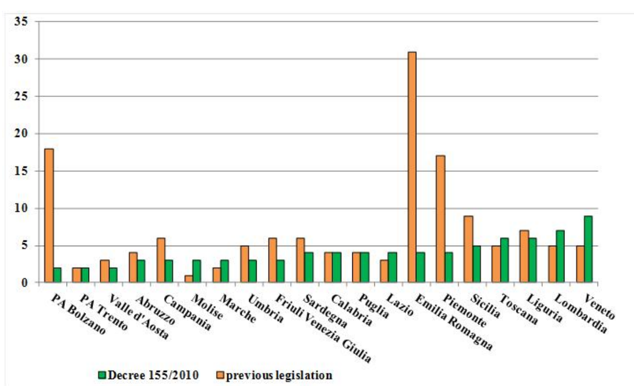

Figure 1. Total number of zones defined in relation to health protection for SO_2, NO_2, PM_{10}, lead, benzene, CO and $PM_{2.5}$

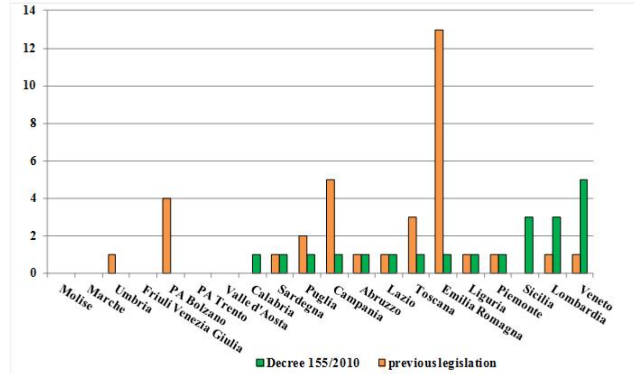

Figure 2. Number of agglomerations for SO_2, NO_2, PM_{10}, lead, benzene, CO and $PM_{2.5}$

The largest decreases in number of zones are in Regions Emilia Romagna and Piemonte and the Autonomous Province of Bolzano. On the other hand, Molise, Marche, Lazio, Toscana, Lombardia and Veneto increased the number of zones. For Calabria, Puglia and the Autonomous Province of Trento the number of designated zones is not changed.

As regards the zoning designation for ozone, benzo(a)pyrene and heavy metals (Pb, As, Ni, Cd), the results are presented in Table 1.

Table 1. Number of zones and agglomerations for ozone, As, Cd, Ni, B(a)P

Region Autonomous Province	*Ozone*		*Pb, As, Ni, Cd*		*B(a)P*	
	N. zones	*N. agg.*	*N. zones*	*N. agg.*	*N. zones*	*N. agg.*
Piemonte	1	1	3	1	3	1
Valle d'Aosta	1		2		2	
Lombardia	5	3	4	3	4	3
Liguria	1	1	2	1	1	1
Trento	1		2		2	
Bolzano	1		2		2	
Veneto	4	5	4	5	4	5
Friuli Venezia Giulia	3		3		3	
Emilia Romagna	3	1	3	1	3	1
Toscana	3	1	5	1	5	1
Umbria	1		3		3	
Marche	3		3		3	
Lazio	2	1	3	1	3	1
Abruzzo	2	1	2	1	2	1
Molise	2		3		3	
Campania	2	1	2	1	2	1
Puglia	3	1	3	1	3	1
Calabria	3		3		3	
Sicilia	2	3	2	3	2	3
Sardegna	1	1	3	1	3	1
Total	44	21	57	21	56	21

Generally the identification of agglomerations is based primarily on population, population density and urban structure, while the topography of the area has been the priority factor which led to the identification of the other zones, which took into account specific situations of orographic complexity and variability of climatic zones and the presence of significant emission contributions as industrial areas.

FINDINGS: CLASSIFICATION OF ZONES AND AGGLOMERATIONS

REGIONAL PROJECTS OF DESIGNATION OF ZONES AND AGGLOMERATIONS CONTAIN EITHER THE DEFINITION OF ZONES AND AGGLOMERATIONS, EITHER THE CLASSIFICATION OF EACH ZONE WITH REFERENCE TO POLLUTANT THRESHOLDS ESTABLISHED IN DECREE 155/2010.

Thus for sulphur dioxide, nitrogen dioxide, particulate matter (PM_{10}, $PM_{2,5}$), lead, benzene, carbon monoxide, arsenic, cadmium, nickel and benzo(a)pyrene, each classified zone may fall in one of the following categories: zone classified above the upper-assessment-threshold (indicated as 'UAT' in the following text), zone classified below the lower-assessment-threshold (indicated as 'LAT'), or zone classified between the two previous thresholds (indicated as 'UAT-LAT'). For ozone, the zones can be classified as above or below the Long term Objective (LTO).

In regional projects, exceedances of the mentioned thresholds are determined on the basis of concentration of each pollutant measured during five years, following the rule that an assessment threshold shall be deemed to have been exceeded, if it has been exceeded during at least three separate years out of those previous five years, for all pollutants other then ozone. Exceedances of long term objective for ozone are determined even if they are registered during one of the five years considered. When less than five years measured data are available, Regions estimated pollution level combining information about available measurement, with measurement campaigns of short duration, emission inventories and modeling results.

The results of the analysis of information related to the classification of zones and agglomerations contained in regional projects for particulate matter and nitrogen dioxide show a higher number of zones exceeding the upper-assessment-thresholds established for PM_{10} (daily and yearly), for nitrogen dioxide (hourly and yearly) and for $PM_{2,5}$ (yearly). For these pollutants, concentrations result critical in particular in agglomerations rather than in other zones. For other pollutants, benzene, sulphur dioxide, lead and carbon monoxide, regional projects show a different situation, with a predominant number of zones or agglomerations classified below LAT and secondly, classified between UAT and LAT. For ozone, all defined zones and agglomerations are classified above the LTO. For benzo(a)pyrene, arsenic, cadmium and nickel there is a large number of zone classified upper UAT: all zones designated in Puglia, Campania, Abruzzo and Friuli Venezia Giulia Regions, some of zones designated in Piemonte, Lombardia, Umbria, Toscana, Sicilia and Sardegna Regions and in both the Autonomous Provinces of Trento and Bolzano.

CONCLUSIONS

In the past, zones were defined mainly on the basis of the assessment of air quality and there was a wide variability in the delimitation of zones in the different Regions; therefore it was quite difficult to make mutual comparison of regional data.

Decree 155/2010 introduced stricter rules for designating the zones. Thus the great variability of the previous zoning was solved and a more harmonized identification was obtained over the whole Country. In addition, a significant reduction of the total number of zones was reached and a complete ambient air quality assessment and management throughout the Country was assured.

Regarding classification, general improvements have been achieved in terms of covered surface and applied assessment methods.

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AIR QUALITY AND CLIMATE CHANGE POLICIES

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***Keywords*:** air quality, climate change, policies, integrated approach

INTRODUCTION

European Union started to deal seriously with air pollution in the late 70s but the first framework directive on ambient air quality was published in 1996, followed by the implementing "daughter directives" and now replaced by directive 2008/50/UE . The general aim of these directives is to define the basic principles of a common strategy to avoid, prevent or reduce harmful effects on human health and the environment. At international level, the Convention on Long Range Transboundary Air Pollution (LRTAP) entered into force in 1983; it lays down general principles of international cooperation for air pollution abatement and sets up an institutional framework bringing together research and policy with the aim to protect citizens and ecosystems from the possible damages of air pollution.

In the same period many Countries joined the United Nations Framework Convention on Climate Change (1992) with the aim of limiting the increase of global temperatures; in 1997 emission reduction targets for the gases mainly responsible for global warming were agreed by the adoption of the Kyoto Protocol.

Since deep interactions between air pollution and climate change occur, it is really important to promote synergies among the sectors and to assure that all policies cooperate in order to achieve good results in protecting human health and the environment.

In the past such a cooperation has not always been assured but something seems to be changed in recent years. The present paper gives some information on this change of approach, both at European and international level.

INTERACTION BETWEEN AIR QUALITY AND CLIMATE CHANGE POLICIES

In the last twenty years many different policies were adopted and implemented to reach the objectives set by the regulations and agreements on air pollution and climate changes.

When we talk about air pollution and ambient air quality we generally mean regulations and measures to reduce air emissions from anthropogenic sources of pollutants which have negative impacts on human health and environment, according to the indications of the World Health Organization. Voluntary reduction commitments come from the LRTAP Convention while mandatory obligations are due to comply with European legislation. In particular, limit values are set for emissions and ambient air concentrations of pollutants; plans and programmes have to be adopted in order to obtain the requested targets and periodically a European thematic strategy on air quality is published containing different measures aimed to help Countries to reduce air pollution.

On the other hand, when we talk about climate change actions are oriented to reduce greenhouse gases levels and fight against global warming. Some greenhouse gases have also a role in air pollution and higher temperatures can contribute to the formation of ozone; therefore their possible impacts on human health and the environment are to be considered. At the same time some air pollutants, such as ozone and particulate matter, can influence climate changes (EEA, 2013 and EPA, 2011).

Up to now, policies were planned and implemented almost independently in the two sectors. Sometimes measures to reduce air pollution can also have a good impact on temperatures and vice versa; but in the last fifteen years some actions implemented to reduce carbon dioxide levels, such as the encouragement of biomass combustion, lead to an increase of some air pollutants, mainly particulate matter and benzo(a)pyrene (Leonardi *et al*., 2016).

The following figures show the trend of emissions of particulate matter and polycyclic aromatic hydrocarbons produced using the national air emission inventories compiled by ISPRA and related to the period 1990-2014 (submission 2016). In each graph, both the total level of emissions and the amount coming from the residential sector are described. It is quite clear that the tendency of national emissions follows that of the residential sector starting from the 2000's, when domestic heating becomes the most relevant contributor; emissions begin to grow up after 2005, even if not in a regular way.

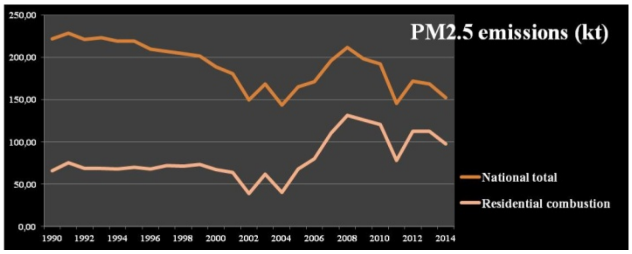

Figure 1. National PM2.5 emissions, 1990-2014

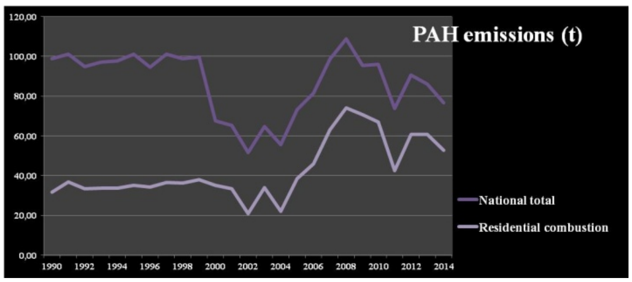

Figure 2. National PAH emissions, 1990-2014

In terms of concentrations, particulate matter and PAH are critical pollutants in Italy and it is necessary to implement all possible actions in order to reduce their levels and protect human health.

A DIFFERENT APPROACH

For this reason, the last "Clean air policy package" adopted in Europe underlined the importance of assuring synergies between the two sectors and in particular reference to this new approach are mentioned in many provisions of one of the new directives foreseen by the policy package, the new NEC (National Emission Ceilings) directive (2016/2284/EU), entered into force on the 31st of December 2016.

Among the recitals, the 7th Environment Action Programme (Decision n. 1386/2013/EU) is recalled aiming to "reinforced synergies between air quality legislation and the Union's policy objectives that have been set, in particular, for climate change and biodiversity". In addition, it is also said that the directive "should also contribute to achieving, in a cost effective manner, the air quality objectives set out in Union legislation and to mitigating climate change impacts in addition to improving air quality globally and to improving synergies with Union climate and energy policies, while avoiding duplication of existing Union legislation".

One of the objectives of the directive, set out in article 1, is that it has to contribute to achieving "enhanced synergies between the Union's air quality policy and other relevant Union policies, in particular climate and energy policies". In order to achieve the above mentioned objective, article 7 of the directive foresees also that the "Commission shall endeavor to facilitate access to existing Union funds", including inter alia "instruments for the funding of environment and climate action such as the LIFE programme". Finally, Annex III establishing the minimum content of the national air pollution control programmes to be adopted by Member States in order to reduce air emissions and comply with the reduction targets, foresees that the national air quality and pollution policy framework in which context the programme has been developed has to be described, including "the policy priorities and their relationship to priorities set in other relevant policy areas, including climate change and, when appropriate, agriculture, industry and transport".

The same approach has been also embraced by the technical and strategic groups of the LRTAP Convention. During the last meetings of the Working Group on Strategies and Review (WGSR) and the Executive Body (EB) of the Convention it was agreed that there is clear overlapping between the two different issues and that it is really important to make aware policy makers about the opportunity to plan policies in a coordinated way. For instance, in the Summary for Policy Makers of the 2016 Scientific Assessment Report "Towards cleaner air" (Maas *et al*., 2016) we can find among the key findings of the document that "an integrated approach to climate change and air pollution could lead to significant co-benefits, as well as to reducing the risk of applying climate change measures with significant negative impacts on air quality".

The new approach seems to be recognized also at national level now: a regulation introducing environmental certification was adopted in November 2017 (Ministerial Decree n. 186, 7 November 2017). It sets a classification of plants (in a range between 1 and 5 stars) based on the emission levels of stoves, fireplaces, cooks and small boilers with a thermal input <= 500 kw and establishes procedures and requirements for environmental authorization system and certification of wood, charcoal and biomass fuel in domestic heating plants. The decree is used by local authorities as a support for adopting specific policies related to this sector, such as banning the use of the most polluting plants with a gradual approach. At national level, new the aim is to grant incentives only in case of substitution of old plants with new more efficient ones.

CONCLUSIONS

It is therefore clear that a complex world as the one we are living in at present with complex environmental problems calls for an integrated approach in order to enhance the effect of the actions adopted to protect it.

In recent years combustion of biomass for domestic heating is quite increased, as shown by the emissions trend. But if biomass combustion is one of the measures producing good results in the framework of climate change actions, it is important that only high efficiency combustion is fostered, in order to assure a good synergy among the different national strategies.

Such approach seems to be recognized also by the policy makers now, who started to deal with environmental problems in a more integrated way.

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HARMONIZATION OF NATIONAL REGULATIONS IN THE FIELD OF ACOUSTIC POLLUTION WITH EUROPEAN LEGISLATION

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Keywords: harmonization, european, directive, environmental, pollution

INTRODUCTION

In Europe, noise pollution continues to be a serious environmental problem with harmful effects on health. The European legislator has adopted the 2002 directive as the main legislative instrument for the protection of citizens from excess noise caused by vehicular, rail, air traffic and large industrial plants.
Many millions of people living in urban areas are exposed to excessively high levels of noise at night. Noise due to night traffic actually has a harmful effect on health. The most important problem is sleep loss. Noise can also affect professional performance and cause disturbance in school activities.
Action is needed to reduce the impact of noise pollution on the health of Union citizens, to better achieve the objectives of the directive and thus to move further towards the values recommended by the WHO.
For noise generated by industrial plants, in compliance with Directive 2002/49/EC - Environmental Noise Directive - END, strategic noise maps have been developed relating to the determination and management of environmental noise.
The Directive is aimed at defining a common approach, aimed at avoiding, preventing or reducing the harmful effects caused by exposure to environmental noise. The data show that most industrial activities, in terms of noise, have a limited impact in a more anthropized environment, as industrial areas are strongly delocalized with respect to urban areas.
The Directive 2002/49/EC, implemented in Italy by Legislative Decree 194/2005, has as a priority objective the reduction of the number of people exposed through the introduction of noise determination and management tools. In order to ensure the determination of the entity of environmental noise, the Directive requires the competent authorities of the Member States to draw up noise maps (see Figure 1 as an example), concerning the agglomerations and the main infrastructures of vehicular, railway and airport transport, using the Lden and Lnight acoustic descriptors introduced in order to establish, respectively, the overall nuisance and noise disturbance induced by noise.

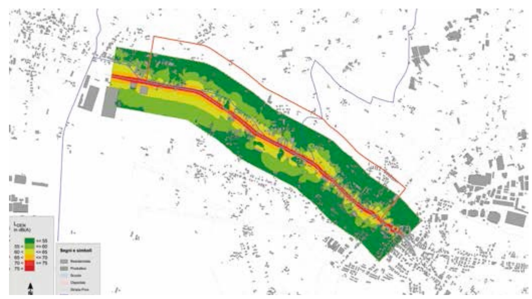

Figure 1. Example of an acoustic map

In 2014, 2,678 noise sources were controlled (see Figure 2). The most monitored sources were service and/or commercial activities (57.5%), followed by industrial activities (28.8%). Among the transport infrastructures, which account for 8.5% of the total, road infrastructures are the most controlled sources (6.5% of the total).

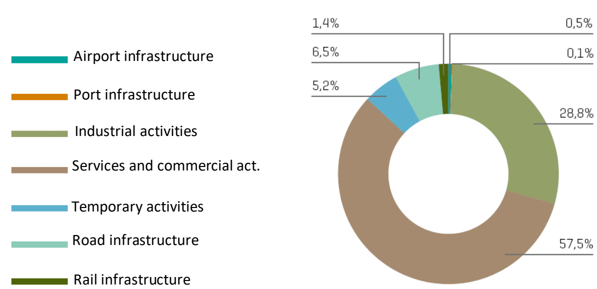

Figure 2. Distribution of monitored sources

This article reports the main points of the publication (ISBN: 978-88-88942-55-1) presented at the seminar on the revision of the legislation on noise pollution, organized by the Italian Association of Acoustics, last October 2017.

The framework law on noise pollution 26th October 1995 n. 447 and the related implementing decrees require a revision and a progressive and gradual adaptation to the progress of technology and knowledge in the field of environmental acoustics. In fact, the article 3, paragraph 3, of the law n. 447/1995 prescribes that the measures pertaining to the State, provided for in paragraph 1 of the same article, must be harmonized with the European Union directives accepted by the Italian State.
With the law October 30th, 2014, n. 161 "Provisions for the fulfillment of the obligations deriving from Italy's membership of the European Union - European Law 2013-bis", article 19, was delegated to the Government regarding noise pollution for the harmonization of national legislation with Directives 2002/49/EC, 2000/14/EC and 2006/123/EC and with Regulation (EC) no. 765/2008.

METHODOLOGY

On 17th February 2017, to complete the entire approval process required by the delegation rule, the President of the Republic signed two new legislative decrees:

1. Legislative Decree 17th February 2017, n. 41
2. Legislative Decree 17th February 2017, n. 42

both published in the Official Gazette of the Italian Republic - Year 158, n. 79 - General Series, Part Before April 4, 2017.
Legislative Decree 41/2017, on "Provisions for the harmonization of national legislation on noise pollution with Directive 2000/14/EC and with Regulation (EC) no. 765/2008, in accordance with Article 19, paragraph 2, letters i), l) and m) of the Law of 30th October 2014, n. 161", concerns substantially modifications, updates and additions to the Legislative Decree 4th September 2002, n. 262, implementing Directive 2000/14 / EC of the European Parliament and of the Council of 8th May 200 concerning the environmental noise emission of machinery and equipment intended to operate outdoors.
Legislative Decree 42/2017 on "Provisions on the harmonization of national legislation on noise pollution, pursuant to Article 19, paragraph 2, letters a), b), c), d), e), f) and h) of the law 30th October 2014, n. 161 "concerns a general revision, update and correction of both the framework law on noise pollution 26th October 1995, n. 447 of the legislative decree 19th August 2005, n. 194, implementing Directive 2002/49/EC concerning the determination and management of environmental noise.

FINDINGS

Legislative Decree 41/2017 has the objective of bringing all the noisy machines operating in the open air, imported from external to the European Union countries and placed on the market in the retail distribution, which lacked the certification and the CE marking. The responsibility in this area is entrusted to importers present on the Community territory, thus filling a regulatory gap and ensuring greater safety for users.
The provision also aims to achieve simplification objectives both in the procedures for the authorization of certification bodies, both for renewals in concomitance with accreditations or their renewal by ACCREDIA. The envisaged sanctioning rules are also strengthened, giving ISPRA greater powers of assessment and verification.
An important aspect that mainly characterizes the legislative decree 42/2017 is the possibility that it offers to introduce with specific legislation the regulation of noise sources previously never considered, such as heliports, propeller systems, cableway and cogwheel systems, simplifying the approval process, transforming these tools by decrees of the President of the Council of Ministers in decrees of the Minister of the environment and of the protection of the territory and the sea.
Furthermore, with the entry into force of the legislative decree 42/2017 it is possible to proceed with the revision of the regulations foreseen by article 11 of the framework law on transport infrastructures, with provisions also simplified through the recourse to the ministerial decree, as well as proceeding with the updating of practically all the decrees implementing the framework law on noise pollution 447/1995.
All this implies that over twenty-five regulatory measures must be issued, updated or supplemented.
The table 1 shows the main regulatory measures must be issued.

Table 1. Main regulatory measures must be issued

Revision of the decree for the preparation of noise recovery plans for transport infrastructures
Decree establishing the commission for the protection from noise pollution
Revision of the decree relating to passive acoustic requirements of buildings and their components.
Decree for the determination of criteria for measuring the noise emitted by wind plants

Legislative Decree 42/2017 establishes the Commission for the protection from noise pollution composed of representatives of the Government of all the realities involved in the problem of noise pollution. The Commission has the task of integrating and harmonizing, within the national legislation, the acoustic descriptors provided for in Directive 2002/49/EC, introducing in the Italian scenario the concept of long-term descriptors, currently only partially present and for some types of sources, and the definition of the type and the limit values.

CONCLUSIONS

Important changes have been introduced to the contents, both of the framework law on noise pollution 447/1995, and of the legislative decree 195/2005, of the implementation of Directive 2002/49 / EC concerning the determination and management of environmental noise, while relating the legislative decree 262/2002, for the implementation of the directive 2000/14/CE concerning the acoustic emission of machines and equipment intended to work outdoors.

These changes refer certain definitions, reiterate and clarify various concepts already contained in the legislation, introduce new indicators for noise, and revise the sanctions set out in the framework law on noise pollution 447/1995, with an update also of the amounts of the sanctions envisaged and clarify the areas of application of the tandemable and urgent ordinances introduced by the framework law on noise pollution 447/1995 in Article 9, review the timing of the consortia of noise mapping, strategic maps and of the action plans provided for by Directive 2002/49 / EC in order to make the process for their forwarding to the European Commission more coherent and effective, review some aspects that have been neglected up to now, such as silent areas, establish the correct flow information, etc.

Further element made by the legislative decree 42/2017 is the revision of the figure of the competent acoustical technician. The table 2 shows the main tasks of the competent acoustical technician.

Table 2. Competent acoustical technician

Phonometric measurements
Verify compliance with the values set by the current regulations
Draw up the recovery plans
Carry out the related control actions

In addition to the establishment of the single national list of competent acoustical technicians, the legislative decree ensures that the preparation and authorization procedures of the competent acoustical technicians are standardized throughout the country. With the legislative decree 42/2017 the profession of competent acoustical technician is included among the professions not organized in orders or colleges under the law of 14th January 2013, n. 4 and therefore assumes a precise identity.

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THE KIGALI AMENDMENT TO THE MONTREAL PROTOCOL FOR A WORLDWIDE PHASE DOWN OF THE POTENT GREENHOUSE GASES, HFCs

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***Keywords*:** Montreal Protocol, Kigali Amendment, Hydrofluorocarbons, HFCs, stratospheric ozone

INTRODUCTION

Concerns that the Earth's stratospheric ozone layer could be at risk from chlorofluorocarbons (CFCs) and other anthropogenic substances first arose in the early 1970s. Scientists warned that the constant releases of these substances into the atmosphere could deplete the ozone layer able to prevent harmful ultraviolet (UV) rays from reaching the Earth.

This would adversely affect ocean ecosystems, agricultural productivity and animal populations, and harm humans through higher rates of skin cancers, cataracts and weakened immune systems. In response, in 1981 the UN Environment Programme (UNEP) launched a negotiating process on an international agreement to protect the ozone layer that brought to adopt, in March 1985, the Vienna Convention for the Protection of the Ozone Layer. Subsequently, binding obligations to reduce ozone depleting substances (ODS) were introduced by the Montreal Protocol on Substances that Deplete the Ozone Layer in September 1987, which entered into force in January 1989.

Since 1987, several amendments and adjustments have been adopted, adding new obligations and additional ODS and adjusting existing control schedules. The last amendment was adopted in Ruanda in October 2016 by the 28th Meeting of Parties to the Montreal Protocol, known as the Kigali Amendment, with the aim to phase-down the production and consumption of the hydrofluorocarbons (HFCs) contributing in tackling climate change. These substance, indeed, even if do not have an ozone-depleting power, have a high global warming power and they have been using as alternatives of the hydrochlorofluorocarbons (HCFCs) in many sectors for their complete phasing-out, by 2030 for developing countries and by 2020 for developed countries. The Protocol and all its previous amendments have been ratified by 197 parties, representing universal ratification (Ozone Secretariat – website).

THE KIGALI AMENDMENT

The Kigali Amendment to the Montreal Protocol builds on 30 years of successfully eliminating ozone depleting substances.

The Kigali Amendment adds powerful greenhouse gases hydrofluorocarbons (HFCs) to the list of substances controlled under the Protocol and which are to be phased down. Use of HFCs is increasing rapidly as substitutes for ozone-depleting substances. HFC phasedown is expected to avoid up to 0.5 degree Celsius of global temperature rise by 2100, while continuing to protect the ozone layer.

Under the Amendment, Montreal Protocol parties are required to gradually reduce HFC use by 80-85 per cent by the late 2040s. First reductions by most developed countries are expected in 2019 due to the amendment will enter into force on the 1st January 2019. Most developing countries will follow suit by a freeze of HFCs consumption levels in 2024, and in 2028 for some of them. Details of the elements of the agreed HFC phase-down schedule are provided in table 1.

OPPORTUNITIES AND CHALLENGES FOR AFRICAN COUNTRIES

African countries have shown several times the willingness to act in reducing HFCs well before the entry into force of their obligations under the Montreal Protocol. Doing so, they would avoid the introduction of HFCs in various sectors, even the most critical, avoiding having to switch to alternatives with low- or zero- GWP later on.

African countries are among those already hit hardest by the growing consumption of high Global Warming Potential (GWP) substances, which impact human health, security and economic growth. However, African countries also face a unique opportunity to directly switch to solutions that do not harm the environment, and to help move towards a sustainable economic transition and positive societal change.

The Kigali Amendment, and its measures for effective ratification, implementation and enforcement, poses opportunities and challenges for African countries. Besides the political and administrative barriers slowing down the Kigali Amendment adoption, the need for enabling activities, institutional strengthening and financial support takes priority.

Table 1. HFCs phase-down steps for A2 and A5 Parties

	A5 parties (developing countries) - Group 1	*A5 parties (developing countries) - Group 2*	*Non-A5 parties (developed countries)*
Baseline formula	Average HFC consumption for 2020-2022 + 65% of (HCFC) baseline	Average HFC consumption for 2024-2026 + 65% of HCFC baseline	Average HFC consumption for 2011-2013 + 15% of HCFC baseline*
HCFC	65% baseline	65% baseline	15% baseline*
Freeze	2024	2028	-
1st step	2029 – 10%	2032 – 10%	2019 – 10%
2nd step	2035 – 30%	2037 – 20%	2024 – 40%
3rd step	2040 – 50%	2042 – 30%	2029 – 70%
4th step			2034 – 80%
Plateau	2045 – 80%	2047 – 85%	2036 – 85%

* For Belarus, Russian Federation, Kazakhstan, Tajikistan, Uzbekistan 25% HCFC component of baseline and different initial two steps (1) 5% reduction in 2020 and (2) 35% reduction in 2025

Notes:
1. Group 1: Article 5 parties not part of Group 2;
2. Group 2: GCC, India, Iran, Iraq, Pakistan;
3. Technology review in 2022 and every 5 years;
4. Technology review 4-5 years before 2028 to consider the compliance deferral of 2 years from the freeze of 2028 of Article 5 Group 2 to address growth in relevant sectors above certain threshold.

As only a few African countries have a refrigeration and air-conditioning (RAC) manufacturing sector, Africa mostly relies on the import of RAC solutions from outside the continent. As a consequence, product strategies adopted by major RAC exporters, in China, Japan, Europe or the USA, have a decisive impact on the adoption of low-GWP technologies in Africa. Moreover, the import of second-hand or pre-charged equipment with high-GWP refrigerants can represent a challenge for the adoption of low-GWP alternatives.

The importance of establishing partnerships within the region or with other developing countries (South-South cooperation), entering into bilateral agreements with RAC exporting countries, and relying on strong public procurement rules to foster low-GWP solutions cannot therefore be underestimated.

The identified priorities for Africa region in implementing the Kigali Amendment are capacity building for policy makers, receiving more support on low-GWP substances and technologies and partnerships with implementing agencies and international bodies. According to the competitiveness of low-GWP technologies, African countries involved in an UNIDO study (UNIDO, 2017), showed that in terms of environmental impact, energy efficiency and performance, safety and reliability, and life cycle cost, low-GWP alternatives would be more competitive than existing technologies. It is expected that the domestic refrigeration will see a quick low-GWP switch to HFC alternatives, such as isobutene and propane, for the highest familiarity levels for low-GWP refrigerants among African officers responded to the survey.

CONCLUSIONS

For the first time, scientists have shown through direct satellite observations of the ozone hole that levels of ozone-destroying chlorine are declining, resulting in less ozone depletion.

Measurements show that the decline in chlorine, resulting from an international ban on chlorine-containing manmade chemicals called chlorofluorocarbons (CFCs), has resulted in about 20 percent less ozone depletion during the Antarctic winter than there was in 2005 — the first year that measurements of chlorine and ozone during the Antarctic winter were made by NASA's Aura satellite (NASA 2018). The Montreal Protocol has put the ozone layer on the road to recovery by phasing out ODSs and in the process has also mitigated climate change. Under the Amendment, parties will phase down production and consumption of HFCs, creating the potential to avoid up to 0.5°C of warming by the end of the century.

Through the Kigali Amendment, the Montreal Protocol takes responsibility for HFCs and plays a leading role in working towards an environmentally sustainable world where no one is left behind, consistent with the 2030 Agenda for Sustainable Development.

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GREEN PUBLIC PROCUREMENT: A LEVER TO CONTRIBUTE TO MITIGATION AND ADAPTATION TO CLIMATE CHANGE AND TO DISSEMINATE CIRCULAR ECONOMY MODELS

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INTRODUCTION

The paper, after defining green public procurement, highlights environmental, economic and social benefits of this environmental and industrial policy tool, describes the Italian regulatory and technical framework, outlines the sectors that have and will be involved in the activities of the Action Plan for environmental sustainability of public administration's and briefly describes the method used to define the "Minimum Environmental Criteria", the environmental requirements defined for certain categories of goods, services and works.
Findings refer the practical effects of the mandatory application of the Minimum Environmental Criteria and the initiatives put in place to facilitate the implementation of this obligation.
Conclusions describe the role that a public research institution, such as the National Research Council (CNR), could have within the GPP framework both as subject obliged to contribute to pursue the Action Plan's environmental sustainability targets and as technical-scientific representative that could reinforce the cooperation with the Ministry in this field to define more effective criteria and to suggest strategic procurement categories on the basis of results of the research carried out in the field of environmental innovation of materials, products, processes and technologies.

METHODOLOGY

Environmental and economic objectives of green public procurement.

The European Commission defines Green public procurement as *"a process whereby public authorities seek to procure goods, services and works with a reduced environmental impact throughout their life cycle when compared to goods, services and works with the same primary function that would otherwise be procured"*[1].
Public expenditure for public procurement in Italy amounts approximately to 10% of the GDP[2] and it represents around 14% of the overall European GDP. Public administrations, through the strategic use of public tenders, have therefore a fundamental role in steering production and consumption models towards sustainability.
The lever effect of green public procurement is determined especially where are used homogenous environmental requirements by contracting authorities in each goods or services public procurement procedures and where is high the volume of goods and services purchased comply with these requirements.
Green public procurement also involves the steps that precede and follow the procurement procedure itself. A robust action to support and promote circular economy and a more efficient use of resources has to consider ways to dematerialise the needs of contracting authorities, to promote an environmentally responsible use of products and extend their life cycle or favour their circularity.
This last objective can be achieved through innovative procurement procedures and environmental requirements able to contribute to close energy and material cycles within supply chains, at the same time minimizing or, in the best cases, avoiding environmental impacts and generating of waste throughout the entire life cycle.
Public procurement has been recognized as an important strategic tool in several European guidelines, starting in 2001 with the COM(2001)68 "*Green paper on Integrated Product Policy*" to the

[1] COM (2008) 400 Public procurement for a better environment.
[2] This estimate is based on the data reported by the National Anti-corruption Authority http://www.anticorruzione.it/portal/public/classic/AttivitaAutorita/Pubblicazioni/RapportiStudiContrattiPubblici

more recent ones, such as COM (2017)572 *"Making Public Procurement work in and for Europe"*.

<u>Environmental, economic and social effects</u>
Green public procurement influences and is influenced by the market, by stimulating and rewarding environmental innovations.
It is therefore a tool that, by tackling environmental impacts along the life cycle of goods and services in public tenders and for its cross-sector approach, can tangibly and measurably contribute to environmental targets, such as:

- minimisation of greenhouse gases
  through environmental criteria that enhance energy efficient products and technologies, promote specific renewable energy sources and low carbon technologies, aim at extending the useful life of products and materials by promoting their preparation for reuse and recycling, aim at avoiding or reducing land take, for example through sustainable timber management or by allowing construction of new buildings only in already suitable infrastructural contexts[3];
- adaptation to climate change
  through specific environmental criteria that promote water efficiency and/or safeguard land's water retention capacity and minimize land take;
- decrease of polluting emissions and of the use of hazardous substances
  trough the definition of environmental criteria aimed at reducing and replacing hazardous substances in materials and products with substances that involve minor risks or no risk at all for health and for the environment or through the enhancement of alternative technologies (for example physical rather than chemical, or low emissive) also in relation to production processes and promoting bio-based products;
- reduction of energy and natural resources consumption, efficiency in the use of materials, promotion of low-emission renewable sources for energy production
  trough innovative tenders that promote circularity and energy efficiency, through environmental criteria for the conservation of natural resources as well as for the reduction of material and energy consumption;
- biodiversity protection
  through specific environmental criteria aimed at making food supply chains and forest management more sustainable, reducing polluting emissions in water bodies, on soil and in the atmosphere, rather than with criteria, for example in the context of group catering services, that safeguard vulnerable species, as well as all those environmental criteria for reducing greenhouse gases emission.

Green public procurement, due its cross-sector approach and for its positive effects on the various environmental targets, can be an implementing tool of the Action Plan on sustainable production and consumption to be defined under the article 21, clause 4 of the Law 221/2015, of the enacting Plan for adaptation to climate change, of the framework document "Towards a model of circular economy for Italy", as well as of all those plans and strategies that approach environmental targets and the best allocation of public financial resources.
With regard to economic benefits, it needs to be taken into account that eco-design of processes and products, management systems innovations and, more in general, all environmental technologies that green and circular public procurement promote, contribute to improving competitiveness of companies and quality of products.
Environmental requirements to improve materials and energy efficiency protect companies from resource scarcity and from their prices fluctuations.
A product or service "with lower environmental impact" will also be more competitive in a cultural context progressively more conscious of the environment and of the health and security issues connected with use and disposal of products.
Green public procurement can be an effective and structural substitute of economic incentives for industrial innovation and for dissemination of environmental technologies, both in mature sectors and in sectors where economies of scale have yet to be developed where it can stimulate growth and promote green jobs.

<u>Regulatory context</u>
In Italy, following the COM (2003) 302 "*Integrated product policy - Building on Environmental Life-Cycle Thinking"*, which encouraged Member States to adopt a National Action Plan on green public procurement by 2006, has been defined, according to article 1 paragraph 1126 of Law n.296 of the 27th December 2006, the GPP National Action Plan approved by the Decree, 11th of April 2008 Minister

[3] Regarding the effects of the introduction of environmental criteria in public tenders in terms of reduction of greenhouse gases emissions consult the website of the project GPP 2020 – GPP procurement for a low carbon economy, co-financed by the programme of the European commission Intelligent Energy Europe (http://www.gpp2020.eu/it/)

for Environment and Protection of Land and Sea with the agreement of the Minister of Economy and Finance and of the Minister of Economic development[4].

This Plan, that aims to promote green public procurement in Italy, provides for the definition and adoption, with specific decrees of the Minister for the Environment and the protection of Land and Sea, of the environmental criteria (Minimum Environmental Criteria) to be introduced in the documentation of public tenders for certain categories of goods and services.

In Italy, green public procurement has been strategic since 2008 thanks to the fact that it has been included in a centralized coordinated policy that, as stated by the first revision of that Plan (DM 10th of April 2013), imposes also a constant dialogue with stakeholders and experts, also of research sector, to develop the Minimum environmental criteria.

The effectiveness of this tool has then been reinforced by article 18 of Law n. 221, 28th December 2015 *"Environmental provisions to promote green economy actions and to contain an excessive use of natural resource*s" and, subsequently, by the article 34 of the Legislative Decree n. 50, 18th of April 2016 *"Code of public contacts"* both of which made compulsory the introduction of "technical specifications" and "contract clauses" defined in the Minimum Environmental Criteria in tender and project documentation as well as taking into account the award criteria when the contract is awarded on the basis of the best price-quality ratio.

Thee obligations apply to procurement procedures of any amount and to any category of goods, services and works for which the Minimum Environmental Criteria have been defined[5].

This legislative provision makes sure that the national policy on green public procurement is effective and that the result of the complex activity carried out to define minimum environmental criteria does not get scattered.

<u>*The procedure used to define*</u> <u>MECs.</u>

A first draft version of the document is defined on the basis of the analysis and the confrontation on a considerable amount of technical and scientific documentation and of environmental legislation, and on the basis of a market analysis. This draft is then shared and discussed among the members of the working group.

The working group has to be composed by representatives of trade associations, and other key stakeholders (experts of contracting authorities, of research sector, central and local institutional representatives etc.).

This document, revisited on the basis of the contributions sent within the working group and further technical insights and shared with the "GPP National Action Plan Steering Committee", is approved by Ministry of Environment, in annex of the decree of adoption.

<u>*MECs product groups*</u>

Until now have been adopted by Decree of the Minister for the Environment the Minimum Environmental Criteria for the folliwing product groups:

- Cleaning products and services
- Copying and graphic paper
- Energy service for buildings
- Food and Catering services
- Gardening products and services
- Incontinence care products: diapers
- Lighting systems design service, purchase of lamps and ballasts
- Office Building Design, Construction and Management
- Purchase of inkjet and toner cartridges; integrated service of collection and supply of cartridges
- Purchase, lease and rent of furniture
- Purchase, lease and rent of imaging equipment, pc desktop and pc laptop, pc monitors
- Purchase, lease and rent of vehicles (car, vans, buses, trucks...)
- Sanitization services for hospital and other health care buildings
- Textiles
- Urban furniture (playgrounds, bins, waste collection bins, benches, outdoor tables ...)
- Urban waste management

And, currently, are under revision or under definition the Environmental Minimum criteria for the following product groups:

- Shoes and other leather products
- Lighting service
- imaging equipment purchase and rent (revision) and copy and print management service (new product group)

[4] http://www.minambiente.it/pagina/piano-dazione-nazionale-sul-gpp.

[5] The only exception in represented by restructuring, demolition and reconstruction works for which criteria apply according to a specific decree (Ministerial Decree 11th of October 2017).

- Purchase of inkjet and toner cartridges; integrated service of collection and supply of cartridges (revision)
- Food and catering services (revision)
- Road Design, Construction and Maintenance
- Laundry service and rent of textile products
- Gardening products and services (revision)
- Cleaning products and services (revision)
- Sanitization services for hospital and other health care buildings
- Urban waste management
- Purchase, lease and rent of vehicles (revision) and boats and public transport service.

FINDINGS

If the mandatory application of the MECs has certainly strengthened their effectiveness it has certainly entailed a stumbling block for those contracting authorities that had never approached this issue.
In order to facilitate the application of the MECs, to promote the maximum dissemination of the information about the MECs among stakeholders and for the professionalization of contracting authorities, a new Action Plan has been defined and agreements have been signed with various key stakeholders, including the National Authority for Anticorruption, called to monitor the MECs application.
Through the results of monitoring activities and, in particular, through economic data (green public spent for each public procurement category), it will be possible to estimate the environmental and economic benefits (p.e. CO_2 saved; lower spending linked to lower energy consumption etc.), quantify the effectiveness of this policy and identify the need for further corrective measures or actions to be taken.

CONCLUSION

The CNR, as a subject obliged to apply the legislation on public procurement, is called upon to contribute to the environmental sustainability objectives envisaged in the National Action Plan by applying the Minimum Environmental Criteria.
In this field, it could also give a huge contribute by transfer the technical-scientific knowledge to prepare and implement this environmental legislation. This showcase aims to suggest how the above transfer could be practically developed.

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INDUSTRIAL AREAS AND HUMAN HEALTH: THE "CISAS" PROJECT

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***Keywords*:** air quality, particulate matter, chemical composition, health effects, Sites of National Interest

INTRODUCTION

The widespread development of human activities in the industrial field, since the post-war period, and the creation of an economy that has placed our country in the eighth place among the world's major industrialized Countries has been causing a complex phenomenon of environmental contamination, with crucial effects on terrestrial and marine ecosystems and on human health. A decisive action of the Government and the Ministries in charge of environmental protection allowed to identify a number of contaminated areas in the Italian territory in need of an urgent and important recovery action. These so-called Sites of National Interest (SINs) are characterized by severe environmental degradation, substantially caused by the development of major industrial activities.

In relation to the environmental characterization of these areas, it has recently been considered crucial and necessary to understand the specific impact of these factors on the health of the people living in proximity of the above mentioned sites. The present research program aims at investigating the environmental pollution and its connection with the ecosystem and with human health, starting from three case studies (SIN's of Augusta, Milazzo and Crotone), true natural laboratories suitable for multidisciplinary investigation.

The primary objective of CISAS ("Centro Internazionale di Studi Avanzati su Ambiente, ecosistema e Salute umana") is to understand processes and mechanisms for the transfer of conventional and emerging contaminants from the environment (as a complex of atmosphere, soil, sediment, inland waters and sea matrices) to the ecosystem and to humans. The atmosphere represents the main intake pathway of contaminants into the respiratory system and for this reason the identification of the concentration, composition and sources of atmospheric pollutants constitutes a cornerstone for the subsequent evaluation of the health effects on the inhabitants of the three SINs.

Task 2.7 of the CISAS project is devoted to the study of particulate matter (PM). Particles suspended in the atmosphere are characterised by different dimensions, shapes, sources, formation mechanisms, chemical composition and ageing. For this reason the effects they exert on the ecosystem are quite complex and an in-depth characterisation of PM is essential for a correct interpretation of the interaction mechanisms with the human body.

METHODOLOGY

The mass concentration, chemical composition and morphology of particles smaller than 10 and 2.5 μm (PM_{10} and $PM_{2.5}$) have been determined during two 3-month study periods, carried out during the winter (December 2016 – February 2017) and during the summer (July – September 2017). The choice of these two size dimensions allows an easy separation between the contributions from anthropogenic sources (mainly combustion sources: traffic, domestic heating, industrial activities), which are almost totally included in the fine fraction ($PM_{2.5}$), and those from natural sources, which are mainly in the coarse faction (difference between PM_{10} and $PM_{2.5}$).

In this project the characterization of atmospheric PM was aimed to the evaluation of people exposure. For this reason we preferred to perform long-duration samplings (each one lasting for one month), instead of the typical 24-h samplings. The latter would have necessarily implied a total duration of the study of no more than two weeks, while the selected protocol was able to give an overview of PM characteristics during a very long period (six months over one year) with affordable cost and man-power.

The choice of the chemical species to be determined was driven by two main criteria: macro-components of PM (macro-elements, ions, elemental carbon, organic carbon) and species that are recognized to exert adverse effects on human health: IPA, PCDD, PCDF, PCB, PBDE.

PM was collected on 4 different filters: - quartz fibre filters were devoted to the determination of elemental and organic carbon by thermo-optical analysis; - polycarbonate filters were devoted to the analysis of particle morphology by Scanning Electron Microscopy; - Teflon filters run by high-volume samplers were devoted to the analysis of micro-organics (IPA, PCDD, PCDF, PCB, PBDE) by High Resolution Gas Chromatography – High Resolution Mass Spectrometry; - Teflon filters run by low-volume samplers were devoted to the analysis of macro-elements by Energy-Dispersion X-Ray Fluorescence, ions by Ion Chromatography, micro- and trace- elements in their soluble (bio-accessible) and residual chemical forms by ICP-MS (Canepari *et al*., 2006). On the latter filter, we also determined the oxidative potential of PM, by the dichlorofluorescein diacetate method (Hung and Wang, 2001).

By determining all PM macro-components (ions, elements, elemental and organic carbon) it is possible to close the mass balance. Moreover, by applying appropriate algorithms, it is also possible to evaluate the strength of the main PM sources: soil, sea, formation in the atmosphere, combustion, biosphere (Perrino *et al*., 2014, 2016).

FINDINGS

Some results regarding the mass concentration and chemical composition of PM during the two study periods are summarized in Figure 1.

PM_{10} and $PM_{2.5}$ concentrations were generally low and did not exceed the European and National limit values set for their annual average value (40 µg/m^3 for PM_{10} and 25 µg/m^3 for $PM_{2.5}$).

During both seasons the coarse fractions were dominated by soil and sea, the two main natural sources of PM. However, while soil-related particles constituted a nearly constant fraction of both PM_{10} (24-32%) and $PM_{2.5}$ (10-20%), sea-spray contribution, dependent on the wind intensity and direction, showed higher variability in PM_{10} (4-20%) and much lower contribution in $PM_{2.5}$ (below 5% during the winter, below 3% during the summer).

The contribution of the traffic source to PM_{10} was around 10% at all three sites; being the particles released by this source confined in the fine range, the contribution to $PM_{2.5}$ was much higher (up to 20%).

Also organics were found mainly in the fine fraction, and constituted the most important contribution to both PM_{10} (21-29% during the winter, 26-39% during the summer) and $PM_{2.5}$ (35-48% and 44-53%, respectively). This group includes a huge variety of chemical species, mostly of secondary origin, that individually yield a low contribution to the PM mass. Secondary inorganic species were mainly constituted by ammonium sulphate. Being of photochemical origin, this species is included in the fine fraction of PM and reaches higher concentration during the warm period. Particularly during the summer campaign, the concentration of ammonium sulphate at the site of Priolo, where two major petrochemical plants are located, exceeded the values measured at Crotone and Milazzo. Nitrate ion was mostly in the coarse fraction of PM: this indicate that the contribution of ammonium nitrate (of secondary origin) was negligible, particularly during the warm period, while the main source of this ion was most likely due to soil abrasion and re-suspension.

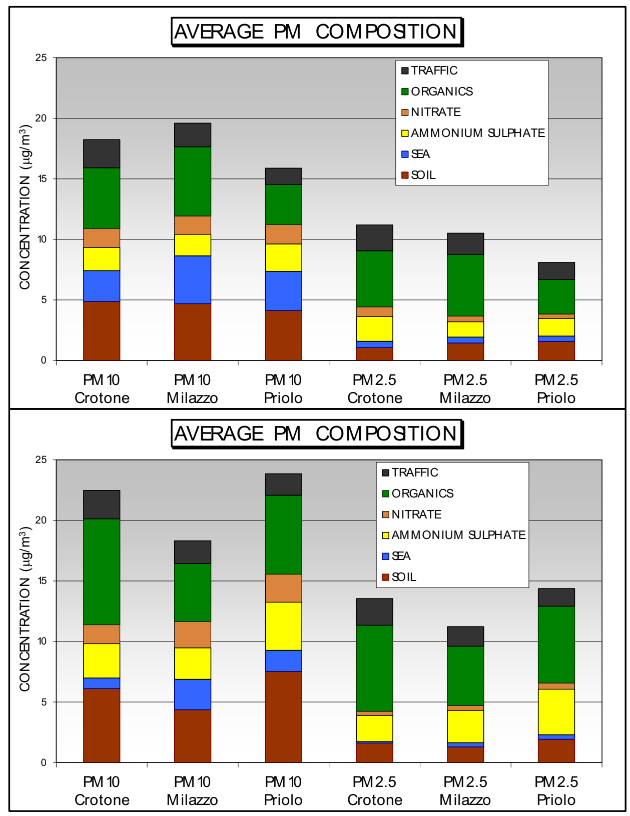

Figure 1. Average composition of PM_{10} and $PM_{2.5}$ during the winter (upper panel) and the summer (lower panel) period at the three SINs

No significant critical issues were identified in the analysis of micro-organics, that were all in the concentration range expected for urban or sub-urban areas.

During this study, an analytical procedure for the detection of flame retardants (PBDE) in PM was developed and optimised. Polybrominated diphenyl ethers constitute an important group of brominated flame retardants that have been, and still are, widely used as additives in many products such as plastics, electronic appliances, textiles and furnishing. Following the banning of penta- octa- and deca-BDE, the industry has turned out to new BFRs, including, among others, decabromodiphenyl ethane (DBDPE), extensively used as replacement for deca-BDE (BDE-209).

The concentration of 42 congeners of PBDEs was measured on the same filter where the other persistent organic pollutants (IPA, PCDD, PCDF, PCB) were detected. The results, summarized in Figure 2, show similar concentrations at the three sites. The most relevant congeners were DBDPE and BDE-209, whose concentrations were 13% and 78%, respectively, of the total PBDE during the winter and 21% and 35% during the summer (average of the six months and the three sampling sites).

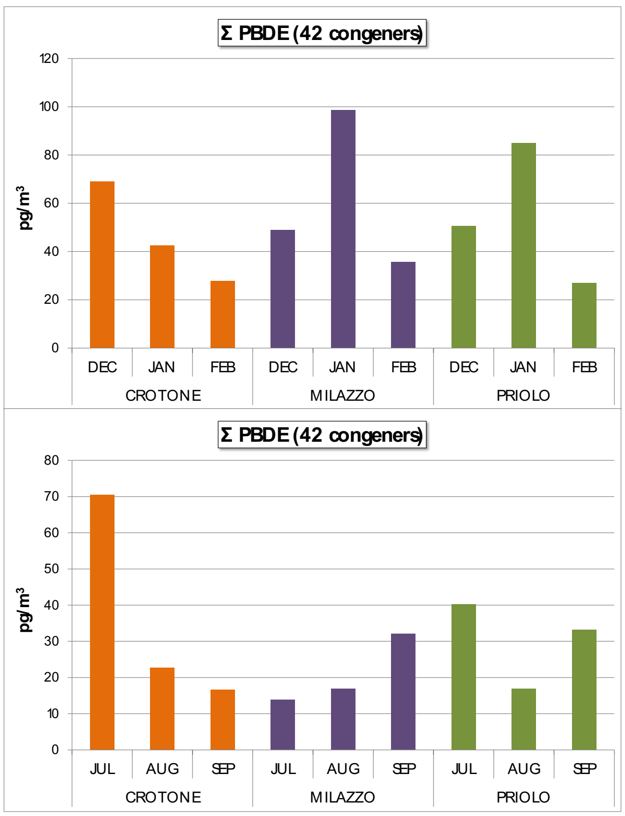

Figure 2. Concentration of flame retardants during the winter (upper panel) and the summer (lower panel) period at the three SINs

THESE RESULTS INDICATE THAT ALTHOUGH BDE-209 HAS BEEN BANNED WITHIN EU IN 2008, THE RELEASE OF THIS TOXIC POLLUTANT, MAINLY FROM WASTE MANAGEMENT, TO THE ATMOSPHERE IS STILL RELEVANT AT ALL THREE SINS.

CONCLUSIONS

As far as atmospheric particulate matter is concerned, the wide set of results collected during the CISAS study did not show relevant critical issues. The concentration and composition of PM was consistent with the results expected for a coastal suburban area, with a low impact of the industrial activity.

The health effects that have been highlighted by the other research groups participating in the CISAS project must be then related to a different intake pathway (e.g.: food) and/or to the exposure to atmospheric pollutant in the gaseous phase. A further field study devoted to the evaluation of these species is recommended.

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THE "AEROTRAZIONE CON BIOCARBURANTI" (ABC) PROJECT: BIOFUELS IN AVIATION

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Keywords: Biofuel, emissions, exhaust gas sampling

INTRODUCTION

In December 2015 all countries that are members of the United Nations Framework Convention on Climate Change (UNFCCC) met in Paris (COP21) and decided to adopt a new climate agreement, which will come into force in 2020. In this framework, CO_2 emissions from the combustion of fossil fuels have been universally recognized as the main cause of the ever-increasing greenhouse effect and the consequent global warming.

The Paris agreement therefore sets the limit of 2°C (or at least 1.5°C) as a long-term target, due to the increase in the global temperature of the planet compared to the pre-industrial period. At the same time, the sum of the INDCs (Intended Nationally Determined Contributions) will not allow to achieve this goal but will lead to a temperature increase of about 3 °C, if the share of individual countries will not be reviewed in a more ambitious way [1]. In this context, biofuels such as fuels can significantly contribute to solving the greenhouse problem. Bioenergy will play a key role in long-term EU energy strategy and in particular in the transport sector, contributing to 9.5% of energy demand in the transport sector in 2020 [2]. The supply of raw materials and the biofuel conversion technologies currently used already make a significant contribution, but it will be necessary to apply a diversification of raw materials and advanced technology to implement this development. In the period up to 2050, aviation worldwide is expected to grow by 5% per year. If fuel consumption and CO_2 emissions grow at the same pace, CO_2 emissions from global air transport in 2050 would be more than 6 times their current figure. Concerning the use of biofuels in aviation, the standards for aircraft engines are very strict and conventional biofuels can be blended up to 20% with fossil kerosene. Therefore, any measures aimed at reducing emissions from air traffic are becoming increasingly important. Indeed, the CO_2 emitted by aircraft that employ "avio" biofuels would be equal to that previously absorbed by the plants that supply these fuels, then subtracted from the atmosphere, with an overall emission-absorption balance very close to zero. When considering the use of aviation biofuels in relation to the release of micropollutants, the impact assessment is most difficult. Since micropollutants' emissions are not regulated, they are largely neglected by evaluation studies on emissions released by the engines according to the fuels used. Among the organic micropollutants, Polycyclic Aromatic Hydrocarbons (PAHs) are a class of compounds of primary importance. Literature data, even if limited, shows a tendency to reduce PAH emissions. Many of these studies, however, have been carried out by examining only the collected particulate, neglecting the vapor fraction; therefore it is not clear if the observed reduction of PAHs is due solely to the reduction of the particulate emitted achieved with the introduction of biofuels, or if it is real, ie if there is also a reduction of PAHs in the vapor phase. Being aware of the environmental consequences of continuing the increase of CO_2, IATA members have committed themselves in 2009 to achieve the following goals:

- improving fuel efficiency by 1.5% per year over the next decade;
- making the sector carbon-neutral by 2020;
- reducing net CO_2 emissions by 50% by 2050, compared to 2005 levels.

It is clear that biofuels will increasingly play a key role in achieving these goals [3, 4]. "ABC Project" is a cooperation agreement between the Ministry of the Environment and the Protection of the Territory and the Sea (MATTM), the National Research Council (CNR), the National Agency for New Technologies, Energy and Development Economic Sustainability (ENEA) and Aeronautica Militare (AM). The main objective of this project is the analysis of aviation biofuel as regards for composition, performance and pollutant emissions. The characterization of avio biofuel (i.e. certification of the bio/fossil fraction, of the efficiency and of the environmental impact), is essential to understand if the large scale diffusion of this new type of fuels could contribute to the reduction of greenhouse gas emissions. This project is organized in 5 macroareas; in this paper, the "preliminary studies" for the first phase are presented: development of methods for the analysis and the on-field sampling system of organic micropollutants, volatile/semivolatile organic compounds, nanoparticles).

METHODOLOGY

Method development

Analytical procedures for the analysis of PAHs, N-PAHs, Oxy-PAHs, VOC, fatty acids, metals were developed. In particular, extraction, clean-up and instrumental analysis vere evaluated. Figure 1 sums up the operating protocol.

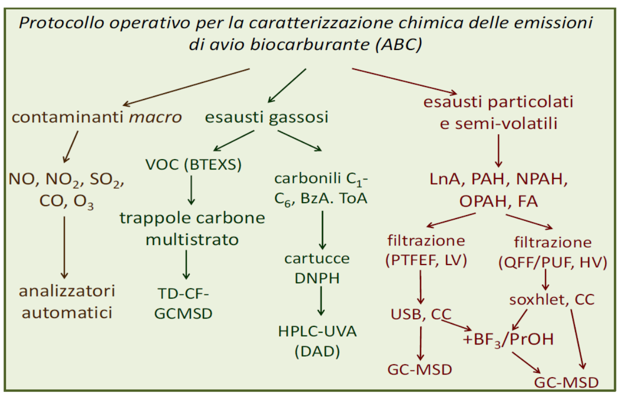

Figure 1. Scheme of analytical procedure

On-field sampling

The sampling system was preliminary optimized in "Campo Sperimentale di Volo" in the Military Airport of Pratica di mare (RM). The goal of this step was to optimize the sampling line of the combustion products emitted from the aircraft engine exhaust.
The following pollutants were sampled:

- aldheydes,
- COV,
- particulate
- semivolatile compounds (PAHS, alkanes).

In addition, a probe was positioned directly in the aircraft's exhaust cone, to collect NOx, CO, SO2, O3 for an automated analyzer. The sampling probe is equipped with a Darcy tube, in order to carry out isokinetic sampling of the particulate and a K thermocouple for temperature detection.

On-field sampling

Sampling campaigns were carried out at the Reparto Sperimentale di Volo di Pratica di Mare (Aeronautica Italiana). Tests were performed on a single-engine attack and reconnaissance aircraft in the two-seater advanced training version (AMX-T), equipped with a 5,000 kg / s Rolls-Royce Avio RB.168-807 Spey turbofan engine.

Test #1

In the first trial, the aircraft was 17m far from the sampling probe, "SONDA" in Figure 2. In that position Aldheydhes and VOCs were manually sampled.
In "B mezzo mobile IIA" position, Aldheydes (1h-sampling at a 1 L/min flow rate), VOCs (5 min and 20 min at 100 ml/min flow rate) and particulate (1h at 6 L/min flow rate) were measured in "B mezzo mobile IIA" and in sampling point "C", chosen as a field blank as not directly hit by the aircraft exhausts. In addition, semivolatiles organic compounds were measured with a week lasting sampling in a position far from the engine test pitch, in order to have a background level.

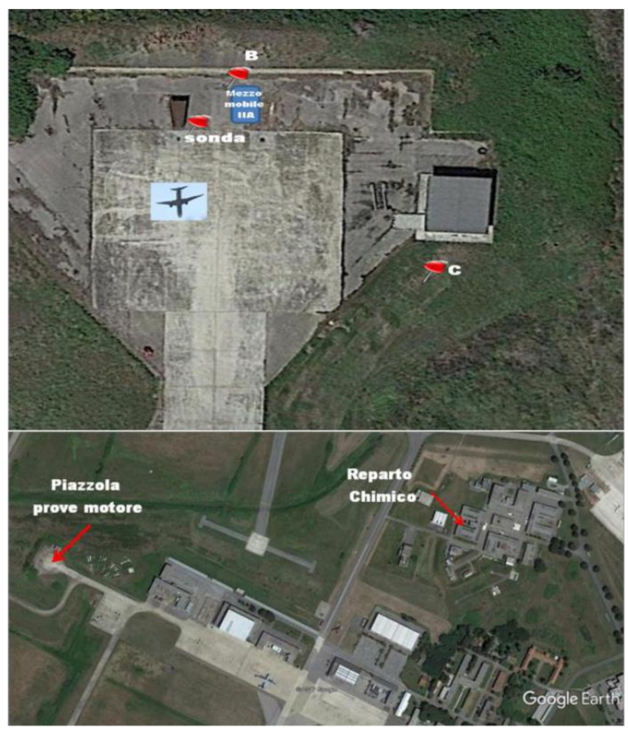

Figure 2. Sampling point – test #1

Test #2

Additional sampling points were added, as presented in Figure 3; positions "A" and "B" were anchored to the two sides of the chute - A is inside the aircraft's exhaust cone. SVOCs, Aldehydes, and VOCs were sampled at 200, 400 and 200 L/min, respectively.

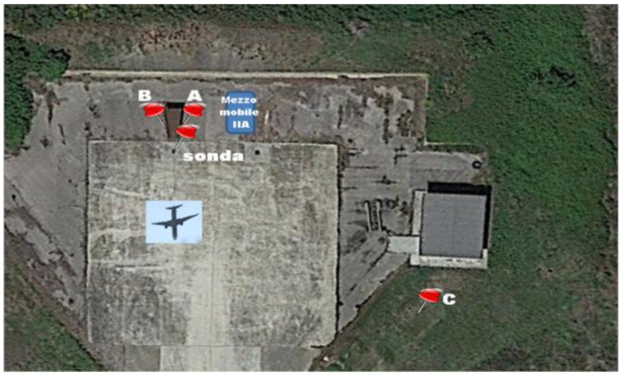

Figure 3. Sampling points – Test #2

Test #3

An SMPS spectrometer (3936, TSI) consisting of an electrostatic classifier to classify the particles according to their electric mobility (DMA) and a CPC to count the filtered particles was installed. A preliminary measurement with the aircraft engine off was carried out (field blank), and the concentration was of about 18000 particles/cm^3. Afterwards, a 8m-length copper sampling line was inserted, the test was repeated and the counts have been reduced to about 15,000 particles/cm^3.

FINDINGS

Macropollutants

NO, NO2, O3, CO, CO2, SO2 were monitored by continuous analyzers in every trial, with different engine power (40% and 60% power) and with engine off; average concentrations of the pollutants show the same trend. Nox concentrations are negligible for background/blank test.

VOCs

Toluene, Ethylbenzene, Xilene and Benzene were sampled at each position, with different sampling volume.

SVOC

The analysis of PAHs and Alkanes were performed from the collected particulate. For both classes a good agreement can be observed between the two tests. For completeness, some diagnostic reports have been evaluated. PAHs originate from a wide variety of sources. A useful method for identifying the possible sources from which they can be generated is the calculation of diagnostic ratios between individual PAHs.

Ultrafine Particulate

The analysis of particle size distribution, shows a bimodal distribution, Dalle prove si osserva una with two max at 25 nm and 100 nm. Particle count was about 10000 particles/cm^3. During the measurement, both the dilution system adjustment and the counts were checked. A second measurement was made with the aircraft engine brought to a power of 60%. In this case, the dimensional distribution of the particles has only one fashion, at 25-30 nm. An additional test was carried out with the aircraft was drawn nearer to the sampling point. The particle size distribution showed a modal peak at 16 nm. It could be assumed that the displacement of the aircraft has resulted in the displacement of the exhaust cone relative to the sampling point.

CONCLUSIONS

The first step of this work involved the development of the analytical protocol for the analysis of VOCs, PAHs, alkanes and Ultrafine particulate and their sampling in different positions, volumes and flow rates. Data evaluated from the comparison between traditional fuels and biofuels will be used to optimize the sampling points. In detail there will be evaluated: exhaust gas by the use of continuous analyzers data, the aircraft exhaust cone and background data from a site far from the engine test pitch. The tests and activities carried out are aimed at the chemical characterizations that will be carried out in 2018, the results of which will be used for the assessment of the environmental impact of aviation biofuel emissions, as well as the expected benefits from its use in place of traditional fuels.

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RENEWABLE ENERGY AND BIOFUELS: THE SUPPORT OF CNR IIA TO THE ENERGY TRANSITION

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Keywords: renewable energy, biofuel, sustainability, waste management, resource efficiency

INTRODUCTION

In the last decades, a growing interest is being observed towards cleaner and safer energy sources. A reduction in the consumption of fossil fuels is regarded as a mandatory target in order to reduce the greenhouse gas emissions and to ensure energy security. In this framework, a transition towards cleaner and safer energy sources can be achieved through bioenergy solutions, including biomass combustion, anaerobic digestion, gasification and pyrolysis. Biomass burning, especially for heat production, is considered an economical and efficient way to reduce carbon emissions, although the proper accounting of CO_2 emissions from biomass combustion in bioenergy systems is still a discussed topic (Cherubini *et al*. 2011 Brandão *et al*. 2013). On the other hand, biomass combustion is becoming one of the main pollution source, with regard to local air quality (Petracchini *et al*, 2017). In order to reduce the local environmental impact of bioenergy without losing its energy potential, alternative biomass exploitation strategies have become a point of high technical interest. Aim of this work is to report the activities performed by CNR IIA in order to support such a transition.

METHODOLOGY

Biomass combustion (SELVA project)
The SELVA project aims to reach the energy objectives set by the Lazio Region. In particular, a survey is being carried out on the short- and medium-term biomass availability using new generation technology; a territorial analysis and an energy requirement will be carried out to establish the introduction and dislocation of plants for the generation of heat and energy from biomass; the analysis of the impact of these systems on air quality will be started by drawing different scenarios; an analysis of the impact on society and on the local economy of these activities will be carried out.

Small scale anaerobic digestion (FORUM project)
In order to allow small communities (towns, districts) to perform a local conversion of municipal organic waste into biogas and compost, a novel pilot scale multi stage semi dry anaerobic digester was developed and tested during Smartgrid project. Subsequently, the Calabria Region funded the implementation of a full scale pilot plant in the town of Cleto, in the framework of FORUM project.

Dedicated solutions for small islands (Smartisland)
In the framework of Smartisland activities, smaller islands are supported in the transition to a virtuous model of environmental sustainability, studying the best solutions in four areas of intervention: Energy, Mobility, Waste and Environment.

Scientific advice for biofuel production
In order to promote the penetration of biofuels in the energy market, CNR IIA supports public agencies and private companies in the identification of optimal solutions for biofuel production. In this framework, the Water Agency of Milan commissioned a study for the monitoring of a pilot plant for biomethane production from sewage sludge.

FINDINGS

Biomass combustion (SELVA project)
During SELVA project, a supply chain was developed and assessed for energy production from woody biomass, including harvesting, transportation, conversion and emission control. Energy and environmental scenarios were evaluated, and a GIS information is available to citizens, as shown in Figure 1. A biomass plant database for the Lazio region is also being built in order to provide a biomass plant registry.

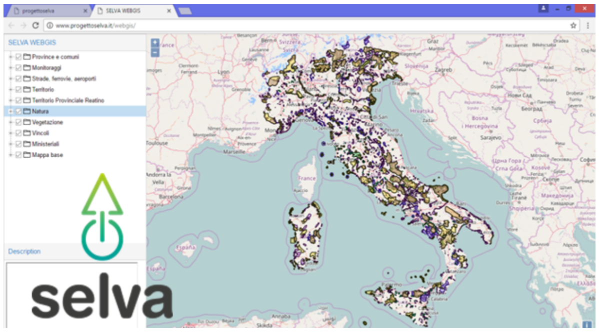

Figure 1. Georeferenced information system of SELVA

Small scale anaerobic digestion (FORUM project)
The anaerobic digestion plant developed during FORUM project includes a set of fist stage (hydrolysis and acetogesis) cells able to extract the energy potential from biomass. The liquid leachate is converted in biogas through acetoclastic methanogenesis in a second stage reactor. The solid residue of the first stage cell is converted into compost through an aerobic process in order to reduce odour emissions.

Figure 2. Pilot plant of FORUM project

Dedicated solutions for small islands (Smartisland)
From an energetic point of view, the connection of many islands to the continent's electricity grid leads to an inefficiency and dependence, due to the use of oversized diesel generation to cover the summer peaks of tourism: for these reasons, the proposed solutions aim to use renewable sources, in order to produce clean energy. In terms of waste, only in recent years many islands are planning environmentally friendly waste management plans, providing for door-to-door separate waste collection: actions are being carried out to promote prevention, information and involvement of citizenship; a management plan that foresees seasonal increase is also being developed. With regard to mobility, actions are aimed to overcome the intensification of road vehicles (both public and private) in the summer season, proposing new cycle paths, car sharing of electric cars and ecological TPL vehicles. Furthermore, unique and peculiar ecosystems from the islands must be protected through dedicated solutions including water saving and reforestation.

Scientific advice for biofuel production
Sewage sludge conversion to biomethane for transportation use was monitored in the pilot plant of Milan Water Agency. The results obtained during the preliminary 2017 monitoring campaign are reported in a recent paper (Paolini *et al*, 2018). Some criticalities emerged in the levels of CO_2 and H_2S due to damage to a valve. At the same time, it was found that the maximum permissible concentration of chlorine was exceeded. Modifications were therefore made to the unit: finally, since March 2017 all parameters were found to be compliant with current regulation. The final plant configuration is reported in Figure 3.

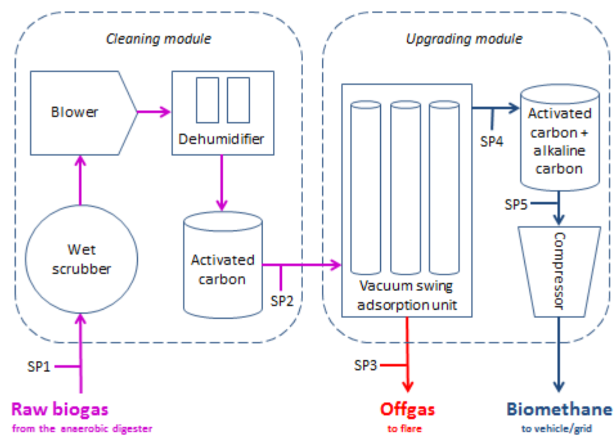

Figure 3. Biogas upgrading unit in Milan

CONCLUSIONS

An energy transition model based on the use of renewable sources with low environmental impact is particularly important, especially in isolated communities such as: islands, mountain areas and small towns. In these contexts the potential improvements would affect both environmental and socio-economic issues. This necessary transition can be achieved with better management of energy and natural resources, especially through the production of energy based on biomass and agricultural byproducts . In fact, among the various sources of energy, the sustainable use of forestry origin biomass together with agriculture and animal waste are a very high energetic and technological potential resource.

In order to boost the bioenergy transition, the following topics need to be further investigated: development of novel prototypes for the energetic exploitation of biomass at small/micro-scale; development of novel, affordable, cost-efficient biogas monitoring and purification systems; assessment of emission factors for alternative biofuel production plants and life cycle assessment of renewable energy processes.

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SMURBS. MIGRANTS IN SMART CITIES: THE CONTRIBUTION OF EO DATA

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INTRODUCTION

According to United Nations (UNs) "World Urbanization Prospects: 2014 Revision" in today's increasingly global and interconnected world, over half of the world's population already lives in urban areas. The study also states that the coming decades will bring further profound changes to the size and spatial distribution of the global population, in view also of increasing migration processes. The continuing urbanization is expected to reach a population of 2.5 billion by 2050 with the world population living in cities increasing to 66%. Under these circumstances, sustainable development challenges will increasingly regards the living and environmental condition of every expanding cities.

The Horizon2020 ERA_PLANET STRAND1 project named *SMart URBan Solutions for air quality, disasters and city growth* (SMURBS) aims to promote and coordinate the "smart city" approach within a European network of cities (http://smurbs.eu/). The project deals with how to serve the needs for a common approach which may enhance environmental and societal resilience to urban pressures. The major emphasis is on how to prevent, monitor and control air pollution, natural disasters (Rapisardi *et al*., 2013), urban sprawl and migration pressures (European Migration Network link; Johansson, 2002). To this purpose, arguments are posed setting the stage for integration of the still fragmented, multi-scale and multi-temporal Earth Observation (EO) resources to provide information and decision making tools to be at hand for individual citizens and local-regional government decisions.

Needless to say, the increasing migration pressure in Europe, due to natural disasters caused by climate change, urban expansion, civil wars, global economic and financial crisis, will have both negative and positive impacts on the quality of life in urban areas. As already reported, many migrants/refugees camps in countries used as preliminary landing areas in Europe have suffered severe deforestation, due to fire-wood shortages in dry-land camp areas, desertification, land degradation, unsustainable groundwater extraction, and groundwater pollution and problems with waste management. In addition, for many countries, uncontrolled migration is already generating inequalities within urban areas. In fact, unless adequately managed, migration can contribute to further deteriorate urban, environmental and social resilience and increase poverty (Esman, 1985, Perrings 1998, Forman 2014).

Although the identification of both legal and illegal refugee camps is made by local/regional authorities, the wellbeing of both refugees and citizens should be based on short term and long-term planning. To this effect, the SMURBS project proposes the use of Earth Observation (EO) data and smart technologies to support public decision-makers in the search of novel, efficient, effective and economic approaches for sustainable governance of the evolving urban complexities.

SMURBS activities, related to urban growth accelerated by migration, which are phased by CNR_IIA researchers, include the following steps:
• Designing and developing a prototype knowledge-driven system based on the integration of multi-sensor and multi-scale EO (in-situ, airborne, satellite) data and Citizens Observatories data, as further development of the system described in (Lucas *et al*., 2015, Lucas *et al*. 2018). The system will provide new downstream services and Urban Essential Variables (EVs), as well as protocols for their systematic monitoring, to support the work of

policy makers, urban planners and humanitarian bodies.
• Building bridges between the project and on-going local, and national programs/initiatives.
• Providing links to relevant decision makers at the European and global level to prove the usefulness of the EO based approach and address Sustainable Development Goal (SDG) 11.
• Promoting the adoption of GEOSS Data Sharing (DSP) and Data Management (DMP) Principles and the use of open specifications in the provision of urban scale data and information.

METHODOLOGY

The SMURBS project is based on the concepts of nature based solutions and urban ecology (Forman 1995, 2014), which consider urban cities as ecosystems, i.e., interactions of plants and animal organisms, built structures (road and buildings), and the physical environment (soil, water and air) where people are concentrated. The urban ecosystem boundaries cannot be considered as stable since they depend on questions and pressures, which are in continuous evolution and must be addressed as such. The use of an ecosystem perspective, representing cities as complex adaptive systems, will allow developing tools for: (i) addressing the monitoring and inter-linkages of nature, food-water sources and sinks, built systems and built areas and then (ii) assessing levels of urban sustainability and resilience. Specifically, within WP3 and WP5, EO available data and new services (products) will be used to identify patterns and processes in support of urban planners, decision makers and urban ecologists to prepare for, withstand and respond faster to the (often uncontrolled) migration process.
The EO data shall be identified on the basis of the requirements of the atmospheric or terrestrial products needed for the tools development (i.e., spatial resolution, revisit time, data/products harmonization).

In such context, much attention will be addressed to: (i) identify new potential areas for hosting migrants and provide useful direct and indirect local measurements on the status of these areas (e.g. proximity to vital resources, such as water, green areas, infrastructures); (ii) improve living conditions for both citizens and migrants by fostering urban biodiversity and its conservation; (iii) interrelate environmental pressures affected or induced by migration. Study areas under observation include critical sites such as Lampedusa and Bari, Athens and Mytilene, in Italy and Greece, respectively.

FINDINGS

The SMURBS project started in September 2017. So far, end-users requirements have been collected A training workshop, which was held in Hamburg in March 2018, was attended by several end-users. The discussion provided evidence that while public authorities have knowledge about in-situ local information, they lack know-how about how to exploit EO data both for urban growth applications and for the solution of migration problems. The discussion also indicated that EO data products might provide information about the most suitable areas to locate migrants, for both short and long-term stays, and may also define air quality, water/soil pollution state, biodiversity and ecosystem services conservation. However, the EO findings may not always be acquired and used by decision makers. In view of the Italian migrant hosting rules, decisions about where to locate migrants depend on different factors including economic and other impediments. Moreover, the lack of confidence with EO data by most public authorities can hamper communication between them and EO researchers, thus impeding applications of EO data and techniques for possible solutions of emerging problems.

Some of the participants in the meeting pointed out the need to train public personnel in order for them to become familiar with EO data and interact productively with researchers. Obviously, many questions were left open for further discussion, pending suitable data obtained by the project in the future.

CONCLUSIONS

EO data and techniques combined with socio-economic data are proposed in the effort to provide smart solutions to complex and costly problems related to urban growth, allocation of migrants, discovery of suitable areas for improve urban resilience. In addition, to these environmental issues, the project also explores strategies to improve communication between researchers, urban planners and decision makers to increase collaboration between the communities and foster new markets for EO products.

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IGOSP – INTEGRATED GLOBAL OBSERVING SYSTEMS FOR PERSISTENT POLLUTANTS

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Keywords: Data Integration, Mercury, POPs, Leveraging, Policy

ABSTRACT

iGOSP, Integrated Global Observing Systems for Persistent Pollutants, is part of ERA-Planet, the "European Network for observing our changing planet", and addresses "Global change and Environmental treaties". iGOSP will build on, and add value to, ongoing work in support of the Minamata (mercury) and Stockholm (Persistent Organic Pollutants) Conventions. This knits seamlessly with the Group on Earth Observations flagship GOS^{4}M and initiative GOS^{4}POPS, and adheres to the objectives of the EU Copernicus Programme.

INTRODUCTION

Central to the iGOSP project is a platform providing a one-stop hub, whereby users can access data, tools, work-flows, monitoring site status, and services. The platform is the project's main interface with the public, policy makers and the scientific community.

While the project essentially aims to strengthen and support existing networks initiatives / programmes, the platform will provide a step-change in persistent pollutant data utilisation, enhancement and exploitation. The platform is envisaged to be a multi-purpose work space to facilitate the production of Insights, Outputs and Products of use to a wide range of 3rd party end-users in formats appropriate and applicable for the users' specific requirements.

The platform will provide:

• Access – observational data, ancillary parameters (chemical, meteo, climate)
• Tools – geospatial selection, temporal selection, category selection (coast, altitude, maritime)
• Workflow applications – trend (spatio-temporal) analysis, plots/maps/advanced visualisation, comparison of dataset characteristics (EMD, superstatistics)

which in turn facilitate:

• Investigations – links, comparable trends, relationships in datasets
• Scenario design – what if? (emissions / climate / socio-economic change)
• Instigation of External Tasks – modelling, the targeting of sites / campaigns / periods / atmospheric parameters, resulting in: *Insights, Outputs and Products*. Thereby promoting the progression from: Observation → Information → Knowledge.

METHODOLOGY

iGOSP is divided into a number of work packages. Two of these deal specifically with conveying the existing monitoring networks for POPs and Hg to the Group on Earth Observations (GEO) initiative Global Observation System for Persistent Organic Pollutants (GOS^{4}POPS) and flagship Global Observation System for Mercury (GOS^{4}M); in line with the Global Earth Observation System of Systems (GEOSS) standards of data availability interoperability and metadata quality. These work packages will also look to extend the current network to areas and environments/ecosystems where currently monitoring data is scarce. The extension of the current monitoring networks will use both established techniques (instrumental and sampling followed by laboratory based analytical techniques) as well as passive samplers, and will begin to deploy newly developed sensor-based detection systems. The trial of newly developed monitoring devices alongside longer established instruments / sampling techniques in a range of field conditions is fundamental before their deployment over a wider scale.

Two further work packages concern the integration of in-situ measurement data with data from satellite observations, one is concerned with land-based sites and the other with marine measurements. These work packages will enhance existing and forthcoming Hg and POPs data, with ancillary data regarding physicochemical characteristics of the atmosphere, and the ocean, which can be used to gain insight into contaminant cycling and fate.

Three further work packages provide data services and tools, both from the project itself and from collated historical data from worldwide monitoring programmes, measurement campaigns and also modelling initiatives.

These will supplement and enhance the current instrument and laboratory based techniques used in the field.

The third in this series of work packages will ensure interoperability, and provide midstream and downstream services. Midstream (or middleware) services connect diverse data systems and harmonize shared data and information content to provide an entry point for the application developers. The mid-stream service layer APIs (Application Program Interfaces) are to be utilized to advance the down-stream services and provide the end users with effective and usable applications. These APIs will then be used to ensure full interoperability with relevant infrastructures (European and international), notably Copernicus services and the GEOSS Portal.

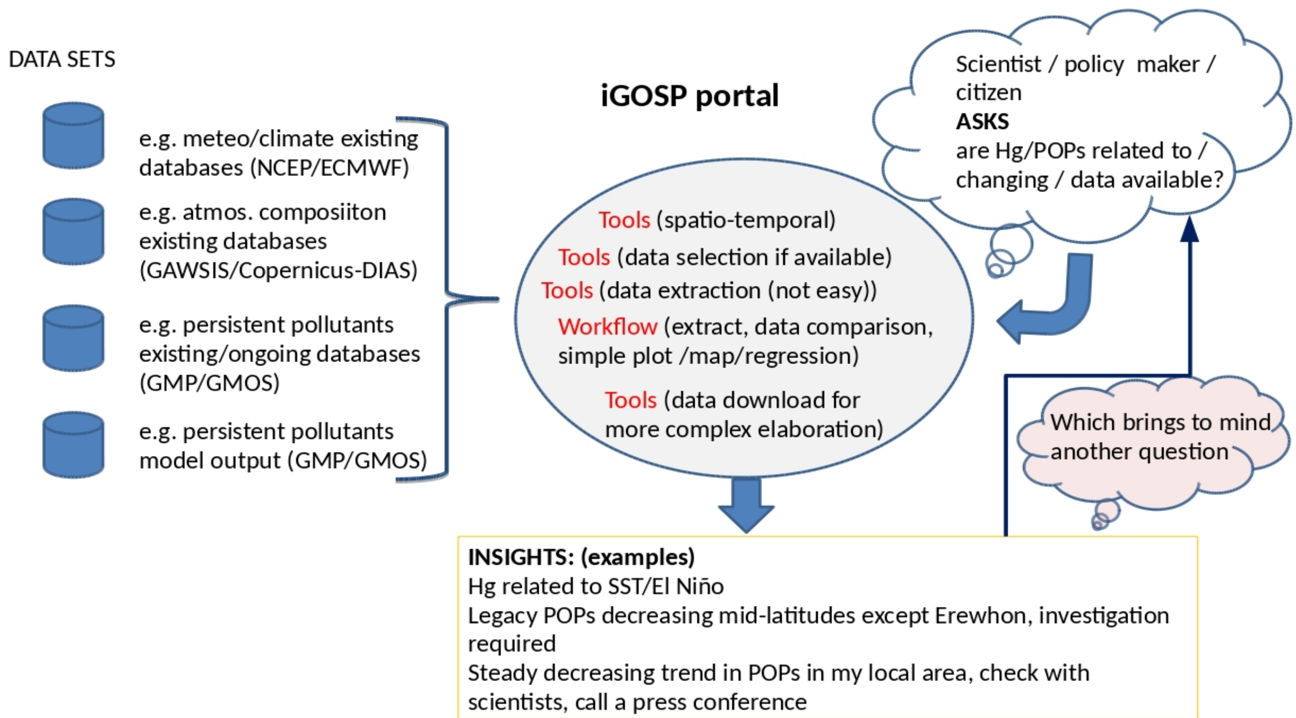

FIGURE 1. **A SCHEMATIC OF THE IGOSP PLATFORM PROTOTYPE**

One work package is targeted specifically at the move "from atmospheric modelling to services and tools", as currently modelling output tends to be published in scientific journals and model output tends to remain on university servers, undiscoverable and unusable by other researchers or 3rd parties. This work package will also investigate the provision of tools to provide emission scenario studies. The two other work packages concentrate on upstream, midstream and downstream services. One concentrates purely on upstream data services, and data sharing/publication. This work package includes the controls familiar in more traditional QA/QC approaches, but with additional tools made available to data providers. The work package also envisages the development of protocols, and connectivity interfaces to encourage the use and development of sensor technologies and multi-sensor platforms.

THE IGOSP PLATFORM

The platform should be a point of reference where researchers, the curious public, our funders and policy makers can primarily see the progress of the project and gain an insight into the project results. However it is intended to be much more than this as can be seen in Figure 1.

The Platform allows users to query the availability of Hg and POPs data in spatio-temporal terms, where and when? It also permits the user to query, and if desired, access, ancillary data for the same and place. Although including this search/query possibility is a technically challenging and potentially laborious task, it will provide a not only a powerful research tool but also contribute to the dissemination and use of the data generated in this and previous projects. This is perhaps most easily illustrated by a couple of simple examples. POPs and Hg concentrations in air and water are influenced by the chemical and physical properties of the atmosphere, the land and the ocean. In searching for the links that can give an insight into the parameters which are most important in determining the variation of measured variables, in this case, atmospheric concentrations, looking for common patterns in data series is often used. A simple example would be plotting a linear regression between and a pollutant concentration and for instance a meteorological variable such as temperature, humidity of boundary layer height.

More complex examples would be investigation of pollutant time series in different locations or in comparison to climate indicators, see Carbone *et al*., 2016, 2018.

Equally it will be possible for policy makers to visualise pollutant time series for monitoring stations in their regions, and to see how modelling studies suggest this may change under differing emission scenarios.

CONCLUSIONS

The potential of the iGOSP project and the iGOSP platform to bring new insights and a wider audience to past and current persistent pollutant monitoring research is huge. It will necessarily highlight the temporal gaps in the monitoring record, and will shine a glaring spotlight on the paucity of monitoring over vast areas of the globe, specifically most of Africa and South America, and the Southern Hemisphere in general. Indeed it seems almost bizarre that there is more widespread and continuous monitoring in the Arctic than there is Africa. Awareness building is a major aspect of leveraging the data available in order to promote wider monitoring coverage.

Making data available in this way also encourages broader cross-disciplinary research initiatives, as researchers, stakeholders and other interested parties will have the opportunity to compare data with which they are familiar, with data obtained by researchers in other fields. This allows more profound and transverse investigations into the processes underlying environmental contaminant cycling by experts in a wide range of fields.

The hope, or rather expectation, is that the iGOSP platform will herald new approaches and with them new discoveries in environmental contaminant research and understanding

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STUDY OF THE SNOW COVER IN THE ICUPE PROJECT

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***Keywords*:** snow cover, remote sensing, Arctic, webcam, snow reflectance

THE ICUPE PROJECT

The iCUPE (Integrative and Comprehensive Understanding on Polar Environments) project is part of the ERAPLANET project. “The overarching goal of ERA-PLANET is to strengthen the European Research Area in the domain of Earth Observation in coherence with the European participation to Group on Earth Observation (GEO) and the Copernicus”.

Goal of the iCUPE project is to provide a picture as complete as possible of the state of the environment in the polar regions, with particular reference to the Arctic regions where significant changes are taking place due both to climatic variations and to the increasing actions of exploitation of natural resources with consequent growing of the anthropized areas (modified by the anthropization). The project, aimed to define the state of the Arctic environment, provides an integrated approach that combines in situ observations of different types (chemical, physical and biological), satellite remote sensing observations and multi-scale modeling.

The iCUPE project is coordinated by University of Helsinki (Finland) and more than 10 European organizations are involved; the beneficiaries are leading European expert organizations (CNR - Italy, NCSR - Greece, AU - Denmark, AWI - Germany, TROPOS - Germany, GFZ – Germany, HZG - Germany, CNRS - France, EULS - Estonia, FMI - Finland, SU - Sweden and PSI - Switzerland) with complementary expertise working in the polar area.

IIA is involved in particular on Task 3.2 that is focused on the characterization of the Arctic surfaces and on the analysis of their changes using Landsat 8 and Sentinel 2 multispectral satellite images. The main effort of this activity will be directed, in particular, to the analysis of snow coverings whose spatial and temporal distribution represents a key element for studying the delicate balance of the Arctic environment.

REMOTE SENSING OF THE SNOW

It is well known that the snow reflectance in the visible and near-infrared wavelengths is controlled by the grain, shape, size and thickness of the snowpack. Furthermore, the occurrence of impurities (dust, soot, pollen and other plant materials) and liquid water content can affect the spectral behavior of snow. The snow reflectance, in particular, is higher in the visible part of the electromagnetic spectrum and it decreases rapidly at longer wavelengths. The increase of grain size determines a decrease of reflectance all over the spectral range from visible to short wave infrared (350-2500 nm). Snow is a highly unstable target and structural changes in grain size and shape may occur quite rapidly so that snow reflectance decreases with time and its value can be used as an indicator of the beginning of the snow melting (Wiscombe & Warren, 1980; Winther *et al*., 1999; Painter *et al*., 2009). Multispectral satellite images, acquired in the spectral range between 350-2500nm, can be therefore successfully used to discriminate snow surface and also to study their microphysical characteristics (Dietz *et al*., 2012, Painter *et al*., 2013).

The most used parameter to describe the distribution of snow on the surface with remote images is the Normalized Difference Snow Index (NDSI) that is computed using reflectance value corresponding to the a visible interval (0.53–0.61 µm) and a near-infrared range (1.55–1.75 µm). In these spectral intervals the snow has a peculiar spectral behavior and it is, therefore, easily differentiated not only by soil and vegetation but also by clouds (Dozier, 1989). The availability of remote sensed images in the Arctic region is unfortunately affected by cloud coverage and low illuminating conditions. This gap has been overpassed combining remotely sensed images and terrestrial photography allowing the reconstruction of the snow cover evolution (Hinkler *et al*., 2002, Hinkler *et al*., 2003).

EXPECTED RESULTS

The purpose of the iCupe IIA activity is the development of a new snow product focused on the estimation of the fraction of snow cover in selected sites at different spatial resolutions. This dataset will be aimed to support the estimation of cryospheric information using remotely sensed data, with a particular attention to data obtained in the framework of the Copernicus program. The availability of this dataset in a "natural" laboratory such as Svalbard islands (Figure 1) will support the reduction of the gap between remotely sensed data and modeling activities. This added value will be very important considering the higher spatial resolution of the sensors recently deployed. The dataset will be based on re-using data obtained from public repositories such as the digital elevation model of Svalbard, the available webcam imageries in Svalbard and satellite products from Landsat, Sentinel and MODIS missions. All the available data will be integrated in order to estimate the fraction of snow cover, at different spatial resolutions, for each satellite mission. These estimations, computed at different sites in Svalbard islands, will offer the opportunity to better integrate results obtained by remote sensing with modeling and air-snow interactions studies. Particular attention will be devoted to the formalization of agreements with raw-data providers in case of not-public licensing policies.

Figure 1. The study area of Svalbard Island

The activity will be focused in the first year on the NyAlesund area, where the Italian Arctic Station is located and a complete setup of cameras and instruments is present. The camera network includes panoramic views of the Brogger Peninsula and plot-scale images of area nearby the Climate Change Tower. In addition of that, spectroradiometric datasets of the same regions are available (Casacchia *et al* 2001, Valt & Salvatori, 2016) and the continuous estimation of the NDSI can be obtained by using the Continuous Reflectance Monitor facility deployed close the CCT tower (Salzano *et al*., 2016). The extension of the studied area will considered in the following years, when additional sites will be included. Cameras are, in fact, available also in Longyearbyen (Central Spitsbergen) and Hornsund (South Spitsbergen).

Furthermore, in order to monitor the snowpack characteristic, in the iCUPE project we are going to develop a methodology to integrate all of these available data with the satellite Landsat images, accessible through the USGS catalog and Sentinel 2 images, made available by ESA.

The starting point of the considered approach will be the snow-nosnow software already developed for webcam images acquired in the Alpine region (Italy) by Salvatori *et al*. (2011). Merging satellite images with ground data and processing webcam pictures with a semi-automatic procedure will make possible to estimate the variation of the snowpack reflectance, to calculate the normalized snow index and the seasonal distribution of the snow cover (Figure 2).

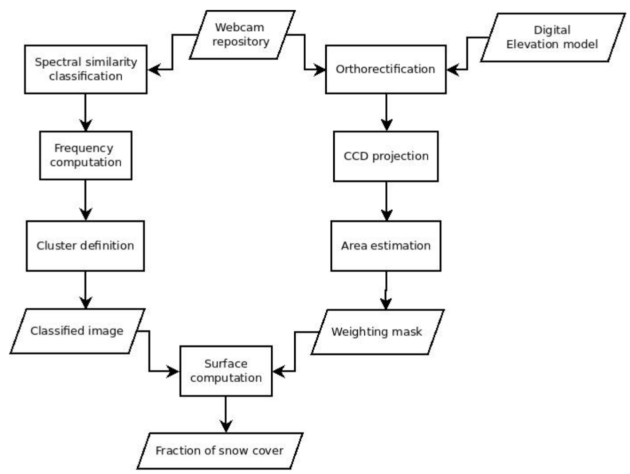

Figure 2. Description of the image processing required for estimating the fractional snow cover area

We expect to export this approach also to other areas, where satellite data and webcam pictures are available, not only located in the Arctic but also in mountain regions at lower latitudes.

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AN INTEGRATED SYSTEM FOR MULTISCALE ANALYSIS OF ECOYSTEM FUNCTIONS AND SERVICES IN PROTECTED AREAS WITH EO DATA IN SUPPORT TO GEOSS IN ECOPOTENTIAL PROJECT

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***Keywords*:** ecosystem monitoring, land cover classification, change detection, gross primary productivity, invasive species, wind field retrieval

INTRODUCTION

ECOPOTENTIAL (2015-2019) addresses the data-to-information-to-decision-making process for ecosystem services, using novel approaches of Earth System and Natural Sciences and building on concepts including Macrosystem Ecology, biogeographical developments and the coupled dynamics of climate-landscape-ecosystem processes. More specifically, ECOPOTENTIAL has the following objectives:

- Extensive use of Earth Observation (EO) data in combination with in situ monitoring. The project products would be accessible through GEOSS (Global Earth Observation System of Systems).
- Create a corpus of innovative, field-tested, monitoring methodology to define the ecological status of current and future protected areas, based on EO and in situ data.
- Develop new ecosystem models for best use of EO and monitoring data.
- Make accessible and available data, scientific results, models and information through a cloud-based Virtual Laboratory.
- Quantify ecosystem services, taking into account social demand.
- Improve evidence-based environmental policy making.

The project involves 4 different communities. Three of them are directly involved in the project partnership: ecologists, remote sensing people and modellers. The fourth community is composed by managers of the protected area that participate as project stakeholders. The *a priori* knowledge of the protected areas dynamics and criticalities were formalized in 22 storylines that serve as guide for the coordination of the 47 project partners.

CNR-IIA participation is two-folds: the group of Florence works to integrate the project outcomes within GCI; the group of Bari works to extract information from remote sensing data.

METHODOLOGY

CNR-IIA researchers are mainly involved in three Working Packages (WPs). The first focuses on Earth Observation (EO) data collection (WP3). The second concerns data processing (WP4) spanning from Land Cover/Use (LC/LU) mapping, plant alien species discrimination, geophysical variable extraction, such as coastal wind estimation from SAR Sentinel 1 data, and time series analysis for change detection and seasonality features extraction of gross primary productivity (GPP). In the third WP, CNR-IIA researchers lead the Virtual Laboratory (VLAB) design and development (WP10). The ECOPOTENTIAL VLAB will be a major contribution to GEOSS through the interoperability with the GEOSS Platform. It will allow publishing ECOPOTENTIAL products reinforcing the GEOSS Data-CORE concept and implementation. New algorithms, products and essential variables, based on improved access (notably via GEOSS) to long-term EO data and information in existing PAs, for the monitoring of ecosystem status and services will be made available by the end of the project.

a) *Land Cover/Land Use classification*

Specifically, the knowledge based classification system (Lucas *et al*. 2015), developed in previous (www.biosos.eu) FP7 BIO_SOS project, has been extended in order to analyze new Sentinel 2 data and provide a framework which can integrate multi-source thematic layers and geophysical variables for ecosystem monitoring. This line of research was carried out in collaboration with Aberystwyth University. The software that implements the approach termed Earth Observation Data for Ecosystem Monitoring (EODESM), can analyze both Very High Resolution (VHR) (WorldView-2) and medium-high resolution data at pixel level or within a Geographic Object-Based Image Analysis (GEOBIA) framework. As output, EODESM can provide LC/LU in the Food and Agriculture Organization (FAO) Land Cover Classification System (LCCS) taxonomy (Adamo *et al*., 2015; Lucas *et al*., 2018) as well as essential geophysical variables.

In the Murgia Alta site, *Ailanthus altissima* alien species distribution was extracted from the VHR LC/LU map produced. The data obtained can favour the quantification of species distribution prior and post-eradication activities. The invasive species mapping work carried out in close collaboration with in-situ activities for validation purposes.

b) Analysis of vegetation indices from dense LANDSAT and Sentinel-2 time series

1) The seasonality of vegetation Primary Productivity (PP), an essential ecosystem variable, can be summarized in the so called Ecosystem Functional Type framework (EFT; Alcaraz *et al*., 2006) using 3 features extracted from EO data time series: mean, coefficient of variation, day of seasonal peak. The ecologists wonder if the latter can be a driver of animal diversity (Gandini *et al*., 2018). Within the cloudy Atlantic mountain of Peneda-Geres different vegetation indices were used, as proxy of PP, to extract seasonality features to place pixels in the space of the Ecosystem Functional Type and correlate it with already available bird biodiversity observations. In order to ensure robust feature estimations in presence of thick cloud cover, we fitted, with a least square approach, an explicit harmonic model having annual, semester and quadrimester components (Forkel *et al*., 2013).
2) The development of satellite sensors, such as Landsat-8 and Sentinel-2, can improve the capability of remote sensing data to follow phenological behaviour of vegetated classes, thanks to acquisition of both high spatial and temporal resolution inter and intra-annual time series. Thus, the reliability of Vegetation Indices time-series seasonality features are being investigated to improve automatic classification of LC/LU and Change detection and class trend extraction in the Murgia Alta site. Landsat 5 TM, 7 ETM+, 8 OLI/TIRS atmospherically corrected (level 2) surface reflectance images are being used to build stacks of cropped clouds and shadows masked images for a set of selected spectral indices. The period understudy extends from 2010 to 2017. All modules are being developed in open source R code.

c) Geophysical variable extraction from SAR data

SAR-derived Sea Surface Wind (SSW) retrieval from Sentinel 1 was carried out for two protected areas with relevant impact of coastal wind: the Wadden Sea (Netherlands, Germany and Denmark) and the Camargue (France). The algorithm applied (i.e., the LG-Mod, Rana *et al*., 2016) allowed providing local wind directions together with their related directional accuracies (expressed as marginal error values). SAR wind directions and the corresponding CMOD5.N-derived (Hersbach, 2010) wind speeds were compared with the ones from global and regional Numerical Weather Prediction (NWP) models and in-situ wind measurements, where available. The LG-MOD algorithm will be further developed to include multi-scale data analysis.

FINDINGS

a) Automatic alien species detection provided an overall accuracy equal to 84% and 97% after 3X3 low-pass filtering. Thus, the proposed methodology can lend support to site managers in the monitoring of the alien plant expansion (Tarantino *et al*., submitted on March 2018).

b.1) Through mean variance explained across pixels, the explicit model approach for the estimator of vegetation index seasonality allowed to identify, on the one hand, MSAVI as the best among the nine vegetation indices tested; on the other, it indicated the harmonic model with the following parameters: three seasonalities and one annual mean, as the best model implementation. Simulation showed both that the model is sufficiently robust for cloud cover typical of the area investigated and that it can yield better results than the empirical seasonal feature estimator.

b.2) The analysis of a set of intra- and inter- annual time series of different spectral indices extracted from Landsat and Sentinel-2 allows not only to characterize temporal trend of vegetation targets used as input of a supervised classification method, but also to improve the accuracy of the Land Cover classification mapping. Changes and break point (abrupt changes) are detected for different object targets of the scene. Trends obtained using different sensors are going to be investigated shortly.

c) The analysis of local winds in the two coastal areas examined, each characterized by very different orography, yielded fruitful indications on the use of SAR wind fields and NWP model wind data in such areas. SAR wind fields retrieval proved capable of reproducing reliable spatial characteristics of local winds. Instead, weather models wind retrieval resulted to be affected by significant estimation errors, especially when the wind blows from the land to the sea. These findings suggest that SAR wind fields may support and complement NWP models for an operational wind monitoring aimed at both conservation and prediction of coastal ecosystems status.

CONCLUSIONS

THE REUSABILITY OF ALGORITHMS AND THE UPDATING OF PRODUCTS OBTAINED IS PARAMOUNT TO PRODUCE USEFUL KNOWLEDGE FOR STAKEHOLDERS. IN THESE PERSPECTIVE, THE MAIN EFFORT OF THE PRESENT PROJECT IS MAKING SCIENTIFIC MODELS FOR KNOWLEDGE GENERATION AVAILABLE AND RUNNABLE THROUGH THE ECOPOTENTIAL VIRTUAL LABORATORY, FULLY INTEGRATED WITH THE GEOSS PLATFORM VISION AND IMPLEMENTATION.

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EARTH BIG DATA CHALLENGES: THE GEOSS EXPERIENCE

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Keywords: information, brokering approach, data sharing

Earth Observation data are growing in size and variety at an exceptionally fast rate. New satellite, airborne and ground-based remote sensing systems characterized by high spatial, temporal and radiometric resolution are, or will be soon, available; the increase of computing power enables simulations at a global scale with unprecedented accuracy; new kind of sensors and applications transform tablets, smartphones and car-navigators in crowdsourcing observing systems delivering an incredible amount of information. That is a great opportunity to enhance our knowledge of the Earth System, but it also poses great challenges to both scientists and information technology experts (Bargellini *et al*., 2013). According to many scientists and technologists, the increasing availability of observations from sensors and models, coupled with the ever-growing computing power provided by new technologies including Cloud systems, would enable an entirely new approach to science based on data intensive scientific discovery. That would entail a real paradigmatic shift, introducing the so-called Fourth Paradigm (Hey *et al*., 2009). However, to make it a reality, it requires innovative enabling technologies for the management, analysis, delivery and presentation of large amount of data. CNR-IIA is carrying out research on the impact of Big Data dimensionalities (commonly known as 'V' axes: volume, variety, velocity, veracity, visualization) on the Global Earth Observation System of Systems (GEOSS) and particularly its common digital infrastructure (i.e. the GEOSS Platform, a.k.a GEOSS Common Infrastructure). GEOSS is a global and flexible network of content providers allowing decision makers to access an extraordinary range of data and information. It is a pioneering framework for global and multidisciplinary data sharing in the EO realm. GEOSS implemented a brokering framework interconnecting several existing federated systems. CNR-IIA designs, develops and operates the GEO DAB (Discovery and Access Broker) providing broker components for Discovery (Nativi and Bigagli, 2009), Access (Boldrini *et al*., 2013) and Semantics-enabled Search (Santoro *et al*., 2012) functionalities. To address Big (Earth) Data challenges for discovery and access, the GEO DAB fully exploits advanced capabilities provided by Amazon Web Services (load balancing, elastic computing and storage, etc.) to enable data search and transformations. It also makes use of a high-performance XML database for metadata storage to provide fast search and results ranking. The GEO DAB allowed GEO to build GEOSS as a system of systems interconnecting more than 150 autonomous and heterogeneous infrastructures.

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GMOS GLOBAL NETWORK AND ITS KEY ROLE IN THE FRAMEWORK OF INTERNATIONAL PROGRAM AND THE MINAMATA CONVENTION IMPLEMENTATION

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Keywords: GMOS, Hg global network, GOS^{4}M, Minamata Convention, UNEP-GEF

INTRODUCTION

Although in the past two decades a number of mercury (Hg) monitoring sites have been established as part of regional networks and/or European projects, the need to establish a global network to assess southern–northern hemispheric gradients and long-term trends has long been considered a high priority not only for scientific purposes but also for policy objectives to support major international program and Conventions on Hg. In 2010, a coordinated global observational network for Hg was established within the funded FP7-GMOS project (www.gmos.eu) to provide high-quality Hg datasets for a global assessment of Hg concentrations and their dependence on meteorology, long-range transport and atmospheric emissions (Figure 1). Hg observations from these sites have been used to validate regional and global-scale Hg models for assessing Hg global patterns, deposition and re-emission fluxes, and to provide a valuable contribution to international policy development and implementation. The Executive Committee of the Global of Earth Observation (GEO) selected GMOS as a showcase able to support the convention and policies as well as pioneering activity in environmental monitoring using highly advanced e-infrastructure developed to allow the sharing of observational and models output data produced. GMOS grown up in fact within the international context and, particularly in the framework of the previous GEO work plan (2009-2011 and 2012-2015), and currently is part of the GEO strategic plan (2016–2025) within the GEO flagship on "tracking persistent pollutants" GOS^{4}M (Global Observation System for Mercury) aimed to develop a global monitoring network for Hg. One of the important objective of this flagship is to support the achievement of current goals in major international program (i.e., GEOSS, UNEP-GEF, UNECE-LRTAP TF HTAP) and Conventions, particularly the Minamata Convention by fostering research and development of new advanced sensors to make sustainable the management costs of long-term monitoring programs on global scale as GMOS is the case, and improve Hg spatial data coverage, particularly in Southern Hemisphere and Tropics throughout the employment of new technologies. In this context, as part of the UNEP-F&T partnership area, a pilot project in cooperation with WHO, has been funded by UNEP-GEF with the aim to develop a Hg monitoring plan for "human exposure to and Environmental concentrations of mercury" to enhance the understanding of Hg concentrations in ambient air through the strengthening of the GMOS network and the development of the complementary passive air samplers (PASs) network for Hg in ambient air.

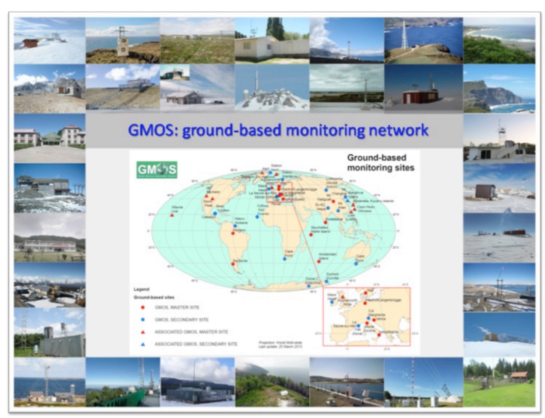

Figure 1. GMOS Master and Secondary monitoring sites worldwide distributed

METHODOLOGY

GMOS network was developed by integrating new GMOS sites established in regions of the world where atmospheric Hg observational data were scarce, particularly in the Southern Hemisphere and

Tropical areas, with previously Hg monitoring stations established by institutions that are part of European and international monitoring programs and managed by GMOS partners and GMOS external partners who have agreed to share their monitoring data and submit them to the central database following the interoperability principles and standards set in GEOSS (Group Earth Observation System of System). GMOS currently consists of 43 globally distributed monitoring stations located both at sea level and high altitude locations, as well as in climatically diverse regions, including polar areas. The monitoring sites are classified as master (M) and secondary (S) with respect to the Hg measurement programs. Master stations perform measurements of gaseous Hg species (both elemental and oxidized) and collect precipitation samples for total Hg analysis, whereas the Secondary stations perform only total gaseous mercury (TGM) measurements and precipitation samples as well. The GMOS objective of establishing a global Hg monitoring network was achieved always bearing in mind not only the necessity to provide intercomparable data worldwide but also international standards of inter-comparability. In particular, GMOS attempts to comply with the data sharing principles set by the GEO that aim to support GEOSS through the use of "observation systems, which include ground-, air-, water- and space-based sensors, field surveys and citizen observatories. Additionally, GMOS makes use of "information and processing systems, which include hardware and software tools needed for handling, processing and delivering data from the observation systems to provide information, knowledge, services and products." It is important to point out that GMOS is a global observational network which includes not only ground-based monitoring sites worldwide distributed but also an (a) Oceanographic Observation Program through oceanographic campaigns performed over major oceans and European seas with the aim to provide key information on Hg species concentrations in the marine boundary layer (MBL), in the top-water microlayer and water column to evaluate the exchange rates of gaseous Hg at the air-water interface, an issue of crucial importance for understanding the global Hg cycle; (b) Aircraft

Observation Program mainly focused on vertical profiling and plume identification/tracking to better quantify and understand the potential range and relative importance of industrial/urban and natural emissions/legacy emissions such as volcanic emissions and forest fires. The program includes aircraft measurements in the lower-middle Troposphere and lower Stratosphere to understand the vertical distribution of elemental and oxidized Hg species at different latitudes both over land and over surface waters on regional and global scale.

DISCUSSION AND FINDINGS

As one of the major finding, GMOS is recognized as unique already existing network developed on global scale which is supporting the objectives of the major international program and Conventions. The GMOS overarching objective to establish a global Hg monitoring network was achieved having in mind the need to assure high-quality observations in line with international quality assurance/quality control (QA/QC) standards and to fill the gap in terms of spatial coverage of measurements in the Southern Hemisphere where data were lacking or nonexistent. One of the major outcomes of GMOS has been an interoperable e-infrastructure developed following the GEO data sharing and interoperability principles which allows us to provide support to UNEP for the implementation of the Minamata Convention from the Effectiveness Evaluation to capacity building, information and public awareness. Within the GMOS network, Hg measurements were in fact carried out using high-quality techniques by harmonizing the GMOS measurement procedures with those already adopted at existing monitoring stations around the world. Standard operating procedures (SOPs) and QA/QC protocols were established and implemented at all GMOS sites in order to assure full comparability of network observations. To ensure a fully integrated operation of the GMOS network, a centralized online system (termed GMOS Data Quality Management, G-DQM) was developed for the acquisition of atmospheric Hg data in near real time and providing a harmonized QA/QC protocol. This novel system was developed for integrating data control and is based on a service-oriented approach that facilitates real-time adaptive monitoring procedures, which is essential for producing high-quality data. The traditional approaches to Hg monitoring QA/QC management that were primarily site specific and manually implemented were no longer easily applicable or sustainable when applied to a global network with the number and size of data streams generated from the monitoring stations in near real time. The G-DQM system therefore, was designed to automate the QA process, making it available on the web with a user-friendly interface to manage all the QC steps from initial data transmission through final expert validation. From the user's point of view, G-DQM is a web-based application, developed using an approach based on Software as a Service (SaaS). G-DQM is part of the GMOS cyber-infrastructure (CI), which is a research environment that supports advanced data acquisition, storage, management, integration, mining and visualization, built on an IT infrastructure (Cinnirella *et al*., 2014; D'Amore *et al*., 2015). In order to increase the GMOS geographical coverage through a consistent number of monitoring sites including rural/background and contaminated sites as well, a fully integrated system of passive samplers for Hg (PASs) based on nano-structured advanced materials has been also developed. In particular, CNR-IIA Hg PASs have been developed with the aim to reduce the costs associated to the monitoring program worldwide and make the program on global scale more manageable and robust. Hg PASs have been employed and tested within the UNEP-GEF pilot study for the developing of a Hg monitoring network on global scale to support policy makers and stakeholders in the implementation of several articles of the Minamata Convention.

CONCLUSIONS

Long-term atmospheric Hg measurements across the GMOS global network and additional new GMOS monitoring sites increasingly incorporated into strategic areas are crucial to continue in the next future in order to provide high-quality measurement datasets which can give new insights and information about the worldwide trends of Hg. The overarching benefit of this coordinated Hg monitoring network would clearly be the advancement of knowledge about Hg processes on a global scale due to model/measurement comparisons, to study long-range transport pathways of persistent pollutants and their precursors. The experience gained during GMOS, the development of SOPs for Hg monitoring and the establishment of the Spatial Data Infrastructure (SDI) along GEOSS lines, which includes the G-DQM system, provide a template to aid countries complying with the requirements of Article 22 of the Minamata Convention. GMOS is currently playing a key role in terms of:

(a) Continuous monitoring of Hg in atmosphere, marine and terrestrial ecosystems in cooperation with UNEP, GEF, WHO and major international programmes;

(b) Technological development of advanced sensors aiming to reduce the investment and running cost of long-term monitoring programmes;

(c) Assist nations in preparing and implementing their National Implementation Plans (NIPs);

(d) As part of UNEP F&T GMOS is supporting the implementation of several articles of the Minamata Convention from the Effectiveness Evaluation (Art.22) to capacity building, information and public awareness (Art.14, 17, 18, 21);

(e) Continuous engagement of the scientific community in the policy making process to assure that decisions will be taken on the state-of-the-art knowledge of different aspects related to Hg emissions, monitoring and exposure evaluation of both environmental ecosystems and human health.

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GMOS NETWORK AND THE UNEP-GEF PROJECT TO DEVELOP A MONITORING PLAN FOR HUMAN EXPOSURE TO AND ENVIRONMENTAL CONCENTRATIONS OF MERCURY

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Keywords: GMOS, global network, mercury, UNEP-GEF, Minamata Convention

INTRODUCTION

The overarching benefit of a coordinated monitoring network for mercury (Hg) on global scale would clearly be the advancement of knowledge of all processes characterizing the Hg distribution in the environmental ecosystems, its spatial and temporal patterns, re-emission rates from and deposition fluxes to aquatic and terrestrial receptors for different emission scenarios. GMOS (Global Mercury Observation System), is a global observational network which includes observations from continuous ground-based monitoring stations worldwide distributed, ad-hoc over-water observation programs, and aircraft-based tropospheric programs. The global network has been established since 2010 with the aim to provide high-quality datasets for a global assessment of Hg concentrations and their dependence on meteorology, long-range transport and atmospheric emissions. One of the major outcomes of GMOS has been an interoperable e-infrastructure developed following the Group on Earth Observations (GEO) data sharing and interoperability principles, which allows us to provide support the objectives and goals of major international program and Conventions (i.e., Minamata Convention). GMOS network is to date recognized as unique global network whose activities are currently part of the GEO strategic plan (2016–2025) aimed to develop a global observing system for Hg and POPs. Particularly GMOS is part of the GEO flagship on “tracking persistent pollutants” GOS^{4}M (Global Observation System for Mercury). One of the important goal of this flagship is to support the technological development by fostering new advanced sensors to make sustainable the management costs of long-term monitoring programs on global scale as GMOS and improve the spatial coverage of observations. Since automated measurement methods for Hg often require power, carrier gases like argon, and significant operator training, they are difficult to apply for understanding Hg air concentrations and deposition across broad regional and global scales. Therefore, the lack of an inexpensive, stand-alone, low-power, and low-maintenance sensor is a primary technical issue to be solved for the sustainability of a global network such as GMOS. In this context, as part of the UNEP-F&T partnership area, a pilot project in cooperation with WHO, has been funded by UNEP-GEF with the aim to develop a Hg monitoring plan for “human exposure to and Environmental concentrations of mercury” to enhance the understanding of Hg concentrations in ambient air through the strengthening of the GMOS network. The overall goal of the project was therefore to provide elements towards harmonized approaches for Hg monitoring, and to strengthen the capacity for Hg analyses in human and in the environment.

METHODOLOGY AND DISCUSSION

Current air-monitoring devices for Hg are amply sensitive to detect Hg background levels but are costly and high maintenance with complicated configurations and electricity requirements. The most common sampling method employed relies on adsorption on gold amalgam and then, either directly or indirectly, through a stepwise process of thermal desorption and final detection (usually by cold-fiber atomic absorption spectroscopy, CVAAS, or cold-fiber atomic fluorescence spectroscopy, CVAFS). Given the uncertainty and restrictions associated with automated and/or semi-automated Hg measurements (Pirrone *et al*., 2013), particularly in responding to the technical needs of an expanding Hg global observation network, CNR-IIA developed a reliable, sensitive, and inexpensive surface for atmospheric Hg detection. In particular, CNR-IIA investigated and demonstrated the utility of composite nanostructured layers of titania decorated with gold nanoparticles (AuNPs) to obtain nanostructured materials capable of adsorbing Gaseous Elemental Mercury (GEM) as a useful alternative system for making regional and global estimates of air Hg concentrations. Previously developed methods and new sampling systems, such as passive samplers, have been used to understand the long-term global distribution of persistent organic pollutants (i.e., POPs). Other passive samplers for Hg collection on the basis of diffusion have been also constructed using a variety of synthetic materials (i.e., gold and silver surfaces, and sulfate-impregnated carbon) and housings but not yet compared each other and in different meteo-climatic conditions. The sampling rates (SRs) using the same passive samplers may in fact depend on the environmental conditions and atmospheric chemistry at each site. The passive sampler, designed and fabricated within CNR-IIA, comprised a nanostructured adsorbing membrane coating a porous quartz slice, a glass vessel and a cap with a protective grid for the exposure to the environment (Figure 1). More specifically, it consisted of an adsorbent membrane made of titania nanoparticles finely decorated with gold nanoparticles (Figure 2). Previously, both the materials (TiO_2 and AuNPs) were successfully used to design and develop novel miniaturized sensors for detecting gaseous elemental Hg in the atmosphere (Macagnano *et al*. 2017a,b), although arranged in different frameworks (specifically, nanofibers for sensors, nanoparticles for passive samplers).

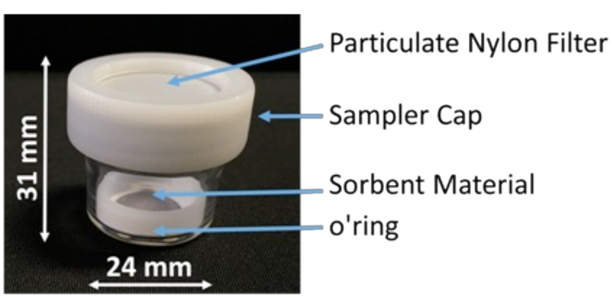

Figure 1. Prototype of Hg Passive Sampler

The nanostructured suspension was deposited on a thin quartz slices (450 μm thick, 20 mm length), dried to 550°C and then incorporated into an axial diffusive sampler in order to be exposed firstly to air polluted with well-known amounts of gaseous Hg for calibration and characterization and secondly to the atmosphere.

Developed and tested Hg PASs have been employed within the UNEP-GEF pilot study for the developing of a Hg monitoring network which included background and contaminated sites to support policy makers and stakeholders in the implementation of several articles of the Minamata Convention from the Effectiveness Evaluation to capacity building, information and public awareness. Six GMOS sites have been involved within the monitoring plan developed within the UNEP-GEF pilot project and involving ten sites worldwide(Figure 3) in order to test active and passive sampling techniques to develop the complementary passive air sampling (PASs) network for Hg concentrations.

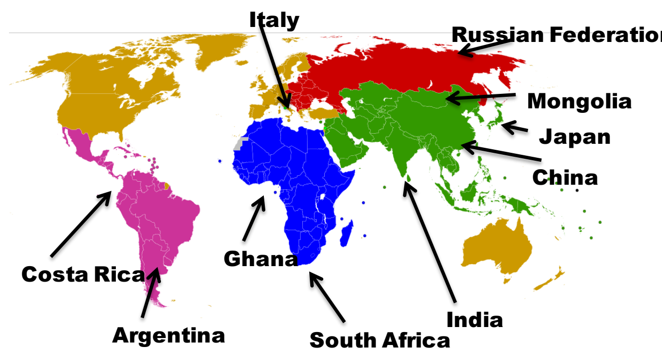

Figure 2. GMOS and UNEP-GEF monitoring sites worldwide distributed

CNR-IIA has selected a set of air monitoring sites composed by two groups of sampling points:

a) the first, at GMOS stations, mostly background/rural sites - for co-exposure of active and passive air samplers;

b) the second, defined in the region where WHO carried out its human-biomonitoring, at highly polluted sites, for exposure of passive air samplers.

The selected air monitoring sites cover all UN regions (i.e., Asia-Pacific, African and Eastern European Groups, Group of Latin America and Caribbean Countries - GRULAC, Western European and Others Group - WEOG) and are located in 10 different countries, as reported in the Table1.

Table 1. Air monitoring sites within UNEP-GEF pilot survey

Argentina –Bariloche-EMMA station	GMOS station, BAR
China - Mount Ailao	GMOS station, MAL
Costa Rica	WHO site
Ghana	WHO site
India	WHO site
Italy - Mount Curcio	GMOS station, MCU
Japan - Cape Hedo	GMOS station, CHE
Mongolia	WHO site
Russian Federation - Listvyanka	GMOS Station, LIS
South Africa - Cape Point	GMOS station, CPO

The sampling pilot survey have been performed over two seasonal campaigns at WHO sites, and over three seasonal campaigns at GMOS stations, in different period of the 2018 yr to study the potential influence of different meteorological conditions on Hg behaviour.

Each air sampling campaign have been scheduled over one month and half during the three different following periods: Feb-March, May- July, Sept-Nov. 2018.

The measurements program has been structured in order to employ a much higher number of PASs that have been co-located and have been exposed for one, two, and three weeks in parallel.

This has allowed to cross check key parameters for the QA/QC: linearity over time, reproducibility, behaviour of samplers at different climate conditions.

FINDINGS

In the UNEP-GEF project the research on the development of new Hg passive samplers and their comparison with the active analysers (Tekran/Lumex) during the three seasonal sampling campaigns at selected GMOS sites was carried out in order to test them in the field.

The campaigns were carried out at six GMOS sites, two of them in the Southern Hemisphere [South Africa (CPO) and Argentina (BAR)]. The developed PAS have been designed to give information about the average Hg levels over time periods of few weeks to months which seem to provide, as a preliminary analysis, acceptable performance compared to active samplers in terms of sensitivity at most of the monitoring sites involved.

On the other hand, some variability and disparities in the data observed at some sites and during some seasonal period could be also due to different meteorological conditions. The PASs have been in fact deployed at a number of sites with a wide range of climatic and local conditions. Some samplers returned from the South Africa, for example, showed the presence of dust inside the passive vials. In these cases, it could be also possible that atmospheric components, i.e., atmospheric particulate matter and oxidants, sorb to or react with the diffusive barrier during deployment. Thus, in addition to meteorological (wind speed, relative humidity and temperature), we also should explore in the next future the effect of other factors which could impact the PAS's Sampling Rate. Another important factor we have to take into account, among the others influencing the response of the PASs, also the protective shield generally are not likely to completely eliminate the influence of wind on the thickness of the air-stagnant layer of the PAS like diffusive barriers.

In addition, some differences could be also due to some limitations of the samplers themselves. While it is believed in fact that the sampler takes up predominantly GEM, we cannot rule out the possibility for gaseous oxidized Hg to also pass through the diffusive barrier.

Additional field performance tests are needed to characterize GEM passive samplers, and further development is needed before we can completely confirm the robustness of the method. CNR-IIA PASs need to be further tested in the field for a larger deployment period, employing in parallel a larger number of PASs to obtain a bigger amount of data for a detailed statistical analysis to assess the robustness of the method and of the sampling devices.

The ease of preparation as well as the high Hg sensitivity, suggests the chance to investigate the devices features by further comparison of the systems. In conclusion, further work is essential to argue PASs validity in every condition to strengthen the GMOS global network, providing an alternately sampling method that will be inexpensive and user-friendly.

CONCLUSIONS

To prevent global mercury pollution and damage to human and environmental health, a new global and legally binding "Minamata Convention on Mercury" has been agreed at the UNEP Diplomatic Conference held in October 2013 in Japan.

The Minamata Convention stresses the importance of Hg monitoring by asking Parties to develop and improve monitoring tools and methods in its Article 19, called "Research, development and monitoring" and by expecting an effectiveness evaluation of the Convention to be conducted six years after its entry into force and periodically afterwards (Article 22). In this context, the Chemicals and Health Branch of the UNEP (UN Environment) in close collaboration with the CNR-IIA and the WHO implemented in 2014 the UNEP- Global Environmental Facility (GEF) project on the "Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentration of Mercury" with the main goal to harmonize approaches for Hg monitoring, and to strengthen the capacity for Hg analyses in humans and in the environment in order to meet the requirements of the Minamata Convention.

The project started with the two major players in monitoring environment and humans: GMOS and WHO. In particular, the GMOS network, supported the project, and is supporting its further development to achieve the goals of the Minamata Convention on Mercury, with particular regard to Article 19 on Research, development and monitoring and article 22 on effectiveness evaluation, providing high quality and coordinated Hg air monitoring activities built on existing monitoring networks.Key scientific information and results generated by the project are contributing to help and develop sustainable plans to assess the human exposure to and environmental contaminations of Hg to serve the Minamata Convention, its parties and the global community.

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GOS^{4}M: THE GEO FLAGSHIP TO SUPPORT THE MINAMATA CONVENTION ON MERCURY

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Keywords: Earth Observation, Monitoring, Interoperability, GEOSS, Copernicus

INTRODUCTION

The Global Observation System for Mercury (GOS^{4}M) (www.gos4m.org) Flagship originates from the former Task HE-02 "Tracking Pollutants" established as a part of the 2009-2011 and 2012-2015 Group on Earth Observations (GEO) Work Plans (Pirrone *et al.*, 2017). Since the beginning, the activity was aimed to develop a coordinated global observation network for mercury and POPs to support the international conventions on toxic compounds, namely the Minamata Convention on Mercury and the Stockholm Convention. The Convention on Long-range Transboundary Air Pollution (UNECE-CLRTAP) of UNECE and other ongoing international programmes (e.g. UN Environment Mercury Program, EMEP) were also targeted with this activity.

This synopsis describes the objectives of GOS^{4}M and activity on data centres and quality control programs to enhance integration of air quality measurements from different national and regional networks, and to establish observational sites in under-sampled, remote regions around the world.

OBJECTIVES

GOS^{4}M aims to: i) increase the availability and quality of Earth Observation data and information to contribute to the tracking of mercury released to the global environment and anticipate changes to the environment; ii) harmonize metadata production, archiving and data sharing collected by mercury networks; and iii) develop advanced web services in support of the Minamata Convention.

The way to attain the above objectives is by i) facilitating cooperation of governments and institutions in tracking chemical pollutants; ii) fostering the adoption of advanced sensors in monitoring mercury and its compounds; iii) better preparing, archiving and sharing information; iv) creating advanced web services for using and discovery information from metadata and data; and v) creating ad-hoc web services for policy.

RELEVANCE TO GEO'S STRATEGIC OBJECTIVES

The GEOSS Strategic Plan 2016-2025 is based on three strategic objectives: (a) advocacy of EO as the foundation of environmental information; (b) engagement with stakeholders to address every-day societal challenges, and (c) delivery of critical data, information and knowledge to inform decision-makers. Along these lines, the contribution of GOS^{4}M will be realized by:

- endorsing full and open access to EO data;
- promoting the use of key data management principles, as well as common standards and interoperability arrangements;
- encourage and act for increased contribution of regional resources directly to GEOSS Data-CORE and Copernicus data portal;
- engage with key stakeholders to identify the needs in observations, and environmental and socio-economic data analyses, which can yield advances in many Societal Benefit Areas (SBAs);
- broadening of the GEOSS and Copernicus user base through well-targeted dissemination and exploitation actions;
- ensuring access to data, information and knowledge, while increasingly promoting interoperability among multiple sources of data; and deliver the tools, knowledge and services suitable for intelligent exploitation by user communities;
- showcasing concrete collaborative schemes (through the strands) relying on integration of regional capacities and skills towards addressing specific challenge priorities.

RELEVANCE TO THE MINAMATA CONVENTION OBJECTIVES

Article 19 of the Minamata Convention on Mercury states that all monitoring activities related to mercury in environment and human health should, build on existing monitoring networks, where appropriate.

Similarly to GMOS, GOS^{4}M will provide a substantial contribute to the Fate and Transport Partnership (UN Environment F&T) by involving regional programmes and networks. The Global Mercury Partnership is a cooperative stakeholder driven effort started in 2006 to protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land. It has been recognised as a fundamental partnership area supporting the preparation and development of technical and scientific knowledge in support of the future implementation of the Minamata Convention. Current monitoring activity of several countries is therefore of fundamental importance in building a coordinated global monitoring network for mercury. The Flagship will provide continuous information on mercury concentrations and fluxes in and between the atmospheric, marine, freshwater and terrestrial ecosystems as well as outputs from validated regional and global scale atmospheric and marine models. The potential contribution of GOS^{4}M to provide key information to all interested parties in evaluating the impacts of the Convention are strategic. Information delivered through the activity of this Flagship may strongly support the periodic assessments and evaluation of the effectiveness of measures that will be undertaken to achieve the goals that will be set by Conference of Parties n. 1. The information that the GOS^{4}M would provide shall be considered as supporting information useful to interested parties in their effort to evaluate the effectiveness of measures.

ENFORCING THE FLAGSHIP

Achievement of established objectives to implement the flagship can be pursued through the activity of Governance bodies. After ad-hoc meetings that discussed in depth this matter, a preliminary Governance document was shaped and a consensus reached on the structure reported in Figure 1.
The main objective of Governance Bodies is to facilitate the involvement of major networks and institutions supporting the collection of mercury atmospheric and environmental monitoring information to guide the work of the flagship effort and report on the process and deliverables.
The organisational structure of the Flagship shall comprise the following Governance Bodies:

- Steering Committee
- Scientific Advisory Board
- Policy Advisory Board

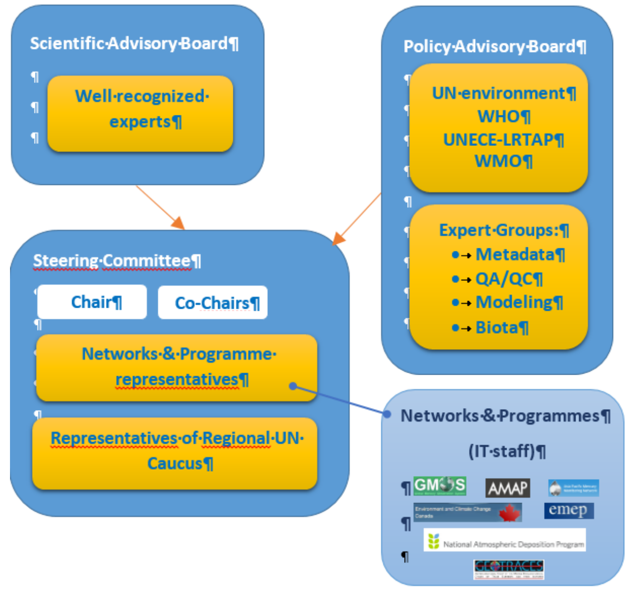

Figure 1. GOS^{4}M Governance structure

As depicted in figure 1 the Steering Committee will drive all activities and will follow-up their implementation, monitoring and evaluation. The Steering Committee is composed by Network and Programmes representatives, and Representatives of Regional UN Caucus.
The Policy Advisory Board is a subsidiary body of GOS^{4}M to support the Steering Committee to render specialised advice in policy matter to the Flagship. It consists of Representatives of UN Environment, WHO, UNECE-LRTAP, WMO, NGOs, and Expert Groups on the domains of Metadata, Quality Assurance and Quality Control (QA/QC), Modelling and Biota.
Finally, the Scientific Advisory Board is a subsidiary body established to support the Steering Committee to render specialised advice in science and technology to the Flagship. Distinguished academic and non-profit researchers will compose this governing body.

Preliminary survey of monitoring networks/campaigns

A survey of in-situ atmospheric mercury measurements and networks was made to prepare a preliminary list of representatives (Table 1) to be involved in GOS^{4}M.
Figure 2 shows distribution of global and regional monitoring networks as well as national and polar sites measuring atmospheric mercury. This map includes both active and inactive monitoring stations

classified between global and regional networks, which summarize to 463 sites mostly distributed in the Northern Hemisphere. It is well clear the synergic benefit brought to GOS^{4}M by the contributing networks. An increase of spatial and temporal coverage can fruitfully support the modelling activity and help identification of gaps.

Table 1. Distribution of active monitoring sites among networks and programmes

Network/ Program	*Active sites*	*Source of information*
AIRMoN	5	http://nadp.sws.uiuc.edu/AIRMoN/
MDN	98	http://nadp.sws.uiuc.edu/MDN/
AMNet	22	http://nadp.sws.uiuc.edu/amn/
CAPMoN	19	https://www.ec.gc.ca/rs-mn/default.asp?lang=En&n=752CE271-1
GMOS	10	http://www.gmos.eu/sdi/
EMEP	7	http://ebas.nilu.no/
APMMN	6	http://apmmn.org/datadb.html
JAPAN	5	https://www.env.go.jp/en/chemi/mercury/bms.html
KOREA	11	https://seoulsolution.kr/en/content/air-pollution-monitoring-network
CHINA	7	Fu *et al*., 2015 (10.5194/acp-15-9455-2015)
MEXICO		de la Rosa *et al*., 2004 (10.1016/j.atmosenv.2004.06.013)
AUSTRALIA	2	http://apmmn.org
UNITED KINGDOM	2	http://www.auchencorth.ceh.ac.uk/node/211
INDONESIA	1	http://apmmn.org
SWITZERLAND	1	https://www.hfsjg.ch

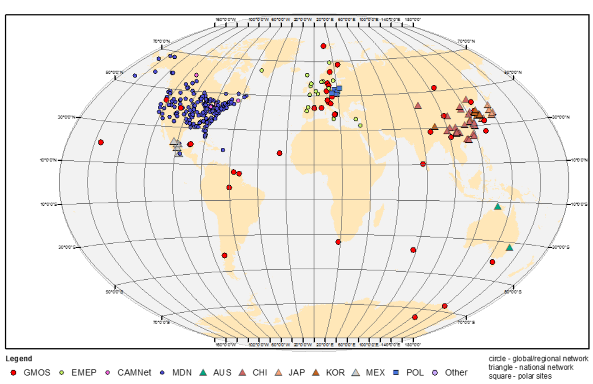

Figure 2. In-situ atmospheric mercury measurements and most important networks

Also responsible of oceanic monitoring campaign are involved as representatives. In particular, MEDOCEANOR and GEOTRACES that have long-term monitoring activity in Mediterranean and World's Oceans respectively will be part of GOS^{4}M.

Preliminary survey on mercury in biota

A global project to collect mercury in biota (Global Biotic Mercury Synthesis, GBMS) was launched by Biodiversity Research Institute (BRI). The database compiles and synthesizes existing data on mercury levels in marine mammals, fish, sharks, skates and rays. It was assembled by gathering samples of more than 33 thousand species, derived from 72 countries and 457 unique locations (Figure 3). As a result, it allows for representative and comparable spatial coverage. This large database will complete the global framework of mercury in the environment.

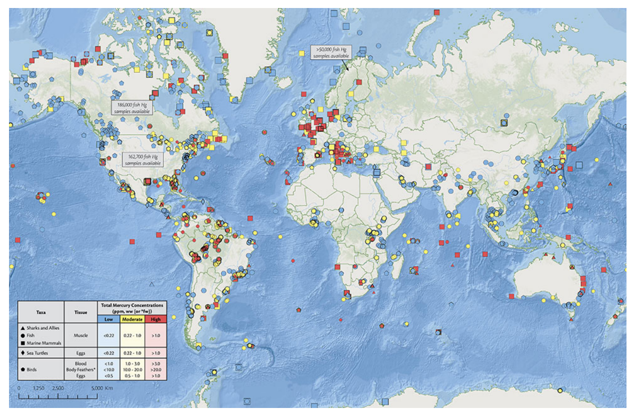

Figure 3. Locations of samples of more than 33 thousand species marine mammals, fish, sharks, skates and rays

THE GOS^{4}M SDI

The purpose of a Spatial Data Infrastructure (SDI) is to archive, access, query, discover, and export metadata and spatial data. In the case of GOS^{4}M the SDI will archive data of networks that agree to share information and will archive metadata of all mercury measurements in media. Effective Minamata Convention implementation rely upon access to spatial information. One of the main advantages of this SDI for integrated environmental management is easy data accessibility, which not only enables scientific analyses, but also facilitates fast and informed decision making.

Implementation of the SDI will require a minimum set of components related to geospatial data management that work together to match user requirements. To be effective the SDI should have all of the following to facilitate ease-of-use and interoperability:

- Policies and Institutional Arrangements: governance, data privacy and security, data sharing, cost recovery, standards;
- People: capacity building, cooperation, outreach;
- Data: single/distributed data storage for geospatial data and metadata;

- Technology: hardware, software, networks, databases, technical implementation plans.

The SDI architecture will consists of three different logic levels: the Data Storage Layer (DSL), the Business Logic Layer (BLL), and the Application Layer (AL) (D'Amore *et al*, 2012). The core of the system will be represented by the Database Management System (DBMS), which will store metadata, mercury measurements and functional data (e.g. users' roles, credentials on datasets). The DBMS will represent the DSL in the SDI architecture and it will be accessed by BLL components. All server components that perform metadata editing, data management, map creation, and data dissemination will be in the BLL. Among them, a map server will be used to export data through OGC compliant services while the metadata server will be used to manage metadata and its related catalog. Server components will export OGC Web Services (OWS) such as Web Feature (WFS), Web Map (WMS), Web Coverage (WCS) and Catalogue Services for the Web (CS-W), through the Hypertext Transfer Protocol (HTTP).

CONCLUSIONS

The need for a Flagship on mercury is timely in light of the recent adoption of the Minamata Convention, which welcomed the scientific communities' efforts to foster the sharing of monitoring data and modelling tools to support policy implementation. Long term and high precision observations and analysis of such pollutant cycles in the different domains of the Earth system (atmosphere, ocean, land), considering also anthropogenic emissions, are furthermore required to better quantify sources and sinks; understand the impact on environment and human health and address their reduction/removal. The Flagship governance will help implementation by:

- Inviting existing mercury monitoring networks including, but not limited to, GMOS, NADP, Asia Pacific Mercury Monitoring Network, AMAP, EMEP, Environment Canada Network, GBMS, to share long-term monitoring expertise, and advance cooperation in monitoring decisions involving data/metadata, data management and distribution, field and lab operations and quality assurance;
- Increasing the availability and quality of EO data and information to track mercury releases and anticipate changes in the global environment;
- Supporting harmonized metadata production, archiving and sharing within the mercury network;
- Developing advanced services in cooperation with nations and UN Environment in support of the policy mandate through the Minamata Convention.

As of its relevance to both GEO's and Minamata Convention objectives, GOS^4M is expected to strongly support the implementation process of the Convention and demonstrate how GEO can contribute to societal benefits with scientific information made available the general public.

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THE ENERGIC OD PROJECT: A BROKERING APPROACH FOR FACILITATING ACCESS AND USE OF GEOSPATIAL OPEN DATA

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Keywords: open data, pan European virtual hub, interoperability, brokering approach

INTRODUCTION

Launched on October 2014, the ENERGIC OD project (European NEtwork for Redistributing Geospatial Information to user Communities - Open Data), was co-funded by the European Union under the Competitiveness and Innovation framework Programme (CIP).
ENERGIC OD involved 15 partners from six EU member states (Italy, France, Germany, Poland, Spain and UK) and was co-ordinated by the (CNR-IIA) Consiglio Nazionale delle Ricerche – Istituto sull'Inquinamento Atmosferico in Italy.

In line with the EU call, the general objectives of the project were:

1) to develop Virtual Hubs at different territorial scales (regions, member states, Europe), providing unique and mutually consistent points of access to heterogeneous data sources for both end-users (via geoportals) and machines (service interfaces, APIs).
2) To demonstrate the validity of the concept, design, implementation and deployment of VHs through the development of a set of ten innovative applications in different domains. The proposed applications will address the needs of businesses, citizens and public institutions, making use of both public and private (open) geospatial data.

DESCRIPTION OF THE PROJECT

In order to reach such objectives, an ENERGIC OD Virtual Hub architecture was designed and implemented adopting an agile methodology, through integration and extension of existing components. The core technology is based on the GI-Suite brokering framework by CNR-IIA with specific extensions to support open data protocols and requirements.
ENERGIC OD has developed and deployed five national Virtual Hub instances in France, Germany, Italy, Poland and Spain. The German Virtual Hub interconnects a Virtual Hub instance specifically deployed to serve the Berlin metropolitan area. On top of that, a pan European Virtual Hub (pEVH) that connects directly or indirectly more than 500 data sources for more than 3,000,000 metadata records discoverable was implemented.
A web data portal, developed by ESA and based on the GEOSS Portal mirror technology, was integrated providing the user interface to the pan European Virtual Hub (www.geoportal.org/community/energic-od). Finally, a multingual pan European Virtual Hub web (www.vh.energic-od.eu/) site was developed as point of access to information for potential end-users, developers and providers. In particular, it provides access to the pan European Virtual Hub data portal for users, and to the Guide for Developers.
The pan-European VH will be available to all users in Europe free of charge in its basic version, thus lowering the barriers of access to it and promoting the use of open data brokered by it (in the long term, leading to increased innovativeness of the firms in the GIS data sector). At the same time, the pEVH has been equipped with tools to continue functioning independently and after the end of ENERGIC-OD project. It will follow a freemium business model, in which certain premium functionalities of the pEVH, such as ability to upload users' own datasets, create complex crowdsourcing applications, or connect sensor networks, will be available for a charge. This charge has been designed to be as low as possible, essentially just covering the operating costs of the pEVH (i.e., the pEVH is a not-for-profit operation). This has been implemented following on the recommendations from pEVH users, as obtained during the contests, in workshops, as well as in other settings (conferences, focus groups, brainstorming sessions).
Ten innovative pilot applications in different domains (ranging from land use, protection of the environment, health, cultural heritage, natural hazard assessment, biodiversity, etc.) have been developed by the ENERGIC-OD partners by using the services offered by the deployed Virtual Hubs. These new

applications are addressing the needs of businesses, citizens and public institutions, making use of both public and private (open) geospatial data, encouraging innovation and business activities.
To demonstrate the benefits of a virtual hub for open data, a subset of four pilot applications was selected for further development towards a cross-border and pan European scope.

CONCLUSIONS

The ENERGIC OD projects achieved its major goals by:

a) creating a pan European Virtual Hub based on a technology that can be effectively deployed at different territorial scales (regions, member states, Europe), providing unique and mutually consistent points of access to heterogeneous data sources for both end-users (via a dedicated web portal) and machines (standard service interfaces, RESTful and Web APIs);

b) releasing ten innovative applications using the ENERGIC OD Virtual Hub in different application domains. An exploitation plan covering the pan European Virtual Hub business model assures the sustainability of the major achievements.

Basic functions of the pEVH are available for free to all users, with some premium features accessible for a low charge (thus embracing the freemium revenue model). The pEVH will function until at least the end of year 2020, and it bridges the gap between a sustainable business model around open data commercialization, as well as bringing research-driven project outputs to the market.

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ISAAC: PROJECT INCREASING SOCIAL AWARENESS AND ACCEPTANCE OF BIOGAS AND BIOMETHANE

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Keywords: Biogas, Biomethane, Social Acceptance

INTRODUCTION

Although Italy is the second European biogas producer after Germany, it still has a great potential for biogas production and market expansion, especially in central and southern regions. According to elaborations of CIB – Consorzio Italiano Biogas e Gassificazione (based on the 2015 annual report of GSE – Gestore dei Servizi Energetici), more than 1550 plants with a total capacity of around 1160 MWel have been installed, but the non-technical barriers, that impede a more widespread diffusion, are still critical.

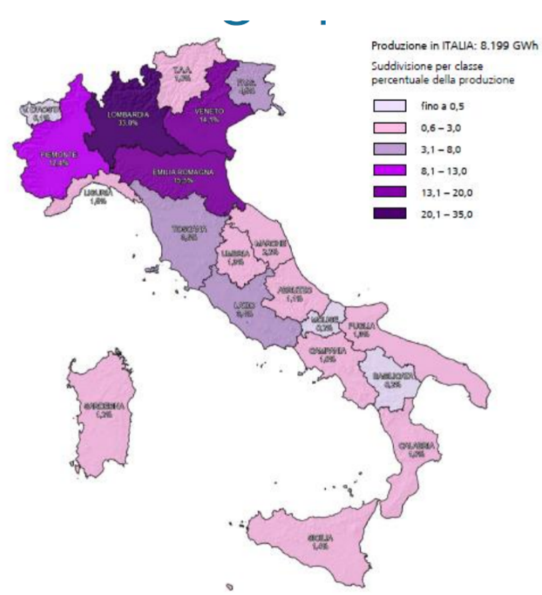

Figure 1. Biogas Plants distribution in Italy (GSE)

Biogas production is a widespread technique for the exploitation of biomass energy, consisting on the anaerobic bacterial fermentation of biomass. The use of biogas as a fuel can reduce the consumption of fossil fuels, decreasing carbon dioxide emissions and the anthropogenic greenhouse effect. Compared to the direct combustion of biomass, the use of biogas can significantly reduce the emissions of particulate matter, heavy metals, sulphur and nitrogen oxides, inorganic acids, organic micro-pollutants (Paolini *et al* 2018).

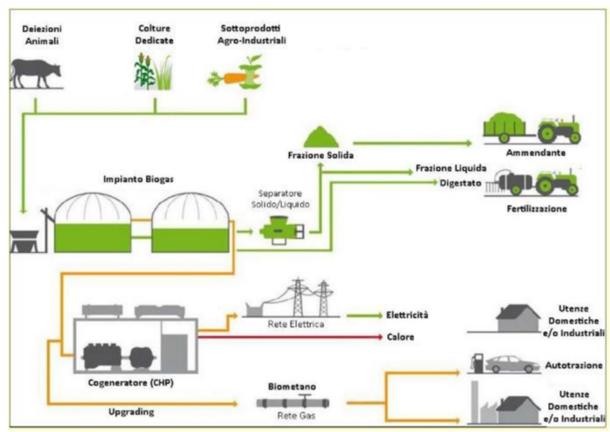

Figure 2. Typical biogas production scheme

METHODOLOGY

ISAAC is a project financed by Horizon 2020 Programme, whose main aim is to remove non-technical barriers, such as lack of public acceptance and coordination for the biogas facilities diffusion, normative and legislative inadequacies, in order to support biogas/biomethane market penetration in Italy and make plants implementation easier within the national context.

Actions are focused on spreading balanced information on the biogas production process and related environmental and economic benefits among the stakeholders potentially involved in the construction of plants. A participatory process model is developed and implemented in two pilot territories to build a common decision-making process and prevent social conflicts. The analysis of biogas production potential from residual biomass constitute the starting point for communication and information activities. Awareness campaigns of the ISAAC Project are also conducted in seven Italian regions to promote discussion, information sharing and co-planning among stakeholders. Specific actions

are focused on reducing fragmentation among individual biomass producers (farmers, breeders, etc.) in order to reach the minimum facility dimension needed and maximise economic advantages. A crowdfunding initiative is proposed to create new opportunities and a sense of ownership and involvement. Proposals for improvements of the current Italian regulations on biomethane and digestate have been prepared and discussed with the authorities in charge.
Increasing the biogas share in the final energy consumption by reducing NIMBY conflicts and fragmentation among stakeholders, as non-technical barriers to the installation of new anaerobic digestion plants:
ISAAC is a Coordination and Support Action, so the outputs that have the most value for the exploitation will be:

• developing a more effective policy at national and regional level by producing clear and concrete proposals for law improvements and harmonization of authorization procedures;
• assessing socio-economic and environmental impacts through surveys, cost/benefit analysis and other methodologies;
• developing tailored financing schemes to fund plants;
• encouraging the uptake of information and news about biogas/biomethane applications and anaerobic digestion process enhancing the knowledge of this method and related benefits among a wide range of stakeholders
• involving farmers and other economic subjects in considering biogas as a new source of revenue and increasing their engagement in energy transition

Encouraging the uptake of information and news about biogas/biomethane applications and anaerobic digestion

ISAAC is the acronym of Increasing Social Awareness and ACceptance of biogas and biomethane, so one of the main goal of the project is the uptake of correct information and news about biogas, biomethane and 5 renewable energies. All activities implemented and the one that have been performed aim to create an “ISAAC community”, made of people with knowledge on topic, ready to discuss about it in a more scientific approach, after checking data, listening to experts, creating an informed opinion. One of the most powerful instrument is the project website (www.isaac-project.it) and the related Facebook page, which is online and available for 4 years after the end of the project, updated with news on biogas/biomethane and renewable energy world. All information published are tailored for the users in order to let them look in depth at the themes of biogas and biomethane, using the website and the connection to other related websites and projects. This will increase the number of persons in the community, and the website double language IT/EN is widening the potential audience not only in Italy, but also in Europe. Another tool to be used is the “Buck Bradley Comic Adventure” APP, used for the activities in the school but available also for other users. The app, through the game, it teaches users on biogas and biomethane technology, and biomass energy potential. The APP has a dedicated website and a Facebook page (www.terrastramba.it), realized around the imaginary world in which the main character Buck Bradley is living. Using the website and the Facebook page, the user can get more detailed information about the story, the characters, what is the idea behind it and its potential future uses, as well as information about renewable energies (biogas in particular).

Involving farmers and other economic subjects in considering biogas as a new source of revenue

The farmers have a huge role in the project, considering that they are potentially the most interested for the biogas/biomethane plant investment. During the project several meetings with farmers and entrepreneurs had already been organised in order to explain the potential of biogas and biomethane on an economic, social and environmental level. The consortium organized as well a visit to a plant, in order people to understand better how a plant works, the effort needed to create and manage it, the potential of energy production. Meetings will be carried out after the end date of the project, as well as the visits to the plants, in order to increase the interest of farmers towards biogas and biomethane technologies, removing eventual doubts on the topic on a financial, environmental and social level.

Developing a pre-feasibility study on the biogas plant

In order to develop a pre-feasibility study on the biogas plant realization, giving an idea on investment, ROI, funding possibility, as well as environmental impacts, the consortium created a computational tool, available on-line on the project website (www.isaac-project.it/tool).The tool gives the user the possibility to insert the exact quantities of available biomass and biogas/biomethane production on the bases of the knowledge of essential input data or calculate it with an expert system. The tool also calculates the possible economical revenue from the available biomasses with a chosen technology, and the relative environmental impacts for the territory. The tool is a powerful instruments for the farmers to have an idea of their situation and the potential cost, investment and remuneration of building a biogas plant. It is a dynamic instruments, and during the project partners are working on it in order to create a better developed tool with updated information and user-friendly approach.

Assessing socio-economic and environmental impacts through surveys, cost/benefit analysis and other methodologies

The results coming out from the diffusion of the project and tools output will be extended by various partners at different levels, expected results will be: increase of the knowledge about local availability of biomasses, increase of the network between partners for design and construction of new plants, expected increase of biogas production, increase of the environmental protection due new plants. The projects carried out surveys in different Italian territories in order to have a better understanding on the population knowledge on biogas and biomethane topics. The data coming out from the survey will be used to produce scientific papers and they will be presented on conferences and meetings among Europe. Moreover, the data will be used to give support to policy makers to understand the population approach in their territories towards biogas plants and production

Increasing biogas share in the final energy consumption by reducing NIMBY conflicts

The methodology developed during the project in order to reduce NIMBY syndrome in Italy on biogas and biomethane plants will be publicly available and ready-to-use for policy makers and stakeholders which will face similar problems in the future, in Italy but also in Europe. The results of activities like participatory processes, events with experts, dissemination material produced and spread, activities in the schools are a good starting point for whoever needs to have a general overview on the population in a “tough” country for the biogas like Italy. The results produced by these actions will foster the creation of new plants well executed and conducted and as consequence the increase of the renewable energy production. Increasing the number of persons with correct knowledge on the topic of biogas and biomethane will lead to a reduced nimby syndrome, and consequently reduced number of conflicts for every new plant construction project. The process will bring to the main results of more renewable energy use in Italy, specifically biogas and biomethane,

Developing a more effective policy at national and regional level by producing clear and concrete proposals for law improvements and harmonization of authorization procedures

The project approach towards local and national administrators is double: from one side, training courses made by experts will be implemented in order to give the proper information on the exploitation of the potential of biogas and biomethane, to better understand the laws on the topic and to open to new entrepreneurship activities; on the other side, normative proposal on regional and national level will be implemented in order the biogas to better penetrate in the Italian market without all the difficulties faced until today. The proposals are focus on the public debate regulation for project with relevant impact at a national level, and on the fragmented administrative path for the biogas plant realization at a regional level. The project implements proposal on improvement of the national law on the biomethane injection in the national grid as well as a proposal on the digestate. The results of this actions will bring to an easier path for the constructions of new plants, for the injection of the biomethane into the national gas grid and for the use of the digestate after the process.

CONCLUSIONS

ISAAC project is expected to deliver a series of results and recommendations around the biogas and biomethane world, and to increase their awareness and acceptance within the population. All partners agree to use the results of the project after its end. All partners will especially try to promote the ISAAC “scientific” approach based on data and on correct information, to bring results beyond Italian borders to European stakeholders and institutions.

The final conference of the Isaac Project will be organized by CNR-IIA in Rome on 12th July 2018.

MERCOX – METROLOGY FOR OXIDIZED MERCURY

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Keywords: Mercury, metrology, oxidised mercury, calibration standards

INTRODUCTION

The objective of the MercOx project is to develop traceable measurements, monitoring and control of mercury (Hg) and its different forms in gas emission sources and in the atmosphere. This will provide significant improvements in measurement comparability and the uncertainty of measurement results. Currently, traceable calibration methods only exist for elemental mercury, but calibration methods are also required for Hg(II) species in order to meet the requirements of EU regulation and for the implementation of the Minamata Convention. MercOx aims to develop and validate traceable oxidized Hg standards and methods for sampling and analysing oxidized Hg species in flue gas emissions and in the atmosphere.

Mercury, as one of the most toxic metals, is regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC. Internationally the Minamata Convention, adopted in 2013, is a global treaty to protect human health and the environment from the adverse effects of mercury. In addition to its elemental form Hg also exists in oxidized forms that are reactive and can be transformed into organic Hg species such as methylmercury (MeHg), the most toxic Hg species and the one most prone to bioaccumulation in aquatic systems. Roughly half of the atmospheric Hg emissions are of natural origin (including secondary re-emission) whilst the rest are from primary anthropogenic sources, particularly from fossil fuel burning and other high temperature industrial processes, such as cement clinker production, waste incineration, ore roasting and steel production.

Development of a reliable real-time direct Hg(II) measurement technique and reliable and traceable Hg(II) standards would solve the traceability problem in the measurement of total and oxidized mercury concentrations originating from different mercury sources. Methods for measuring oxidized mercury and to accurately compare the total mercury concentration in generated standard elemental and oxidized mercury gases are also needed, as well as sample transportation methods, traceable reference standards, validated methods for the on-line measurement of mercury under field conditions and a comparison of mercury species inter-conversion.

Knowledge of Hg speciation both in air and in stack gas emissions is critical when validating models for predicting Hg emissions, transport, deposition and fate on regional and global scales. Atmospheric Hg isotopic signatures that can be used to trace the origin and fate of atmospheric mercury also need full metrological support and development.

In addition, to meet future global and European requirements (in relation to the Minamata Convention and European Directives) standardisation bodies have recognised the importance and need to standardise the method for measuring mercury in industrial flue gases and in the atmosphere.

METHODOLOGY

The overall objective is a traceable on-line and sorbent-based measurement for the monitoring and control of mercury in its different oxidized forms in emission sources and in the atmosphere in order to achieve significant improvements in measurement uncertainty. Specific objectives are addressed in individual Work Packages:

To develop, establish and implement a traceable calibration methodology for the most important oxidized mercury species, especially for $HgCl_2$. Possible methods are; evaporation of known mercury chloride solutions, sublimation of solid mercury chloride or oxidation of elemental mercury. This could include quantitative confirmation of the output of liquid evaporative $HgCl_2$ generators, development of a real-time on-site $HgCl_2$ measurement technique or transfer standard, or the development of reliable portable $HgCl_2$ reference gas materials and sources. (WP1)

To study, develop and compare different methods of measuring oxidized mercury. To accurately compare total mercury concentrations in generated standard gases for elemental mercury Hg(0) and oxidized mercury. The most common measurement method for different mercury species is via conversion to Hg(0) but also direct measurement of $HgCl_2$ or other oxidized species is an option. Also, high accuracy bulk and species-specific [e.g. Hg(0) and Hg(II)] isotope ratio measurements can be evaluated for origin discrimination and to determine migration pathways of mercury and mercury species interconversion. (WP2)

To compare, develop and establish conversion and sample transportation methods employing traceable reference standards developed for Hg(0) and oxidized mercury. Regarding species inter-conversion, different measurement methods and their long-term efficiency and reliability in different matrices have to be taken into account. This can include, for example, the validation of currently available conversion methods with new (more accurate) calibration standards, addressing more theoretical approaches for predicting mercury chemistry or employing more advanced techniques based on compound specific mass spectrometric measurements. (WP3)

To apply the developed methodologies in order to test and validate new and existing methods for on-line mercury measurement under field conditions by employing the gas standards or generators developed. This will include typical direct measurement of mercury via different conversion and optical detection methods, but also sorbent traps commonly used for mercury measurement. The methods developed will be also applied to the measurements of stack gas emissions and atmospheric mercury speciation. Mercury stable isotope ratio measurements of Hg(0) and Hg(II) will be applied in the field. (WP4)

To facilitate the take up of the technology and measurement infrastructure developed in the project across the measurement supply chain (accredited laboratories), organisations which develop standards (such as CEN/TC264/WG8 and those linked to the IED Directive 2010/75/EU, the Air Quality Directive 2004/107/EC and the Waste Incineration Directive 2000/76/EC) and end users (environmental monitoring, research community, regional and global programmes). (WP5).

IMPACT

Environmental impact:

Typically, mercury is released into the atmosphere in one of three forms: i) elemental mercury, which can travel a range of distances and may remain in the atmosphere for up to one year (GEM); ii) particle-bound mercury, which can fall out of the air over a range of distances (PBM); and iii) oxidized mercury (GOM), which is predominantly found in water-soluble forms. Recent emission estimates of annual global mercury emissions from all sources, natural and anthropogenic, which are highly uncertain, are about 5500 - 8900 tons per year. MercOx will join American expertise in this field with European metrological expertise, building a global metrological framework for the determination of mercury in stationary source emissions and atmospheric measurements. Ultimately there is a need by Industry and others for the implementation of validated measurements that are comparable and compliant with those required by legislation. A better metrological infrastructure will improve the comparability of measurements. It also means that measures to reduce mercury emissions and releases will be based on credible and defensible data.

An important component of the project will also be awareness building and training of users of measurement results from various industrial sectors on the outputs of the project. Traceable measurements with defensible uncertainties will help to demonstrate trends in mercury concentrations with improved confidence and this will lead to a more accurate understanding of the presence of mercury in the environment, thereby informing abatement strategies and future mercury policy.

Scientific impact: In the UNEP 2013 document "Global Mercury Assessment" it is stated that large uncertainties remain in global estimates of mercury emissions to the air. This uncertainty stems from various sources, including the availability of information on activity levels, but mainly from the lack of information concerning the mercury content of some raw materials and the validity of assumptions regarding processes and technologies employed to reduce mercury emissions, including their rates of application and effectiveness.

Mercury science will advance significantly by having methods and protocols developed by the project, which the project will disseminate worldwide. Novel datasets generated will provide a greater understanding of the presence of mercury in the atmosphere and in the environment.

The scientific community has made significant advances in the use of isotopic analysis of Hg for identifying sources of Hg, species interconversion and sinks of this toxic element. The use of these techniques has largely been restricted to solid samples, biota and similar. Measurements in the atmosphere and stack emission are rare, but much needed to understand the global geochemical mercury cycle. The outcome of this study should provide the scientific community with a more profound insight into the phenomenon of instrumental mass discrimination, a more solid basis for selecting a suitable method for correcting for bias and ultimately, higher quality data. Obviously, higher quality data will aid in the study of the complicated biogeochemistry of Hg compounds, formulating realistic hypotheses and adequately assessing the environmental impact risks associated with real-life situations.
Additionally, it will provide the community with a solid basis for producing primary calibration standards. Quantitative determination of Hg is of the utmost importance for a variety of applications.

Health and Social impact: Mercury can seriously harm human health, and is a particular threat to the development of foetuses and young children. It damages the central nervous system, thyroid, kidneys, lungs, immune system, eyes, gums and skin. Neurological and behavioural disorders may be signs of mercury intoxication, with symptoms including tremors, insomnia, memory loss, neuromuscular effects, headaches, and cognitive and motor dysfunction. Recent studies have also shown mercury to have cardiovascular effects. In the young it can cause neurological damage resulting in symptoms such as mental retardation, seizures, vision and hearing loss, delayed development, language disorders and memory loss (UNEP, 2013, "Mercury, Time to Act"). By providing comparable measurements of Hg species in emission sources and in the global atmosphere, the accuracy of models that predict the Hg concentrations in fish, because of reduced emission, will be significantly improved. This will guide the public health sectors on advising population on the consumption of fish.

Economic impact: Anthropogenic processes have increased the exposure of humans and wildlife to toxic MeHg. Mercury emissions are increasing by about 25 % between 2005 and 2020 if the present trajectory is maintained. A global assessment of societal damages caused by the ingestion of MeHg, based merely on loss of IQ (Intelligence Quotient), suggests that the annual cost will be approximately US$3.7 billion (2005 dollars) in 2020. Based on European wide human biomonitoring (HBM) results it was estimated that, within the EU, more than 1.8 million children are born every year with MeHg exposures above the safe threshold of 0.58 µg/g, and about 200,000 births exceed a higher limit of 2.5 µg/g proposed by the World Health Organisation (WHO). The total annual benefits of exposure prevention within the EU were estimated at more than 600,000 IQ points per year, corresponding to a total economic benefit between €8,000 million and €9,000 million per year. These estimates document efforts to combat mercury pollution and to reduce exposure to MeHg, which will have very substantial economic benefits in Europe, mainly in southern countries. Large economic benefits can be achieved by reducing global mercury emissions.
Defensible and traceable mercury measurements will accelerate highly cost-beneficial action plans and will allow credible estimation of economic savings as a result of reductions in the presence of mercury in the environment.
Furthermore, in terms of industries which emit mercury, traceable measurement with lower uncertainties will also help European industry meet the requirements of mercury abatement and emissions legislations with greater confidence and at lower cost, resulting in huge overall savings across the EU.

DISCUSSION

Article 8 of the Minamata convention adopted in 2013 [1] addresses emissions to the atmosphere and calls for a reduction in the emissions of mercury and its compounds in particular from point sources addressed in Annex D (coal-fired power plants, smelting and roasting processes, waste incineration and cement clinker production facilities). It also calls for comparable measurements and harmonized methodologies for Hg and its compounds in emission sources (Article 19) and information on environmental cycling including long-range transport and deposition, transformation and fate of mercury and its compounds in different environmental compartments, taking appropriate account of the distinction between anthropogenic and natural emissions. It also calls for awareness building and education in Article 18 as well as capacity-building, technical assistance and technology transfer (Article 14).
Oxidized mercury species are a serious environmental concern, primarily due to their reactivity and high water solubility, and because

Hg(II) species act as intermediates between elemental and organic Hg compounds [2]. Their availability is essential for methylation resulting in an organic form called methylmercury, which is the most toxic form of mercury. However, currently there exists no metrological infrastructure for traceable, validated and accurate measurements of oxidized mercury species in the atmosphere and emission sources. This infrastructure is of paramount importance for the implementation of the Minamata convention on mercury and European Directives 2004/107/EC and 2010/75/EU, [3,4] that regulate atmospheric and industrial mercury emissions.

The most important open issues pending to be resolved are:
A lack of traceable calibration method and traceable oxidized mercury generator output as evidenced by European and USA standards for mercury measurements in air (EN15852 and EN1853) [5,6] and for mercury measurements in emissions (EN13211 and EN 14884; US EPA methods 30A and 30B), [7-10] which are still inadequate in-terms of validated and comparable measurements procedures for oxidized Hg species.

Difficulties of formation of artefacts and interspecies conversion during sampling, processing and storage may influence the sample integrity and thereby the measurement results of mercury in atmospheric and stack gas emissions [11-14].

Reliability of field measurements due to temporal and spatial variations in the composition of air and emission sources are a big concern according to the latest findings by researchers in the field [15,16]. Intercomparison of validated methods for field measurements of atmospheric and stack gas emissions are of vital importance for development of traceable validated methods for oxidized Hg quantification.

Migration from sources of pollution and provenance of mercury species are of great importance for compliance assessment monitoring where recent developments in Hg isotope ratio measurements might unravel the differences between contributions of different emission sources [17]. These techniques are still under development and verification with urgent need for implementation of metrological concepts.

Capacity building, training and knowledge transfer between NMIs and DIs, monitoring laboratories, instrument providers, international organisations, industrial stakeholders, researchers in the field and the public are needed to empower the community for effective mitigation of mercury related issues.

The project will address all of these issues and is supported by the major stakeholders as is evident from the letters of support provided by standardisation body (CEN ISO/TC 158 and ISO/TC 264) international organisations and programmes (UNEP, GEO, AMAP, CEMBUREAU, IEA CCC, Ekokem), governmental organisations (US EPA, EA UK, INECC, non-EU NMI's (NIST, CENAM)

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HOW SCIENCE SUPPORTS POLICY IN THE IMPLEMENTATION OF THE MINAMATA CONVENTION

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INTRODUCTION

Mercury (Hg) is one of the hazardous chemical of global concern due to its persistence into the environment, its long-range atmospheric transportation, its ability to bio-accumulate in ecosystems and its significant negative effects on human health and the environment. Hg has been therefore recognized as a toxic, persistent, and mobile contaminant that requests immediate global action to reduce emissions of and human exposure to mercury on both regional and global scale. The UN Environment Chemicals and Waste Branch is the focal point in the UN system for developing concerted global actions to foster environmentally sound management of hazardous chemicals, including mercury. In its technical work, the Chemicals and Waste Branch builds and relies on partnerships with various governments, international organizations and non-governmental organizations to reduce mercury pollution and its negative impacts. Hg is a naturally occurring element used in numerous products and industrial processes. It is released into the environment trough both human and natural activities. Several studies have been conducted on Hg emissions into the environment in order to understand the magnitude of this environmental pollution issue (Pirrone *et al*., 2010; Pacyna *et al*., 2010; UNEP, 2013a; Pacyna *et al*., 2016). According to the 2013 report by the United Nations Environment Programme (UNEP, 2013a) the anthropogenic sources of mercury emissions account for about 30% of the total amount of mercury entering the atmosphere each year. The combustion of fossil fuels (mainly coal) for energy and heat production in power plants and in industrial and residential boilers, as well as artisanal and small-scale gold mining, are the major anthropogenic sources of Hg emissions to the atmosphere at present. These sources account for about 37 and 25% (Pacyna *et al*., 2016) of the total anthropogenic Hg emissions globally, estimated to account for about 2000 t of Hg emitted annually (Pirrone *et al*., 2010; Pacyna *et al*., 2016). The current estimates of mercury emissions from natural processes (primary mercury emissions and re-emissions), including mercury depletion events, were estimated in the EU Global Mercury Observation System (GMOS) project (www.gmos.eu), to account for about 5200 t of Hg emitted annually, which represents nearly 70% of the global mercury emission budget. Oceans are the most important sources (36 %), followed by biomass burning (9 %) (Pacyna *et al*., 2016). In 2009 the Governing Council of UNEP agreed on the need to develop a global legally binding instrument on mercury by convening an Intergovernmental Negotiating Committee (INC), supported by the Chemicals Branch of the UNEP as secretariat, and the 25/5 Governing Council decision welcomed the UNEP Global Mercury Partnership for their progress in developing and implementing the Partnership as a vehicle for immediate action on mercury (UNEP, 2009a). The overall goal of the UNEP Global Mercury Partnership is to protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land (UNEP, 2009b). The mandate to INC was reaffirmed in 2011, through the Governing Council decision 26/3 and in 2013, countries signed the Minamata Convention on Mercury, a legally binding agreement intended to “protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds” (Article 1 in UNEP, 2013). The scope of this presentation is to give an overview of the Minamata Convention with a focus on its main targets, highlight the links between the scientific activities carried out by CNR-IIA in the framework of initiatives, programs and projects carried out in cooperation with the UN Environment, NGOs, stakeholders and national bodies such as the Italian Ministry of Environment, among others.

ANALYSIS OF POLICY TARGETS

The Minamata Convention builds upon scientific knowledge of global sources and supply, and reservoirs of Hg, coupled to health impact aspects.

To reach the policy goals of targets of the Minamata Convention, and other relevant policies aiming at the reduction of mercury pollution, is necessary: a) to assess the current and future levels of mercury pollution into the environment and its behaviour; b) to identify critical and emerging areas of investigation, as done in a recent work (Gustin *et al*., 2016) and, where possible, to identify relevant metrics related to mercury control, as done for the effectiveness evaluation by Evers (Evers *et al*., 2016); c) to properly manage mercury as a persistent and toxic contaminant globally. The approach of the current work is to present the on-going activities on mercury research and transfer of knowledge to policy sector, carried out by the CNR-IIA, according to a three-steps approach: i) to analyse specific targets of the Minamata Convention or science-based concerns for consideration regarding mercury assessment and mercury monitoring, when implementing this international agreement; ii) to make linkages between the Minamata Convention targets and current activities carried on by the CNR-IIA; iii) to establish possible contributions and metrics to be considered by the scientific sector.

i) THE CONVENTION'S PROVISIONS

The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury (art. 1 in UNEP, 2013b). It was agreed at the fifth session of the Intergovernmental Negotiating Committee on mercury in Geneva, Switzerland on 19 January 2013 and adopted later on 10 October 2013 at a Diplomatic Conference (Conference of Plenipotentiaries), held in Kumamoto, Japan. The Minamata Convention entered into force on 16 August 2017, on the 90th day after the date of deposit of the 50th instrument of ratification, acceptance, approval or accession. The updated Status of the Convention is reported in Table 1.

The Minamata Convention includes a variety of provisions to control, reduce or eliminate major sources on Hg that emit to air and release to land and water Hg into the environment. Major highlights of the Minamata Convention include, inter-alia, a ban on new mercury mines, the phase-out of existing ones, the phase out and phase down of mercury use in a number of products and processes, control measures on emissions and releases, and the regulation of artisanal and small-scale gold mining (ASGM) (UNEP, 2013b).

The provisions of the Minamata Convention can be grouped in three areas, as suggested by Selin *et al*. (Selin *et al*., 2018) to which the scientific community can contribute: 1) Uses, emissions and releases; 2) Support, awareness raising and education; 3) Impacts and effectiveness.

Table 1. Status of Signatures and Ratifications of Minamata Convention on Mercury (at 10 April 2018)

Objectives	
Countries that have signed	128
Countries that have ratified (updated at mid of April 2018)	91
Italy has signed the Convention on	10/10/2013

Table 2. Key Minamata Convention areas

Art. 3 – Supply and trade	Uses, emissions and releases
Art. 4 – Products	
Art. 5 – Processes	
Art. 6 – Exemption of phase out	
Art. 7 – ASGM	
Art. 8 – Emissions	
Art. 9 – Releases	
Art. 10 – Storage	
Art. 11 – Waste	
Art. 12 – Contaminated Sites	
Art. 13 – Financial mechanism	Support, awareness raising and education
Art. 14 – Cap.Build., tech. assist., tech.t.	
Art. 16 – Health	
Art. 17 – Information exchange	
Art. 18 – Public inform, awareness, ed	
Art.15 – Implementat. & compliance	Impacts and effectiveness
Art. 19 – Research, development and monitoring	
Art. 20 – Impl. plans	
Art. 21 – Reporting	
Art. 22 – Effectiveness evaluation	

ii) THE ROLE OF SCIENCE IN POLICY

1) From November 2017 the CNR-IIA is amongst the list of the experts nominated by the General Secretariat of the Council of the European Union, for the Experts Group on 'Establishing arrangements for providing comparable monitoring data and elements of an effectiveness evaluation framework'. The Group met in Ottawa in March 2018. The main challenge concerning the effectiveness evaluation and reporting processes is to gather comparable monitoring data on the presence and movement of

mercury and mercury compounds in the environment and on the levels of mercury and mercury compounds observed in biotic media.

- *The Science-Policy Link*

Recognizing the urgent needs for a framework for research, development and monitoring (Art. 19 in UNEP, 2013b) and for the effectiveness evaluation (Art. 22 in UNEP, 2013b) of the Minamata Convention on mercury, the pilot study on global Hg monitoring made by UNEP, CNR-IIA and WHO, based on the experience from the GMOS, can support the policy goals and needs to further improve tools and networks for global mercury monitoring and to provide to provide baseline data for the effectiveness evaluation.

2) Furthermore, the CNR-IIA is amongst the list of the experts nominated by the Italian Ministry for the Environment Land and Sea, within the "Mercury Expert Working Group" officially constituted for technical-scientific support necessary for the implementation of European Regulation 2017/852 (European Union, 2017) and the Minamata Convention on Mercury (UNEP, 2013b).

- *The Science-Policy Link*

This group will contribute to all articles of the Minamata Convention with particular regards to the assessment of mercury pollution in Italy and will support the technology transfer from the scientific to the policy sector.

3) The UNEP Global Mercury Partnership currently has eight identified Partnership areas (identified also as Priorities for Action) that are reflective of the major source categories of mercury and its compounds. The Partnership Areas include the Mercury Air Transport and Fate Research Partnership (UNEP F&T).

The UNEP Global Mercury Partnership represents an helpful input to understand the whole mercury pollution issues in deep and the outcomes of the partnership areas have contributed to the negotiation process. The Partnership is a voluntary network among governments, NGOs, industry, academia, and other stakeholders to work to reduce mercury pollution. The Overarching Framework of the UNEP Global Mercury Partnership has established a Partnership Advisory Group to encourage the work of the partnership areas, that meets once a year.

UNEP F&T started its activity in 2005 aiming to improve the global understanding of international mercury emission sources, fate and transport and to encourage collaborative research activities on different aspects of atmospheric mercury cycling at local, hemispheric and global scales.

At the beginning of 2006, Italy started leading the UNEP F&T in close cooperation with other interested partners. At today the CNR-IIA of Italy leads the F&T together with the Biodiversity Research Institute (www.briloon.org) Portland, Maine, USA.

At today (as far as to March 2018) UNEP F&T has 39 partners within the UNEP Global Mercury Partnership.

The specific objectives of the Partnership are to support the Decisions of the UNEP Governing Council and specifically the activity of the UNEP Global Mercury Partnership by, inter-alia:

• Accelerating the development of sound scientific information to address uncertainties and data gaps in global mercury cycling and its patterns (e.g., air concentrations and deposition rates, source-receptor relationships, hemispheric-global air transport/transformation, emission sources);

• Enhancing compilation and sharing of such information among scientists and between them and policymakers;

• Enhancing the development of a globally-coordinated mercury observation system to monitor the concentrations of mercury species into the air and water ecosystems.

Considering the importance of an integrated evaluation of mercury impacts on the whole environment, the scope of the Partnership's research activities is being extended to include aquatic transport and fate of methylmercury to biota as well as human exposure.

- *The Science-Policy Link*

The F&T will continue to act as an integrator of scientific information among the partnerships and will also continue to support the overarching goals of the UNEP Mercury Programme and the Minamata Convention, including contributing to, coordination and liaison with various organizations and programs. F&T aims, in general, to increase global understanding of international mercury emissions sources, fate and transport and will then support the necessary assessment to be made within the Minamata Convention.

4) As requested by the UN Environment Assembly (Decision 27/12: Chemicals and waste management, 2013), UN Environment is currently developing with

many scientists an update of the Global Mercury Assessment (GMA) 2013 to be finalized by the end of 2018.
The work will include two reports:

• A Technical Background Report, a fully referenced scientific report (prepared in cooperation with the Arctic Monitoring and Assessment Programme (AMAP), and a
• Summary report for policy makers (the UN Environment's GMA report to UN Environment Assembly).

CNR-IIA in close cooperation with many international scientists has lead the Chapter 3 *'Levels of mercury in air'* in the Technical Background Report. The aim of the chapter is to provide an up-to-date overview of Hg levels in air (since the GMA 2013). In particular, the chapter focuses on atmospheric Hg measurements and regional/worldwide spatial and temporal trends with an overview of measurements currently collected in regional monitoring networks around the world.

- *The Science-Policy Link*
Integrated and updated global assessments, based on valid data and information from regional and national levels, are essential for global understanding and for predicting trends, with particular regards to the effectiveness evaluation (in Art. 22 of UNEP, 2013b). A better understanding of mercury pollution and behaviour is also essential for a proper management of the entire Minamata Convention.

5) UN Environment in close collaboration with WHO and CNR-IIA are executing the UN Environment - Global Environmental Facility (GEF) project entitled "Develop a plan for global monitoring of Human exposure to and environmental concentration of Mercury". The main aims of the projects are to provide elements towards harmonized approaches for mercury monitoring, and to strengthen the capacity for mercury analyses in humans and in the environment.

- *The Science-Policy Link*
The project contributes to scientific knowledge for development of effectiveness evaluation mechanism as required by Article 22 (UNEP, 2013).
The experience made within the project suggests that there is an urgent need to coordinate the global effort in mercury monitoring and to this end to consider building on regional and global existing monitoring programs in cooperation with other on-going programs such as for example the GEO (Group on Earth Observation, www.earthobservations.org) Strategic Plan (2016-2025) and to its Flagship "Global Observation System for Mercury (GOS4M)", which is aimed to contribute to the implementation of the Minamata Convention

iii) CONTRIBUTIONS AND METRICS
The nature of effectiveness evaluation of the Convention will evolve over time and could be based on following aspects:

• In the shorter term, this will have to be assessed on the basis of monitoring key information indicators of anthropogenic mercury pollution that can include supply, trade, use and emissions of mercury;
• In the longer term, reduced mercury pollution would be translated in reduced levels in the environmental and living organisms, which will allow a full evaluation assessment.

Reliable monitoring data is needed (art. 19 and 22 in UNEP, 2013b) and the Global Mercury Observation System (GMOS) and other regional information sources available, will substantially contribute.

CONCLUSIONS

Scientists can support international, national, and local efforts of Hg pollution reduction policies through multiple institutional mechanisms. Internationally, scientists can contribute to scientific assessments and can also highlight linkages between science and policy and possible metrics or indicators to be used for the more appropriate implementation of policy goals.

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ERA-PLANET MANAGEMENT: SOME KEY ASPECTS

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INTRODUCTION

The H2020 Program - ERA NET COFUND ERA-PLANET - The European Network for Observing our Changing Planet (Grant Agreement No. 689443) of five-year duration (www.era-planet.eu) coordinated by CNR-IIA (www.iia.cnr.it), sees the participation of 34 research organizations, including research centers and universities, belonging to 14 EU countries and an associate country, all leaders in the domain of Earth Observation (EO) in coherence with the European participation to Group on Earth Observation (GEO) and the Copernicus.

ERA-PLANET's main objective is to strengthen European leadership in the EO domain in synergy with other international and national programs such as the European participation in the GEO (Group on Earth Observations) intergovernmental program and the development of Copernicus, the European program on 'Earth Observation, coordinated by the European Commission (DG GROW) in which all Member States participate together with ESA, EUMETSAT, ECMWF and other agencies. In addition, the ERA-PLANET will provide advanced decision support tools and technologies aimed to better monitor our global environment and share the information and knowledge in different domain of Earth Observation.

Key program features are reported in Figure 1 while actors involved in Figure 2.

Specific objectives of ERA-PLANET are:

1. To prepare and launch a two-stage joint transnational call structured along the following Strands:
   - Strand 1 - Smart cities and resilient societies addressing issues such as urban growth, air quality, disasters, health, contaminated sites.
   - Strand 2 - Resource efficiency and environmental management including water, energy, food security, biodiversity.

Figure 1. Main program features

Figure 2. Actors involved in ERA-PLANET

   - Strand 3 – Global change and Environmental treaties addressing global observing systems for toxic and persistent pollutants, harmonization of monitoring and coupled atmosphere-ocean-terrestrial models, evaluation of ecosystem response to regional/global emission changes, support to policy implementation. Climate forcing is one of the major variables to be

considered in assessing global change patterns and analysis of policy scenarios.
   - Strand 4 – Polar areas and natural resources in a highly climate-sensitive regions including the evaluation of the impact of energy resource exploitation, the impact of long-range transport of air pollutants and their atmospheric deposition, air-surface exchange mechanisms, and environmental pressure from increasing anthropogenic activity in areas with sensitive ecosystems.
2. To fund projects according to a priority list set by external experts.
3. To monitor funded projects and to report progress accordingly.
4. To develop a strategic research agenda to reinforce the ERA and to coordinate the cross- and inter-cooperation of European and national programs in key and selected EO domains.
5. To coordinate initiatives with the aim to improve the interoperability among the existing and future projects on EO and links to the GEOSS Common Infrastructure.

This work presents main activity led to implement ERA-PLANET.

OBJECTIVES OF ERA-PLANET

Main activity of ERA-PLANET was the launch of a Joint Trans-national Call, open to the beneficiaries of the Program. A two-step selection process, (September 2016 - May 2017) was adopted to evaluate submitted projects by two External Panels of Experts.
The Management Support Team (MST) is guiding day-by-day activity of the Consortium and maintains contacts with Work Package Leaders, European Commission, the Coordinators of the four funded projects, and with national Programme Owners and Managers. The Management Support Team also assists and acting as Secretariat for the Chairs of the Expert Panels. It also assisted the consortium and the coordinator of the four selected projects in preparing the Grant Agreement and all the necessary documents needed for the negotiation.
MST in close cooperation with all WP Leaders is helping partners to produce timely and high quality deliverables as well as accomplishments of contractual obligations with EC. Within Work Package 1 the MST will ensure efficient logistic and financial management of the project and monitor ERA-PLANET progress and prepare reports, ensuring respect of commitments.

ERA-PLANET IMPLEMENTATION

To ensure an efficient governance of the consortium and its activity in the preparation and launch of the Call, in the evaluation and selection of the projects, in the follow up of projects, in the communication and dissemination of major outcomes of projects and in establishing a close cooperation with European research policy on Earth Observation and support the EU and international environmental policy process ERA-PLANET is structured in 6 WPs (Figure 3) which are briefly presented below.

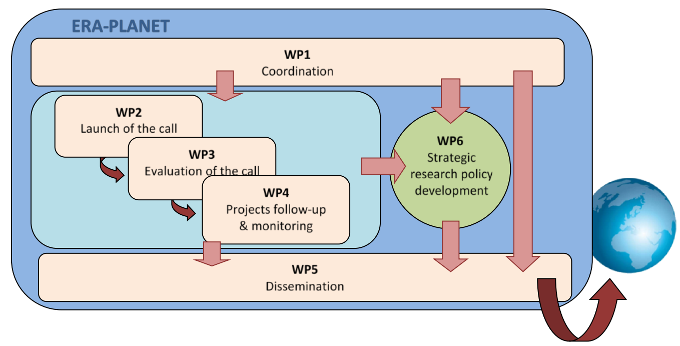

Figure 3. ERA-PLANET Workpackages

WP-1: Consortium coordination and management
Lead: CNR (IT)
The overall coordination and management of ERA-PLANET will be led by CNR in close cooperation with all WP Leaders and members of the Steering Committee. As responsible leader, the CNR will help partners to produce timely and high quality deliverables as well as accomplishments of contractual obligations with EC. The main goal of the WP is to assure an efficient coordination of all WPs and Tasks of the project.
WP-2: Preparation and launch of the co-funded Call
Lead: MU (CZ)
The WP-2 will implement all necessary actions to ensure an efficient and transparent ranking of submitted proposals and to promote a wide participation to submit innovative ideas. The process will be based on preparation of the Two-step Call for Proposals related to the four Strands;
WP-3: Evaluation and proposal selection
Lead: CNR (IT)
The aim of this WP is the identification of External Evaluation Panel and support for the Second Step evaluation. This WP will also interact with the coordinators of the four selected proposals in the negotiation phase according to the rules laid down in the H2020.

WP-4: Follow-up and monitoring of projects
Lead: CREAF (ES)
WP-4 is designed to ensure that ERA-PLANET projects are developed following their proposed agenda, generate results of excellent quality and achieve all objectives and expected results reported in their work plan.
WP-5: Communication, Exploitation and Dissemination of the results
Lead: NOA (GR)
WP-5 describes the strategy and means that the Consortium will use to optimize the communication, dissemination and exploitation paths to be followed and consequently maximize the impact of the ERA-PLANET project.
WP-6: Strategic research policy development, coordination of European programs and supporting International Policies
Lead: CNR (IT)
This WP is designed to ensure that ERA-PLANET projects develop their activities in the context of the European research policy on EO.

LAUNCH OF THE CALL AND RESULTS

Preparation of the call included the text of the call and Guidelines for Evaluators.
The call followed a two-step submission and evaluation procedure. In Step-1, proposers responding to the transnational call submitted a short proposal, which were evaluated by and external panel of experts. Only the best short proposals (up to three per thematic area) were invited to submit a full proposal for final evaluation. A different panel for evaluation was established in Step-2 and all activity was followed by and independent observer appointed by the European Commission.
Forms and evaluation criteria were those established in H2020 Program to select the best innovative and competitive projects that may better contribute to realize the ERA-PLANET scope and objectives, in relation to key aspects characterizing each of the four thematic areas of ERA-PLANET.
At the end of the process four projects were approved and financed:

- SMURBS (SMarturban Solutions for air quality, disasters and city growth);
- GEOEssential (Essential Variables workflows for resource efficiency and environmental management);
- IGOSP (Integrated Global Observatory Systems for Persistent Pollutants);
- iCUPE (Integrative and Comprehensive Understanding on Polar Environments).

Each project started his activity on September 1st 2017 and will last in 36 months. The sum of total declared cost (Direct plus Indirect Costs at a flat rate).
As expected each partner reshaped his budget following real estimates and distributed budget amount to each project. Few partners withdrawn their participation. All considering an amendment was proposed and accepted by the Commission, which revised the matter. Table 1 shows key figures of the budget for each project.

Table 1. Key figures of ERA-PLANET projects

SMURBS ERA-PLANET	
Coordinator	NOA (GR)
Partners	19
Total eligible costs	9 150 151 €
Requested EU contribution	2 750 000 €
GEOESSENTIAL ERA-PLANET	
Coordinator	UNIGE (SWISS)
Partners	15
Total eligible costs	10 401 932 €
Requested EU contribution	2 712 256 €
iGOSP ERA-PLANET	
Coordinator	CNR-IIA (IT)
Partners	13
Total eligible costs	8 351 396 €
Requested EU contribution	2 750 000 €
iCUPE ERA-PLANET	
Coordinator	UHEL (FI)
Partners	13
Total eligible costs	9 339 798 €
Requested EU contribution	2 750 000 €

PROJECTS' ACTIVITY

The negotiation phase takes a while to prepare Consortium Agreements (CAs) for each project that were based on the general CA approved in ERA-PLANET.
Eighty-one (81%) of payments to Parties of each project were made in accordance with the art. 21 of Grant Agreement, the ERA-PLANET Consortium Agreement and after the approval of the Report for the First Reporting Period by the Commission.
A specific activity involved Italian beneficiaries (CNR, UNICAL, UNIPD, ISPRA) as they can receive from the Ministero dell'Istruzione, dell'Università a della Ricerca (MIUR) an additional

cofund amount of 1.4 M€ (14.15% of total eligible costs).
These partners were required to submit additional documentation for evaluation.

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RECENT CLIMATE CHANGE: FROM CAUSES TO IMPACTS ON EXTREME EVENTS AND AIR QUALITY

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Keywords: Neural network modelling, robustness, tornadoes, heat waves, pollution

INTRODUCTION

Climate change related to the recent global warming is a challenge for both science and society. Science has to understand and predict the behaviour of this complex system, under natural and anthropogenic external forcings, and internal variability. Society is strongly affected by the impacts of climate change on territories, ecosystems and humans, and therefore has to mitigate and adapt, but, in the meantime, it must use science for achieving a better knowledge of the characteristic features of these impacts and for understanding their relationships with the climate change itself.

In this framework, scope of this work is to briefly review two studies performed in this Institute and related to investigations about the causes of the recent global warming and the behaviour of tornadoes in Italy under sea surface temperature (SST) changes. Furthermore, the consequences of climate change for air quality in Italy are discussed.

THE ATTRIBUTION PROBLEM

Attribution is defined as *'the process of evaluating the relative contributions of multiple causal factors to a change or event'* (Bindoff *et al.*, 2013). In climate studies this is usually performed through Global Climate Models (GCMs). In particular, once obtained validated models – i.e. models which are able to reconstruct a climate variable such as global temperature in a satisfying manner when fed by real values of external forcings –, these models can be used for numerical "causal" experiments. For instance, GCMs may run with altered values for anthropogenic forcings, simulating no change from preindustrial levels. In doing so, one clearly find that the recent warming would not have happened, because the increase of temperature (in the last 50-60 years) disappears and the temperature behaviour remains quite constant: see Figure 10.1(b) of Bindoff *et al*. (2013). In short, human influences appear as the fundamental causes of the recent global warming.

Because all GCMs provide this common result, it could be considered a clear signal of the robustness of this result, provided that given conditions, such as the independence of the models involved, hold. But GCMs do not seem so independent, given that they are all historically linked together by a common origin and relations of mutual generation, they follow the same modelling/methodological dynamical scheme, etc.

Thus, only the adoption of a distinct approach of investigation can confirm or "falsify" the attribution results from GCMs. Here we consider an attribution analysis performed through a neural network model. See Mazzocchi and Pasini (2017) for more details on different data-driven models which can be adopted for analysing the topic of robustness.

A NN tool, specifically developed for modelling relationships among variables in small datasets (Pasini, 2015), can be adopted for attribution studies. A training-validation-test procedure must be applied for obtaining a nonlinear relationship between inputs and targets (to be approximated by outputs) which can be generally valid. In particular, the connection weights (the free parameters of the NNs) have to be fixed on the training set – by stopping the training phase when the error on the validation set begins to increase – and the generalization performance must be measured using a third set (unknown to the NNs), the test set. The tool used here – by adopting a generalized leave-one-out procedure – permits to maximize the members of the training set, while leaving good generalization performance. More information on this NN tool can be found in Pasini (2015) and Pasini *et al*. (2017).

For attribution purposes, we can search for some NN models that are able to well reconstruct the temperature time series once considered all observed values of forcings as inputs, then apply their transfer functions (the validated NN models) to new

inputs, in which we mimic the fact that some of their values show no trend since 1850, finally obtaining new outputs in terms of "simulated" T. In this case one can appreciate the roles of the real changes in different forcings on the behaviour of T.
In particular, if one sets the total anthropogenic radiative forcing as constant at the value of 1850, he can perform the same attribution experiments as in the GCM ones cited above. The result of the NN attribution is depicted in the following Figure 1.

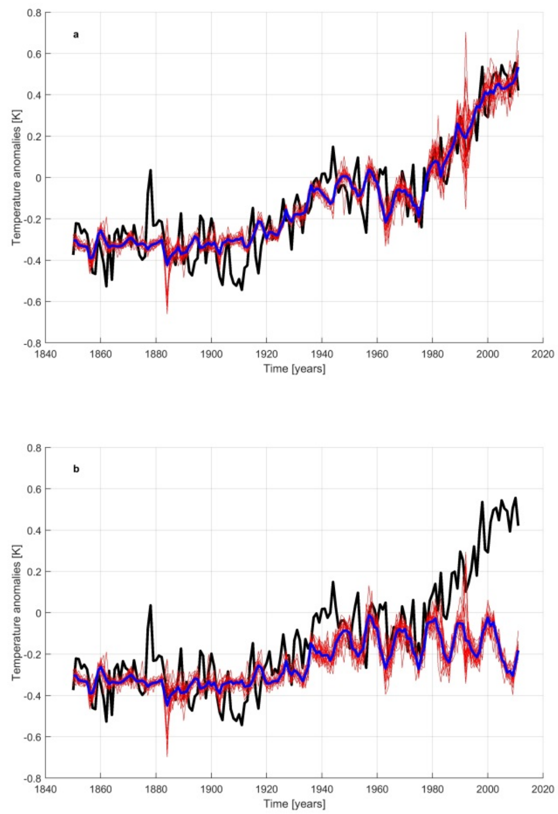

Figure 1. Results of NN attribution

The outputs of NNs (red lines) and their ensemble mean (blue line) are able to reconstruct the global temperature (black line) when all the real data of external forcings are supplied to them (a). When we mimic the situation of constant anthropogenic forcings fixed at their estimated values of 1850, the recent global warming is no more caught by the NN models (b).
Incidentally, this new approach contributes also to the climate debate on the media, where the anthropogenic influence on the global warming is often denied, basing on the critics to the GCMs. Here we show that, even using a very different type of models, the final result is essentially the same: the man had and has a fundamental role in causing the recent global warming.
In addition to this "corroboration" of the results previously obtained by GCMs, new attribution results are now achieved on the role of the Sun, irrelevant for the trend of the last decades and quite strong at the middle of the 20th century, and for the influence of anthropogenic sulphate emissions on both the temperature hiatus during the period 1945-1975 and the behaviour of the Atlantic Multidecadal Oscillation (AMO) since 1866. Further details may be found in Pasini *et al*. (2017).

TORNADOES IN A WARMER MEDITERRANEAN SEA

As well known, global warming leads to changes in water cycle, energy fluxes and atmospheric circulation. All these effects can have important impacts on territories and inhabitants.
One of the major concerns is now the possible increase in frequency and/or intensity of the so-called "extreme events". Among them, tornadoes are local-scale dangerous phenomena affecting also Italy: see Miglietta and Matsangouras (2018) for an Italian "climatology" of tornadoes and waterspouts.
At present, an assessment of the behaviour of tornadoes in future climate scenarios is not achievable by climate models, because GCMs (and also Regional Climate Models – RCMs) do not "see" tornadoes, due to their low resolution. Furthermore, evaluating if – with global warming – there will be changes in regional/local circulation that could favour a higher frequency of tornadoes, or hinder it, is not simple, and models do not supply us with clear signals at regional scale.
In this framework, studying evolution of tornadoes through high-resolution meteorological models appears a good idea, since it enables us to evaluate the role of warming on their intensity under particular circulation conditions. In doing so, we establish on the robust thermodynamic part of meteorological models, involving in particular sea-atmosphere flux exchanges. In short, even if probably we are not able to assess if tornadoes will become more frequent, we could achieve information about their intensity and violence, when they happen.
In a recent paper (Miglietta *et al*., 2017) a tornado originated as a waterspout over the Ionian Sea and landed near Taranto on November 28, 2012, has been studied by means of Weather Research and Forecasting (WRF) model, version ARW-3.5.1. Three one-way-nested domains are implemented (9-

3-1 km): see Miglietta *et al*. (2017) for further details. This configuration permitted to catch the supercell which originated the tornado and to simulate correctly its path. In Figure 2 this supercell is identified in terms of vertical vorticity (red dot), when it was approaching Taranto.

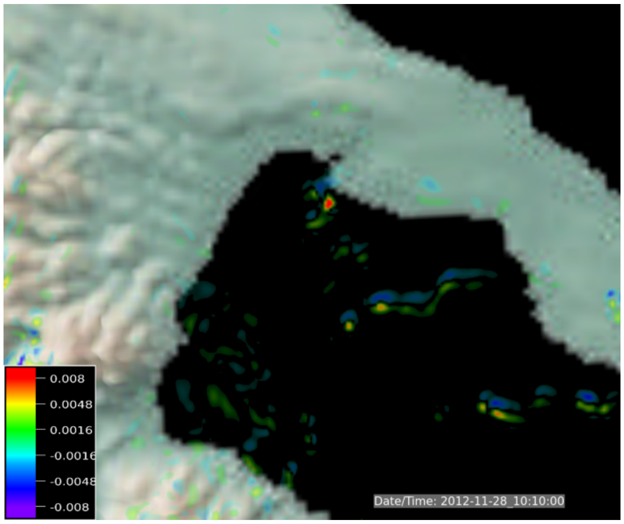

Figure 2. Vertical vorticity (red dot) of identified supercell

Observations about sea surface temperature (SST) of the Ionian Sea in that period show that it was about 1°C warmer than the climatological mean (1985-2005) at the end of November. Thus, model runs with decreased and increased SST (+/-1°C) of the sea were performed. The results were very clear. In the colder run (SST = climatological mean) no supercell forms. In contrast, the case with the warmest SST produced a strong non-linear intensification of the updraft rotation in the supercell. More details can be found in Miglietta *et al*. (2017).
SST in future decades is predicted to increase almost everywhere in the world. In the Mediterranean Sea, in particular, we have shown that small increase in SST can have dramatic consequences for tornadogenesis. Our study gives no information about future circulation in the Mediterranean basin, so that we cannot infer anything about the future frequency of tornadoes in this area. Nevertheless, this research shows that, when tornadoes will happen, the increased SST will have a direct effect on their intensity.

IMPACTS ON AIR QUALITY

Among the numerous impacts of global warming and related climate changes, one of critical importance is that on air quality. As well known, particular atmospheric states can lead to accumulation of pollutants in the boundary layer or to insurgence of peaks for secondary pollutants.
How will the situation evolve in the next future? This is a question to be answered at regional scale, so that, first of all, the importance of downscaling systems has to be stressed: see, for instance, the study presented in this volume by Amendola and Pasini (2018). Furthermore, RCMs do not always supply us with reliable results on many areas of the globe, but on the Mediterranean basin their projections are converging in a greater influence of the African high pressures, because of a future extension northwards of the Hadley cell of the general circulation (see Figure 3), already observed recently (Birner *et al*., 2014).

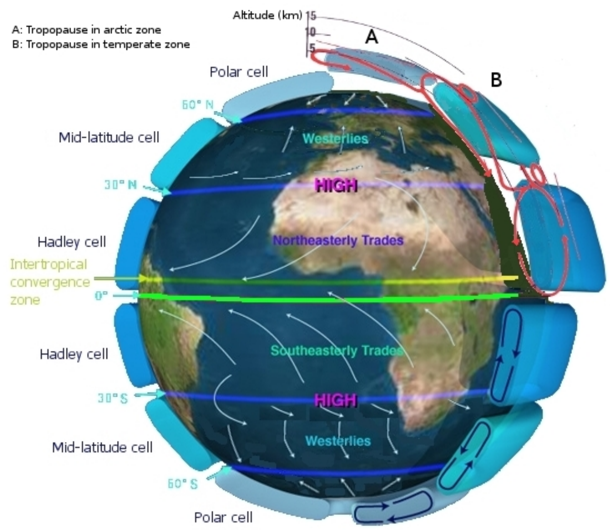

Figure 3. Hadley cell of the general circulation (from Wikipedia)

This could generally lead to more insolation and less precipitation, even if the decrease in wet days may be joined with an increase in precipitation amount during the wet days themselves, that is more intense rainfall in short time intervals.
In this situation, just a few studies were performed on boundary-layer impacts in Italy: see, for instance, Pasini and Cipolletti (2007), Caserini *et al*. (2017). The results are quite interesting. First of all, the increase in temperatures should lead to favour convective motions and consequently instability of the lowest layers. Nevertheless, together with increase in temperatures, also pressure tends to higher values, so that the temperature destabilizing effect is counter-balanced by the subsidence effect of increasing pressure and this leads to more events of long-lasting stability conditions during winter. The destabilizing effect of temperature increase

becomes to be important only in the transition seasons. Even the vertical structure of the troposphere is perturbed and leads to future situations which are critical enough (see Caserini *et al*., 2017). Thus, stagnation periods are not projected to decrease, but seem to become more frequent and strong. This represents obviously a clear predisposition of the low layers for dangerous pollution events, especially for PM peaks.
Furthermore, the influence of heat waves will affect our summers and the highest temperature and insolation will favour the creation of photochemical pollutants, such as ozone, so dangerous for our health.
In short, in the field of air-quality impacts of future climate change in Italy, a big effort has to be devoted to research. The expertise present in this Institute will allow us to deal with this scientific problem inside an interdisciplinary approach.

CONCLUSIONS

In this brief review three important topics have been presented. Both in attribution studies and in impact researches, original results have been achieved.
Following these results, a call for further research has to be opened, but some clear action is also necessary to be performed. The former can improve our understanding on more details of the climate system and its impacts, while the latter can lead to effective mitigation and adaptation activities: we may not further postpone them.

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NEW CHEMICALS AND PERSPECTIVES IN THE HEALTH AND ENVIRONMENT RISK EVALUATION

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Keywords: Environmental toxicity, indoor pollution, endocrine disruptors, psychotropic substances, pharmaceuticals

INTRODUCTION

Recent developments in environmental chemistry and health risk assessment deal with pollution of interiors as well as new substances affecting atmosphere, waters, soil, biota and foods (Richardson and Ternes, 205; Monneret, 2017). In fact, population is known to spend over 85% of its life indoors; there, several chemicals affecting air and surfaces can fight human health though acute and long-term actions. Apart from cancer that was the focus in the past, attention is now paid to non-cancer diseases like skin and gorge irritation, cough, asthma, cardiovascular problems, lung emphysema, cell damages, obesity, diabetes, allergies, weakness, depression, neuropathies, reduced sex functionality, etc. (Bergman *et al.*, 2015; Castiglioni *et al.*, 2018). Most diseases are induced or favoured by hormone interfering substances, usually known as "endocrine disruptors" (EDs). Lists of EDs have been released by EU, Japan, and USA (Table 1).

Table 1. List of EU priority endocrine disruptors (EDs)

Group 1: ascertained EDs	*Group 2: probable EDs*
Chlorinated pesticides	Resorcinol
Hydrocarbons (styrene)	Chlorophenols, phenol, naphthol
Arochlors (PCB)	Alkylphenols
Brominated biphenyls	Chloro, aza & sulfur pesticides
Dioxins	PCDD, PCDF
Tributyltin	CS_2; DMF
Stannane and stannates	C_2Cl_4, $C_2H_4Br_2$
Bisphenol A	4-Nitrotoluene
Phthalate esters	Benzophenone
Sulfur pesticides	Octachlorostyrene
Aza pesticides	DEHA
	Phthalic acid, phthalates
	Ethylene glycol
	Al, Cd, $CuSO_4$
	PBDE
	Hg, $HgCH_3$

As for macro-toxicants, the focus of scientists is on ultra-fine particles (concentration and number) and biogenic pathogens; among micro-contaminants the groups of interest are plasticizers, flame retardants, pesticides, household, personal care and smoking products, which means: phthalates and organic phosphates, brominated diphenyl ethers, fragrances including isoprenoids, fluorinated surfactants, psychotropic substances, drugs; allergens; PAHs. To assess the health risk, distinct work lines are often approached, including: chemical speciation of vapours, suspended particulates and dust; micro-climate and its effects on chemicals, biota and and humans; relationship between exposure and intake through inhalation, contact and ingestion; sources and fate of toxicants; indoor/outdoor pollution relationships.

METHODOLOGY

Our most recent investigations aim at chemically characterizing school, office and home interiors with regard to phthalate esters, psychotropic substances and pharmaceuticals. Phthalates are the most important plasticizers ascertained as endocrine disruptors, while drugs have been found to affect non-users' interiors at levels similar to open air. Pharmaceuticals in air look as a potential issue of big concern, due to their spreading in waters and the general (and often uncontrolled) use by population. Their occurrence is also checked in outdoor air, while toxicants (e.g., PAHs, PM_{10}, $PM_{2.5}$, benzene) are measured to picture the classical pollution.

For this purpose, volatile hydrocarbons are collected from air through both aspiration on carbon traps and passive sampling devices, then they are thermally or solvent desorbed and analysed through GC coupled to MSD or FID. Organic particulates require more complex procedures, including collection (on filters through pumping air, or mechanically removing dusts from surfaces), solvent extraction, clean up through alumina column chromatography, and GC-MSD analysis; pharmaceuticals require the further derivatisation with silylating agents (BSTA).

FINDINGS

Classical and emerging toxicants show well distinct behaviours indoors. In fact, volatile and polycyclic hydrocarbons usually occur indoors and outdoors at comparable concentrations, within the respective limits fixed by normative (exceptions are kitchens and canteens, wood or charcoal stove heated rooms, smokers' homes). Instead, emerging contaminants (ECs) are much more rich indoors, and accumulate both in air and particulates; despite no regulation exists for them, the EC occurrence looks sufficient to depreciate ambient quality. As for example, Table 2 reports the phthalate loads found in urban PM_{10} collected during March 2013 in Amsterdam [AMS], Rome [RM] and Rende [RD] (Italy), and in dust (Rome). Besides, Figure 1 shows mean indoor and outdoor concentrations of psychotropic substances in PM_{10} of Rome (2013).

Table 2. Phthalate loads in urban PM_{10} and settled dust

City	*Type*	*DiBP*	*DBP*	*DEHP*	*DOP*	*DNP*
AMS	PM_{10}, ng/m^3	4.9	1.59	1.22	0.00	0.00
RM		0.63	0.57	8.1	0.32	1.58
RD		0.79	0.55	9.7	0.49	2.5
RM	dust, ng/(m^2*d)	388	280	972	27	220

Symbols: DiBP = diisobytyl phthalate; DBP = dibutyl phthalate; DEHP = dietylhexyl phthalate; DOP = dioctyl phthalate; DNP = ninolyl phthalate (mix of isomers)

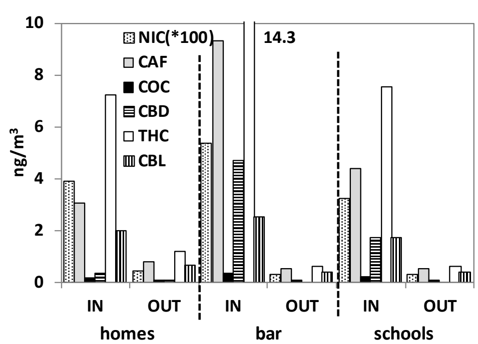

Figure 1. Mean concentrations of particulate nicotine (NIC), caffeine (CAF), cannabidiol (CBD), tetrahydrocannabinol (THC) and cannabinol (CBL) in Rome (winter 2013)

With regard to outdoor environment, ECs seem to affect overall water bodies and wastes, while a little is known about their occurrence in air, sediments and soil.

CONCLUSIONS

Ambient quality is heavily influenced by the occurrence of unregulated ECs, which affect all environmental compartments at every increasing levels, whilst classical toxicants tend to decrease owing to technical progress and limitations posed by normative. Besides, ECs are usually more abundant in interiors, enhancing their adverse effects on population exposed.

Among ECs some groups are recognized as of concern, whilst much more are still underestimated and passed over in environmental studies. Despite that, the growing attention to non-carcinogenic (epigenetic) contaminants and the contemporary discovery of unexpected chemicals require further extensive monitoring investigations and more appropriate approaches to estimate exposure, intake and risk associated to them.

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CHEMICAL CHARACTERIZATION OF ULTRAFINE PARTICLES EMITTED FROM CEMENT PLANTS

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Keywords: ultrafine particles, cement plant emission, particle size segregation, sampling set-up

INTRODUCTION

Cement plants are responsible for particle and gaseous emissions into the atmosphere. With respect to particle emission, the greater part of it is in the range from 0.05 to 5.0 µm in aerodynamic diameter (Kalacic, 1973; Meo *et al*., 2002). Aitken *et al*. (2004) and Luther (2004) summarized various types of device which might be or have been used to provide measurement information about nanometer size aerosols. Burtscher (2005) described the two principal classes of methods used to investigate aerosol particles: methods based on the analysis of filter samples and in situ methods. In the last years, although much attention has been paid to submicron particles, there is a few literature data on their emission from stationary sources.

Experimental campaigns were carried out by Rotatori *et al*. (2015) in order to develop a sampling line for the measurement of the concentration and size distribution of the emitted particle at the stack of four cement plants through condensation particle counter (CPC) and scanning mobility particle sizer spectrometer (SMPS). Average total particle number concentrations were between 2000 and 4000 particles/cm3, about 8-10 times lower than those found in the corresponding surrounding areas. As for size distribution, for all the investigated plants it was stable and showed a unimodal distribution (120-150 nm), independently of the fuel used.

Further investigation comprehend the chemical characterization of the inorganic fraction of ultrafine particles and nanoparticles emitted by the cement plant by offline aerosol mass spectrometry (Daellenbach *et al*., 2016). The same characterization of the particulate matter will be carried out in the ambient air surrounding the plant, in order to evaluate the possible correlation between the particulate matter present in the environment and the emission due to the cement plant.

Due to the low mass of UFP emitted by the cement plant, an extended sampling time is required; a greater collected amount could increase the possibility of mass overloading on the larger fractions.

Flue gas emitted from the kiln is hot (90-130°C), highly concentrated, and made up of volatile gaseous compounds that tend to condense, leading to an under-/over-estimation of emitted particles due to either nucleation or condensation during the cooling phase. Usually, a permeable membrane dryer is used to remove water vapor and other light, polar compounds from the flowing sample stream (Clarke and Bartle, 1998).

In this paper, the development of a sampling system able to directly transfer the sample from the stack to a multistage impactor will be evaluated and optimized.

METHODOLOGY

Instrument set-up and experimental specifications

Experimental campaigns were performed at the stack of Italian cement plants of Buzzi Unicem Group located in Guidonia (Rome).

A flange has been installed on the ground, at the base of the stack, on the pipe at the end of the bag filter. The sampling probe was equipped with a tubular Nafion membrane (E. I. Dupont de Nemours, Inc., Wilmington, DL), a copolymer of tetrafluoroethylene and fluorosulfonyl monomer, that is coaxially mounted within larger tubing (Perma-Pure Products, Inc.). The sample flow rate to the measurement system, through tubular Nafion membrane, was 0.3 L/min. The dried sample was sent to the measurement system, a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc.) able to measure the size distribution of the aerosols in the range from 10 to 800 nm. Then, the same dried sample was sent to two different commercially available size-segregated PM samplers:

• a nano-microorifice uniform deposit area impactor (Nano-Moudi-II™, MSP Corp., USA Model 125R) equipped with PTFE filters, operating at an inlet flow rate of 10 L/min; this impactor effectively separated the particulate matter into 13 stages (0.010 – 10 µm);
• an electrical low pressure impactor ELPI™ (Dekati Ltd., Tampere, Finland) equipped with PTFE filters, operating at an inlet flow rate of 10 L/min; this impactor effectively separated the particulate matter into 13 stages (0.007 – 10 µm). The ELPI™ External Heating Assembly Set allows the ELPI™ charger and impactor to be heated up to 200 °C.

In order to eliminate water vapour from the flue gas, condenser-type diffusion denuder was used. Briefly, cold water (20°C) flows in the denuder, cooling the sampling probe; the condensate is removed by collecting it in a slightly depressurized tank.
Particulate matter in the area surrounding the plant was simultaneously collected by MOUDI II 120R operating at an inlet flow rate of 30 L/min with 10 collection stages spanning a size range of 0.056–18 µm.

FINDINGS

Once the sampling probe has been installed in place, and the flows and any leaks verified, the same has been connected to the multistage impactor. At the same time, another multi-stage impactor for air-environment sampling has been installed. Before starting the sampling, preliminary measurements were made with the SMPS - upstream and downstream of the sampling system - to evaluate the number of ultrafine particles emitted. On the basis of these tests, the minimum sampling period was established in 15-20 days.
After the measures with the SMPS analyzer, the probe was connected to the multistage sampler NanoMOUDI.
After a few hours, abundant condensate was found on the filters inside the multistage impactor, making the filters wet and useless.
The difference between the sampling lines of SMPS and NanoMOUDI is in the sample flow: 0.3 and 10 L/min, respectively. Accordingly, the sampling conditions have been modified, acting on the parameters of the dryer (increasing the purge flow, as the NanoMOUDI operates at a flow rate of 10 L/min). Another measurement has been carried out but, again, condensation was found on the filters.
Since humidity of the flue gas of this cement plant is about 10 % (v/v) and the average temperature is about 110°C, it was attempted to remedy the condensation problem by thermostatically controlling the sampling system. This goal was achieved both by heating the NanoMoudi with a homemade heating system (about 35°C) and by using the ELPI with the External Heating set (about 55°C). Although a reduced amount of water has been observed on the filters, this method has not been decisive for the total removal of the condensate.
Taking into account the negative results of the described experiments, it was considered to eliminate the water vapor in the flue gas using a condenser-type diffusion denuder with the probe (set temperature: 20°C) in order to send almost dry flue gas to the Nafion membrane and then to the NanoMOUDI impactor (Figure 1).

Figure 1. Optimized sampling system

With this optimized system, the temperature (°C) and the relative humidity (% RH) of the flue gas at the inlet of the impactor were 22°C and 57%, respectively. These conditions, comparable to ambient air, allowed an extend sample collection of 15 days.

CONCLUSIONS

In this study, some critical issues have been identified in the sampling of ultrafine particles emitted by a cement factory through a multistage impactor system.
The critical issues in sampling the fumes emitted by the cement plant with a system suitable for ambient air are the temperature and humidity of the sample. The high temperature (100 °C) changes the viscosity of the air, influencing the cutting-off of the impactor stages; the humidity (10% v/v) causes condensation on the filtering membranes, degrading the sample.
THE COMBINED USE OF A DRYER (NAFION MEMBRANE) AND A COOLER CONVERTED THE FLUE GAS TO AMBIENT CONDITIONS (T 22 °C, RH 57%), ALLOWING A RELIABLE

SAMPLING USING INSTRUMENTS SUITABLE ONLY FOR AMBIENT AIR.

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OVERVIEW OF TECHNOLOGIES FOR IMPROVING ENERGY EFFICIENCY FROM ENERGY INTENSIVE INDUSTRIES DERIVED FROM THE ITALIAN NATIONAL EXPERIENCE IN IPPC PERMIT LICENSING

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INTRODUCTION

Over the past years the growth rate of global primary energy demand has been one of the key points in the political agenda of industrialised countries in determining their economic development.
In EU-28 the largest share of energy is consumed by transport, followed by industrial activities and residential consumption. Within the industrial sector, most of the primary fuels are used in thermal power stations (27%), followed by the iron and steel (19%) and chemical sectors (18%) (Eurostat, 2014).
Some recent studies provide a comprehensive overview of energy savings potentials and related environmental impact reduction in different industrial sectors (Kimura and Noda, 2014; Thollander *et al*., 2015; Stede, 2017).
In particular, some analyses provide a very comprehensive assessment of those technologies applied in energy intensive industries especially in relation to climate change mitigation (Napp *et al*., 2014; Fleiter *et al*., 2012; Pardo and Moya, 2013).
Several other studies explore barriers to energy efficiency improvements in order to develop recommendations for policy makers (Fleiter *et al*., 2012; Stede, 2017).

In the EU emissions from relevant industrial activities are currently regulated under the Directive 2010/75/EU on industrial emissions - Integrated Pollution Prevention and Control (IPPC-IED) that requires operators to improve their own environmental performance by implementing the Best Available Techniques (BAT) also with regard to how to use efficiently the energy resources (Directive 2010/75/EU, 2010; Mazziotti *et al*., 2014).
The present paper provides a glimpse into the main achievements in Mazziotti *et al*., 2017 and focuses on the implementation of BAT with reference to energy efficiency in relevant industrial sectors, having being licensed IPPC permits by the Ministry for the Environment, Land and Sea (Decree n. 152/2006), namely:
1. integrated iron and steelworks (primary fusion);
2. refineries of mineral oil and gas within the category installation with a production over > 500 Mg per day of coke and shale oil;

Such an analysis is carried out on the basis of any documentation on the IPPC permits licensed under the mentioned Integrated Pollution Prevention and Control (IPPC-IED) legislation and made available to the public on the Ministry for the Environment, Land and Sea web site, on the so-called "AIA Portal" (AIA Portal, 2015 and 2016; Mazziotti *et al*., 2014).
Moreover, since energy efficiency is at its best at the beginning of the life cycle of the plant, operators, whenever necessary, periodically shall monitor and measure the actual energy performance of their own installations for process control and maintenance purposes.

METHODOLOGY

According to the IPPC-IED, operators are required to achieve a general improvement on the entire environmental performance of their industrial installations with regard to emissions into water, air, soil as well as to energy efficiency, waste production, recovering and recycling, restoration of the site upon definitive cessation of activities.
For this purpose, the main instrument to trigger innovation is the provision of implementing Best Available Techniques (BAT), that is the technology used and the way in which the installations is designed, built, maintained, operated and decommissioned, providing an effective level of protection of the environment under economically and technically feasible conditions, as addressed by relevant BAT Conclusions (Evrad *et al*., 2016; Mazziotti *et al*., 2014).

Along with the mentioned legislative framework, a voluntary certification system, i.e. the recent revised version EN ISO 14001:2015, Regulation (EC) No. 1221/2009 (EMAS), as recently amended by Regulation (EU) 2017/1505 and EN ISO 50001 (EN ISO 50001, 2011), specify any requirement for establishing, implementing, maintaining and improving the management system at the installation.

FINDINGS

Iron and steel industry

The iron and steel industry is an intensive energy sector. For the sector of primary iron and steel production the following techniques, synthetically described in Table 1, are specifically set out for energy management, as reported in the BAT Conclusions adopted with Decision 2012/135/EU (Commission, 2012) and in the Reference Document on Best Available Techniques (BRef) for iron and steel production (European Commission 2013a).

For the present paper the integrated iron and steel installation (primary fusion) located in Piombino (Livorno) is taken into account, although the production is now ceased.

In particular, the installation in Piombino, that has not adopted any voluntary certification system, the IPPC permit released in 2013 specifically foresees

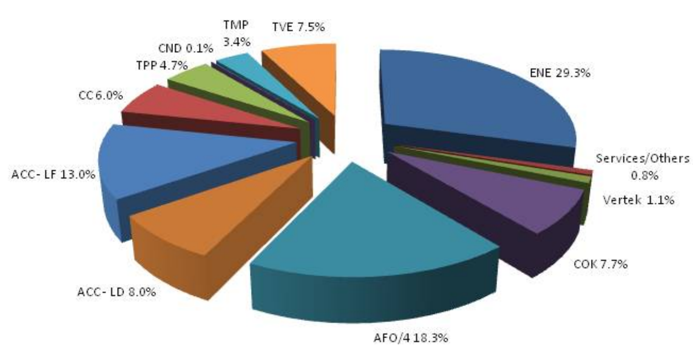
- the implementation of periodic energy audits to identify effective energy savings opportunities also by means of revamping of existing units;
- a study that demonstrates that the installation is managed taking into account Best Available techniques (BAT) as defined in the BRef for energy efficiency and in any relevant BAT Conclusions for the sector concerned.

In such an installation, the energy power for internal use and for operation of auxiliaries of the installation are either acquired from an external power plant either produced internally.

The exchange of raw materials and energy with the thermoelectric power installation located nearby is significant and it involves the siderurgical gases (Coke gas and Blast Furnace gas) produced during steel production processes, that are used as fuel by the same thermoelectric power installation. On the other hand, the power plant produces energy and vapour for the units of the siderurgical installation. Thus, the installation is highly integrated in the industrial-parks with exchanges of by-product and services to minimise waste and maximise the use of resources.

Table 1. Techniques for the sector of primary iron and steel production according to Commission Implementing Decision 2012/135/EU of 28th February 2012 establishing BAT Conclusions for iron and steel production - BAT 2, 3 and 4 (European Commission, 2012)

BAT 2 Reduction of thermal energy consumption by using a combination of the following techniques	I. Improved and optimised systems to achieve smooth and stable processing, operating close to the process parameter set points by using
	II. Recovering excess heat from processes, especially from their cooling zones
	III. An optimised steam and heat management
	IV. Applying process integrated reuse of sensible heat as much as possible
BAT 3 Reduction of the primary energy consumption by optimisation of energy glows and optimised utilization of the extracted process gasses such as coke oven gas, blast furnace gas and basic oxygen gas.	
BAT 4 Use of desulphurised and dedusted surplus coke oven gas and dedusted blast furnace gas and basic oxygen gas (mixed or separate) in boilers or in combined heat and power plants to generate steam, electricity and / or heat using surplus waste heat for internal or external heating networks, if there is a demand from a third party.	



COK: Coke Oven Plants
AFO: Blast Furnace
ACC: Basic oxygen furnace
CC: Casting
TVE, TMP, TPP, CND: processing
ENE: Gas, electric energy, steam and water distribution network

Figure 1. Total energy consumption per division in an iron and steel installation (AIA Portal, 2015)

According to 2005 data, the ENE division was the one with the most relevant energy consumptions. In fact, it represents almost the 30% of energy consumptions of whole installations. It follows the basic oxygen furnace with the 21%, the blast furnace with the 18.3%, the Coke Oven Plants with the 7.7% and the division of Treno Vergella (TVE) with the 7.5%. The main technical intervention for the blast-furnace and the basic oxygen furnace carried out by the company in 2007, before the IPPC permit release were mainly addressed to the blast-furnace that is the main responsible for the consumption of energy and raw materials, such as coke and other fossil fuels (AIA Portal, 2015).

Refineries of mineral oil and gas

In 2015 there were 12 refineries of national relevance in Italy, while to date they are 11; their permit is released at national level by the Ministry for the Environment, Land and Sea (AIA Portal, 2015).
Similar to other industrial sectors, the majority of the Italian installations already applies the following techniques (Table 2 and Figure 2) in relation to energy efficiency, since, in principle, energy costs represent more than 50% of global operating costs and an increase in the energy efficiency reduce the total operating costs (Commission, 2014; European Commission, 2009 and 2013b).

Table 2. Techniques for the sector of the refineries of mineral oil and gas (BAT 2) according to Commission Implementing Decision 2014/738/EU of 9th October 2014 establishing BAT Conclusions for the refining of mineral oil and gas (Commission, 2014; AIA Portal, 2015)

Design technique	Heat integration
	Heath and power recovery
	Pinch analysis
Process control and maintenance techniques	Process optimisation
	Management and reduction of steam consumption
	Use of energy benchmark
Energy efficient production techniques	Use of combined heat and power
	Integrated gasification combined cycle (IGCC)
Further intervention proposed by the operator after the first round of IPPC permit release	Set up of a new co-generation of heat and power - CHP / Revamping of existing combustion plants inside the refinery; Vapour recovery unit; Substitution of blowers; New production process – green refinery.

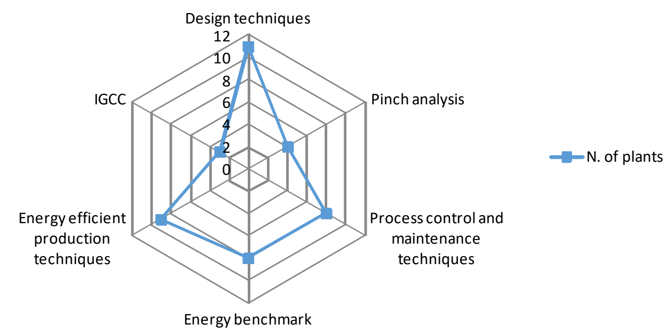


Figure 2. Analysis of the documentation for the IPPC permit release and following updates (AIA Portal, 2015)

In Figure 3 it is shown a diagram on example of raw material and energy consumption fluxes in an Italian refinery, to show the highly integrated and interdependent nature of most processes, where the thermal recovery is maximized (AIA Portal, 2016). Furthermore, it should be noted that some national installations are highly integrated in a symbiotic industrial network with exchanges of energy and vapor as well as water reuse in the cooling / cutting process operations.

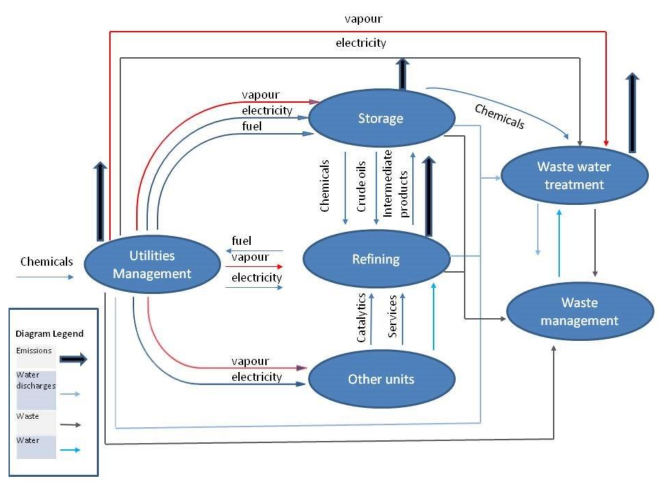


Figure 3. Raw material and energy consumption fluxes in a refinery where the thermal recovery is maximized (AIA Portal, 2015)

Furthermore, it should be noted that integrated gasification combined cycle (IGCC), i.e. gasification, air separation, gas cleaning and combined cycle, is a highly-integrated process technique for the production of steam, hydrogen and electric power. In particular, the gasification of heavy residues is a rather new technique. In fact, IGCC plant can convert almost any refinery residues (atmospheric residues, vacuum residues, visbroken or thermal tars, etc.) to heat and power. On the other hand, such residues have a high sulphur content (European Commission, 2015).

CONCLUSIONS

This paper presents the picture of the status of implementation of BAT related to energy efficiency in the main Italian industrial installations on the base of the analysis on the IPPC permits released by the Ministry for the Environment, Land and Sea. The implementation of Best Available Techniques according to BAT Conclusions and Integrated Pollution Prevention and Control Reference Document (BRef) has been assessed in relevant national energy-intensive industry taking into account technical documents provided by operators related to the IPPC permit released as well as periodic communication on self-monitoring.
However, the implementation of cross-cutting technologies and measures as well as the recent improvement in computer aided services in order to automatically adjust key process parameters, show that there is still a potential for further reducing the energy demand within the installation and to promote a prudent and sustainable use of resources in complex installations as it is emerging in the large combustion sector (AIA Portal, 2016; Mazziotti, 2017).

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CHARACTERIZATION OF EMISSIONS FROM A STRAW-FED THERMAL POWER PLANT OF WHEAT AND RICE STRAW

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Keywords**:** Biomass Fuel, emissions, Organic micro-pollutants, Inorganic micro-pollutants, Emission factors

INTRODUCTION

Biomass production is an integral component of farming systems leading to generation of huge amount of crop residues worldwide annually. Rice is an important cash crop, and it is estimated that 739 million tonnes were produced in 2016, leaving a significant amount of residue burned after harvest in the field, such as roots, stubbles and straw (Oanh *et al.*, 2010). Over recent decades, it is an emerging and important issue contributing to the intensification of smog, especially in Asian countries. Open burning of straw is a common practice in rice straw management in Asia (Gadde *et al.*, 2009). Mass ratio between the obtained biomass waste and the rice produced is equal to 1.76 while the total waste burned in the world is about 20% (Street s*et al.*, 2003). From these data, it is clear that the annual burnt biomass of the world is equal to 260 million tons. This study determines the role of the burning of rice straw and wheat straw biomass and its contribution to air pollution, since burning can emit considerable amounts of atmospheric organic and inorganic macro and micropollutants. This study is aimed at the evaluation of emission factors due to the combustion of biomass deriving from rice straws.

METHODOLOGY

The experimental campaign was carried out on wheat straw of the variety *Triticum Aestuvum L.* produced by CREA (Consiglio per la Ricerca E la Sperimentazione in Agricoltura, Monterotondo) while the basmati rice straw (*Oryza sativa*) was specially imported from Pakistan from three different areas including Punjab, Azad Jammu and Kashmir (AJK) and Sindh. The biomass has been shredded and open-air dried in order to reduce the size and the moisture, thus facilitating the combustion process.

The moisture content was measured by means of the Memmert UFP800 drying oven and according to the UNI EN 14774-1 (2009). In particular, the biomass sample was dried at 105 ± 2°C and the moisture content was calculated taking into account the weight loss of the sample due to the drying process that lasted 24 h, until constant weight.

For the characterization tests of heating value, elemental composition and ash content, the dried sample was grinded first with the Retsch SM 100 cutting mill for a preliminary size reduction and thereafter through the Retsch ZM 200 rotor mill.

The higher heating value (HHV) was determined by means of the Anton Paar 6400 isoperibol calorimeter and according to the UNI CEN/TS 14918 (2005). The sample was prepared in a pellet form of about 1 g through a pellet press and then it was inserted into the bomb. The sample was connected through a cotton wire to the electrodes for the ignition of the combustion reaction that occurs in a high-pressure oxygen atmosphere. The lower heating value (LHV) was calculated from the higher heating value, depending on the hydrogen content.

The elemental composition in terms of carbon (C),hydrogen (H), nitrogen (N) and sulphur (S) was measured by means of the Costech ECS 4010 CHNS-O elemental analyzer and according to the UNI-EN 15104 (2011). Tin capsules containing about 1 mg of sample were prepared and then inserted in the combustion furnace of the analyzer through a pneumatic carousel. The oxygen content has been calculated by difference on a dry basis. The ash content was measured by means of the Lenton EF11/8B muffle furnace and according to the UNI-

EN 14775 (2010). The sample of about 1 g was placed on a porcelain dish and then inserted in the furnace. The temperature of furnace was set with two different heating rates related to two steps: the first up to 250°C and the second from 250°C to 550°C.

Table 1. Characterization of biomass before being burned in the boiler

	Wheat Straw Triticum aestivum L.	*Rice 1 Punjab*	*Rice 2 AJK*	*Rice 3 Sindh*
Characterization of Biomasses				
Moisture on a dry basis %	10,59	9,33	9,64	10,15
Ashes average %	7,6	18,2	17,1	15,6
Highest Calorifying Power MJ/Kg	17,0	14,7	14,5	14,9
Lower Calorific Value (M) MJ/Kg	15,7	13,5	13,4	13,7
Elementary Analysis				
C %	43,2	36,4	38,3	37,3
H %	6,1	6,0	5,6	6,0
N %	0,6	0,8	0,7	0,5
S %	1,7	0,1	0,1	0,1
O %	40,8	38,6	38,4	40,5

The metal content was determinate by means of the ICP-MS 7700 Agilent according to the UNI EN ISO 17294-2 (2016) after the mineralization of the samples with a microwave Milestone START D.

Boiler GSA/80 (D'Alessandro Termomeccanica Serie GSA 80KW) was used for combustion; the fuel was extracted from the circular modified hopper (for the combustion of straws) by means of special motorized blades that convey it towards the fall hole in the upper auger.

The star valve, has the dual function of dosing the fuel towards the auger feeding the burner and breaking the continuity of the fuel between the two augers, preventing the return of any flames that could rise up to the hopper of the fuel. The rotation speed of the lower auger determines the correct feeding of the furnace and it is therefore a determining factor for the correct operation of the hot air generator. The fuel in the furnace is burned with the introduction of primary and secondary air combustion. During operation, the high pressure air generated by the centrifugal fan rear side strokes the outer walls of the combustion chamber and the tube bundle, heating and exiting the upper plenum at high temperature.

Biomasses were chopped to 4 mm before being sent in boiler as feed. The same biomasses were milled with a ball mill, homogenized and subsequently characterized to determine its chemical and physical characteristics.

The boiler's stack was provided with several flanges to accommodate different kind of probes for flue gas sampling. Two online gas analyzers were used, including a FID for Total VOC detection and a multi-gas portable analyzer for measurements of NOx, SOx, CO, CO_2 and a paramagnetic detector for oxygen detection. An isokinetic sampler was used for particulate matter detection. The multi-gas portable analyzer was Horiba Model PG-250 specifically designed for compliance with 40 CFR 60, as a backup instrument and for conducting relative accuracy test audits. Each gas constituent can be monitored over multiple ranges: NOx extending up to 2,500 ppm, four ranges for SO_2 extending up to 3,000 ppm, five ranges for CO over the span of 0 to 5,000 ppm and three ranges each for CO_2 and O_2. The chemiluminescence NO detector used a low-temperature NO_2 to NO converter to achieve measurement of NOx. Separate NOx and NO measurements can be made. NO_2concentrations can be measured by taking the difference between the sequential NOx and NO measurements.

PG-250 also incorporates a built-in sample conditioner consisting of a dual-stage moisture removal system that includes a gravity drain separator and thermal-electric cooler. Sampling was accomplished with a 316 stainless steel unheated sample probe equipped with an external primary filter.

Total gaseous hydrocarbon concentrations were instrumentally determined using a Ratfisch Model RS 53-T heated flame ionization detector (FID) calibrated against propane in air standards. The THC concentration was continuously monitored by extracting a slipstream of exhaust gas by means of a heated probe and filter holder. A heat-traced Teflon line (180°C) transported the sample gas from the filter holder outlet to the analyzer inlet. Each of the laboratory methods for PM has a standard operating procedure including the frequency of running the standards and the repeatability that was expected when the standard was in run. Additionally, data for the standards were plotted to ensure that the values fall within the upper and lower control limits for the method and that there is no obvious trends or bias in the results for the reference materials. The plant was stabilized for about 30 minutes as a test run for emissions. The exhaust concentration of gaseous emissions were measured and recorded for the last 3 min.

For Particulate Matter (and Anhydrosugars), Metals, PCDD/Fs, PCBs and PAHs, the sampling system was equipped with a sampling probe heated at 120±5 °C, a cooling device (6±2°C=, a 47mm quartz fiber filter, and a pumping system able to ensure isokinetic conditions, necessary to avoid error caused by sampling the particulate matter, as requested by the European method UNI EN 13284-1 (2017) and EPA 201A (2018).

According to UNI EN 13284 (2017), each sampling lasted an average of 30 min and was performed with an automatic isokinetic sampler (ST5, Dadolab) equipped with a Pitot tube and a thermocouple. A heated titanium probe with a heated out-stack (47mm) filter holder (Dadolab), both equipped with quartz microfiber filters without binders (MK-360 Munktell), have been utilized.

PCDD/Fs and dl-PCBs and PAHs were isokinetically sampled following methods EN-1948-1 and 4 (2006) and ISO 11338-1 (2003), respectively. The metals were isokinetically sampled with the same system, replacing the adsorbent part (condenser and XAD-2) for the semi-volatile organic compounds with 3 bubblers containing HNO_3/H_2O_2 as absorbing solutions. As for the sampling of Anhydrosugars (Levoglucosan, Mannosan and Galactosan) emitted by the consequent pyrolysis of carbohydrates, such as starch and cellulose, a new method has been developed. For this purpose, the aforementioned isokinetic system for the sampling of metals has been used replacing the oxidizing solutions used for metals with simple absorbent H_2O MQ. The volatile organic compounds were sampled following UNI CEN/TS 13649 (2015) method by self-made ACF adsorbent traps suitable for subsequent thermal desorption.

The determination of PCDD/Fs and PCBs was performed using the method EN 1948-2,3,4 (2006-2014). PAHs were quantified by following method ISO 11338-2 (2003). PCDD/Fs, PCBs and PAHs were determined with triple quadruple gas chromatography-mass spectrometry (GC-MS) system Thermo Scientific TSQ 8000 Evo (Guerriero *et al*. 2009). Metals were determined by method EN 14385 (2004). Volatile organic compounds were determined as a thermo sorbent, MarkesTD 100-xr and a triple quadruple gas chromatography-mass spectrometry (GC-MS) system Agilent (GC 7890A and MS/MS 7000).

The Anhydrosugars were determined by the individual bubbler solutions and by the solution obtained by extracting the sampled filter in an ultrasonic bath with H_2O MQ. The solutions had an acidic character due to the acidity of the combustion fumes. This acidity interfered with the subsequent analysis in ionic chromatography. With the addition of Ammonia, the pH was brought to neutrality.

Analytical determination was performed by high–performance anion–exchange chromatography coupled to pulsed amperometric detection (HPAEC–PAD). We used an IC mod. DX–500 (Dionex Corporation, USA) consisting of a DC ICS–3000 Chromatography Oven, a GP40 Gradient Pump and a Dionex ED50 Electrochemical Detector utilizing disposable gold electrodes. Separation of the individual anhydrosugars was achieved using a Dionex CarboPac PA10 Analytical Column with an 18 mM aqueous sodium hydroxide (NaOH) eluent at a flow rate of 0.5 mL min^{-1}. The analytical limit of detection was estimated to be better than 0.002 ng/ml. The quantitative analysis was carried out by analysing a 1 ppm levoglucosan standard solution immediately before and after each sample (Perrino *et al*. 2011).

RESULTS

As expected, flue gas emissions from the combustion of rice and wheat straw produced high concentrations of most pollutants.

The concentration of particulate emitted were high but the concentrations of PAHs are impressive. These values obtained from the combustion in the boiler are however of an order of magnitude lower than the combustion of rice straw in open burning (Oanh *et al*., 2011).

The values of PCBs do not vary between rice straw and wheat straw, while a different PCDD/Fs profile was obtained. Table 2 shows that the total concentration of both PCDD/F and PCB, expressed as toxicity equivalent to 2,3,7,8 Tetra Chloro-p-dibenzodioxin (TEQ pg/Nm^3), in the combustion of the rice straw are an order of magnitude higher than that of wheat straw. It is thought that it could mainly due to the catalytic effect of the higher concentration of copper in rice straw. In fact, copper is the main catalyst in the formation of organo-chlorine compounds during combustions, according to the Deacon synthesis (Huang *et al.*, 1995, Vogg *et al.*, 1994).

The VOC-BTEXs emitted from the combustion of rice straw are higher than those emitted by the wheat straw, despite the continuous measured TOC value being higher during the combustion of wheat straw.

The ash content in rice straw is twice that of wheat straw, and this results in a related higher metal content in emissions. Moreover, the high concentration of ashes influences the combustion, in the sense that even operating in excess of oxygen, high concentrations of carbon monoxide were

Table 2. Values found in emission during biomass combustion

Values in emission Stack				
	Wheat Straw Triticum Aestuvum L.	*Rice 1 Punjab*	*Rice 2 AJK*	*Rice 3 Sindh*
Sum PCDD / PCDF (pg/Nm3)	39	1493	4557	856
Sum PCDD / PCDF TEQ(pg/Nm3)	2,9	210,7	759,8	94,3
Sum PCB dioxin-like (pg/Nm3)	6196	6074	13003	32998
Sum PCB dioxin-like TEQ (pg/Nm3)	15,8	12,0	52,8	18,2
Sum PCDD / PCDF and PCB TEQ(pg/Nm3)	18,7	222,7	812,6	112,5
Sum PAH (µg/Nm3)	362	460	488	483
VOC(BTEX)				
µg/Nm3				
Benzene	1,84	1,86	4,96	5,86
Toluene	1,13	2,29	1,75	2,25
Etil bz	0,34	0,52	0,25	0,42
(m+p)-Xylene	0,64	1,53	0,58	1,20
o-Xylene	0,15	0,31	0,12	0,22
Styrene	0,77	1,29	0,74	1,16
	5	8	8	11
Levoglucosan µg /Nm3	8,3	2,7	10,3	8,3
Metals µg/Nm3				
Li	3,8	1357,9	3132,3	8,5
Na	1524,7	796,4	1579,9	1980,2
Mg	48,0	321,3	610,9	691,3
Al	35,0	82,0	53,3	97,8
K	724,4	13665,7	29629,2	111875,1
Ca	63,8	361,6	485,9	369,9
Cr	5,5	4,9	2,2	4,3
Mn	1,7	18,3	30,4	32,9
Fe	84,7	112,7	77,5	106,3
Co	0,4	1,3	0,1	0,2
Ni	4,4	11,1	9,9	6,2
Cu	10,6	35,0	47,5	21,7
Zn	39,5	133,8	89,2	92,6
Sr	2,0	4,9	22,2	16,6
Ag	0,5	0,1	0,1	0,2
Cd	0,6	0,9	0,8	0,4
Ba	0,0	1,9	4,4	3,8
Tl	0,4	0,1	0,1	0,1
Pb	4,0	13,5	14,5	14,4
Bi	5,4	4,0	7,2	8,8
Total Particulate Matter mg/Nm3	31	26	61	89
Gas in Emission				
CO (ppm)	2843,5	2805,6	3626,7	3101,6
CO2 (%)	2,1	2,3	4,2	2,5
Nox (ppm)	56,2	58,9	94,5	49,8
O2 (%)	18,9	18,0	16,3	18,4
SO2 (ppm)	26,0	22,3	30,5	24,1
TOC (mgC/mc)	498,6	358,9	182,4	397,5

recorded. It means that the combustion of straw is a "bad combustion", since the high content of ash does not allow combustion in a homogeneous phase between the comburent and the fuel.

In this measurement campaign a new method for sampling levoglucosan in emission has also been developed. It has been observed that the levoglucosan itself behaves like the semi-volatile organic pollutants and therefore the volatile fraction must also be sampled at the sampling temperatures (around 120 °C).

In fact it has been observed that the ratio of Levoglucosan in the sampling absorber (H_2O MQ) with respect to the filter containing the particulate in the samples ranges between 31% and 171%.

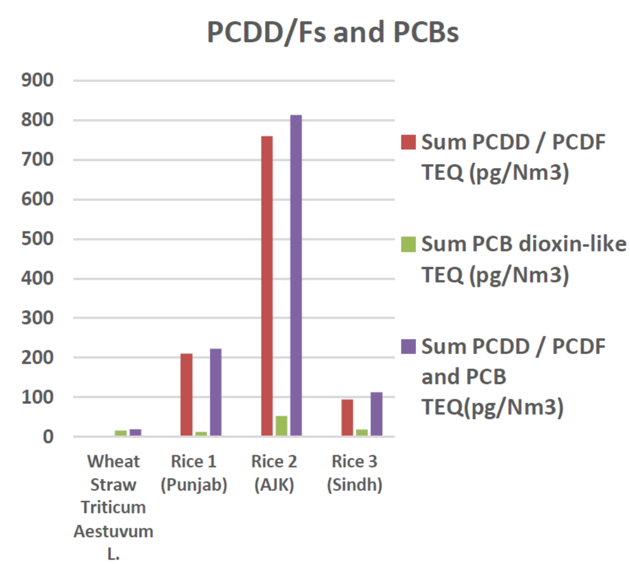

Figure 1 Sum of PCDD/Fs and PCBs expressed as toxicity equivalent to 2,3,7,8 Tetra-Chloro-p-dibenzodioxin (TEQ pg/Nm^3)

CONCLUSIONS

The experimental campaign highlighted the high concentrations of pollutants that are emitted in the combustion of wheat straw and rice straw.Surprisingly, high concentrations of PCDD/Fs and PCBs in combustion were found probably due to the presence of copper present as a fungicide in seed production.

PAHs concentrations are also high, often correlating with the high CO concentrations found during experimentation.

Using the hyphenated thermodesorption technique-mass spectrometry, high concentrations of VOC-BTEXs have also been found, and all the other VOCs determined but not yet quantified will have to be processed.

A method for sampling the Levoglucosan has been developed, and it has shown that sampling it only on the particulate matter coould lead an underestimation. As a further step, this method will be validated and extended to other Anhydrosugars.

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TECHNOLOGIES FOR BIOGAS AND BIOMETHANE

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***Keywords*:** biogas, biomass, zeolite, pressure swing adsorption

INTRODUCTION

Biogas production is a widespread technique for the exploitation of biomass energy, consisting on the anaerobic bacterial fermentation of biomass. The use of biogas as a fuel can reduce the consumption of fossil fuels, decreasing carbon dioxide emissions and the anthropogenic greenhouse effect. Compared to the direct combustion of biomass, the use of biogas can significantly reduce the emissions of particulate matter, heavy metals, sulphur and nitrogen oxides, inorganic acids, organic micro-pollutants (Paolini *et al* 2018). In order to further reduce the environmental impact of biogas combustion, and furthermore to obtain a more efficient fuel, biogas can be upgraded to biomethane. Indeed, biogas obtained from the anaerobic digestion is a gas mixture, whose two main constituents are methane (40-75%) and carbon dioxide CO_2 (15-60%). Secondary components are also present, including hydrogen sulfide and organic sulphurs, ammonia and organic amines, nitrous oxide, siloxanes, hydrogen and water. The removal of carbon dioxide from biogas is commonly called biogas upgrading. It aims to obtain a fuel gas with a higher calorific value. Moreover, the presence of carbon dioxide changes the density and does not allow to use the normal methane pipelines and plants. Biogas upgrading techniques are divided into the following categories: absorption in liquids, adsorption on solids, membrane separation and cryogenic separation (Rychebosch *et al* 2013). Zeolites are known for their ion exchange and gas adsorption properties. Syntectic zeolites have been succesfully used for the removal of carbon dioxide from biogas, both in the pressure swing adsorption technique and as a membrane. Recently, a comparison between synthetic and natural zeolites for biogas upgrading was performed (Alonso Vicario *et al*, 2010). Aim of this work is to report recent advances in biogas and biomethane technology, in terms of environmental sustainability and upgrading efficiency.

METHODOLOGY

Anaerobic digestion

A prototype anaerobic digester was developed and tested for the conversion of food waste into biogas and compost. Hydrolysis and acetogenesis are performed into three parallel batch reactors, whose leachate is mixed and recirculated. A fraction of leachate is continuously fed to a second stage, consisting in a continuously stirred tank reactor (CSTR). Waters obtained downstream the CSTR are treated in a nitrification unit with natural zeolites, and finally recirculated in the leachate collection tank. The whole system is represented in Figure 1 and described in full details in Petracchini *et al* (2018).

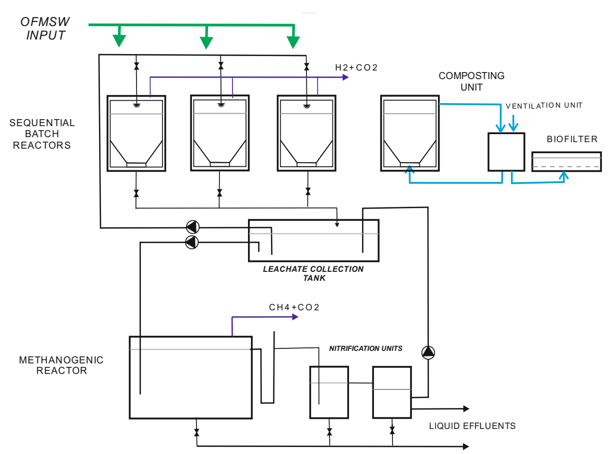

Figure 1. Schematic of the anaerobic digester

Biogas upgrading

The adsorption of carbon dioxide and hydrogen sulphide on natural zeolites was performed on a lab scale, using natural zeolite chabazite with the charcteristics described in Aquino *et al* (2016).
Subsequently, a continuous adsorption/desorption cycle based on two adsorption columns was tested using a prototype described in Petracchini *et al* (2017) and reported in Figure 2.

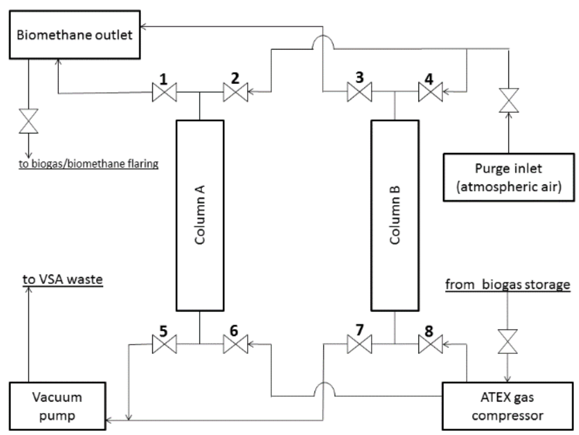

Figure 2. Schematic of the biogas upgrading unit

FINDINGS

Anaerobic digestion

Table 1 shows results obtained in the anaerobic digester in terms of gas composition and flow rate.

Table 1. Performances of anaerobic digester

Parameter	*1st stage reactors*	*CSTR*
Flow rate m^3/day	1.2-2.5	1.0-1.4
CH_4 % v/v	10-25%	75-85%
CO_2 % v/v	60-80%	15-25%
H_2 % v/v	5-10%	<2%

Data obtained show that the reactor is able to reach a specific methane production of 0.54-0.82 L^3 g^{-1}_{TVS} (methane litres per gram of total volatile solids). This result is higher than other specific methane production obtained in similar studies. (Grimberg *et al* 2015, Schievano *et al* 2010 Cavinato *et al* 2012).

Biogas upgrading

Figure 3 (taken by Paolini *et al*, 2016) reports the adsorption breakthrough curve for carbon dioxide and hydrogen sulphide. It can be observed that a simultaneous removal of these contaminants can be achieved through natural zeolites.

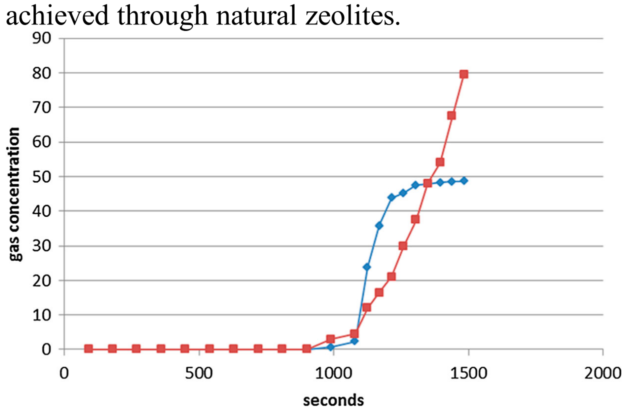

Figure 3. Outlet concentration of CO2 (%v/v, red dots) and H2S (ppmv, blue dots)

In terms of adsorption capacity, natural zeolites are less efficient than synthetic materials. However, they can be considered a valid alternative because of their lower cost. Adsorption capacity is reported in Figure 4, based on data obtained in Aquino *et al* (2016).

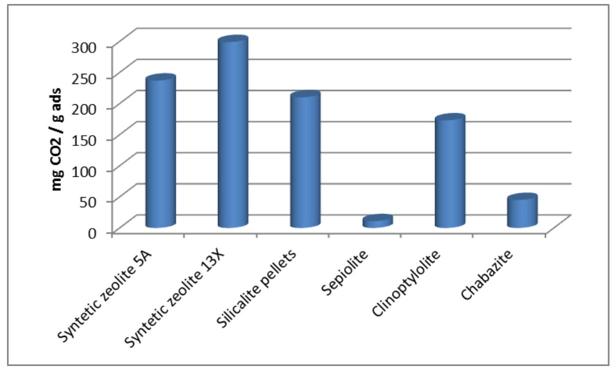

Figure 4. Adsorption capacity of zeolitic materials

A long term adsorption/desorption stability of natural zeolites was observed with the biogas upgrading prototype. Biomethane composition is shown in Table 2 based on data reported in Petracchini *et al* 2017.

Table 2. Performances of biogas upgrading

	Biogas	*Biomethane*
CH4 [%-vol]	48 ± 2	98.45 ± 0.02
CO_2 [%-vol]	49 ± 2	0.060 ± 0.003
H_2S [mg/Nm^3]	6 - 12	3 - 10.5
O_2 [%-vol]	2 ± 0.6	0.53 ± 0.06
N_2+H_2 [%-vol]	1.7 ± 0.8	0.96 ± 0.01

CONCLUSIONS

In this work, the advances in biogas and biomethane technologies were reported, in terms of biogas production and upgrading. A dual stage semi dry anaerobic digester was described for the conversion of food waste into biofuel and compost. Furthermore, a vacuum swing adsorption methodology based on natural zeolites was assessed in terms of biomethane purity and adsorption efficiency.

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METHODOLOGY FOR EVALUATION AIR QUALITY AND MOBILITY POLICY IN 14 BIG ITALIAN CITY 2006-2016

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Keywords: Air quality, mobility policy, management

INTRODUCTION

"Transport represents almost a quarter of Europe's greenhouse gas emissions and is the main cause of air pollution in cities. Europe's answer to these challenges is an irreversible shift to low-emission mobility in terms of carbon and air pollutants." (EU, 2016).

Figure 1 shows that road transport was responsible for more than 73% of total greenhouse gas emissions by different mode transport. 44,5% of road transport is due to car transport (Figure 2) (EEA, 2017).

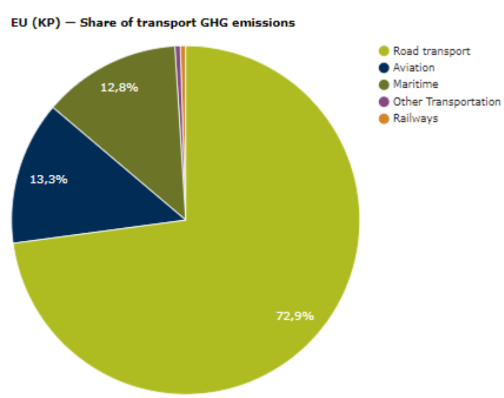

Figure 1. Share of transport GHG emissions (EEA, 2017)

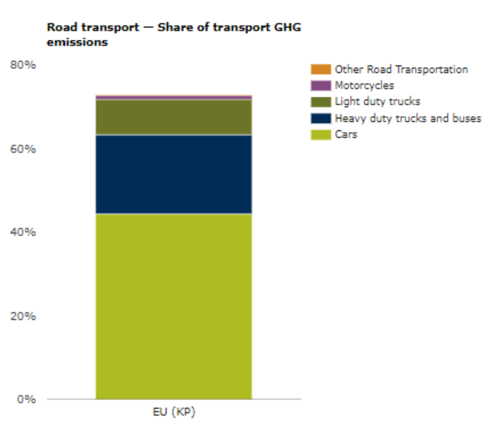

Figure 2. Road transport — Share of transport GHG emissions (EEA, 2017)

Therefore, "Decarbonise transport" is the key word in European mobility policies, necessary to achieve Paris Agreement goals such as reducing greenhouse gas emissions.

2030 climate and energy framework sets key targets for years 2030 and 2050. Europe aims to reduce greenhouses emissions from non-ETS sectors by 30% (compared to 2005) in 2030 and by 60% below 1990 levels in 2050.

European Commission issued a new package for air quality in 2013 for short-term achievement of existing objectives and for the achievement of new air quality limits by 2030. These new rules will have a strong impact on cities that will have to deal with increasingly restrictive limits.

Though air quality in Europe has improved, thanks to adopted policies and technological developments still underway, high concentrations of following atmospheric pollutants that are most troublesome for human health are still detected: Atmospheric matter (PM); nitrogen dioxide (NO_2) and Ozone (O_3) (EEA, 2016, 2017).

In 2015, PM_{10} concentrations exceeded the EU daily limit value for 19% of EU stations in 20 of the 28 EU Members States and in other five countries. $PM_{2,5}$ exceeded annual limit value for 6% of EU stations in 3 Member States and other 3 courtiers.

In the same year, annual limit of NO_2 was largely exceeded in Europe. The 10% of all EU stations registered values above the limit in 22 of EU-28 and in other 3 European countries. 89% of the stations with exceeded value are traffic ones.

In 2015, 41% of EU stations registered concentrations above the O_3 target value protecting human health in 18 of EU countries and other 4 European countries.

Even if it's another important pollutant deriving from road transport, Black Carbon is not measured yet.

Table 1 shows urban European population exposed to air pollution. Larger percentage exposed to PM, O_3 and BaP both for EU and for WHO limits (EEA, 2017).

Table 1. Percentage of the EU-28 urban population exposed to air pollution over EU and WHO concentrations (min-max observed between 2013-2015)

Pollutant	EU reference value (•)	Exposure estimate (%)	WHO AQG (•)	Exposure estimate (%)
$PM_{2.5}$	Year (25)	7-8	Year (10)	82-85
PM_{10}	Day (50)	16-20	Year (20)	50-62
O_3	8-hour (120)	7-30	8-hour (100)	95-98
NO_2	Year (40)	7-9	Year (40)	7-9
BaP	Year (1)	20-25	Year (0.12) RL	85-91
SO_2	Day (125)	< 1	Day (20)	20-38

Key				
Key	< 5 %	5-50 %	50-75 %	> 75 %

EEA (2015) uses two different ways to estimate health impacts: Years of life lost (YLL), "the years of potential life lost owing to premature death" and Premature deaths, "deaths that occur before a person reaches an expected age" (the age of standard life expectancy for country and gender).
EEA estimated that Years of life lost (YLL) attributable to $PM_{2.5}$, O_3 and NO_2 exposure in 2012 in the EU- 28 are 4,494,000, 800 000 and 197,000, respectively. At the same time, premature deaths attributable to $PM_{2.5}$, O_3 and NO_2 exposure in 2012 EU- 28 countries are 403,000, 16,000 and 72,000 respectively (EEA, 2015).

WHO (2015) estimated the economic cost of premature deaths from Ambient Particulate Matter Pollution (APMP) in European Region. In 2010, the cost of premature deaths is 1,156,118 US$, higher than in 2005 (1,007,223 US$).

Therefore, the reduction of atmospheric pollution in urban area will provide several benefits both on health and on environment, such as to save tens of billions of euros and deaths.

On the base of such considerations, main goal of this work is to develop a methodology to evaluate air quality compared to mobility policies in force, in order to take best actions and measures to improve air quality, mobility, and urban space.

There are different instruments where sectoral data are gathered and processed such as research institutes, ministries, agencies, observatories, associations, local authorities, but there is no place where urban mobility data are integrated each other and with trend of air quality. Frequently, data are often partial, contradictory, and no systematic, without shared methods of detection.
There is a similar analysis realized by The German environmental and consumer associations NABU, BUND, VCD and DUH call "The European City Ranking", but this work define the state of different European city by an aggregate score for single macrotopic. Instead, MobilitAria Report provides to define a real status about current urban mobility and air quality in the 14 larger Italian cities in last 10 years, by using several air quality and mobility parameters.

METHODOLOGY

Air quality and mobility data collection

First step of data collection was the identification of parameters involved in analyses and the period analysis. Parameters identified take into account different aspects: general information about the city, weather and climate data, air quality, urban mobility and mobility policies and measures. Parameters having an influence on mobility or air quality has been considered main ones while the period analysis has been chosen equal to last ten years.
Air data has been collected by Regional agencies for environment protection and Municipalities, having control units located in the cities for monitoring the values using methodologies respecting the legislation in force.
Urban mobility data has been collected thanks to mobility metropolitan agencies, ISTAT, Municipalities and Associations. Reconstruction of main mobility measures was been implemented by study of main measures taken (PUT, PUM, PUMS).
Last group of data, weather and climate data, has been collected from National Center for Aeronautical Meteorology and Climatology, Regional agencies for environment protection and local Agencies.

Data Analysis

The mobility analysis was carried out by analysing approved instruments and measures implemented, as well as a brief history of the main actions undertaken during the period considered. Many parameters have been calculated for each city to identify the current state of mobility such as: the supply and demand for public transport, modal split, car sharing, bike sharing, motorization rate, types of vehicles and cars, accident and mortality rates, the extension and regulation of LTZs, taxi licenses and NCC.

NO_2, PM_{10} e $PM_{2,5}$ are primary air pollutants emitted by motor vehicles and have been considered as reference pollutants for air quality study.
Trends concentration have been calculated and analysed in order to define traffic and background stations average, city average and exceedances of the city for each polluted between 2006 and 2016.
Concentration average and stations with maximum number of exceedances have been calculated for 2016, also have been localized every air monitoring stations considered.
Furthermore, growth rate has been calculated for each mobility and air quality parameter in order to verify if it increases or decreases compared to 2006.
Last analysis provided allowed to identify any correlation between mobility parameters and air quality values.
For general variables such as: city width, inhabitants, cycle paths, green area, limited traffic area extension, methodology proposed in this study calculates the current state and the growth rate for some variables.
Weather and climate analysis has been developed considering both last 10 years for detailed analyses and last 30 years data from the "Atlante Climatico d'Italia 1971-2000" for general analyses.

Data representation

Data collected have been represented by using an innovative graphics allowing the reader to look the state of the city. The reader can be compare a city with others by only 4 summary sheets in which the parameters are shown (Figure 4). Used graphic, tables, box and level of change, time line to capture the reader's attention.

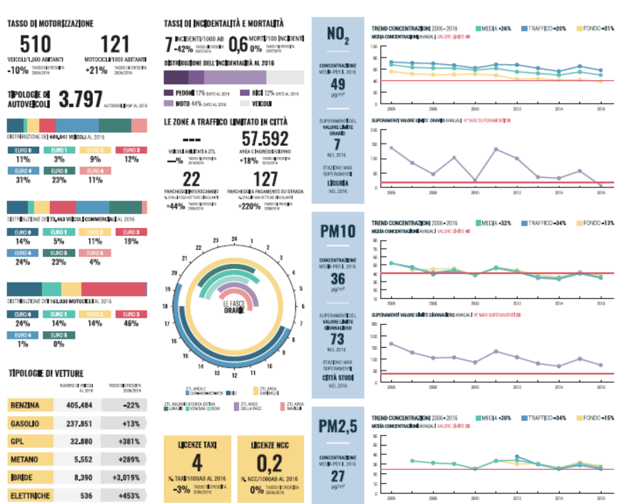

Figure 4. Examples sheets

RESULTS

Study led to develop a methodology for analysis and identification of most critical and positive aspects of each city.
Main goal of the methodology proposed is to lead towards the improvement in air quality, mobility and urban space in cities.
Applied methodology allows to show the current status of main Italian cities, with an approach that can be replicated in other Italian cities or European cities regardless their width.
Moreover, this innovative representation of data collected and analysed, allows both an immediate comparison of the same parameter between the different cities and the comparison between the actual status with the past (2006).

Analysis and comparison of data between 2006-2016 shows a real commitment to the sustainable mobility of big Italian cities. However, the situation is uneven between the different areas of the country, especially the cities in the South Italy that still need to do much more to improve the situation.
Air quality has improved overall in all cities, the improvement due to the measures taken, the economic crisis that has reduced travel and the improvement of vehicle emissions, but very critical situations of pollutants concentrations and exceedances compared to limits set by regulations is observed.

Therefore, considering this results, this study can be a tool for local authorities to highlight intervention areas for local policies aiming to improve services and environment quality.

CONCLUSIONS

The applied methodology allows to evaluate the current and past status of cities in order to guide the political choices to be implemented.
Further developments of this methodology may include the extension to all metropolitan Italian cities, and the parameters for evaluation such as traffic, train lines, or extraurban lines buses data.

ACKNOWLEDGEMENT

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CHEMICAL CHARACTERIZATION OF PM_{10} AND PBAPs DETERMINATION IN INDOOR ACADEMIC ENVIRONMENTS

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Keywords: IAQ; mass closure; infiltration, bioaerosol, epifluorescence microscopy

INTRODUCTION

It is well known that more than 80% of our time is spent in enclosed areas, including private homes, schools and universities, offices, transports and meeting places [1-2]. Nevertheless, the indoor levels of most health-related air contaminants are not regulated by any legislation and the mechanisms causing the health effects related to poor indoor air quality (IAQ) are far from being understood. In the case of particulate matter (PM), health effects related to PM exposure may strongly depend also on its chemical composition; for this reason, besides the determination of the mass concentration, is also important to investigate the chemical composition of inhaled particles.

The present study aims at giving the main results of an experimental study carried out in several academic environments, ranging from small laboratories to very wide classrooms. The objective of this work was to evaluate the mass concentration and chemical composition of indoor atmospheric particulate matter (PM_{10}) and to investigate the role of the presence/absence of the students, the volume of the classroom, the height from the ground and the distance from outdoor sources in the definition of indoor air quality (IAQ). Furthermore, the morphological characteristics and mass contribution of Primary Biological Aerosol Particles (PBAPs) to PM_{10} and organic carbon concentrations were also evaluated by applying a simple and comprehensive method for the detection and the quantification of atmospheric bioaerosol.

METHODOLOGY

Simultaneous samplings were performed at an outdoor reference site and in five confined environments at the Physics Department of Sapienza University of Rome. Indoor sites included a Lecture Hall, two classrooms, a computer room and a laboratory. The Lecture Hall was located at the ground floor and can accommodate about 300 students, one classroom (suitable for about 130 students) and the computer room were located at the second floor, the remaining classroom (identical to the previous one) and the laboratory were at the fourth floor. Outdoor site was located in the courtyard as close as possible to the indoor sites. The sampling schedule was carried out during a six-week period during the winter season and arranged in order to collect PM_{10} samples separately during the day-time, night-time and weekends. The weekly samplings were performed by using low-volume, quiet sampling units operating at 10 l/min, equipped with a sequential unit able to automatically manage the sampling program.

PM samplings were simultaneously carried out on Teflon, quartz and polycarbonate fiber filters. The determination of mass concentration (by gravimetry), of the total elemental content (by energy-dispersion X-ray fluorescence, XRF), of the soluble and residual fractions of elements (by inductively-coupled plasma mass spectrometry, ICP-MS) and of the anions and cations (by ion chromatography, IC) were carried out on Teflon membranes; quartz filters were used for the determination of the organic and elemental carbon (by thermo-optical analysis); polycarbonate filter were devoted to bioaerosol assessment.

For the determination of PBAPs, three triangular sections, about 1 cm in width at the edge, were cut from each polycarbonate filter. Each section was dyed with a 1% solution of Propidium Iodide, a fluorescent dye that binds to the nucleotide pairs of guanine and cytosine in DNAs and RNAs. Ten consecutive fields were chosen in each one of the three sections and observed at the epifluorescence microscope. The microscope was equipped with a high-resolution camera allowing a 1000x total magnification and the observation of particles down to 0.4 mm in length. Numerical density and morphological characteristics of the bioparticles were determined by an automated digital image analysis. Particles are approximated to ellipsoides and, using the most common density value reported in the literature for bioaerosol (1.1 g / cm^3), the mass and the atmospheric concentration of fluorescent particles are finally estimated. The method is extensively described in Perrino and Marcovecchio, 2016 [3].

RESULTS AND DISCUSSION

The determination of the macro-components (elements, ions and organic content) led us to obtain a satisfactory mass closure and to evaluate the impact of the main macro-sources (*soil, sea, organics, secondary inorganics and traffic*) on air quality both indoors and outdoors [4]. Figure 1 shows a comparison between the contribution of the five macro-sources in four of the six sites; the data are shown following the sampling schedule that separated the samplings among diurnal, nocturnal and week-end hours.

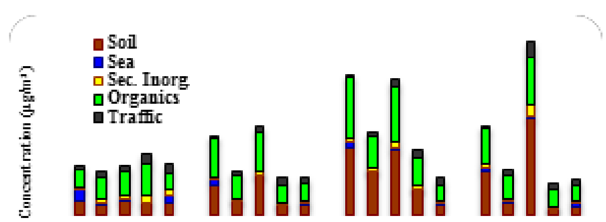

Figure 1. Contribution of the five PM macro-sources in the Lecture Hall, in a classroom, in a laboratory and outdoor during the same sampling week

The contribution of organic components was the main responsible for a significant decrease of PM mass concentration during the night-time and weekends in comparison to day-time samples. In all the indoor environments, this contribution was characterized by a relevant fraction of primary biogenic particles, mainly related to the ratio between the number of occupants and the classroom volume as well as to the duration of the lessons. A typical image of the bioaerosol collected on polycarbonate filters inside a classroom during daily hours is shown in Figure 2. The contribution of PBAPs to the total PM mass was associated to the presence of human skin debris and natural fibers. It is worth noting that the amount of spores, pollens and bacteria is very low in comparison to the corresponding samples collected outside.

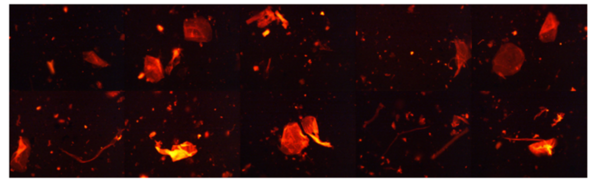

Figure 2. Bioaerosol collected on polycarbonate filter in a classroom during daily hours

The indoor concentration of crustal-related elements, which mainly originate from abrasion and mechanical processes and belong to the coarse mode, showed a lower correlation with outdoor values because of the presence of indoor sources (re-suspension) and because of the difficult infiltration of coarse particles. A vertical gradient was observed for these species, particularly during a short period when public works were taking place in the courtyard of the building.
The infiltration from outside constituted the main source of secondary inorganic species, whose concentrations were governed by the mixing properties of the lower atmosphere.

The discrimination between the soluble and residual fraction of micro- and trace-elements allowed to speculate about the potential toxicity of indoor PM and to trace its main sources, particularly those generating fine particles. For instance, some species associated to biomass burning, industrial processes and vehicular traffic, traced by specific elements in the appropriate solubility fraction, showed high infiltration coefficient both during day-, night- and week-end periods.

CONCLUSIONS

The present study highlighted that IAQ in academic environments is strongly influenced by organic compounds of biogenic origin and by the contribution of soil-related species generated by the re-suspension of settled dust. Both processes are governed by the occupancy rate and the volume of the classrooms. Particularly, the contribution of PBAP's was in the range 10-30%, in comparison to a contribution in the range 1-10% in outside air and in unoccupied classrooms. Infiltration processes of outdoor air contaminants, in particular micro- and trace-elements originated from combustion and industrial processes, were also important in the definition of PM toxicity in indoor environments.

This study has been carried out in the framework of the INAIL BRiC Research Projects n. 22/2016 ("Studio integrato numerico sperimentale delle modalità di trasferimento del materiale particellare sospeso in atmosfera all'interno di ambienti di lavoro indoor in area urbana, in funzione dei fattori fisici, chimici, micrometeorologici e delle caratteristiche costruttive degli edifici").

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POTENTIAL OF INDOOR DUST ANALYSIS IN THE AIR QUALITY ASSESSMENT

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Keywords: Indoor, Settled dust, $PM_{2.5}$, PAHs, Air quality assessment

INTRODUCTION

The awareness that, especially in urban areas, people spend much of their time in indoor environments has given rise to marked interest of scientists and legislators about the air quality in places such as homes, workplaces and schools (Ma and Harrad, 2015; Nehr *et al*., 2017). For instance, it has been evaluated that Italian citizens spend 84%-93% of their time in enclosed spaces and this issue highlights the relevance of the indoor air quality in terms of health of population (Fuselli *et al*. 2013). As a consequence, the accurate evaluation of the indoor contribution is necessary in order to reliably assess the citizen exposure to pollutants and evaluate the associated risk. A number of studies have been dedicated to the effect of outdoor air intrusion into the interiors, but many sources of toxicants exist inside. Among them, typical indoor activities such as cooking, smoking, the use of cleaning products, cosmetics, biocides, and the presence of textiles, furniture, electronic devices influence the air quality in the living environments; besides, very important effects outcome from indoor activities conducted at workplaces (Romagnoli *et al*., 2014; Mohammadyan *et al*., 2017; Colman *et al*., 2018)

Studies carried out by CNR-IIA showed that indoor environment can be very different from outdoors in terms of air quality and wide variability exists also among distinct points within a unique enclosed space (Cecinato *et al*., 2014; Romagnoli *et al*., 2016). Figure 1 shows the $PM_{2.5}$ bound PAHs concentrations measured indoors and outdoors over one month in a home (60 m^2) whose inhabitants were smokers. Simultaneous samplings were carried out in the living room, in bedroom and outdoors at their balconies which overlooked, respectively, the street and a courtyard inside the building. The investigation was carried out in winter; heating plant run 4-5 hours/day and normal daily activities such as cooking and dusting were carried out there. The indoor concentrations were higher than the outdoors, highlighting the importance of internal sources. Outdoors, the PAH distributions and neat concentrations were very similar (the two data sets correlated very well, y=1.022x+0.026, R^2=0.994).

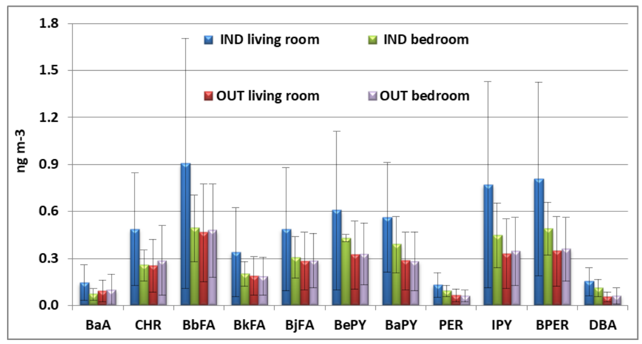

Figure 1. $PM_{2.5}$ bound PAH concentrations detected indoors and outdoors in the winter in an apartment in Rome.
Benz[a]anthracene = BaA; chrysene = CHR; benzo[b]fluoranth-ene = BbF; benzo[j]fluoranthene = BjF; benzo[k]fluoranthene = BkF; benzo[e]pyrene = BeP; benzo[a]pyrene = BaP; perylene = PER; indeno[1,2,3-cd]pyrene = IP; benzo[g,h,i]perylene = BPER; dibenz[a,h]anthracene = DBA

By contrast, marked differences were observed between PAHs in the two rooms (in living room +60% compared to bedroom). Thus, at local scale, the air mixing outdoors looked enough to make PAH appearing released by area sources rather than point sources. The same behaviour could not be applied to interiors, where point emission (in this case, smoking) became important and wide differences existed among rooms or close spaces (Marc *et al*., 2018). Hence, the choice of sampling point looks crucial to reliably assess the exposure to contaminants and the related risk for humans. At this regard, any preliminary approach easy to apply, quite rapid and not perturbing at all the target sites is welcome. Investigations have been performed by CNR-IIA to assess the suitability of non-standard procedures of dust collection and analysis. Indeed, the dust collection approach allows multiplying the sampling points, furthermore the whole experiments are costly friend. Whenever pollutant concentrations in dust show meaningful differences among indoor locations, the results obtained in this way can drive more specific extensive investigations of air quality and provide also insights about risk associated to non-dietary intake (Mercier *et al.*, 2011).

METHODOLOGY

To collect dust, horizontal surfaces (≥1.2 m above floor, ≥1 m from vertical walls), were pre-cleaned with cotton wads and exposed to particle deposition; after 15 days, surfaces were cleaned again with cotton wads which retained dust. Wads were wrapped with aluminium, sealed in plastic bags and stored at 4°C. Before analysis, samples were spiked with deuterated internal standards suitable for chemicals investigated (i.e., alkanes, PAHs, psychotropic substances and phthalates). Samples were extracted through sonication (3 x 20 min) with dichloromethane/acetone, then extracts were dried and purified by column chromatography. Quali-quantitative characterizations were carried out by means of GC-MSD. Samplings were made between 2014 and 2017 at schools, hospitals and houses in Ouargla, Algeria (Boudehane *et al.*, 2016), while homes and an airport were examined in Rome and Fiumicino, Italy. (Cecinato *et al.*, 2014-2017).

FINDINGS

Table 1 reports the mean concentrations of total PAHs found in Algeria and Italy. The maximum concentration were observed in the apartment in Algeria, and at the airport in Italy.
In Ouargla the mean concentration in the apartment was exceeded 5 times that measured in the school, showing distinct pollution rates there. Analogously, important differences were found in Italy between homes and airport.

Table 1. PAHs in settled dust

Country	*Site type*	*PAHs, ng m^{-2}*
Algeria	university	18 ± 3
	hospital	23 ± 10
	school	15 ± 4
	apartment	89 ± 32
Italy	apartments	20 ± 3
	airport	60 ± 30

Settled dust samples were also collected in the living room and in the bedroom where wide difference in the $PM_{2.5}$ bound PAHs were recorded. Figure 2 reports the PAH loads on dust (in ng m^{-2} units). Total amounts of PAH detected in the living room and in the bedroom reached 68 ng m^{-2} and 28 ng m^{-2}, respectively, confirming a higher occurrence of this group in the living room, in accordance with that resulting from the $PM_{2.5}$ analysis. Examining the PAH profiles in the two matrices (see Figures 1-2), differences can be put in the evidence. In dust, the concentrations of unstable dibenz[a,h]-anthracene and perylene were below the detection limit and the ratio BePY/BaPy was higher due to the ageing of the investigated compounds in the matrices. In particular the BePY/BaPY ratio was equal to ≈ 1.1 in the $PM_{2.5}$ whereas it was ≈ 3.6 in the settled dust.

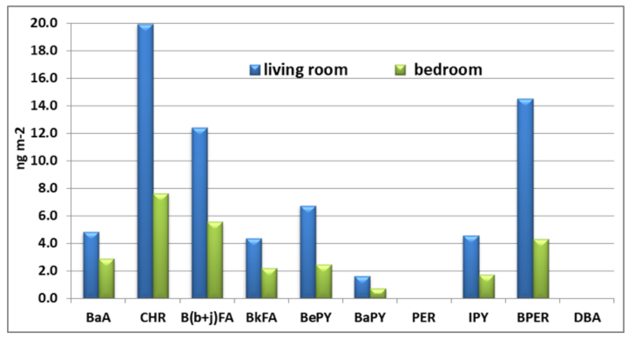

Figure 2. PAH contents in dust collected during the winter in an apartment of Rome, Italy. PAH symbols: see Figure 1

CONCLUSIONS

Though settled dust is overall constituted by coarse particles and characterized by some ageing of the transported pollutants, preliminary studies carried out by the CNR-IIA suggest that their chemical characterization in interiors looks feasible to capture differences of PAHs occurrence in different sites. Besides, while the coarse and fine particles have, in general, distinct sources and chemical composition, which results in wide difference between dust and suspended particulate, in interiors this difference seems less pronounced, maybe due to increase of effectiveness the fine particles deposition indoors. More deep investigations are underway aimed at identifying, if they exist, relations between pollutants concentration in aerosol/gas-phase and in settled dust in indoor environments. When this goal will be achieved, dust collection in interiors will become a suitable approach to preliminary assess the air quality, draw indicative information about the chemical contour of living environments and increase the reliability of successive extensive investigations.

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BUILDING UP THE NATIONAL DATABASE OF PM CHEMICAL SPECIATION IN THE FRAMEWORK OF IAS – ITALIAN AEROSOL SOCIETY

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Keywords: PM_{10}, $PM_{2.5}$, urban aerosol, chemical speciation, PM database

INTRODUCTION

Within the territory of Italy an extended work of chemical characterization of airborne particulate matter (PM) has been carried out in the last decades. Size segregated PM collected at rural, residential, urban and industrial sites has been studied from Northern to Southern Italy.

Studies concern short- or long-term field campaigns, to identify site-related sources, advection/transport and secondary formation processes, and to evaluate how, to what extent and by which seasons each source influences the measured PM mass and composition. Despite the large number of available studies, and the consequent possibility of gaining national-level knowledge on the status of PM pollution in Italy, the representativeness of these studies is limited by the years, time windows and specific sites considered. Furthermore, Italy features wide differences of local topography and meteorological conditions, that may affect the variability of PM composition at sites of the same type (thus sharing, reasonably, the same source categories), under equal conditions (e.g. the season). The linkage between territorial peculiarities and variability of the PM composition at comparable sites is actually missing, as well as a national-level picture of the PM composition, both issues representing thus knowledge gaps. A national-level awareness would instead support, on the one hand, the scientific and environmental protection communities improving the products of, respectively, source apportionment and air quality modelling (e.g. source chemical fingerprints, regional previsions on ambient air concentrations, etc.). On the other hand, the public availability of this information would help the general population to upgrade awareness on the quality (more than quantity) of local respirable PM.

Within this picture, the Working Group 1 (WG1) *'Sorgenti e Processi di Generazione degli Aerosol'* (*sources and formation processes of aerosol*) of the IAS – Italian Aerosol Society, started in 2013 a collection of PM speciation data from published and unpublished individual studies on urban/urban background sites, to the goal of building up a database having national representativeness.

At present, the database comprises 23 large and medium-size cities of Italy, including port (i.e. Venice, Genoa, Civitavecchia, Naples, Bari and Brindisi) and inland urban sites, and covering the period 2005 – 2016. Data are provided on a voluntary basis by the WG1 members and by the related research groups, from Italian universities and public research institutions (Table 1). Previous initiatives of PM chemical data collection from different studies and geographical areas concern those carried out by Puteaud *et al*. (2004; 2010) at European level. PM mass and main components are analyzed versus the spatial scale and the increasing anthropic impact, in these studies. Differently, the IAS database of PM chemical speciation is being designed to be an usable tool, by which possible hidden information can be extracted on PM sources (trace elements are explicited, in example) and their relationships with territorial peculiarities.

The structure of the database is being finalized, and the informative potential is thus under investigation. The first analyses were focused on: - evaluating the soundness of the database when it is used to estimate missing seasonal averages; - highlighting possible unexplored or hidden relationships among species; - assessing the possibility of applying receptor modelling to the chemical speciation data array. Main related goals are, respectively: - to test the database as a tool to provide speciation data, where these are missing in the PM modelling; - to identify possible minor source contributions, that could be strictly related to the type of urban sites (e.g. high/low anthropic impact, port/inland character, etc.); - to obtain source chemical fingerprints that can be considered representative at national level of the Italian territory.

Table 1. Italian universities and research institutions contributing the IAS database of PM chemical speciation

Università degli Studi di Firenze
Università degli Studi di Modena e Reggio Emilia
Università degli Studi di Genova
Università degli Studi di Bologna
Università degli Studi di Perugia
ARPA Lombardia
Università degli Studi di Milano-Bicocca
ENEL Ingegneria & Ricerca S.p.A.
Università degli Studi di Venezia
Università degli Studi di Napoli Parthenope
Università degli Studi di Milano
CNR Ist. sull'Inquinamento Atmosferico (IIA-MLib)
CNR Ist. di Scienze dell'Atmosfera e del Clima (ISAC-Lecce)
CNR Ist. di Metodologie per l'Analisi Ambientale (IMAA)

METHODOLOGY

Data collection

Data collection was agreed within the WG1 and carried out by means of periodical calls opened to all the IAS community. An *ad-hoc* form to be filled and sent by email was created to this aim.

Calls following the first one were launched after updating the IAS community on main lacks of information (e.g. uncovered areas, regions, years) and on actual needs of the database.

Seasonal averages were selected by the WG1 as best option of chemical data aggregation, to provide site-representative information not affected by time contingency. Additional information were also asked to be provided, like site/area-related modeling results of source apportionment and source fingerprints, analytically determined source profiles, as well as typical meteorological conditions and site description/local topography. Besides constituting the necessary knowledge basis for every investigation on the chemical speciation data, the additional information included in the database can be used independently to perform further statistical and environmental analyes.

Chemical speciation data

Data concern both PM_{10} and/or $PM_{2.5}$, although the latter is less represented, being available by ab. 50% of the total. Chemical species closing the PM mass balance (Perrino *et al.*,2014) are available from most contributing authors, as well as micro and trace elements, while PAHs, levoglucosan and organic acids are available only in few cases.

At present, the two data arrays of PM_{10} and $PM_{2.5}$ chemical speciation include 110 and 70 cases, respectively, grouped by hot and cold seasons.

The spatial coverage of the database is shown in Figure 1; Southern Italy is the less covered part, with data provided only for Naples, Bari, Brindisi and Lecce. In addition to Figure 1, however, it is worth specifying that for Northern Italy data coverages of PM_{10} and $PM_{2.5}$ are almost equivalent (with the exception of Milan area), while the areal coverage of PM_{10} in Central Italy is far more detailed than that of $PM_{2.5}$ (not available for the Rome area), and the opposite is observed for Southern Italy.

Figure 1. Spatial distribution of data within the IAS National Database of PM_{10} and $PM_{2.5}$ chemical speciation

FINDINGS

Since collected data originate from independent studies and experimental designs, both arrays of PM_{10} and $PM_{2.5}$ are incomplete due to eventual missing data. Linear regression analysis (LR) was thus employed, to the goal of investigating the soundness of the database in estimating reliable species averages, with respect both to chemical ratios commonly expected in the PM, and city types. LRs were performed manually, to check the goodness of regressions over the whole variability range. Outliers were excluded by LRs on a case-sensitive basis, to the same aim. Pearson's R-squared was adopted as indicator to assess the goodness of regressions. An R-squared value of 0.6 was assumed as threshold of good quality of LRs; however, only regressions with R-squared values above 0.7 were considered reliable for using in the modelling. Good or reliable linear regressions were observed in many cases, concerning either major, or minor / trace species. This result constitutes an indication of the good quality of collected data.

It should be noted, indeed, that matrix elements of this database are average quantities, instead than point ones, and are generated by totally independent studies. Concerning the PM_{10} data array, seasonal variations of regression slopes are shown by inorganic ions related to secondary aerosol formation, as expected, but also by some minor and trace species. In example, the slope of Ti vs Mn increases from 1.76 to 2.30 from cold to hot season, and a similar behaviour is observed for the regression of Ti vs Fe. Given that Ti is a source tracer of desert dust, these findings provide a national-level quantitative measure of the influence of long-range advection of air masses on the Ti fluctuations in the PM_{10}. Another notable finding concerns the reciprocally overall good regressions in the PM_{10} between As and EC (elemental carbon), Ni, Pb, Cu, Cr and Zn, regardless of the season. Since all these species are allocated to traffic-related sources (vehicle exhausts, mainly), the quantitative relationships among them (that is, the chemical ratios indicated by regression slopes), found by means of the IAS database, improve significantly the definition of the related source profiles.

This result confirms that, investigating the fluctuations of the PM composition by considering seasonal averages along a topographical scale, provides an key added value with respect to contingent time-series along daily time-scale. Indeed, some of above species are only sporadically determined in the field studies, and the quantitative relationships among them couldn't be still univocally established. This may affect the performances of source apportionment models (Belis *et al*., 2015), that depend strictly on the reliability of source profiles.

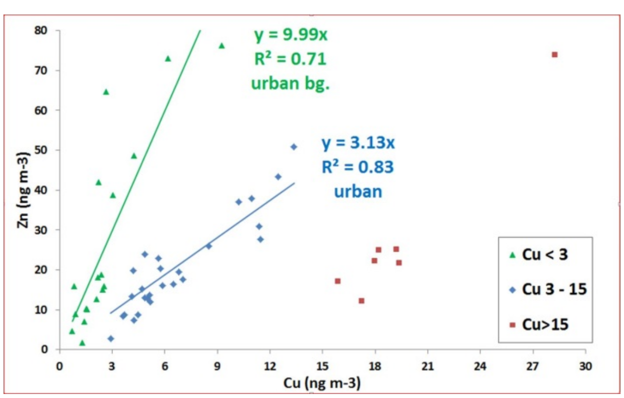

Figure 2. Influence of the increasing anthropic impact from residential to urban sites in the PM_{10}

The variability of some traffic related chemical ratios may also be influenced by the extent of the anthropic impact. This is the case of the Zn vs Cu relationship. As shown in Figure 2, the variability range of Cu increases from < 3 to 3 – 15 ng m^{-3}, going from residential to urban sites, while similar ranges are observed for Zn irrespective of site type. This behaviour has been currently observed in the PM_{10}, but it will be investigated also in the $PM_{2.5}$ to evaluate the role of PM size fractions.

Results above described are only few examples of the complex informative network that can be explored within this database. To this purpose, multivariate statistical tools are required, either to explore hidden relationships, and to quantify them. Factor Analysis (FA) is thus being applied to the database to fulfill the first scope, and Positive Matrix Factorization (PMF) will then be used to provide a quantitative estimate of the impact of PM sources with respect to the territorial differences. The database content of source apportionment data (provided by the contributing authors) will be used to investigate fluctuations of source impacts among the sites included, and to compare these with the findings from the PMF applied at the PM chemical speciation array. Further investigations will involve the meteorological data.

CONCLUSIONS

The IAS database of PM chemical speciation represents the first initiative of national-level collection of PM complete speciation data within a properly designed structure. By its actual status, the database allows obtaining reliable estimates of seasonal averages of major, minor and trace species. This information may supply missing data of chemical species, that are instead needed by both air quality modellers of regional environmental agencies and the source apportionment scientific community. The database shows the potential of providing added, as well as hidden, information on the influence of the anthropic impact and of the local topography on the PM average composition in Italy. Having collected in the database average chemical concentrations allows to perform statistical multivariate investigations, besides data description. The informative content of the chemical data and related meta-data is suitable to be made available to scientific communities and to the general population by means of an informative tool (i.e. a web repository). The future developments of this database constitutes the actual core of the IAS WG1 scientific activities.

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RADON PROGENY IN THE ARCTIC REGION

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Keywords: Radon progeny, Arctic, Svalbard islands, soil emanation, atmospheric stability

INTRODUCTION

The presence of radioactive nuclides in the Arctic represents a key tracer of air-mass pathways (AMAP, 2010). Naturally occurring isotopes, emitted by geologic sources and associated with cosmogenic processes, can describe air-masses origin and residence time (Baskaran, 2016). This is a key information for studying the fate of pollutants in the Arctic region, which is controlled by the meteo-climatic conditions occurring in the different seasons and in the different days of the year (Baskaran and Shaw, 2001). Radon (^{222}Rn and ^{220}Rn have half-lives, respectively, of about 3.8 days and 55 s) and its progeny represent an important tracer of the meteo-climatic conditions occurring in the lower atmosphere. The use of naturally-occurring nuclides, and in particular of radon, for pollution purposes was extensively investigated at lower latitudes (Perrino *et al*., 2001; Chambers *et al*., 2015), especially in urban settings. These case studies support the scientific community to use ^{222}Rn as a comparatively simple and economical approach for defining the stability conditions of the lower troposphere and for estimating the mixing height (Pasini and Ameli, 2003; Salzano *et al*., 2016). The low emissive conditions of the ground, controlled by the permafrost dynamics, limit the application of this approach in Polar Regions.
This study will focus the attention on the technique based on the not-in-equilibrium progeny, where high-volume sampling is not required. This is a single-filter approach coupled with beta counting and it represents, now, the best compromise for our logistic resources between detection efficiency and required man intervention. Furthermore, the disequilibrium issue is less invasive compared with the most common approach available in literature about the Arctic region, where the near-constant progeny is involved.
The present study tests the potentiality to study hourly variations instead of daily samples. We will describe the high-frequency behavior of radon progeny looking at the persistence of stability conditions and we will combine these results with the air-mass characterization based on back-trajectories.

METHODOLOGY

The study, described in details in Salzano *et al*.(2017), was carried out at the Gruvebadet observatory, located in Ny Ålesund (79°N, 11°E, 50 m a.s.l.). The site is located in the Brøgger Peninsula and different glacial valleys converge from the reliefs where the highest altitude is 1017 m above the sea level. The survey covered the period from 1 April to 28 October 2015, including the melting season and the entire summer season.
The natural radioactivity was measured using an automatic stability monitor (PBL Mixing Monitor - FAI Instruments) with a sampling height of 3 m above the ground. The system comprises an air sampler for the collection of particulate matter on filter membranes and a Geiger-Muller counter for determining the total β activity of radionuclides attached to the particles.
The estimation of the soil Rn flux was obtained using a stationary model where the major controlling factors are the soil radon emanation power and the soil water saturation (Salzano *et al*., 2016).
The analysis of the back trajectories was approached calculating the air mass path with the HYSPLIT model. We considered 5 days trajectories using the GDAS meteorological dataset. Simulations were targeted on the study site at different altitudes (500 and 1000 m a.s.l.) in order to evaluate the circulation without the influence of orography on trajectories.

FINDINGS

The evolution of the three radioactive components was the result of the overlapping of different sources and processes: local emission, oceanic income, slope flows and atmospheric stability. The data analysis was focused firstly on isolating the local-source component, which is controlled by the emissive condition of the local surface. Two periods were defined and while small fluctuations in the short-lived progeny were detected during the low-emanation period, the long-lived component seemed to be very close to the limit of detection and the near-constant progeny was frequently detected. The high-emanation period was, on the other hand, characterized by sharp variations in terms of the short-lived progeny, by significant variations concerning the long-lived component and by an occasionally detectable amount of the near-constant progeny. Furthermore, while the long-lived progeny followed the trend described by the short-lived component, the near-constant progeny showed the opposite. The two different emanation periods can be identified also looking at the soil Rn exhalation rate, which is controlled by the thermal behavior of the permafrost layer. The final output of the stationary emanation model indicated a limited soil emission until the end of May with a maximal emissive condition of local soils reached after 30 days at the beginning of July. Referring to the impact of permafrost dynamics, we can distinguish between a low-emanation period (which includes the ablation, the fusion and active-layer development phases) and a high-emanation period (as soon as the ground reached the maximal thickness of the emanating active-layer). The transition between the two periods can be positioned approximately in 8-9 July 2015 within a very short time interval.

Looking at the occurrence of isotopic mixtures with different relative percentage of each component, the most frequent situation during both emanation periods was, of course, the condition dominated by the short-lived progeny, with a frequency ranged between 72% and 78%. The partition of contributions between the near-constant isotopes and the classes dominated by the long-lived progeny represented the most significant difference between the two periods. While intermediate conditions between short-lived and near-constant progenies were more consistent during the low emanation period, the terms between short and long lived progenies were almost dominant during the second period. The first behavior is consistent with the end of the Arctic winter, when the Arctic haze enriches polar air masses with nuclides such as ^{210}Pb and consequently ^{210}Bi. On the other hand, the presence of the long-lived progeny could trace the contribution of local sources or the arrival of recently emitted air masses. The relationship between each radon-progeny mixture and the wind features highlighted that the $^{214}Pb_{eq}$-$^{212}Pb_{eq}$ ratio (Figure1) was strictly controlled by the occurrence of wind calm conditions.

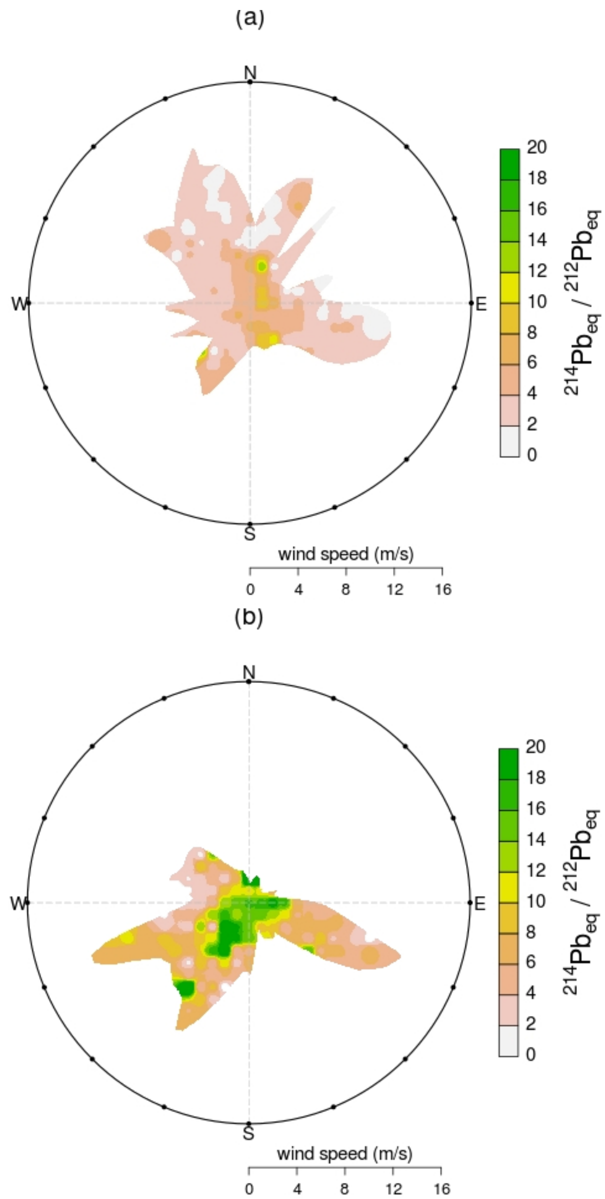

Figure 1. Polar bivariate plots of the ratio between the equilibrium short-lived progeny ($^{214}Pb_{eq}$) and the equilibrium long-lived progeny ($^{212}Pb_{eq}$) during the low emanation period (a) and the high emanation period (b)

The occurrence of periods characterized by high $^{214}Pb_{eq}$ - $^{212}Pb_{eq}$ ratios or by significant near-constant activities were, in fact, associated with atmospheric stability and advection of flows arriving from the open sea or from the glaciers. The first driving factor is the persistence or not of winds below 4 m s^{-1} and this distinction was controlled by atmospheric stability. Atmospheric stability can be traced looking at the residence time of air masses above Svalbard islands in the last 5 days. This information is not completely exhaustive since it does not consider the vertical intrusion of air masses through the inversion layer. The decoupling between the above-inversion and below-inversion air circulation in the fiord seemed to play an important role especially during the summer period when a long wind-calm window occurred. During this event the radon-progeny ratio was permanently high but the residence time of air masses was very low. The evolution of absolute humidity provided some confirmations about the importance of this process. The general increasing trend over the whole campaign was, in fact, combined to accumulation windows, probably related to atmospheric stability, and to abrupt decrements (more than 1 g m^{-3}) that were probably associated with glacier flows. These slope flows, with a katabatic behavior indicated also by high wind speed (more than 8 m s^{-1}), were coincident with significant near-constant activities.

CONCLUSIONS

The detection of β emission from airborne particles with a high-time resolution offers the opportunity to increase the capability of studying atmospheric processes in polar areas. The reduction of soil exhalation during spring may appear as a limitation, but it represents an important challenge. The composition of the radon progeny in the Arctic region supported the identification of air masses dominated by long-range transport in presence or not of near-constant radionuclides instead of long and short lived progenies. This study, presented in details in Salzano *et al.* (2017), supports to extend this approach from the definition of the accumulation processes involving isotopes present in the lower atmosphere, to the identification of the stability conditions of the lower atmosphere, to gather information about air masses and the soil-exhalation conditions. Two different emanation periods were defined in accordance to the permafrost occurrence at the ground. Furthermore, accumulation windows were recognized coherently to the meteo-climatic conditions occurring at the study site.

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CONDUCTIVE AND OPTICAL SENSORS FOR TOLUENE DETECTION BASED ON ELECTROSPINNING TECHNOLOGY

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Keywords: Toluene monitoring, electrospinning technique, nanofibers, conductive and optical sensors, transducers

INTRODUCTION

Toluene, a common indoor pollutant widely used in consumer products (rubber, chemical, paint, dye, glue, printing) is a flammable and toxic molecule with effects on the central nervous system. Inhaling small amounts of toluene vapors (<200 ppm) causes irritation of the eyes and nose, weakness, exhaustion, confusion, euphoria, anxiety, muscle fatigue, insomnia, numbness or tingling of the skin and dermatitis. Inhalation of high levels of toluene vapors (200–500 ppm) for a short period may cause dizziness, nausea, visual changes, muscle spasm and loss of coordination. Exposure to extremely high levels of toluene can cause permanent toxicity to the brain or even death (Juntunen *et al*., 1985; Donald *et al*., 1991; Yücel *et al*., 2008; Filley *et al*., 2004; Benignus *et al*., 2005). Considering the harmful effects associated with toluene, it becomes highly desirable to detect the presence of toluene in indoor climate, without using expensive analytical instruments.

To make this aim available to anyone, novel sensors for environmental monitoring have been designed and developed to obtain consistent values comparable, to those provided by standard methods and technologies. To date, among nanotechnologies, electrospinning is considered as one of the most versatile and inexpensive manufacturing technologies to design and develop nanostructured sensors to detect gases and volatile organic compounds (Macagnano *et al*., 2015). Sensors based on nanofibers sensing-material look extremely attractive for the low cost and great versatility of the raw materials that can be easily tunable, according to the transducer used and the application of interest.

Herewith, different types of transducers capable of detecting toluene vapors are presented:

• Interdigitated Electrodes (IDEs) coated with Polystyrene (PS)/ Polyhydroxybutirrate (PHB)/ Mesoporous Graphitized Nanoparticles (MGC) fibers;
• IDEs covered with TiO2 nanofibers decorated with gold nanoparticles;
• CdSe/ZnS quantum dots (QDs) decorated TiO2 nanofibers.

The features of the sensors changed upon interaction with different concentrations of toluene vapors causing variation in photoluminescence for the TiO_2 fibers decorated with QDs sensor, or current changing for the IDEs covered with electrospun fibers (PS/PHB/MGC nanofibers and gold nanoparticles coated TiO_2 nanofibers).

The sensors performances depended on the type of interaction and the affinity of the material and could be use in some case for detection of small or high level of toluene in air.

1. NANOFIBERS ON IDES AS CONDUCTIVE SENSORS

Herewith, two sensing materials, based on different interaction with the pollutants, are showed and are compared.

PS/PHB/MGC nanofibers were produced through the usage of two incompatible polymers (polystyrene and polyhydroxybutyrate, recyclable and biodegradable polymers, respectively) a peculiar conductive nanopowder (MGC), a proper mix of organic solvents and a surfactant salt. The fibrous layer possessed high porosity and a lot of interfaces among the phases of the composite, hence favoring the gas diffusion. A general decrease of sensitivity to toluene upon increasing temperature (40-80°C) was reported. Such a result suggests that the sensor adsorb into the polymer matrix changing the conformation of the conductive nanoparticles (MGC). (Avossa *et al*., 2018).

TiO_2 nanofibers were UV-light irradiated into a $HAuCl_4$ (tetrachloroauric acid) water solution to grow gold nanospheres. The role of gold is to improve the signal-noise ratio, favouring the detection of toluene at room temperature. The sensor is capable of sensing vapour concentration lower than 0.04 p/p_0.

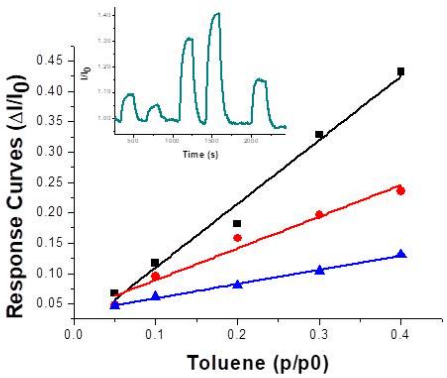

Figure 1. Response curves of PS/PHB/MGC sensor to increasing concentration of toluene when temperature increased (black square: 40°C; red sphere: 60°C; blue triangle: 80°C). Inset: plot of transient responses to various percentages of toluene vapours

2. Fluorescent nanocomposite fibers for Toluene detection

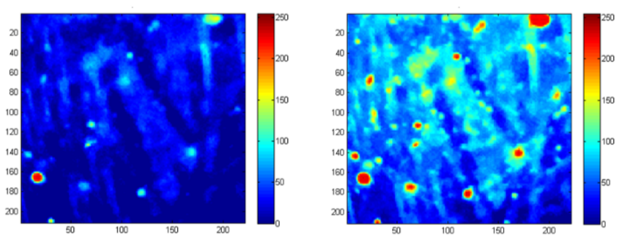

Figure 2. Image Analysis of green lumiscent intensity of fluorescent fibers UV-LED irradiated before (left) and after (right) exposure to a 0.16 p/p_0 of toluene for 10 min

TiO_2 nanofibrous layers have been decorated with fluorescent core/shell nanoparticles (CdSe/ZnS) and investigated as potential optical sensors for Toluene detection. The fibrous sample, placed in a very compact device, designed and fabricated by a 3D-printer in IIA-CNR, was irradiated by a low power LED (390 nm, 5 mW). Using an image analysis programme (MATLAB) the average luminance has been calculated and related to the toluene concentration. Upon injection of 0.16 p/p_0 (partial pressure/ vapour tension) an increase of the luminance was registered at 50% relative humidity.

CONCLUSIONS

The nanofibers properties (resistance or photoluminescence) changed upon toluene interaction with nanofibers sensing material enabled the real-time measuring of the pollutant concentrations in air. According to the type of interaction, the sensor response varied. For the current type of sensor, the photodegradation of toluene phenomenon, on the TiO_2/gold fibers, directly modified the current leading in a higher response of the sensor, while the toluene adsorption into the PS/PHB/MGC fibers caused a reorientation of the conductive particles causing a less intense current variation.

Optical sensors are generally preferred for their high sensitivity, fast response time and low power consumption. Indeed, fluorescent TiO_2/QDs fibers showed remarkable sensing properties regards to toluene, hence it could be used as possible indoor sensing material.

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ENVIRONMENT–GENE INTERACTIONS AND SUSCEPTIBILITY TO NEURODEGENERATIVE MERCURY EFFECTS

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Keywords: Mercury, Neurodegeneration, Risk assessment, Environmental genetics, Alzheimer's disease

MERCURY: A WORLDWIDE CONCERN

Mercury (Hg) is a global pollutant and well–known neurotoxin that has raised great fear in the international scientific community, due to a variety of significant and documented adverse effects on human health and the environment throughout the world (WHO, 2007). The pathological input of Hg on humans and other organisms is widely proven, and the overall picture is quite complex. This is because in the environment Hg is present in various physical and chemical forms, which have different characteristics of transport, deposition and impacts on ecosystems. Methylmercury (MeHg), the major organic Hg form, is produced by industrial processes and indirectly from biological sources by microbial action. The brain and nervous system represent the primary MeHg target tissues for adults, children and neonates. Therefore, MeHg exposure represents a hazard for neurodevelopment, with several symptoms including sensory impairment, cognitive dysfunction, and motor disabilities. Instead, a long–term or acute exposure of Hg vapor can result in the impairment of pulmonary function and psychotic reactions, as well as neurodegeneration. The broad range of symptoms potentially arising from Hg exposure considerably complicates accurate diagnosis (Clarkson *et al*. 2003; Rice *et al*., 2014).

To aggravate such a delicate situation, Hg toxicity and associated health effects can vary at individual level, depending not only on its chemical speciation, concentrations, and time of exposure, but also on the individual susceptibility to Hg exposure (Gundacker *et al*. 2010). As a result, the real negative influence on humans is difficult to evaluate within a multifaceted clinical framework, where chronically exposed people due to lifestyles, cultures, socio–demographic characteristics, and working activities still play a leading role (WHO, 2008). Epidemiological studies on populations exposed to inorganic Hg (e.g., dentists and miners) or MeHg (e.g., fish consumers) are showing that DNA sequence variations (polymorphisms) can better explain variations in Hg biomarker values and health outcomes (Barcelos *et al*., 2013; Engström *et al*., 2013; Goodrich *et al*., 2011; Harari *et al*., 2012; Wang *et al*., 2012). Hence, the creation of a promising research field, which combines the concepts of response to Hg action, individual genetic "makeup", and adverse health effects. Actually, children are recognized as having a significant susceptibility to Hg toxicity, displaying extreme variability in mainly neurological outcomes (Julvez J, and Grandjean P. 2013). In addition, in occupational health there is a long–standing controversy regarding genetic screening that might identify workers at great risk (hypersusceptible) from workplace exposure (Grandjean, and Landrigan, 2006). Some disadvantaged ethnic groups that might have a higher incidence of certain susceptible genes, making them more vulnerable to adverse effects of Hg, represent another sobering example. For all these reasons, identifying molecular markers for variation in susceptibility to Hg poisoning is very crucial in terms of a more accurate individual risk assessment for children and adults (Andreoli *et al*., 2017). This work briefly discuss emerging knowledge in Hg susceptibility on neurodegenerative disease, such as Alzheimer's disease (AD), focusing on the potential role played by the gene–Hg interactions in this context.

THE ROLE OF THE GENETIC BACKGROUND IN MEDIATING INDIVIDUAL MERCURY SUSCEPTIBILITY

It is well known that the pathogenic action of Hg can alter a wide array of molecular pathways and clinical presentations, but the exact mechanism of toxicity is globally very complicated to determine. Several mechanisms have been proposed. At the cellular level Hg is surely a potential toxicant, capable of causing alterations in membrane permeability, interfering with macromolecular synthesis of DNA, RNA and protein, inducing oxidative stress and mitochondrial dysfunction, increasing radical oxygen species levels and lipid peroxidation (Syversen and Kaur, 2012). All these pathological processes initiate a cascade of molecular alterations, which may result in permanent impairments of the cellular structure or the catalytic activity of metabolic/DNA repair enzymes, altering the expression patterns of numerous genes. With this background, many studies emphasized the potential of the genetic heritage in modulating human susceptibility in the context of Hg exposure, response, and biomarkers identification. There are many genes evaluated as potential mediators or moderators factors, which act in response to environmental stimuli of Hg (Basu et al. 2014). **Figure 1** shows a simplified, theoretical model of how genetic variants, environmental risk factors and different personal stressors may interact to shape the repercussions of Hg on human health. In this context, a person's complete genomic sequence with its molecular differences at the DNA level (genotype) may create individuality (phenotype), acting in combination with environmental influences, while genes and their products do not function independently, but they participate in networks that interact between themselves (synergistic effect). Actually, emphasis is placed on a particularly important type of coding genetic variants, the non–synonymous single nucleotide polymorphisms (nsSNPs), occurring in a gene–coding region. Since these latest variants may induce differences in primary molecular structures at the DNA level, they alter the encoded amino acid sequence, thus potentially affecting proteins composition, function, and their interactions with other molecules (Shastry, 2009). Therefore, it is important that ever–increasing number of gene–environment studies may focus on those nsSNPs providing an opportunity to develop prevention strategies and to identify high–risk individuals for early intervention.

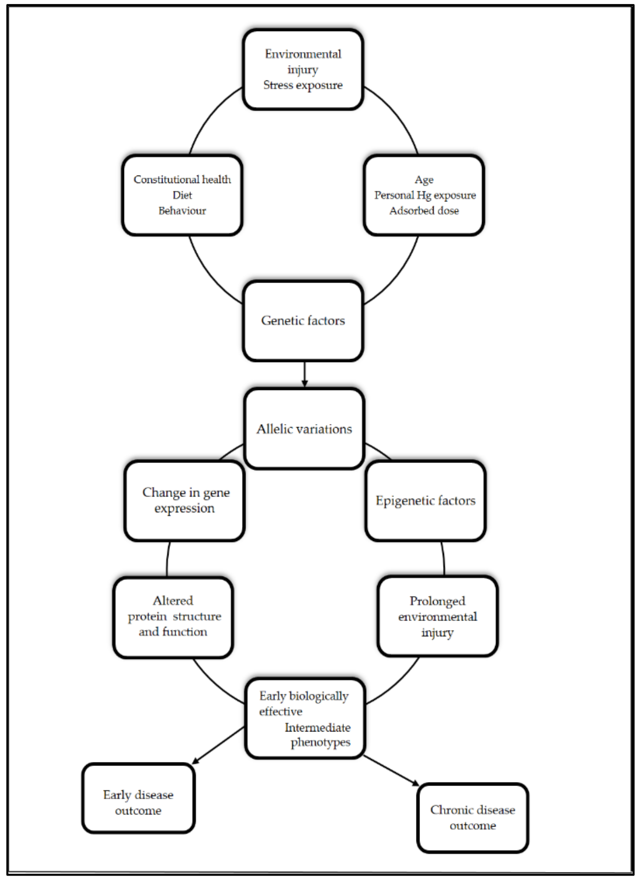

Figure 1. The expanded environmental–genomic heuristic model related to Hg. Genetic and environment interactions contribute to the development of pathological conditions (Andreoli *et al.*, 2017)

MERCURY EXPOSURES AND GENETIC VARIATIONS AS RISK FACTORS FOR NEURO-DEGENERATIVE DISORDERS

In the last years, experimental evidence has primarily highlighted the toxicity induced by Hg in exacerbating neuropathological conditions, because of its ability to produce neurodegeneration. Some results have also suggested that this exogenous factor may be involved beside genetic risk factors in amplifying the risk of developing Alzheimer's disease (AD). The existence of a potential link between Hg exposures and AD was therefore emphasized. In vitro experimental studies with neural cells have shown that Hg induces glial cell reactivity (a hallmark of brain inflammation), increases the expression of the amyloid–beta (Aβ) peptide, and produces abnormal forms of tau protein, causing senile/amyloid plaques and neurofibrillary tangles, two key features of AD (Ye *et al.*, 2005). In addition, Hg deposition in some human brain regions, as hippocampus and amygdala, which are fundamental to perform the cognitive functions, has highlighted its active role in AD etiopathogenesis still further. Finally, higher Hg concentrations in brains of deceased and in blood of living patients have confirmed this heavy metal seems increase the AD risk. AD, the most common cause of dementia in the world, is multifactorial and heterogeneous (Bird, 2008). Over 99% of AD cases represent the so–called sporadic form of the disease, which is not associated with any known mutation. This form itself probably involves several different etiopathogenic mechanisms. Neuroinflammation, head trauma, and diabetes have been implicated as risk factors for AD. In the sporadic AD, the presence of one or two alleles of Apolipoprotein E (APOE) $_4$ as opposed to $APOE_2$ or $APOE_3$ increases the disease risk by several fold. Interecsantly, an important role for APOE as a genetic susceptibility factor against the Hg neurodegeneration has also been found. In fact, human association studies supported a differential detoxification capacity regarding Hg of the APOE ε_4 allele, which may amplify the neurocognitive damage in chronically exposed AD patients (Godfrey *et al*. 2003; Mutter *et al*. 2004). The versatility of ApoE protein arises from having three isoforms changing from one another, because different amino acids are present at position 112 and 158: Apo-E4 has an arginine in position 112 and 158, where Apo-E2 has two cysteines, and Apo-E3, the most common variant, an arginine and a cysteine. However, only the cysteine contains a sulfhydryl, which is capable of binding bivalent metals like Hg. This means that the E2 and E3 isoforms, with cysteine rests, could better bind and then detoxify Hg, when for example it crosses the blood–brain barrier and causes damage in the brain. In contrast, the E4 isoform, which is therefore devoid of sulfhydryl groups, probably fails to connect with Hg, thus performing a less efficient elimination process that increases the intensity of the symptoms of Hg toxicity. Consequently, APOE genotyping (ε2-ε3-ε4 alleles) may represent an additional link between presumptive Hg–related neurological symptoms and increased risk of developing AD, by acting as important protective (ε2) or risk (ε4) factor. These findings show that the potential association between Hg and AD is of high clinical relevance, because its public health impact may be enormous.

FUTURE PERSPECTIVES

In summary, we emphasize a new genetic and personalized dimension for a more accurate Hg risk assessment. This is effectively the goal of environmental genetics, to understand how genetic variability influences individual responses to environmental effects, based on the assumption that high–risk genotypes accumulate more damage and therefore are at greater risk of developing exposure–related diseases. To accomplish this goal, it is important to evaluate the functional impact and disease risks associated with these polymorphisms. At present, with its background of crucial mediating factor in neurological and cognitive processes, the APOE ε_4 allele is a major genetic risk factor investigated for its association with not only dementia forms and cognitive development, but also with neurological adverse effects Hg–induced. Obviously, definite knowledge about the causal role of Hg in neurodegenerative diseases, such as AD, may only be derived from large, long–term prospective epidemiological studies examining the occurrence of disease in subjects exposed to Hg risk in various sources, compared with those at lower risk. In addition to the APOE $\varepsilon_2/\varepsilon_4$ polymorphisms in coding sequence, APOE contains other interesting functional polymorphisms in the promoter at multiple regulatory sites, able to influence gene transcription, and finally the quantitative expression of APOE levels. Therefore, the consideration of haplotype–based analysis involving structural polymorphisms in the APOE promoter area, in addition to the functional variants located in the gene–coding region may be helpful in terms of a more accurate individual risk assessment. In this framework, additional data and evidence should also involve new functional polymorphisms in interactively–candidate genes, for example through Genome–wide association studies, to clarify the genetic basis of personal vulnerability to Hg toxicity, and assess the clinical relevance particularly on exposed subjects. Finally, while the detection of genotypes associated to Hg damage is an inalterable phase, a comprehensive evaluation of Hg impact on health should retrospectively take account of dynamic interactions with other variables, arising from both the essence of Hg itself (i.e. source, duration and levels of exposure, speciation, corresponding biomarkers analyzed), and environment. In this case, for example simultaneous exposure to multiple heavy metals could trigger final health outcomes with either additive or synergistic effects, which would have marked influence in estimating the individual risk due to Hg exposure. The hope is that all new information will be used to implement a comprehensive public health action plan in a context of global Hg risk assessment, for identifying and protecting susceptible individuals from Hg hazards. While genetic susceptibility is clearly important and more studies are needed to identify increasingly specific interactions, high priority should, however, begiven to reducing Hg pollution exposure in general.

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SUPPORTING ACTIONS TO BASILICATA REGION GOVERNMENT: ENVIRONMENTAL QUALITY IN AGRI RIVER VALLEY

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Keywords: Environmental toxicity, air pollution, Agri river Valley, emission sources, in-field measurement campaigns

INTRODUCTION

During the last century, the oilfield exploitation at Viggiano e Grumento Nova (PZ, Italy) excited the hope of an important social-economic development of the Agri Valley in the Basilicata region, Italy. On the other hand, strong puzzlements existed about the twisting of land's talent and the pollution of all environmental compartments (i.e., air, waters, soil and underground). Nowadays, the Agri Valley is among the richest areas of Southern Italy but is also the theatre of protest marches and sit-ins, legal disputes and political debates with regard to pollution and health impact on population.

The Agri river Valley area is under observation by Regional Agency for Environment Preservation (ARPAB), which manages five monitoring stations located in zones characterized by distinct environmental contours. An important role is also played by the Ministry of Environment and Preservation of Territory and Sea (MATTM), promoter of studies dealing with ambient pollution (not restricted to regulated toxicants) and epidemiology over the area. Nevertheless, the investigations conducted till now look as inconclusive (Calvello *et al.*, 2017). Indeed, all chemical indexes meet the requirements fixed by normative (data are much lower than concentration limit or alarm values); nevertheless, some exceedances occur for benzene concentrations together with episodes of smells causing illness and trouble. Besides, tumour incidence in the Agri Valley exceeds that of the remaining of Basilicata, though no specific tracers have been identified for assessing the impact of industrial plants running there or the health risk induced.

In this context, Basilicata Region and CNR-IIA have signed in 2016 a Convention (Basilicata Region and CNR-IIA, 2016), covering all industrial districts of the region, including Agri Valley. It is comprised of two work packages; the first work package (WP1) deals with environmental impact assessment and authorizations, while the second (WP2) is committed of monitoring.

METHODOLOGY

In the frame of WP2, two measurement campaigns were conducted in 2017 (May to June and October to November). The two campaigns differed not only for year time (and occurrence of season-modulated pollution sources), but also for operating status of industrial district; indeed, plants were shut-off in the spring and on in the autumn. As total, to implement WP2 the participation was needed of 11 researchers and 7 technicians plus administrative staff.

Table 1. Names and geographical co-ordinates of the monitoring sites over Agri river Valley

ARPAB name		*municipality*	*latitude*	*longitude*
A	Viggiano	Viggiano (Guardemauro)	40.3141 01	15.9045 88
B	Viggiano 1	Viggiano (Santa Caterina)	40.3348 66	15.9006 88
C	Masseria de Blasiis,	Viggiano	40.3242 35	15.8673 62
D	Grumento 3	Grumento Nova (Carpineto M.),	40.2884 12	15.8914 87
F	Costa Molina Sud 1	Viggiano (Valloni)	40.3137 75	15.9547 41
PC	Protezione Civile	Viggiano	40.3353 86	15.9032 83

Six sites were selected for measurements; five of them coincided with the ARPAB stations; the sixth was set inside the Civil Protection Agency estate (Table 1 and Figure 1, PC site).

Our study included the regulated toxicants but was extended to a list of unregulated substances, in order to draw a more comprehensive evaluation of ambient quality and infer insights about the nature of sources, with special reference to oil treatment plants. In particular, attention was paid to:

- • regulated pollutants: CO, SO_2, H_2S, O_3, NO, NO_2, benzene, PM10; PM2.5; benzo[a]pyrene in PM10; heavy metals (Pb, Cd, As, Ni);

- • unregulated contaminants: VOC (toluene, xylenes), aldehydes and ketones, PAHs in PM10 and depositions, particulate n-alkanes; cations and anions in PM10, PM2.5 and depositions; organic and elemental carbon.

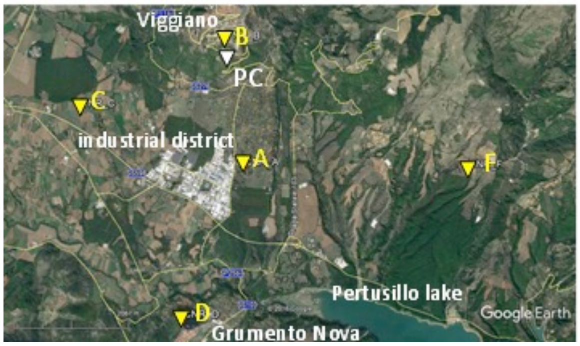

Figure 1. Map of Agri Valley area with the six monitoring sites. A-F: ARPAB stations; PC: Protezione Civile estate

Three distinct approaches were applied to monitor target compounds; they were: *i)* monitoring in continuous modality, applied to gaseous regulated toxicants; *ii)* active sampling (air and particulates were collected by pumping and filtering through traps or filter membranes); and *iii)* passive sampling (collection of contaminants through samplers based on principle of gas diffusion or settlement of matter). The toxicants' time behaviours were acquired by the first two approaches, while the passive sampling provided the concentrations over weeks of the whole investigation periods.

Both for sampling and chemical characterizations standard, reference or consolidated procedures were used. In particular, chemical analyses were performed through solvent extraction and GC-MSD, HPLC-UVA, ICP-MS and XRF methods. PM_{10} and $PM_{2.5}$ were determined by gravimetry on micro-balance. Molecular signatures (diagnostic ratios, percent distributions) were investigated in addition to net concentrations to draw information about the sources

FINDINGS AND CONCLUSIONS

The results of in-field studies have been presented in two Technical Reports sent to Basilicata Region Government (Cecinato and Perrino, 2017, 2018a). These results are property of Basilicata Region, and can be asked for to Regional Government.

A third Report has been released to provide a comprehensive analysis of our findings (Cecinato and Perrino, 2018b). This report holds suggestions for further investigations actions aimed to better assess the impact of Viggiano plants on Agri Valley and preserve the environment quality in that area.

Anyway, the pollution rates look low both in spring and autumn even at industrial district, though in the second period the plants were running. The Agri Valley seems to undergo the presence of plants as a consequence of co-related activities rather than of direct release of toxicants. Natural sources impact on the occurrence of particulate hydrocarbons and light carbonyls, while wood burning exhaust is detectable in the cold season. Despite that, hot spots episodes of benzene, acetaldehyde and acetone seem to merit further investigations.

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ORGANOMERCURY COMPOUNDS IN BIOLOGICAL SAMPLES: ANALYTICAL APPROACH FOR A THOROUGH DETERMINATION

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INTRODUCTION

Mercury (Hg) is one of the most toxic pollutants ubiquitously present and persistent in the environment. Hg is emitted from natural and anthropogenic sources and is globally dispersed because, in contrast to other metals which tend to exist in the atmosphere in the particulate phase, Hg exists almost (>95%) in the gaseous phase as elemental Hg (Hg^0) which is relatively inert and stable with a long residence time (6 to 1 yr) (Pirrone *et al*., 2010; Pirrone *et al*., 2013). Long-range transport of Hg^0, followed by wet and dry deposition after its oxidation, is an important process by which Hg is input to terrestrial and aquatic ecosystems. Through this process, aquatic receptors are subjected to Hg contamination and consequential bioaccumulation in the food chain, causing negative impacts on wildlife and humans through consumption of contaminated fish. Once in the water, Hg can be present in different forms. The main Hg forms are elemental mercury [$Hg^0_{(aq)}$], complexes of oxidized Hg with various organic and inorganic ligands, and organic Hg forms, mainly as monomethylmercury cation ($MeHg^+$, CH_3Hg^+) and dimethylmercury (DMHg, CH_3HgCH_3) (Horvat *et al*., 2017; Kotnik *et al*., 2015). The environmental fate of Hg in water is quite complex since its toxicology, toxicity, mobility, and bioaccumulation depend on its chemical form (Horvat *et al*., 2017). Therefore, the study of Hg speciation in seawater is of key importance to understanding the Hg cycle in the global environment, and more specifically, its fate in the biotic and abiotic components of marine ecosystems, improving our understanding of patterns that may affect human health (Fantozzi *et al*., 2013; Horvat *et al*., 2017). The principal form of Hg in biota is methylmercury ($MeHg^+$), an oxidized species of Hg with the addition of one covalently bound carbon atom. Organomercury compounds, especially $MeHg^+$, are toxic because of their penetration ability through biological membranes, high stability and long-term elimination from tissues. $MeHg^+$ is highly absorbed by the gastrointestinal tract and it can pass blood-brain and placenta barriers causing serious damages, especially to the central nervous system. Due to its toxicity and its ability to bioaccumulate and biomagnify, monitoring programs of $MeHg^+$ concentrations are a critically important issue.

METHODOLOGY

Different techniques have been developed for the determination of both total mercury (THg) and Hg species. The appropriate analytical method for monitoring depends on the nature of the sample and concentration level. THg can be quantified by cold vapor atomic fluorescence spectroscopy (CVAFS). This technique consists of (a) sample digestion, (b) oxidation by BrCl to convert all mercury species to Hg^{2+} in solution, (c) addition of a reducing agent to generate Hg^0, (d) amalgam formation of Hg^0 vapor with gold traps, (e) thermal desorption of the mercury from the trap and (f) detection of the Hg^0 by CVAFS (Cizdziel, Tolbert, & Brown, 2010). CVAFS can be performed by using the Tekran 2600 instrument that relies on dual stage Hg pre-concentration onto gold traps, virtually eliminating all interfering compounds. This technique is better suited to measure Hg in small tissue quantities and has lower detection limits, down to pg L^{-1} depending mainly on the purity of the reagents and the inert gas used as well as on the cleanliness of the working procedures. The concentration of THg can also be determined with thermal decomposition technique by means of Direct Mercury Analyzer (DMA) instrumentation. Solid or liquid samples are weighted and introduced into the DMA (Barst *et al*., 2013); they are dried and then thermally decomposed under an oxygen flow. The combustion products are carried off and further decomposed in a hot catalyst bed. The Hg vapors are trapped on a gold amalgamator and subsequently desorbed for detection by atomic absorption spectrometry (AAS). Compared to CVAFS, thermally decomposition technique is faster and allows for the direct Hg determination, but among the main drawbacks, there are the higher values of the lower limit of quantification and the lower sensitivity.

Hg speciation investigation requires coupling of separation techniques and element-specific detection techniques. Different analytical separation methods can be used for Hg speciation analysis in tissue; usually, chromatographic methods are employed, as high-performance liquid chromatography (HPLC) and gas chromatography (GC) which are able to separate all Hg species in a single step. HPLC is applied for analyzing mercury in biological samples where Hg concentration is relatively high (in parts per billion to parts per million levels). GC is the most commonly used technique for separation of Hg species owing to its high separation efficiency, lower detection limit and capability to easily couple with highly effective pre-concentration methods. In gas chromatography, Hg species need to be derivatized in order to become volatile and thermally stable. Moreover, solid samples cannot be directly injected into a chromatographic system; therefore, the extraction of Hg compounds from the samples is necessary. Indeed, Hg speciation analysis in environmental samples requires three steps: extraction/pre-concentration of Hg from the matrix, separation of different Hg species, and quantitative detection. Hg species are usually extracted by acid leaching and microwave digestion. In the first case, the solid sample is dissolved in an acid/acid mixture solution for an appropriate period of time that can be shortened by sonication. Microwave digestion can be used as a suitable alternative to acid leaching, reducing extraction time and solvent consumption. Among sensitive and selective detection methods, mass spectrometry (MS) and inductively coupled plasma mass spectrometry (ICP-MS) are suitable alternatives to atomic absorption/fluorescence spectrometry that can reach detection limit in the ng L^{-1} range or lower.

DISCUSSION

Organomercury compounds in the biological material can be analyzed by GC-MS. For sample preparation and extraction of Hg species, acid leaching can be used. This procedure includes homogenization of the sample in aqueous solution, strong acid addition (usually HCl or HBr) to separate Hg species from proteins, derivatization reaction (by alkylation with $NaB(Pr)_4$) and organic solvent extraction, usually by toluene, methylene chloride or dichloromethane. Before derivatization, a pre-concentration step with an aqueous ethanolic solution containing a thiol-compound (as cysteine) can be carried out in order to concentrate $MeHg^+$ because of its affinity for cysteine groups. A valid alternative to acid leaching is the use of microwave mineralization, which is performed by digesting an aliquot of biological sample with the use of strong acid (usually HCl) into a closed vessel under pressure. It allows an increase of the sample dissolution efficiency, improving Hg solubility into the extract, reducing extraction time and acid consumption, and minimizing the risk of loss of volatile elements (Korn *et al*., 2008). After microwave digestion, propylation reaction is performed to derivatize the Hg before solvent extraction. Afterward, the derivatized organomercury compounds can be extracted using an organic solvent as dichloromethane. Finally, an aliquot of the combined extracts is injected into a gas chromatograph for quantification. As reported in the literature, the combination of microwave mediated extraction with the GC-MS analysis is the optimal combination for $MeHg^+$ determination in biological sample (Chen, Chou, & Hwang, 2004).

CONCLUSIONS

Hg is a persistent pollutant enriched in the environment by human activities, and cycling between different environmental compartments. The impact of Hg on ecosystem health is related not only to the magnitude of regional and global emissions and deposition, but also to the potential of the water ecosystems to convert oxidized Hg to $MeHg^+$, and of the food webs to biomagnify $MeHg^+$. Therefore, monitoring $MeHg^+$ concentration in biota is an accurate indicator of Hg impact on human and biological health (Pirrone *et al*., 2013). Global concern of widespread $MeHg^+$ contamination has motivated international initiatives to assess current knowledge on atmospheric Hg emissions, transport, deposition, and its effects on terrestrial and aquatic ecosystems. These include activities of the United Nations Environment Program (UNEP) and that of under the UNECE-LRTAP Task Force on Hemispheric Transport of Air Pollution (TF HTAP). The UNEP initiative is aimed at decreasing human health and environmental risk from the release of Hg, as well as improving the understanding of international Hg emissions and their transport and fate. CNR-IIA is currently coordinating the GMOS network, a global observational network, which includes to date more than 40 ground-based monitoring sites worldwide distributed as well as an oceanographic monitoring program to assess Hg species in water samples including the biota, as a fundamental part of the biogeochemical cycle. GMOS is currently supporting the major goals of international program and Conventions, such as the Minamata Convention, which was signed in January 2013 to control the global release of Hg to the environment, and is currently under implementation. Together with measurements of Hg levels into atmosphere and hydrosphere, the analysis of biological material allows an accurate comprehension of all mechanisms that regulate its distribution among the different environmental compartments. Therefore, the analysis of biological samples represents a necessary support to air and water quality monitoring, because these specimens accumulate atmospheric contaminants at levels above the ambient concentrations.

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INVESTIGATION OF CARBONACEOUS COMPOUNDS AND TRACE ELEMENTS OCCURANCE IN PARTICULATE MATTER AT MONTE CURCIO OBSERVATORY

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INTRODUCTION

PM is one of the major pollutant groups emitted from both natural (volcanoes, dust storms, and forest fires) and anthropogenic (vehicles, power plants, and charcoal combustors) sources. Primary particles are directly emitted as liquid or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruption, and wind-driven or traffic-related suspension of the road, soil, and mineral dust, sea salt and biological materials (plant fragments, micro-organisms, pollens, etc.). Secondary particles, on the other hand, are formed by gas to particle conversion in the atmosphere (Lohmann and Feichter, 2004). The suspended airborne particles undergo various physical and chemical interactions and transformations (atmospheric aging), that is, changes of particle size, structure, and composition (e.g. coagulation, restructuring, gas uptake, and chemical reactions).

The components of PM can generally be classified as carbonaceous fractions including organic carbon, elemental carbon, carbonate carbon and inorganic components consisting of crustal elements, trace metals, and ionic species. Each of these components typically contributes about 10–30% of the overall mass load. Depending on aerosol properties and meteorological conditions, the characteristic residence times (lifetimes) of aerosol particles in the atmosphere range from hours to weeks. The particles with a diameter from some nm to tens of µm can remain buoyant in the atmosphere for days and thus can be transported over a long distance from the original source resulting in an enhanced level of ambient PM concentrations even at rural or background sites.

A particular PM component that is known to exert toxic effects on a human being is the metallic fraction. Many elements, like Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn are widely distributed in PM and, hence, are suspected to be an important source of PM toxicity. Therefore, trace element analysis of PM is highly demanded to assessing air quality and health risks. Many epidemiological studies have demonstrated that exposure to such metals can cause adverse human health effects at concentrations commonly found in urban areas around the world.

The carbonaceous aerosol is composed of an organic fraction, named organic carbon (OC), and by a refractory light-absorbing component generally referred to as soot. Soot is generated by incomplete combustion of organic material from traffic, residential heating, industrial activities, and energy production using heavy oil, coal or biofuels. Depending on its empirical determination, soot is reported as elemental carbon (EC) or equivalent black carbon (eBC). EC is quantified by thermal-optical (TOT) methods, while eBC is derived from optical measurements. Elemental carbon being directly emitted into the atmosphere has a long photochemical lifetime and this makes it a good indicator of primary anthropogenic air pollution (Xiao *et al*., 2011). Organic carbon originates from a variety of processes. It can be released into the atmosphere from anthropogenic (fossil fuel combustion, domestic heating and cooking, biomass burning), and biogenic sources (vegetation, wind-lifted biological particles, fires, emissions from marine environments), as primary OC (POC), or produced within the atmosphere by photochemical reactions through gas-to-particle conversion of volatile organic compounds, as secondary OC (SOC).

METHODOLOGY

The most common technique for the measurement of airborne PM is the manual measurement method, which is based on the combination of filter sampling and gravimetric analysis using a microbalance. The introduction of advanced on-line instrumentation such as aerosol mass spectrometers (AMS) has allowed for fast and descriptive characterization of chemically speciated mass distributions of atmospheric aerosol components (PM_1 and $PM_{2.5}$) in some studies (Sandradewi *et al*., 2008). For the continuous measurements of airborne PM, many researchers have commonly relied on the automated sampling system. In this respect, beta gauge particulate and tapered element oscillating microbalance (TEOM) particulate samplers have been the common choices. For such automated system, the amount of particulate deposited on a filter tape during a fixed sampling interval is determined continuously by measuring the extent of beta ray attenuation through the filter on which the particles have been deposited.

After sampling, sample preparation is the most important passage for trace metals analysis. Acid digestion has always been the most widely used method for extracting trace metals, with microwave assisted acid digestion that has taken hold in the last decades among researchers. Usually, for both methods are used H_2SO_4, HNO_3 and HCl acids in a different ratio based on the research carried out with the possibility to use a small percentage of HF acid to aid the digestion of silicate compounds. The advent of a new ICP-MS/MS instrument has encouraged the development of new applications. In one (Pappas *et al*., 2015) three cell modes: single quadrupole (Be, Pb, and U); MS/MS with NH_3–He (Co, Cr) and MS/MS with O_2 (As, Cd, Mn, Ni, and Se) were used for quantification in cigar smoke, and similar strategy is also carried out in our laboratories. Using an ICP-MS instrument as a detector for the on-line measurement of particles is a fertile, interesting but challenging research area. Researchers in Austria described (Sommersacher *et al*., 2016) a system for measurement of the time-resolved release of Cl, K, Na, Pb, S, and Zn from single particles during biomass combustion. Researchers in Switzerland developed (Zhao *et al*., 2016) an SMPS-ICP-MS system coupled with a rotating-drum device for the simultaneous determination of both the size distribution and elemental composition of NPs. Meanwhile, in the Czech Republic, researchers used (Benešová *et al*., 2016) substrate-assisted laser desorption to introduce Au NPs from a plastic surface into an ICP-MS instrument. A 61% transport efficiency was achieved using 56 nm-sized references NPs.

Regarding the analysis of the carbonaceous species were determined on one punch (area: 1 cm^2) cut from the quartz fiber filters employed for collecting the 24-h PM_{10} and $PM_{2.5}$ samples. The analysis of OC and EC was performed by the thermo-optical method (TOT) using a Sunset Laboratory OC/EC analyzer (Sunset Laboratory, Tigard, OR, USA). Briefly, samples were heated in a completely oxygen-free helium atmosphere, through four increasing temperature steps, to remove all organic carbon on the filter. The transition from the third temperature to the fourth (from 500 to 700 °C) also decomposes carbonate carbon. Then, the pure helium eluent is switched to a 2 % oxygen/helium mixture in the sample oven and the temperature is stepped up to 850 °C for EC determination. Organic and elemental carbons were detected by a flame ionization detector after oxidation to carbon dioxide that is finally reduced to methane.

FINDINGS

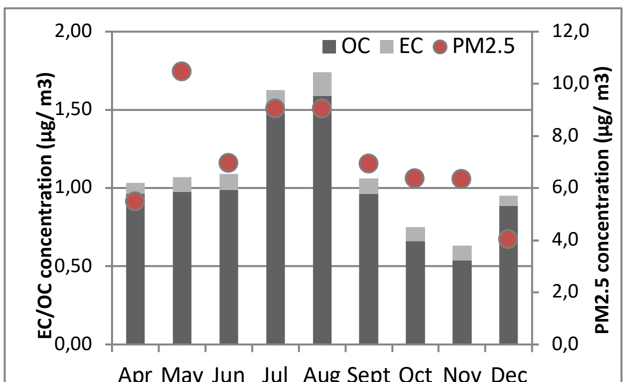
Some of the methodologies described above had been used on measurements taken at the Monte Curcio Observatory (MCU), the regional station of the Global Atmosphere Watch program (GAW-WMO). The Observatory (39°18’57.2” N 16°25’23.6” E; 1780 m a.s.l.) is located in a strategic position within the Sila National Park in the Calabria region (South Italy).

The sampling method used at the observatory was an automated sampler using beta gauge system for identification of particulate mass on the filter.

The analysis of trace metals offers important information that can be combined with the concentrations of other pollutants (i.e. carbonaceous fraction, ions) to obtain the information on source apportionment. Numerous source apportionment (SA) methods, such as positive matrix factorization (PMF), enrichment factor (EF), principal component analysis (PCA) and chemical mass balance (CMB) have been implemented to identify the main sources that emit $PM_{2.5}$and PM_{10} with the major sources that include coal burning, vehicular emissions, biomass burning, secondary aerosols, soil dust, and industrial emissions.

The monthly average of EC and OC concentrations at MCU in PM_{10} and $PM_{2.5}$ is reported in Figure 1 which shows that the carbonaceous component is mainly segregated in the $PM_{2.5}$, caused by the contributions of combustion sources which affect mainly the fine fractions of atmospheric aerosols. The OC and EC concentration trends observed in PM_{10} and $PM_{2.5}$ fractions are similar, with the highest concentrations observed during the warm period (April-August), while during the coldest months (September-December) lower carbon levels are observed as in a previous work (Dinoi *et al*., 2017). A t-Student test was performed to investigate these differences were statistically significant. Results indicated that seasonal variability was significant for both species (OC and EC) ($p < 0.01$). This trend was observed also in high altitude remote site in Italy (Sandrini *et al*., 2014) and could be explained considering that during the cold period they are decoupled from the Planetary Boundary Layer (PBL), where emission sources are located, hence representative of the free troposphere, in fact dispersion and transport of lower atmospheric pollutant depend largely on the local PBL structure, and the turbulence is the dominant mechanism mixing particulate matter (PM) and ambient air. By acting as a lid to the pollution vertical mixing extent, PBL height is one of the important factors affecting pollution concentration and large-scale transport.

In this study, a good correlation was observed between EC and OC both in PM_{10} (Pearson 0.79, $p < 0.05$) and in $PM_{2.5}$fraction (Pearson 0.74, $p < 0.05$). The relationship between OC and EC could provide useful information regarding the origin of carbonaceous aerosols. It confirms that, at this high altitude rural site, most of the carbonaceous species are transported by long-range air masses and that the time series of EC and OC concentrations are modulated by synoptic and local meteorology, increasing in this way the correlation between the two chemical species. While the high concentration of PM in both fraction in May and in PM_{10} in October is due to Saharan dust event occurs in this months.



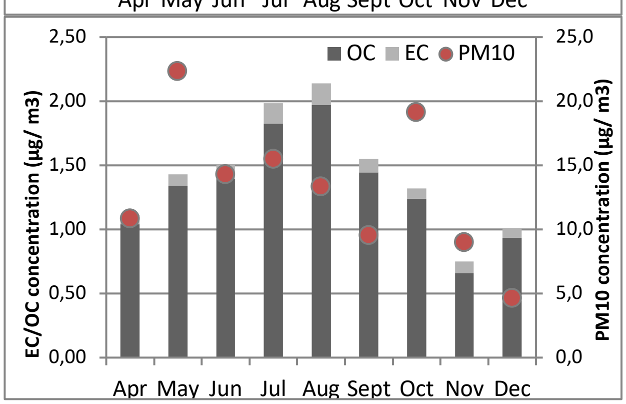


Figure 1. Monthly averages of EC and OC concentrations in $PM_{2.5}$ (a) and in PM_{10} (b).

CONCLUSIONS

The study on OC and EC concentration show similar trends observed in PM_{10} and $PM_{2.5}$, with the highest concentrations observed during the warm period (April-August), while during the coldest months (September-December) lower carbon levels are observed. The similar trend observed also in high altitude remote site in Italy and could be explained considering that during the cold period they are decoupled from the Planetary Boundary Layer. The concentration of PM tends to increase during the summer months, passing from 5 $\mu g/m^3$ in $PM_{2.5}$ during April to around 10 $\mu g/m^3$ in the months of July and August falling again to 4 $\mu g/m^3$ in December. The content of PM_{10} increases from about 10 $\mu g/m^3$ in April to 15 $\mu g/m^3$ in July and then back to 5 $\mu g/m^3$ December. The high concentration of PM in both fraction during May and in PM_{10} in October is attributed to Saharan dust event, indeed eliminating the concentrations of this event in May the $PM_{2.5}$ decrease from 10.2 $\mu g/m^3$ to 6.8 $\mu g/m^3$ and PM_{10} from 23.3 $\mu g/m^3$ to 14.1$\mu g/m^3$; while during October the concentration of PM10 decrease from 19.1 $\mu g/m^3$to 10.2 $\mu g/m^3$. The analysis of trace elements will be performed and used to carry out the source apportionment method and obtain information on sources.

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MICROEXTRACTION TECHNIQUES AND MICROWAVE-ASSISTED EXTRACTION: A NEW COMBINED APPROACH FOR THE ANALYSIS OF THE POLLUTANTS ASSOCIATED TO THE AIRBORNE PARTICULATE MATTER

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INTRODUCTION

Until a few decades ago, sample preparation was carried out using traditional techniques, such as liquid-liquid extraction (LLE) and solid-liquid extraction (SLE), which use large volumes of organic solvents. Although with the advent of solid-phase extraction (SPE) much less solvent has been used than LLE, the volume can still be significant. Furthermore, this approach is not applicable to solid matrices for which the Soxhlet extraction is still the most used technique in the official methods of analysis.

These preparation methods are expensive, time-consuming and environmentally unfriendly. Recently, a great effort has been made to develop new high-throughput analytical methods able to perform analyses using alternative ways for the pollutant extraction from solid matrices such as microwave-assisted extraction. This methodology has in recent years attracted growing interest as it allows rapid extractions of solutes from solid matrices, with extraction efficiency comparable to that of the classical techniques (Camel 2000). In addition, compared to other extraction techniques, optimization of MAE experimental conditions is rather easy owing to the low number of influential parameters (i.e. matrix moisture, nature of the solvent, time, power, and temperature in closed vessels) (Sanchez-Prado *et al*. 2010). After extraction, a cleaning step is often required along with a concentration of the analytes to improve the method sensitivity. Indeed, gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) can be used when analyzing a broad range of organic analytes, thereby improving the method sensitivity and specificity (Cavaliere *et al*. 2012; Naccarato and Pawliszyn 2016; Naccarato *et al*. 2018). However, before the chromatographic run, the target pollutants must be extracted and pre-concentrated to make them detectable. For this purpose, a great effort has been recently made to develop new analytical methodologies able to perform direct analyses using miniaturized equipment, thereby achieving high enrichment factors, minimizing solvent consumption and reducing waste. These microextraction techniques improve the performance during sample preparation, particularly in complex environmental samples (Naccarato *et al*. 2014; Padrón *et al*. 2014) and can be used as a suitable strategy to connect analytes extraction with the instrumental detection.

METHODOLOGY

Our work focuses on the development of new analytical methods for the determination of analytes bound to the airborne particulate matter (PM). The proposed protocols provide for the microwave-assisted extraction (MAE) of the analytes from the PM followed by solid-phase microextraction gas chromatography-tandem mass spectrometry determination (SPME-GC-MS/MS). In the developed method, the pollutants were extracted by MAE using a green hydroalcoholic mixture. Design of Experiment (DoE) was used for the multivariate optimization of the parameters affecting both the MAE extraction and the SPME analysis, thereby achieving the optimal working conditions.

The assay of the analytes was performed by using tandem mass spectrometry in selected reaction monitoring (SRM) acquisition mode. The proposed method was carefully validated in terms of linearity, accuracy, precision (intra- and interday) and limit of quantification. The developed protocol can be put into practice by short sampling campaigns of PM10 performed in an air monitoring station located in Rende, in a suburban area close to the CNR-IIA.

FINDINGS

We have been using the proposed approach for the extraction of pollutants with different environmental fate and occurrence such as the organophosphate esters. A single MAE run allowed for the extraction of up to 15 sample simultaneously by using a hydroalcoholic mixture composed of water and ethanol, and eco-friendly organic solvent widely used in green chemistry. After the extraction, SPME was used for the sampling of the analytes from the MAE extract and the direct introduction into the gas chromatographic equipment. Design of experiment was successfully used for the optimization of the experimental conditions affecting the MAE and SPME. The method was applied to a real case scenario by analyzing PM10 samples collected at the monitoring station of the CNR-IIA in Rende. The results showed the presence of some of the investigated pollutants at a concentration above the lower limit of quantification of the method. These findings can be due to the closeness of the sampling area to the industrial area of Cosenza and the motorway which crosses the area at about 1 Km East of the measurements site.

CONCLUSIONS

A new approach for the determination of the pollutants bound to the airborne particulate matter was set up. The analytical strategy is based on a microwave-assisted extraction of the analytes from the particulate matter using a hydroalcoholic mixture followed by an SPME-GC-MS/MS analysis. In comparison to the protocols generally used, which mainly use Soxhlet as extraction technique, the developed approach does not provide for the use of environmentally damaging organic solvents, is faster and automatable. The final protocol reached satisfactory values in terms of linearity, sensitivity, LOQs matrix effect, accuracy, and precision.

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ANALYTICAL APPROACHES FOR THE DETERMINATION OF TOTAL AND SPECIATED MERCURY IN ENVIRONMENTAL WATERS

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***Keywords*:** environmental waters, total mercury, mercury speciation, gas chromatography-mass spectrometry, CVAFS

INTRODUCTION

Due to its high toxicity and its capacity for long-range transport in the atmosphere, mercury (Hg) is a ubiquitous pollutant involved in a complex biogeochemical cycle characterized by exchanges between different environmental compartments: atmosphere, hydrosphere, and biosphere. It originates from both natural and anthropogenic sources, including volcanic emission and industrial activities. Moreover, it is distributed in various chemical forms that determine environmental impact, mobility, and bioavailability as well as toxicity and negative effects on human health. Main forms consist of elemental mercury (Hg^0), inorganic mercury (Hg^{2+} and its complexes) and organic mercury (monomethyl mercury and dimethyl mercury). All of these species are involved in the biogeochemical cycle. Considering that the main exposure pathway of Hg to humans is through the seafood consumption and that mercury has an extremely high bioaccumulation factor (up to 10^6) in the marine food chain, an accurate monitoring of mercury and its species in the hydrosphere is fundamental for risk assessment on human health (Nicola Pirrone *et al*., 2013). Therefore, hydrosphere plays an important role: wet deposition from the atmosphere constitutes the greatest source of mercury in both freshwaters, as rivers and lakes, and seawater. Then, aquatic organisms accumulate mercury species, which biomagnify through the food chain. In general, mercury content in natural waters varies in a wide concentration range: very low concentrations of sub ng L^{-1} can be found in open ocean water (Kotnik *et al*., 2007), values of few ng L^{-1} can be found in non-contaminated freshwaters (K. Leopold, Harwardt, Schuster, & Schlemmer, 2008) and in wet depositions (Xu *et al*., 2014). The biogeochemical transformation, mobility, and fate of Hg rely not only on its total concentration but also on its chemical forms. Therefore, in addition to the monitoring of total mercury concentration, speciation analysis in the environmental waters provides very useful information. A continuous monitoring of each form in aquatic ecosystem is therefore necessary by means of innovative, fast, simple and sensitive methods (N. Pirrone & Mahaffey, 2005).

METHODOLOGY

Concentration levels of mercury species in environmental waters are often below a few ng L^{-1}; therefore, analytical procedures for mercury determination have to fulfill requirements as high sensitivity and selectivity. Cold vapor atomic fluorescence spectroscopy (CVAFS) is one of the most common techniques for total mercury (THg) quantification in aqueous samples. As explained in EPA1631 method revision E, it uses fluorescence spectrometry to detect elemental mercury vapors, obtained after reduction of the inorganic mercury species of the sample (US-EPA, 2002). Prior to analysis, an oxidation step is strongly recommended in order to convert all mercury species into the divalent form Hg^{2+}, especially in freshwater samples where most of the mercury species are complexed by organic matter. This pre-treatment process is generally realized by means of oxidant solutions, as BrCl, which also acts as a preservative. The reductant solution (usually tin chloride $SnCl_2$ or sodium borohydride $NaBH_4$) is then added to reduce all Hg^{2+} to volatile elemental mercury, which is purged out from the sample solution and collected into a gold trap. After thermal desorption, mercury vapor is detected by atomic fluorescence spectrometry (AFS). As regards mercury speciation analysis, it is mainly realized by hyphenated techniques involving separation techniques (usually chromatography) and elemental specific detection techniques, e.g., atomic spectroscopy or mass spectrometry. Among chromatographic techniques, gas chromatography (GC) is surely among one of the most commonly used, since it allows a quantitative transfer of analytes from the chromatographic column to the detector, without sample nebulization, which considerably improves the limits of detection with respect to liquid chromatography (LC). A drawback of the GC is the need for derivatization of the ionic mercury species to obtain volatile organomercury forms, which are chromatographically separable. The most common approach for the derivatization of mercury species in aqueous samples is by means of alkylation reactions using reagents such as sodium tetraethylborate $Na[B(Et)_4]$ (Bravo-Sánchez, Encinar, Fidalgo Martínez, & Sanz-Medel, 2004), sodium tetrapropylborate $Na[B(Pr)_4]$ (Kotnik *et al.*, 2007), and sodium tetraphenylborate $Na[B(Ph)_4]$ (Carro, Neira, Rodil, & Lorenzo, 2002). Since the concentration of Hg in environmental samples might be at trace level, the Hg distribution analysis requires preconcentration step before chromatographic separation in order to achieve quantifiable mercury levels. These methods involve the adsorption of target analytes onto the surface of solid materials, sorbents, and then eluting with an appropriate solvent for analysis. For the effective pre-concentration purpose, the sorbents must be chosen with functional groups, which show a high affinity towards Hg chemical species. SPE is one of the most commonly used alternatives, featuring with simple operation, fast separation, and various adsorbents available. In addition, SPME can be applied for off-line preconcentration of the ethylated or phenylated mercury species. Sulphydryl cotton fibers and complexing resins are the most used sorbents for mercury speciation analysis of water samples (Kerstin Leopold, Foulkes, & Worsfold, 2010).

In order to quantify all mercury species, several element specific detectors are employed, as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), mass spectrometry (MS) and inductively coupled plasma-mass spectrometry (ICP-MS). All these techniques have found to be robust, precise and sensitive (Kerstin Leopold *et al.*, 2010). The use of AAS allows for the detection of Hg compounds with low detection limits for Hg^{2+}, methylmercury and ethyl mercury. A drawback is that some spectral interferences may interfere with the mercury species determination. As previously stated, AFS detector is more sensitive, extremely selective, relatively inexpensive and simple. In addition, the use of MS and ICP-MS in speciation analysis has increased in recent years; both MS and ICP-MS have the advantage to perform speciated isotope dilution mass spectrometry (SID-MS) (Kotnik *et al.*, 2007). Thus, mercury species transformations can be checked by labeling analytes with enriched Hg isotopes as tracers. For a correct determination of both total mercury and mercury species, it cannot be forgotten that it is extremely important to assure proper sampling, pre-treatment, and storage of the aqueous sample, because sample integrity must be preserved and special care has to be paid not to alter the speciation (Parker & Bloom, 2005).

DISCUSSION

The described analytical approaches for total and speciated Hg determination can be applied to the samples collected during oceanographic cruises in the Mediterranean Sea performed in the context of the Med-Oceanor measurement program. During the cruise campaigns, the depth profile of total mercury was assayed for different sites in the Mediterranean Sea. Seawater samples were collected into PTFE bottles (cleaned following GMOS SOPs) using a stainless-steel rosette system. Simultaneous sensing of temperature, conductivity, salinity, and oxygen was obtained by CTD measurements. After sampling, seawater was preserved by adding 0.8% HCl solution to the bottles. Total mercury determination was achieved following EPA1631 method revision E, described in the previous section, by means of Tekran 2600 mercury analyzer. Prior to analysis, 1% BrCl solution as an oxidizing agent was added to seawater samples and left for at least 12 hours; hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was then added to destroy free halogens. Samples were subsequently analyzed by Tekran 2600, as previously stated. Average THg concentrations ranged between 0.51 and 1.17 ng $L^{-1}$and were comparable to those obtained in previous studies of the Mediterranean Sea (Kotnik *et al.*, 2007) (Horvat *et al.*, 2003). Speciated mercury determination can be performed by gas chromatography-mass spectrometry (GC-MS), after sample derivatization with $Na[B(Pr)_4]$, in order to investigate the distribution of mercury species and their proportion compared to THg. In addition, in the context of GMOS network aims, also wet deposition samples collected in the Amsterdam Island remote site were analyzed for total mercury determination. Rainwater samples were collected into PTFE bottles and acidified by 0.8% HCl solution. Analyses were performed by CVAFS, following the same protocol for seawater samples with the difference of 0.5% BrCl solution addition (rather than 1%) because this amount is sufficient to oxidize all mercury species from this type of matrix. Results showed a THg concentration in the range 0.59-1.99 ng L^{-1} in rainwater samples from Amsterdam Island.

CONCLUSIONS

Owing to its volatile nature and long atmospheric residence time, mercury is one of the toxic elements among environmental contaminants. It exists in different forms, interchanging in atmospheric, aquatic and terrestrial environments. Studies on the transformations of mercury in natural waters are an important part of research into the global biogeochemical cycle of mercury and its adverse impact on human health and the environment. Measurements for total mercury determinations can be carried out in wet deposition, freshwater or seawater samples by means of CVAFS. This technique uses fluorescence spectrometry to detect elemental mercury vapors, obtained after reduction of the inorganic mercury species of the sample. Speciation analysis should be considered to further understand mercury emission, transport, deposition, and biogeochemical cycling. There are advanced instruments that can be used for ease determination of Hg chemical species at trace level, usually requiring different sample pre-treatment and pre-concentration approaches. In general, speciation analysis is commonly achieved by the coupling of a separation technique (usually gas chromatography) with an element selective detector, with or without a previous preconcentration step (usually SPE or SPME). Highly sensitive and element-specific detection approaches consist of atomic absorption spectrometry (AAS), atomic fluorescence spectroscopy (AFS), and inductively coupled plasma mass spectrometry (ICP-MS). Among these approaches, CVAFS and GC-MS were applied for the determination of total and speciated mercury concentrations in seawater and rainwater samples.

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MARINE AEROSOL STUDY ACROSS THE MEDITERRANEANEAN SEA: SPATIAL DISTRIBUTION AND POTENTIAL SOURCES OF ORGANIC COMPOUNDS

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Keywords: Mediterranean Sea, PAHs, Airborne particulate, Anthropogenic sources, Cruise campaign

INTRODUCTION

Marine aerosol is a complex mixture of chemicals and a big receptor for organic species derived from both continental and sea sources. According to literature (Ravindra *et al*., 2008; Zhao *et al*., 2016), organic compounds are overall generated by the incomplete combustion of carbon containing fuels (biomass burning, road transport, domestic heating); besides, biogenic natural emission (wax plants and suspension of pollens) can be important. Long range transport from urban and industrial sources has been ascertained as the predominant origin of organic pollutants over the Mediterranean basin; meanwhile, shipping related sources (engine exhausts) may be important along transport routes and modify chemical composition of atmosphere. The Mediterranean Sea basin, because of its semi-enclosed configuration, is one of the marine areas the most affected by air pollutants. During the last decade, this marine atmospheric environment has received considerable attention because of the high level of industrialization and population density around the coastal zone; meanwhile, this area is duty influenced by natural emissions including volcanoes and Saharan dust. Despite considerable advances reached recently in marine research, the chemical nature and origin of particulate organic fraction over marine regions still remains poorly understood, mainly due to plurality of sources and to complex chemical-physical mechanisms developing there (Fu *et al*., 2013). Besides, so far, its composition is largely unclear, mainly because of: *i)* the insufficient spatial-temporal coverage of in-situ measurements; *ii)* the variability in the emission from the sea surface resulting from change of biological activity in seawater; *iii)* from complex transfer of gases and particles at the air-sea interface; and finally, *iv)* the insufficient chemical characterization (identification and quantification) of organic compound groups and individual organic species due to the low and variable concentrations. The main aim of the three monitoring campaigns conducted in the frame of three scientific cruises across Mediterranean Sea was to understand the marine aerosol organic composition over the region, with a special focus on chemical analysis combined with information regarding air mass origin as well as meteorological and photochemical parameters, in order to elucidate the characteristics of marine environments and draw information about their main sources. For this purpose, apart from neat concentrations of targeted compound, attention was paid to group percentage profiles and to selected diagnostic concentration ratios of congeners. Suitable statistical methods (Anova, t-test, Pearsons' correlation) were applied to the results drawn for various pollutants, by comparing the respective distributions among the sets of samples. In addition, gaseous pollutants and meteorological parameters were continuously recorded using standard or well consolidated monitoring procedures.

METHODOLOGY

In the framework of *MEDOCEANOR* measurement program, air samples were collected on-board the “RV Urania” and “Minerva Uno” ships during three Mediterranean cruises carried out during the summer season (July-August 2013, June-July 2015 and August-September 2017). The Southern-Eastern Mediterranean (SEM), Western Mediterranean (WM) and Mediterranean basin characterized by elevated volcanic zones (Aeolian Area) were investigated. Airborne particulate and gaseous pollutants were collected along the sea routes, depending on geographical and shipping situation, i.e. in front of the harbors (2 km or some km from coast), offshore at stops and during transects between stops. At some stations, the sea area was far and free from important stationary anthropo-genic emission source (open sea) and atmospheric transport was expected to be the principal source of pollution. In front of harbors, the marine environ-ment might be affected by breezes and general air movement driving the contaminants from mainland as well as from human activity. In addition, during transects relatively high contamination could be observed as a consequence of intense maritime traffic for commercial activities. Chemical characterization of PM_{10} and $PM_{2.5}$ fractions of particulate included regulated toxicants but was extended to a list of unregulated substances, in order to draw a more comprehensive evaluation of ambient quality. In particular, attention was paid to polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes and phthalate esters. Our concern was focused on carcinogenic/mutagenic PAHs: benz[a]anthracene BaA, benzo[b]fluoranthene BbF, benzo[j]fluoranthene BjF, benzo[k]fluoranthene BkF, benzo[a]pyrene BaP, indeno[1,2,3-cd]pyrene IP, dibenz[a,h]anthracene DBA and benzo[ghi]perylene BPE, as well as on perylene PE and benzo[e]pyrene BeP. The sampling apparatuses and procedures used to collect airborne PM are described elsewhere (Romagnoli *et al*, 2016) with the respective features. The PM monitoring method was based on active sampling at high volume conditions on quartz or PTFE filters, and on use of a consolidated procedure comprising the GC-MSD determination of substances.

Meteorological data were collected by means of an automatic station and chemical parameters (O_3, NO_x and SO_s) were recorded by using the automatic analyzers based on absorption, chemiluminescence and fluorescence detection methods, respectively. In order to discriminate possible source influences, the origin and pathway of the air masses crossing the ship were analyzed by calculating 48h backward trajectory, besides wind roses.

FINDINGS AND CONCLUSIONS

The results of investigations performed in the cruises during 2013 and 2015 have been already presented separately in three short abstract books and in an international research paper (Romagnoli *et al.*, 2016). Specific routes characterized by distinct site typologies were chosen in the basin, with the goal of better understanding the air quality over Mediterranean Sea region.

As for PAH concentrations calculated during the 2013 and 2015 cruises, wide data variability was recorded with the maximums corresponding to harbours. The PAH loads varied similarly, from 0.06 to 1.83 ng/m^3 and 0.03 to 1.94 ng/m^3 in the two years, with the respective means not significantly different ($p<0.05$). Compared to results obtained in the summer 2010 cruise (Mulder at all, 2014), our data suggest that the PAH levels remained fairly unchanged.

Table 1 shows the total PAH averages calculated for the three environmental contour types, i.e. harbors, transects (cruising) and stops. The means for the three site types were significantly different ($p <0.05$) and the percentage distribution of the congeners was different, in agreement with the values of the rates of PAH concentration diagnostic ratios, proposed by literature as suitable for drawing information about the intensity and type of sources of atmospheric pollution.

Table 1. Mean concentrations of airborne pollutants measured during 2013 and 2015 Mediterranean Sea cruises

ng/m^3	*harbors*	*stops(offshore)*	*cruising*
PAHs, 2013	1.53±0.23	0.22±0.06	0.16±0.17
PAHs, 2015	0.58±0.53	0.07±0.02	0.08±0.04
n-alkanes, 2013	-	-	14.2±7.5
n-alkanes, 2015	27.3±28.0	23.7±15.9	25.3±20.2
∑ phthalate esters, 2013	9.4±1.7	22.8±19.9	20.4±15.5
∑ phthalate esters, 2015	38.1±31.4	0.8±0.5	35.7±65.6

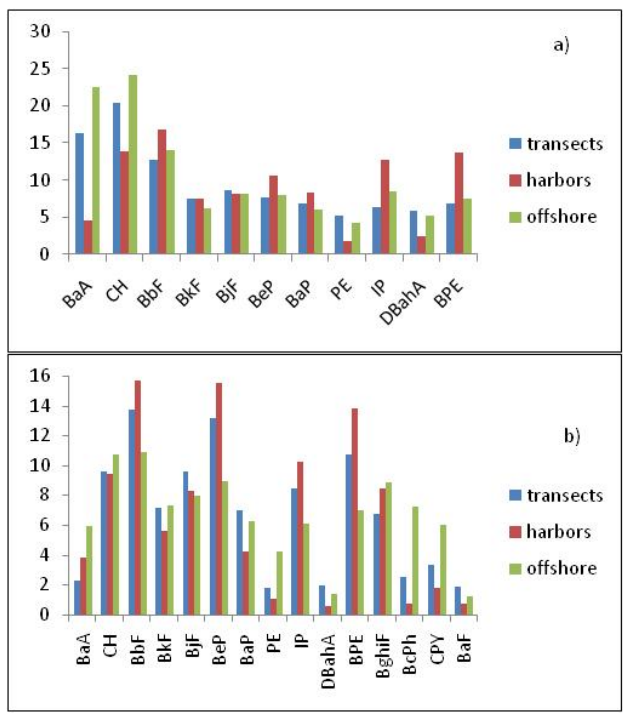

Figure 1. Mean percentage distributions of PAH compounds during a) 2015 cruise campaign b) 2013 cruise campaign

The observed differences originated from the distinct impacts of sources other than ship plumes (e.g., industrial and harbour plants along coasts, transport from land) as well as from chemical reactivity developing in the marine atmosphere. The highest PAH values were observed along the 2013 track.

Regarding benzo[a]pyrene (the index of air toxicity associated to airborne particulates), this compound never exceeded 0.2 ng/m^3.

Figure 2 shows the variations of PAH percent distributions observed over Mediterranean Sea during the 2013 and 2015 campaigns. In particular, in 2015 the offshore samples exhibited relatively high concentrations of benzo[a]anthracene.

With regards to n-alkanes and phthalate esters, the concentrations ranged widely across the two cruises. The analysis of alkanes has confirmed the distinct contributions of natural and anthropogenic emissions at the three types of sites. Total concentration rates (C_{18}-C_{38}) ranged from ca. 6.7 to 43 and 8.7-90 ng/m^3, while the "carbon Preference Index" CPI_{25} (which parameterizes the importance of natural sources) ranged between 1.4 and 4.5, and 1.1-3.0, during the 2013 and 2015 cruises, respectively. According to that, particulate n-alkanes were mainly originated from incomplete combustion of fossil fuels in the Mediterranean marine atmosphere whereas the contribution of higher plant waxes was only minor but nonetheless not negligible. Furthermore, a bimodal distribution of these congeners was always present with high percentages of odd-carbon homologues (maximum at C_{29}) merged with a bell-shaped sequence centred at C_{25}-C_{27}.

The overview of data presented in this paper looks of scientific interest in that it fills in part the gaps of knowledge concerning organic pollutants over the Mediterranean Sea basin atmosphere. These results should be considered as an important ensemble of investigations, which nevertheless calls to further investigations. As a work in progress, we are now examining the aerosols and data collected during the third cruise campaign performed in 2017.

ACKNOWLEDGMENTS

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ASSESSMENT OF CARBONYL COMPOUNDS IN INDOOR AND OUTDOOR AIR

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Keywords: Aldehydes, Indoor Air, Passive sampling, Biogenic and anthropogenic hydrocarbons

INTRODUCTION

The occurrence of carbonyl compounds in the atmosphere is ruled by a trade-off of concurrent mechanisms of formation, by photo-oxidation of anthropogenic/natural organic compounds (Possanzini *et al*., 2002), by the incomplete combustion of biomass and fossil fuels (Schauer *et al*., 2001; Zhang and Smith, 1999), and by removal through photolytic reactions (Lowe and Schmidt, 1983).

The main sources of aldehydes are vehicles, power plants, and residential wood burning (Altemose *et al*., 2015). The most important global source of formaldehyde and acetaldehyde in the atmosphere is of secondary origin. Formaldehyde, in particular, is an intermediate in the oxidation of hydrocarbons to carbon monoxide. Even in the indoor environments, aldehydes can be released by ozone reactions with unsaturated VOCs (Zhang *et al*., 1994).

Contributors to the indoor pollution are building materials, cigarette smoke, perfumes (containing mostly long chain aldehydes ≥C7), home renovations (Herbarth and Matysik, 2010), indoor activities such as cooking; inadequate ventilation plays also an important role in the concentration build up.

Aldehydes are indoor and outdoor chemical pollutants of particular interest due to their potential adverse health effects on humans.

Both in occupational and residential indoor environments, the predominant carbonyls are light aldehydes, mainly formaldehyde and acetaldehyde, together with acetone. The most abundant aldehyde in air is formaldehyde, classified as Group 1 (human carcinogen) by the International Agency for Research on Cancer (IARC,2006), while acetaldehyde is classified in Group 2B as possible carcinogen for humans (IARC,1999,WHO,1995).

Furthermore, benzaldehyde and acrolein are suspected as probably carcinogens and mutagens, as well as other low-molecular-mass aldehydes, whose reactivity and possible mutagenicity are similar to those of acetaldehyde (Liu *et al*., 2007, US EPA 2003).

The objective of our study was to estimate the exposure of occupants of different offices inside IIA building to carbonyl compounds, to assess the possible emissions of these species by the new furniture over the years and to evaluate their seasonal trends.

METHODOLOGY

The monitoring site, located inside the CNR (Italian National Research Council) research estate about 30 km NE of Rome centre, was semirural; thus, it was impacted by moderate vehicular emissions and occasionally by pollutants transported by winds from the metropolitan area. The sample collection was carried out in three points, two inside the IIA building and one outdoors.

The two indoor points were respectively: an office at the ground floor (20.0 m^2 of surface), close to the main entrance of the building, where the door was always kept open, and a small office (14.5 m^2) situated at the first floor, where the door was usually closed. The furniture of the ground floor office was already in use since several years, whereas the first floor office was newly furnished.

Seven measuring campaigns were conducted between 2015 and 2017. Carbonyl compounds were measured for 2 non-consecutive periods during summer (from 27 to 31 July, and from 3 to 7 August) and in the autumn 2015 (from 30 November to 4 December). The sampling operations continued in 2016 in spring (from 10 to 13 May), in summer (from 18 to 22 July) and in autumn (from 24 to 28 October). The last campaign was carried out in winter 2017 (from 27 February to 3 March).

The diffusive samplers were placed at an height of 1.5-2 m from ground, about 20 cm far from the walls; the outdoor samplers were protected from rain. Sampling was carried out over five days from Monday morning (approximately 9 a.m.) to Friday afternoon (approximately 5 p.m.), representing a typical working week. In total 36 indoor and 18 outdoor samples were analyzed.

The Radiello® passive samplers (from Fondazione S. Maugeri, Padova, Italy) were used for monitoring carbonyl compounds. Radiello® passive samplers consist of a stainless steel cartridge filled with 2,4-dinitrophenylhydrazine-coated Florisil® inside a diffusive body.

At the end of sampling the cartridges were kept in their sealed glass tubes and stored in the dark and refrigerated (< 4°C) until the analysis, which was carried out within 7 days after sampling. For this purpose, the DNPH cartridges were extracted with acetonitrile (V = 2 mL) and the solutions obtained were processed by means of a high performance liquid chromatographic system (HPLC) (Shimadzu Corporation, Kyoto, Japan) equipped with a photodiode array detector (SPD-M20A) set at a wavelength of 360 nm. A second wavelength (420 nm) was recorded to verify the occurrence of acrolein. A reversed-phase column (Ultra C-18, 100 A, 150 × 4 mm, 5 µm, from Restek, Milan, Italy) kept at 30°C by means of a column oven (CTO-10AS VP) was used to carry out the separation of the hydrazone derivatives of carbonyls.

The mobile phase consisted of acetonitrile (LC ultra-gradient, 99.9%, Romil, Delchimica, Naples, Italy)/water mixture; a linear solvent gradient was applied from 40/60 ACN:W up to 50/50 for the first 27 min, then it was increased up to 100% of ACN for column cleaning. The flow rate was set equal to 1 mL min^{-1}.

The aldehyde concentrations were calculated using a three points calibration curve (1.0 µg mL^{-1}, 0.5 µg mL^{-1}, 0.25 µg mL^{-1}) prepared by opportune dilutions of standard solutions containing the corresponding DNPH-aldehyde derivatives in acetonitrile (Alde-hyde/Ketone-DNPH Stock Standard, 1 µg mL^{-1} of each component in acetonitrile, certified reference material, purchased from Sigma, Milan, Italy).

The amounts of carbonyls found were corrected taking into account the blanks values.

FINDINGS

The concentrations of carbonyl compounds showed a clearly recognizable distribution at the two internal sites.

The first floor smaller office exhibited higher concentration values for most of the carbonyls compared to the ground floor office; this was true in particular for formaldehyde and hexanal. The indoor/outdoor ratio (I/O), generally used to evaluate the rate of penetration of outdoor pollution into indoor environments, ranged between 3 and 10, clearly indicating the presence of indoor sources. Similar results were obtained for acetaldehyde and propionaldehyde (I/O = 2-4), however the indoor levels of these carbonyls were quite low in all sampling sites. For the remaining carbonyls, I/O ratios close to 1 were calculated.

Descriptive statistics and ratios of acetaldehyde to formaldehyde concentrations were calculated to summarize the data and compare results to those coming from other locations. The main statistical parameters calculated processing the dataset are reported in Table 1.

Table 1. Aldehydes concentrations inside IIA building (µg m^{-3})

Compound	*Site*	*N*	*Mean*	*SD*	*Min*	*Max*
Formaldehyde	I1	7	5.3	3.0	1.6	9.5
	I2	7	15.2	8.2	6.8	30.0
Acetaldehyde	I1	7	2.4	1.1	1.3	4.0
	I2	7	3.9	2.1	1.6	6.8
Propionaldehyde	I1	7	3.5	1.1	2.0	5.0
	I2	7	6.3	1.4	4.6	8.3
Butanal	I1	7	18.5	4.7	12.3	25.0
	I2	7	23.9	7.2	15.7	33.0
Benzaldehyde	I1	7	1.3	0.4	0.8	2.1
	I2	7	1.4	0.6	0.5	2.4
Pentanal	I1	7	6.7	4.4	1.7	14.4
	I2	7	6.7	3.9	1.7	11.8
Hexanal	I1	7	3.3	2.7	0.3	7.3
	I2	7	9.2	6.9	3.4	21.4

Symbols: N=number of observations (number of samples), I1 = Ground Floor, I2= First floor.

In Figure 1 the trends over different years and seasons for formaldehyde, acetaldehyde and hexanal are reported.

It can be observed how the concentrations decreased over the years, overall at site I2 where ventilation conditions and furniture characteristics were significantly different from I1 site.

According to aldehyde plots in Figure 1, it is also evident that during the Summer the concentrations were higher than in the Winter and Autumn seasons of the same year.

The ratio between formaldehyde and acetaldehyde can be used as a criterion for determining the impact of biogenic hydrocarbons with regards to local photochemistry (Villanueva *et al*., 2015). Indeed, biogenic hydrocarbons are ascertained as the main precursors of formaldehyde (HCHO), whilst anthropogenic hydrocarbons of acetaldehyde (CH_3CHO). $HCHO/CH_3CHO$ ratios were reported to vary from ca. 1 in urban areas (Feng *et al*., 2005, Pang and Mu, 2006, Xu *et al*., 2010) up to 10 in deciduous forests (Shepson *et al*., 1991).

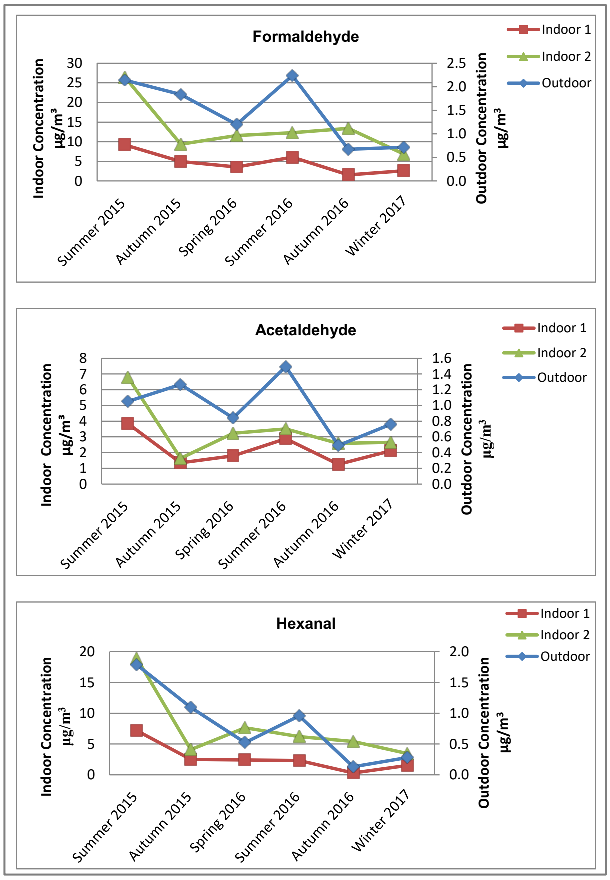

Figure 1. Trends of carbonyl compounds over the period investigated. Indoor 1 = ground Floor; Indoor 2 = 1st floor

In Table 2, the average C_1/C_2 ratio calculated in this study was in agreement with that reported by Possanzini *et al.*, 2000 and Villanueva *et al.*, 2015). Instead, higher ratios were obtained by Possanzini in 2007 at the same site likely owing to the seasonal (July-September) contribution coming from biogenic VOCs during that study.

CONCLUSIONS

The results of our investigation confirmed the expected seasonal trend of aldehydes caused by the photochemical formation in air, particularly impacting on formaldehyde concentrations. C1/C2 ratio rates likely indicated a slight predominance of biogenic hydrocarbons compared to anthropogenic sources.

The indoor survey showed a relevant difference between the two offices examined. Many concurrent factors could affect the air quality of the sites, however on the basis of the results obtained it was possible to infer that the presence of new furniture at site I2 might explain the gradient of concentration observed.

Table 2. Formaldehyde/acetaldehyde (C1/C2) concentration ratio reported in the literature

Locations	C1/C2	Range	References
Montelibretti, Italy (suburban)	1.5	0.9-2.0	This work
Montelibretti, Italy (suburban)	1.2		Possanzini *et al.*, 2000
Langmuir Lab., Mexico (forested)	2.3		Villanueva-Fierro *et al.*, 2004
Socorro, Mexico, (rural)	2.4		Villanueva-Fierro *et al.*, 2004
Montelibretti, Italy (urban)	3.1	1.9-4.2	Possanzini *et al.*, 2007
Beijing, China (urban)	1.1	0.6-3.1	Xu *et al.*, 2010
Hillsborough County, FL	2.2	1.8-3.0	Evans *et al.*, 2011
UST, Honk Hong (background)	2.2		Cheng *et al.*, 2014
Puertollano, Spain	1.3	0.7-3.0	Villanueva *et al.*, 2015
Orléans; France (suburban)	2.4	1.2-7.6	Jiang *et al.*, 2016

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IMPLEMENTATION OF SENSORS ON MONITORING SYSTEMS FOR ENVIRONMENTAL, AEROSPACE AND FOOD APPLICATIONS

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***Keywords*:** Sensors, UGV drone, electronic, environment, technologies

INTRODUCTION

Our research group has been involved, in the context of various projects, in the realization of *ad hoc* sensors for environmental monitoring. The sensors used, chemical and physical, were either commercial or experimental, made by us. Each system realized responded to particular needs in terms of measures to be performed and adaptation to the scenario in which they were to operate. In this paper we present a review of some of our developed systems with the environments where they have operated.

EXPERIMENTAL AND RESULTS

The environmental monitoring systems we have developed have some substantially different characteristics. In fact, for example, a terrestrial drone has been developed that is capable of moving on rough terrain and that can operate in potentially dangerous places for health (Figure1).

Figure 1. Terrestrial drone

One of the scenarios where we used this tool was a landfill in which measurements of gases of environmental interest, relative humidity, temperature and fine dust were performed (Zampetti *et al*. 2018, Manzo *et al*. 2017, Zampetti *et al*. 2017). The drone was driven remotely using a system of radio controls that, in addition to making the vehicle move, allowed to view the terrain through a camera and to receive and store the data collected in real time. A completely different system is that consisting of a widespread system of gas sensors interconnected with each other by a local wifi network. (Figure 2)

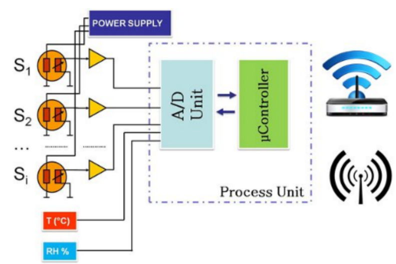

Figure 2. Sketch of the distributed system

These objects were used for environmental monitoring in the port of Crotone. Once they were placed in points deemed of interest (passage of trucks, docking of ships, goods handling equipment, etc.), these systems were able to collect data from the various sensors and send them both to a computer and to a smartphone to be able to check and record. This kind of system makes it possible to compare data taken at the same time in places also distant from each other to highlight particular pollutant dynamics. In order to allow targeted interventions in areas where fast and wide analyses are required, it is useful to use a system that is easily portable, has a wide range of energy, an adequate number of sensors as well as calculation capacity and autonomous connection at internet we have developed a system that has been used in the "SmartIsland project, MIUR 2014- 2016" (Figure 3)

Figure 3. Compact set for outdoor monitoring

In the Aerospace field we have developed (in collaboration with INAF-IAPS and Politecnico Milano) an innovative, small and lightweight device based on a new concept of Piezoelectric Crystal Microbalance able to discriminate the volatile content in planetary environments (ESA projects CAM, CAMLAB). This device (Figure 4) will be applied in planetary in-situ missions to perform: a) measurement of water ice and dust mass flux b) analysis of the amount of water and organic compounds bounded to the dust, by Thermo Gravimetric Analysis (TGA) up to 773K (Dirri *et al.*, 2016)

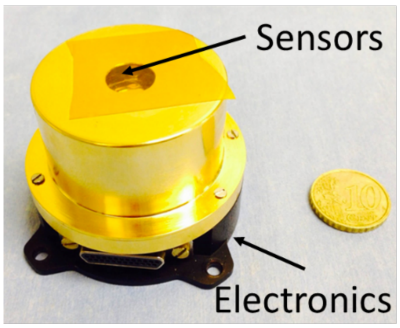

Figure 4. CAM Sensor Head.

A system that goes beyond the environmental monitoring but which has been designed and produced for the anti-confusion control of wines is based on the use of the so-called "Electronic Nose". This apparatus (Figure 5) measures the natural vapours emitted by wines and is able to determine if the product is natural or if it has been adulterated using a customized data analysis

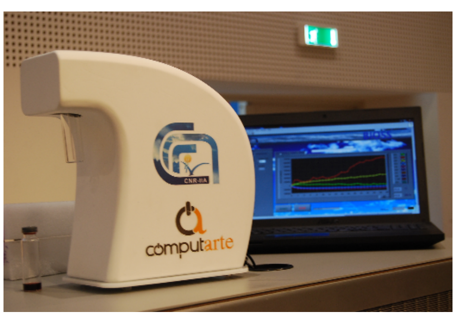

Figure 5. Prototype of an Electronic Nose based system for smart wine analysis (photo taken during an event held in EXPO 2015)

CONCLUSIONS

The use of integrated sensor systems implemented on appropriate platforms can facilitate environmental monitoring campaigns in the most varied situations. The main contributions that these systems offer to the users, are to be found in their simplicity of using, portability and the possibility of avoiding exposure to dangerous or otherwise unhealthy substances.

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"Notte dei Ricercatori" Area della Ricerca di Tor Vergata, Rome September 2016 and 2017

EMPIRICAL MODE DECOMPOSITION AND LONG-TERM HG0 EVASION FROM THE OCEANIC SURFACE DRIVEN BY TEMPERATURE

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Keywords: Atmospheric Transport, Turbulence, Intermittency, Signal decomposition

INTRODUCTION

One of the principal characteristics of complex dynamical systems is their intermitten behaviour [1-5].

Intermittency represents the strongly correlated fluctuations that lead to deviations from a normal probability distribution function (PDF).

In the atmospheric boundary layer, intermittency is an important part of a continuous spectrum of atmospheric motions [6-8]. Within large-scale temporal variations of atmospheric motion, fluctuations in pollutant species concentrations result from interactions of a large ensemble of mesoscopic phenomena, occurring contemporaneously in the atmosphere: turbulence, variation in anthropogenic and natural emission sources [9,10], variation in deposition velocity, loss through chemical reactions which is in turn determined by fluctuating reactant/oxidant concentrations, and other extreme events.

In the specific case of Hg^0 these extreme events would include phenomena such as convective storms, forest fires, and atmospheric Hg^0 depletion events. Understanding the dynamics of these emergent extreme events, meteorological, chemical and anthropological, represents the key to understanding complex dynamical systems.

Due to their complexity, the analysis of these systems has focused on the understanding of where certain features are exhibited by a large class of phenomena, regardless of the details of their structure [5].

Multiple works have shown that complex non-equilibrium systems (and non-stationary), are described by an entangled superposition of fast and slow oscillating modes on different timescales.

Classical timefrequency analysis methods, i.e. Short Time Fourier Transform (STFT) or Wavelets are considered the more appropriate techniques to handle non-stationary signals, but each method presents certain drawbacks: STFT is unable to precisely localize the signal in time, while simultaneously maintaining an adequate frequency resolution [11], requires piece-wise stationarity of the data, and assumes that the stationarity scales coincide with the sliding window length used in the decomposition. Wavelets, need a fixed basis function to be specified “a priori”, and the precise choice of this basis is not always a trivial problem. On the other hand, Empirical Mode Decomposition is a relatively new method in signal [12]. Despite the fact that it is primarily an empirical method, it has proved its worth in the analysis of non-stationary and non-linear signals. The principal advantage of EMD is that it is totally adaptive and data driven, without the need for a-priori basis function selection (i.e., mother wavelet) for signal decomposition.

EMPIRICAL MODE DECOMPOSITION

Within the EMD framework, the data are decomposed into a finite number k of empirical oscillating basis functions, known as intrinsic mode functions (IMFs), characterized by an increasing time scale τ, and a residual r(t) which describes the mean trend, if one exists.

The decomposition (known as sifting) procedure includes two stages: first, the local extrema of the dataset are identified and subsequently connected through cubic spline interpolation. Once connected, the envelopes of local maxima and minima are obtained.

Second, the mean is calculated between the two envelope functions, then subtracted from the original data. This difference is an IMF only if it satisfies the following criteria: (i) the number of local extrema and zero crossings does not differ by more than 1; (ii) at any point t, the mean value of the extrema envelopes is zero. When the difference does not meet the above criteria, the sifting procedure is repeated using the difference extracted as the new raw data series, and a new set of envelope is generated. The sifting procedure is repeated m times until the difference betwee two subsequent step satisfies the above criteria. A general rule to stop the sifting is introduced by using a standard deviation σ, evaluated from two consecutive steps (usually fixed at 0.05).

EMD ANALYSIS OF THE HG^0 TIME SERIES

The Hg^0 time series recorded at the Mauna Loa Observatory (MLO) in Hawaii between 2002 and 2009 has been analyzed using Empirical Mode Decomposition. The MLO in Hawaii (19.5° N, 155.6° W, 3397 m above sea level) is best known for its long-term monitoring of greenhouse gases (http://www.esrl.noaa.gov/gmd/obop/mlo/).
Between 2002 and 2010 the U.S. Environmental Protection Agency made speciated Hg measurements at the Observatory. The MLO was chosen to evaluate the long range transport of Hg species and to investigate Hg^0 oxidation in the free troposphere.

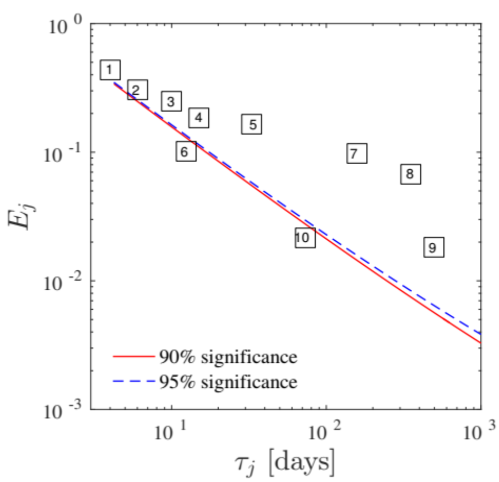

Figure 1. Significance test for the IMFs The full line and the dashed line represent the 90 and 95% confidencebounds for the test. All modes over the boundary lines are physicallysignificant modes. The IMFs 6 and 10 are not significant with respect to the test

The statistical significance of the information contained in each IMF, compared to white noise, is obtained by plotting the IMF energy content, E_j, against the natural periodicity τ_j.
The results are shown in Figure 1, where the lines correspond to the confidence levels, 90 and 95%.
All the IMFs, with the exception of 6 and 10, are significant at the 95% level when compared to white noise. The j = 5, 7, and 8 IMFs are the most significant, while j = 1, 2, and 9, with E_j values are closer to the curve, are the least significant. To interpret the process underlying each IMF, it is necessary to associate a characteristic period, τ_j, with them. There are four characteristic time scales within the Hg^0 concentration time series.
The first has a period of less than a month and is split into two IMFs (j = 3, 4) of comparable significance. Exploiting the orthonormality of IMFs, the partial sum IMF 3 + IMF 4 gives an oscillation mode of the system which gives a period of ≈ 7 ±3 days. The IMF j = 5 represents a monthly mode of the system, which is also energetically important. The IMF j = 7 defines an intrayear, possibly seasonal mode, while the j = 8 represents a roughly annual oscillation in the time series. As shown above, EMD reveals modes in the data set characterized by long time periods and which are significant with respect to white noise. These modes should be related to physical or chemical processes, such as atmospheric transport phenomena, variation in atmospheric composition, etc. The complexity of many atmospheric phenomena and, for some variables, a lack of data mean that identifying the processes behind the IMFs and their characteristic times can be a daunting task. However, given the location of the MLO and the role of oceanic reemission of Hg in the global atmospheric Hg cycle, oceanic variables were chosen for investigation.
To investigate links between variations in SST and the Hg concentration, data from the TAO/TRITON network (Tropical Atmosphere Ocean/TriangleTrans -Ocean Buoy Network) have been analyzed.
The position of the buoys used in the analisys is reported in figure 2.

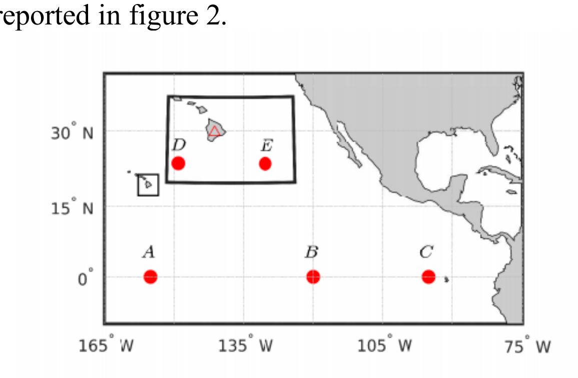

Figure 2. Location of the MLO. The red triangle in the inset is the location of the Observatory, the red dots are the buoys located on the equator 95°, 125°, and 155° W (A, B, and C) and near the island (D and E)

Figure 3 shows the time evolution of IMF 2 for three buoys data sets, superimposed on the yearly Hg_0 mode 8. These modes are correlated with a time lag, which can be estimated through a cross correlation analysis between the yearly modes of the SST and Hg^0 data sets.

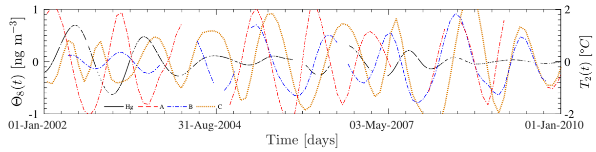

Figure 3. Comparison of the yearly modes 8 of the Hg0 time series (left y axis) and 2 data (right y axis) for buoys A, B, and C. All data sets cover January 2002 to January 2010

The behavior of the cross-correlation coefficient against the lag Δ shows oscillations with numerous peaks of similar amplitude. These occur at both negative and positive lags, which is typical when oscillating signals of similar frequency are compared. In this situation the leading and following processes are identified because Hg0 is observed after the evasion from the sea. An estimate of the lag corresponds to the first significant positive peak, approximately Δ = 8 months, at 0° N, 95° W (buoy A), Δ = 5 months for 0° N, 125° W (buoy B), while Δ = 1 month at 0° N, 155° W (buoy C) (see Figure 4).

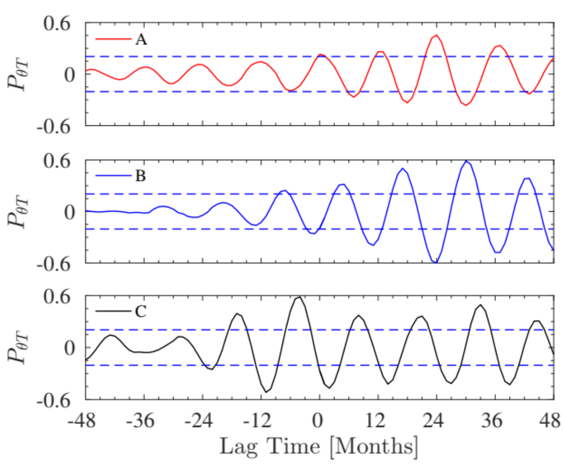

Figure 4. Cross correlation between the yearly modes 8 and 2 for buoys A, B, and C, respectively. Horizontal dashed lines represents the standard 2σ significance

However, evidence of a yearly oscillation mode can be observed by defining an average lag time ⟨Δ⟩ =⟨Δi+1 − Δi⟩, in other words ⟨Δ⟩ measures the average difference in months between two consecutive lag peaks: i-th and (i + 1)-th. In this case ⟨Δ⟩ is the same for all three buoys (A, B, and C): $\langle \Delta \rangle_{(A)}$ =11 ± 2 months, $\langle \Delta \rangle_{(B)}$ =11 ± 3 months, and $\langle \Delta \rangle_{(C)}$ = 12 ± 1 months (Figure 5).

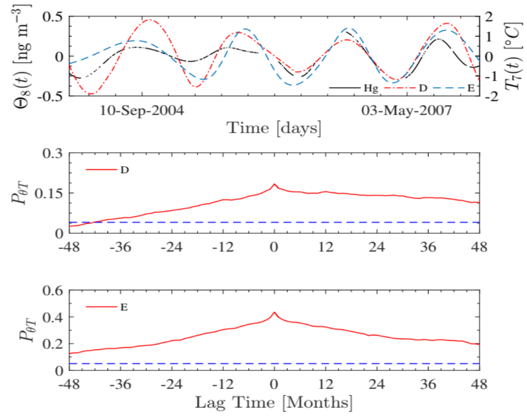

FIGURE 5. (TOP) COMPARISON BETWEEN THE YEARLY MODE 8 AND THE MODES 7 OBTAINED AFTER THE SIFTING PROCEDURE ON THE SST DATA FOR BUOY E. (CENTRAL) CROSS CORRELATION BETWEEN THE MODES 8 AND 7 FOR BUOY D. (BOTTOM) CROSS CORRELATION BETWEEN THE MODES 8 AND 7 FOR BUOY E

CONCLUSIONS

The EMD is a technique based on the local characteristic time scale of the data, whose basis functions (IMFs), used to represent the Hg^0 data, are nonlinear functions directly extracted from the data. The periodicities observed in the tropical Pacific sea surface temperature (SST), through the data collected from five buoys, are also observed in Hg^0 concentrations measured at the MLO. The lag times in the observed periodicities are related to the position of the buoys with respect to the measurement site. This demonstrates a direct link between climatological phenomena, in this case SST, and measured Hg^0 and reflects the influence of ocean SST on Hg^0 evasion. This is the first long-term experimental evidence of such a direct effect on Hg^0 evasion from the oceanic surface driven by temperature.

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TELECONNECTIONS BETWEEN ENSO, NAO AND MERCURY: GLOBAL ATMOSPHERIC PATTERNS DURING 2001-2015

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Keywords: Hg pollution, Climate Change, ENSO, NOA

In the latest decades, numerous advances have been made in our understanding of the atmospheric cycle of mercury (Hg) at global scale, which include better estimates of Hg atmospheric concentrations and new insights regarding the exchange processes between atmosphere and oceans. These, and other advances allow new policies to be implemented under international agreements, to reduce Hg release to the atmosphere, with the final aim to mitigate the risk of the exposure to Hg pollution. However, the temporal extent of such policies can be as long as decades. Therefore, it becomes relevant to correlate the atmospheric cycling of Hg with the ongoing global changes to predict the effect of any policy over the next future. In this preliminary work, we used a global Hg CTM to illustrate how the changes in the North Atlantic Oscillation (NAO) and El Niño–Southern Oscillation (ENSO) afflict atmospheric concentrations, ocean evasions, and total deposition of Hg worldwide.

INTRODUCTION

The management of Hg pollution require global efforts to be effective (De Simone, 2017). There are a number of initiatives to mitigate Hg pollution exposure, and the Minamata Convention (Minamata, 2018), the unique global treaty on Hg, ratified during 2017, is now entering the implementation phase. These initiatives have benefited of recent advances in our understanding of the major physical and chemical processes Hg undergoes in the atmosphere and at interfaces (Selin *et al*. 2007; Holmes *et al*. 2010; Horowitz *et al*. 2017). However, the rate of potential recovery and therefore the temporal extent of such policies, is uncertain, because of the remaining uncertainties in the atmospheric cycle of Hg. In this regards it is relevant to evaluate the processes involving Hg within the atmosphere in the face of ongoing global changes.

The North Atlantic Oscillation (NAO) is one of the most prominent teleconnection patterns in all seasons (Barnston and Livezey, 1987), and consists of a north-south dipole of anomalies, which centers are located over Greenland and over central latitudes of the North Atlantic (around 35°N). The positive phase of the NAO indicates below-normal pressure across the high latitudes of the North Atlantic and above-normal pressure over the central North Atlantic, the eastern United States and western Europe, whereas the negative phase reflects the opposite patterns of pressure anomalies over the same regions.

El Niño-Southern Oscillation is a periodic fluctuation in the temperature of sea surface (El Niño) and in the air pressure of the atmosphere (Southern Oscillation) across the equatorial Pacific Ocean, between observation stations at Darwin, Australia and Tahiti. El Nino affects strongly the climate since it disrupts normal circulation patterns, at both regional and global scale, resulting in wetter weather in some areas and dryer in others (see for example, Wang *et al*., 2000).

In this preliminary study, we used the global Hg chemical transport model ECHMERIT (Jung *et al*. 2009) to evaluate the effect of ENSO and NAO on three major atmospheric variables related to the Hg atmospheric cycle, during the period 2001-2015. Determining how the variations of these indices have impacted the cycling of Hg in the recent past is a useful exercise to assess the potential impact of the global changes on the next future.

METHODOLOGY

The global Hg chemical transport model ECHMERIT (De Simone *et al*., 2014) has been used to simulate the annual atmospheric cycle of Hg for the period 2001-2015. All the simulations were performed on a T42 horizontal resolution and 19 vertical levels up to 10 hPa, considering the O3/OH oxidation mechanism. Although there is some uncertainty regarding the atmospheric Hg oxidation pathway (see Ariya *et al*., 2015), no other oxidation

mechanism has been included in this preliminary work.
Since we were aimed at assessing the direct impact of indexes on the atmospheric cycle of Hg, for all simulated years, we included in the model the same AMAP/UNEP (AMAP, 2013) global inventory of Hg anthropogenic emissions. The response of fires to the forcing of ENSO is complex (van der Werf, *et al.*, 2004) and has not been evaluated systematically across different continents. Therefore, in this study we used GFED v4 inventory (van der Werf, *et al.*, 2017) to calculate and to include Hg emissions from fires for the year 2013, that is recognised as ENSO neutral (ENSO Events at NOAA, 2018). Emissions of Hg from oceans have been calculated on-line in the model following De Simone *et al.* 2014.
Anomalies are formed by subtracting the 2001-2015 base period of monthly means. For each season (three months), model data anomalies are regressed onto the standardized Niño-3.4 (NAO) index. All datasets were de-trended, prior to calculate the regression. The ENSO and NAO impacts on the model fields analysed over the globe are largely linear, as indicated by goodness of the linear fit (R^2 close to 1). The correlation coefficients illustrated in the figures, and expressed in unit fractions, represent the "strength" of the linear fit (Peng at NOAA, 2018). This means that the positive state (warm or El Niño in the case of ENSO) is generally associated with the anomalies displayed by the positive half of the colorbar in the figures. On the opposite, the negative state (cold or La Niña in the case of ENSO) is associated with the anomalies that are displayed by the negative half of the colorbar in the figures.
The seasonal data was then aggregated to give an evaluation of the correlation with ENSO (NAO) over the entire period, by reporting for each cell on maps the maximum correlation, either positive or negative.

FINDINGS

Panels in Figure 1 show how La Niña is usually associated with lesser than average emissions of Hg over the entire equatorial Pacific oceans, that drive lesser Hg concentrations and deposition over the same basin. During La Niña, the Hg concentrations also appear to be lesser than average on the southern area of the Australia, and over most of the Arctic. On the opposite, El Niño results to be associated with increased Hg concentrations over Japan and increased deposition over Indonesia. This is particularly interesting, and will require further model investigations using yearly fire emissions, because the increasing of fire emissions in the region during drier conditions (Chen *et al.*, 2017) will probably enhance the deposition of Hg over the same region.
The impact of NAO on the atmospheric cycle of Hg is quite different, as evident in Figure 2, especially regarding the release of Hg to the atmosphere from oceans. In particular the positive state of NAO is associated with an increased Hg evasion from a large area over the equatorial Pacific and over two band in the North Atlantic, causing increased Hg concentrations over the entire Mediterranean basin and over a large fraction of Arctic. The impact of NAO on Hg deposition causes irregular patterns over Pacific and Indian oceans and also over the Arctic.

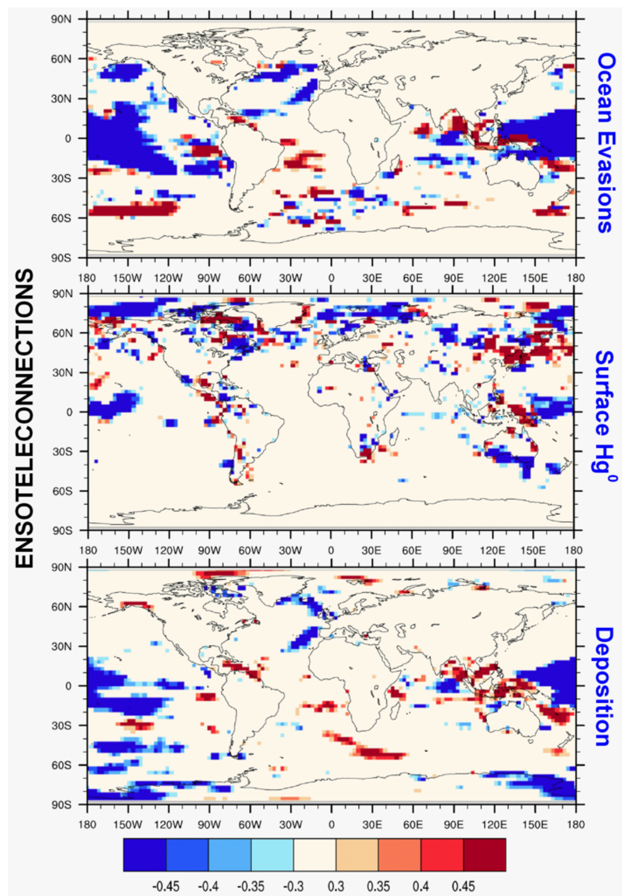

Figure 1. "Strength" of ENSO teleconnections on Hg global patterns

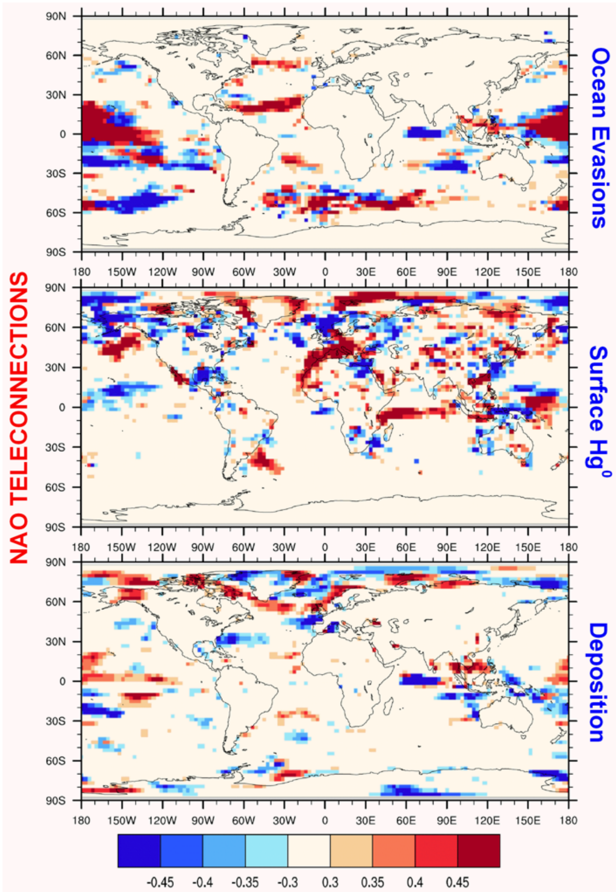

Figure 2. "Strength" of NOA teleconnections on Hg global patterns

CONCLUSIONS

In this preliminary study, we presented the impact of ENSO and NAO on the Hg global dynamics during its cycle within the atmosphere. The cold state of ENSO (La Niña) is associated with decreases in ocean emissions of Hg over the entire area of equatorial pacific, whereas the positive state of NOA is strongly correlated with increased Hg concentrations over the entire Mediterranean basin.

A more detailed analysis, eventually considering some of the uncertainties related to the processes Hg undergoes within the atmosphere, is required to better investigate the teleconnections between ENSO and NOA and the atmospheric cycle of Hg. The advances in our understanding of Hg cycling within the atmosphere have been many in the latest years, but it is necessary to evaluate the impact of the simultaneous ongoing global changes to predict the effects of policies on human Hg exposure.

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Minamata, 2018, http://www.mercuryconvention.org

Dataset

3-month averages of the Nino-3.4 index, which is also known as the Oceanic Nino Index and is based on ERSST.v3b data. http://www.cpc.ncep.noaa.gov/data/indices/oni.ascii.txt

LAND COVER CHANGE DETECTION USING COPERNICUS SERVICES AND SENTINEL-2 DATA

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Keywords: Biodiversity, Change detection, Copernicus, Sentinel-2

INTRODUCTION

The detection of changes in ecosystems for the monitoring of biodiversity is one of the main goals in the commitments undertaken not only by the European Union Habitat Directive (92/43/EEC) and the Convention of Biological Diversity (CBD) but also by the United Nations Sustainable Development Goals (UN SDG, 2016). To meet this aims, regular mapping and assessing extension and state of ecosystems and their services are required. The process involves determining the scale of habitats through translation from Land Cover/Land Use (LC/LU) maps by integrating auxiliary information (e.g., water salinity, lithology) (Tomaselli *et al*., 2013; Adamo *et al*., 2014). Earth Observation (EO) data and related techniques are the most promising tools for monitoring changes at multiple scales and high temporal frequencies. These approaches can provide new services for a wide user community including ecologists and decision makers (Nativi *et al*., 2014; Nagendra *et al*., 2013; Pettorelli *et al*., 2014).

Several European programs, as Copernicus (www.copernicus.eu), can offer useful support, under free and open data policy, favoring the harmonization of satellite and in-situ data to detect changes in the land cover.

In the literature, two main approaches for change detection between two date T_1 and T_2, with $T_2>T_1$, are reported. If two compatible (in terms of scale and taxonomy) maps are available, the Post Classification Comparison (PCC) can be adopted by evaluating two classified LC/LU maps, independently obtained.

Alternatively, either two calibrated surface reflectance images (atmospherically corrected) or specific features extracted from them, can be compared (unsupervised approach) (e.g., difference of reflectance images or NDVI features). The PCC approach can allow the recognition of the from-to transitions classes. In this case the output accuracy depends on the accuracies of each input classified map. On the other hand, the unsupervised approach provides no information about the LC classes transitions and it can be affected by several radiometric and thresholding problems. In Tarantino *et al*. (2016a; 2016b), an alternative approach called Cross Correlation Analysis (CCA) was investigated. The effectiveness of CCA which uses a LC/LU map at time T_1 and a single multispectral remote sensed image at time T_2, at Very High Resolution (VHR) (from Worldview-2) and HR (from Landsat 8) satellites, was assessed. Since the algorithm employed can detect changes, for a known target class at time T_1 changed to other unknown classes at time T_2, asking for only one satellite image, the findings reported can be considered encouraging.

The present work investigates the usefulness of free available data (according to the Global Earth Observation System of Systems (GEOSS) data sharing principles) for LC/LU change detection by CCA algorithm. Copernicus service (semi-) natural grasslands and satellites Sentinel-2A images, as LC/LU map at time T_1 and multispectral image at time T_2, respectively, were exploited.

The findings which have been obtained for (semi-) natural grasslands changes of OA%=94.21±0.10% are encouraging and thus the proposed methodology can be considered a useful support to policy makers.

METHODOLOGY

According to CCA change detection method (Koeln *et al*., 2000; Civco *et al*., 2002), all pixels of the T_2 image belonging to a specific thematic layer (target class) extracted from the T_1 map are, first, analysed to determine the expected reference class metrics in T_2 (i.e., class average spectral response and standard deviation). Then, the Z-statistic measure is computed, for each pixel in the layer, to evaluate the distance between its spectral signature and the reference class metrics at T_2. High values of Z-measure evidence the high likelihood of class changes. The Z-statistic describes how close pixel response is to the expected spectral response of the target class. Changed pixels will produce large Z-statistic values while pixels that have no change will produce small Z-statistic values.

Thresholding set of $\mu+1\sigma$, $\mu+2\sigma$, $\mu+3\sigma$, based on the output Z-statistic image histogram, was tested: this issue represents a crucial tuning for the algorithm. The selection of the threshold value producing reliable accuracy results could yield a binary change map (change/no change).

As time T_1 data, the Pan-European HR (semi-) natural grasslands layer dated 2012 at 20 meters spatial resolution was considered while as time T_2 data, a Sentinel-2A image, dated August 7th, 2015, (referring to 9 bands in the visible and infrared spectrum), 20 meters spatial resolution, atmospherically corrected, were chosen.

The area investigated is the "Murgia Alta" Protected Area (PA), from Natura 2000 network, which is located in Apulia Region, Italy (Figure 1). "Murgia Alta" consists of a calcareous upland covered with (semi-) natural dry grasslands ecosystem for almost 24% of the total site. Its main pressure is represented by fragmentation of rocks and stones belonging to natural grasslands to increase cultivated areas in addition to fire events.

This PA belongs to the ECOPOTENTIAL H2020 European Project (www.ecopotential-project.eu). The investigation provided evidences of several LC/LU changes from (semi-) natural grasslands to other classes which may have resulted, from 2012 to 2015, in according to the main pressures in the area (http://www.ecopotentialproject.eu/sitestudies/protected-areas/19-murgia-alta.html).

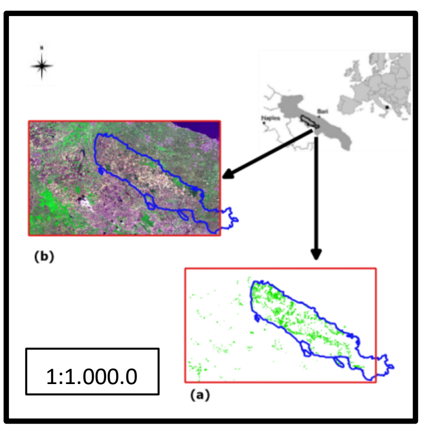

Figure 1. "Murgia Alta" protected area in blue line. Analyzed are in red line. (a) Copernicus service layers (2012; time T_1): (semi-) natural grassland; (b) Sentinel-2A image (RGB false color composition: Red-Nir-Blue; August,7th 2015; time T_2)

FINDINGS

A total amount of 673 polygons corresponding to ≈ 2390 ha ≈ 9% of the analyzed area were considered. In details, 284 polygons targeted as changes from (semi-) natural grasslands to other classes whereas 389 polygons as no changes, were identified. The changed polygons considered were mainly subjected to transitions from (semi-) natural grasslands to cultivated areas.

The accuracy assessment of the change map was based on stratified random sampling weighting the Overall Accuracy (OA) by the proportions of the study area represented by the map classes (Olofsson *et al.*, 2014). When the sampling intensities differ for the considered classes (i.e. change and no-changed areas), correct calculation of OA requires that the within-class accuracies be weighted by the proportions of the study area represented by the map classes. Some meaningful close-up windows can be recognized on the change map and appreciated hereafter (Figure 2). In details, changes due to fire events in Figure 2(a) and to cultivated areas in Figure 2(b) are highlighted. The findings reported are in agreement with the known main pressures for that PA.

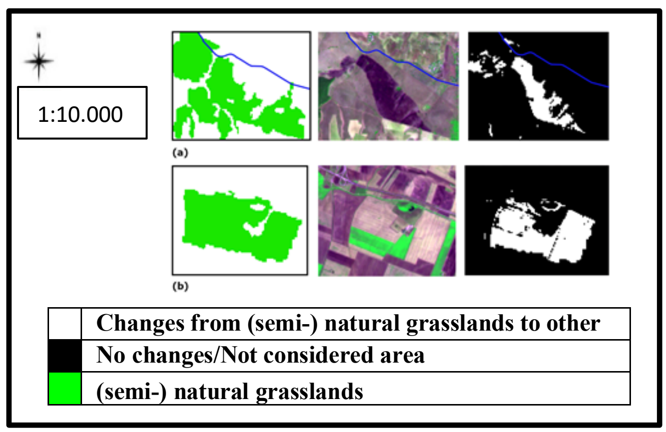

FIGURE 2. CLOSE-UP WINDOWS RELATED TO SIGNIFICANT CHANGES FOR (SEMI-) NATURAL GRASSLAND DETECTED IN "MURGIA ALTA" IN THE PERIOD 2012-2015. FROM LEFT TO RIGHT, RESPECTIVELY, COPERNICUS LAYER, SENTINEL-2A IMAGE, CHANGE MAP. CHANGE INTO: (A) BURNED AREA (B) CULTIVATED AREA

Results of the quantitative analysis carried out are reported in Table 1. Using the threshold value of TH= $\mu+1\sigma$, the highest values of OA%, User's and Producer's Accuracies, in change and no change classes, were evaluated. Using this TH value, the stratified changed area estimate, with its error, results quite similar to the mapped changed area (Table 1, last column). The error on the stratified changed area remains high, due to the coarse spatial resolution.

frequency will be able to assure a continuous monitoring of changes in LC/LU.

Table 1. Change detection matrix obtained from CCA for "Murgia Alta" site

TH	*Change User's Acc.%*	*Change Producer's Acc.%*	*No Change User's Acc.%*	*No Change Producer's Acc.%*	*Overall Acc.%*	*A_m (ha)*	*Stratified changed area estimate with 95% conf. interv. (ha)*
μ+1σ	94.64±0.23	70.68±0.33	94.14±0.10	99.16±0.04	94.21±0.10	3456.16	4628.19±51.03
μ+2σ	99.66±0.08	33.07±0.22	88.63±0.14	99.98±0.01	89.22±0.13	1420.84	4281.38±68.72
μ+3σ	100.0±0.01	10.17±0.08	83.54±0.15	100.00±0.01	83.84±0.15	486.88	4788.57±80.77

Almost 13% of (semi-) natural grasslands in the analyzed area results changed in the period from 2012 to 2015 because of transition to cultivated areas. Some changes were detected as transitions from (semi-) natural grasslands to forest land cover. This change appears to be caused by a tree growth process. The invasion of tree growth is hard to justify in a short period of 3 years. The finding was found to have been influenced by errors in the overestimation by the Copernicus (semi-) natural grasslands layer in areas populated by mixed grasslands and forest cover.

CONCLUSIONS

The findings suggest that a great support for the monitoring of ecosystems changes, which is one of the main European Commission actions (European Commission, 2011), is represented by the free availability of a large collection of Sentinel-2(A/B) satellite regular acquisitions. The spatial resolution (20-10 meters) of Sentinel-2(A/B) images can be considered suitable for change detection applications if no too fine details are requested. Furthermore, the free available Copernicus services can represent another useful support even though in need of a finer revision before products delivery.

At present, Copernicus service layers represent valid landmarks, at a spatial scale compatible with Sentinel-2(A/B) images. Future advancements may be represented by the exploitation of other Copernicus service layers as for example the forest service layer.

Moreover, the findings demonstrates that the CCA algorithm needing only one multispectral remote sensed image (at time T_2) can be considered suitable for automatic change detection when free data as Sentinel-2A, launched recently (i.e., June 2015) are unavailable in the past. In the near future a larger collection of Sentinel-2(A/B) images may be available and the high temporal acquisition

In particular, the change maps for (semi-) natural grasslands yielded data with high accuracy and low uncertainty (OA%=94.21±0.10%).

The findings encourage suggestion that the combined use of the CCA change detection algorithm with Sentinel-2A data and Copernicus service layer could favor long-term monitoring of natural ecosystems in support to conservation management of PA by allowing also the discovery of illegal changes.

The information thus obtained could help design and monitor strategies for implementing the following UN SDG: a) "protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss" (SDG 15); b) "take urgent action to combat climate change and its impacts" (SDG 13). As clearly evidenced in (Blonda *et al*., 2013) and in (Turner *et al*., 2015) agreements between space agency and national authorities should be encouraged to reduce costs for a widespread EO data application to ecosystems monitoring.

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SENTINEL-1 SEA SURFACE WIND IN COASTAL AREAS

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INTRODUCTION

Sea Surface Wind (SSW) represents an essential variable that may be exploited in a wide range of applications, e.g. ecosystems status monitoring in coastal areas.
A number of wind sources, such as in situ meteorological observation stations, Synthetic Aperture Radar (SAR) sensors and Numerical Weather Prediction (NWP) models, can be used to retrieve coastal wind information.
Although marine stations (e.g., instrumented buoys) can collect high accuracy/precision wind observations, their costs however do not allow a sufficient spatial and temporal coverage of coastal zones at global scale.
Moreover, the exploitation of wind estimates provided by NWP models may be problematic in such areas. Local winds variability may be influenced by complex coastal orography. NWP model data may be affected by significant estimation errors, especially when the wind blows from the land to the sea (i.e., offshore wind). As consequence, winds in coastal areas are often not well reproduced by both global (Zecchetto and Accadia, 2014) and regional (Accadia *et al*., 2007) NWP models.
SAR imagery can be also employed to derive SSW field by measuring radar energy backscattered by the sea that is a function of the roughness of the sea itself. Assuming the wind as the dominant environmental factor responsible for this roughness, SAR images can be then fruitfully exploited to obtain both SSW direction and speed.
Most techniques for SAR SSW field retrieval adopt the so-called scatterometry-based approach. Wind direction is first either extracted from wind-aligned features (hereafter named wind rows) when visible onto SAR amplitudes (Wackerman *et al*., 2003; Koch, 2004; Zecchetto *et al*., 2008, 2016; Rana *et al*., 2016) or provided by NWP models (Pichel *et al*., 2015). Then, wind speed is inferred through the inversion of a backscattering semi-empirical model, i.e. Geophysical Model Function (GMF) (Stoffelen and Anderson, 1997; Hersbach *et al*., 2007; Hersbach, 2010; Nirchio and Venafra, 2013; Li and Lehner, 2014), which assumes wind direction as a priori information.
Even if several studies on SSW direction and speed retrieval from SAR (e.g., Sentinel-1) have been already published, the exploitation of SAR wind fields in coastal areas is still problematic and in need of further investigations.
This paper offers a contribution to the employment of new C-band Sentinel-1 SAR data for wind field retrieval in coastal areas. In particular, SAR-derived SSW estimation was carried out in a coastal Natura 2000 site, i.e. the Camargue (France) protected area. The Local Gradient Modified (LG-Mod) algorithm (Rana *et al*., 2016) was applied for wind direction extraction from ten Sentinel-1 images, downloaded from the Copernicus Open Access Hub (scihub.copernicus.eu). For wind speed retrieval, the inversion of the GMF CMOD5.N (C-band MODel 5.N) (Hersbach, 2010) was then employed.
To evaluate SAR SSW estimation trough the LG-Mod (followed by the CMOD5.N inversion) at medium (12.5 km grid) and high (5 km grid) spatial output resolutions, both the Ground Range Multi-look Interferometric Wide Swath High Resolution (GRD-IW-HR, briefly IW) and Extra Wide Swath Medium Resolution (GRD-EW-MR, briefly EW) Sentinel-1 Level 1 products were processed.
Findings achieved show that the exploitation of Sentinel-1 IW images should be recommended for retrieving high resolution SSW fields in coastal areas.
SAR SSW fields were compared with wind data from both global and regional NWP models, i.e., ECMWF, European Centre for Medium-Range Weather Forecasts (Dee *et al*., 2011) and SKIRON (Zodiatis *et al*., 2003), respectively.
Comparison results confirm that the exploitation of SAR Normalized Radar Cross Section (NRCS) for wind direction as well as for wind speed retrieval allows detailing the spatial characteristics of local winds, at both high and medium output resolutions.

METHODOLOGY

By means of the ESA (European Space Agency) Sentinel Application Platform (SNAP) (step.esa.int/main/toolboxes/snap/), Sentinel-1 co-polarised (VV or HH) images were initially pre-processed, i.e. calibrated and geocoded, and auxiliary products (i.e., land-sea mask and incidence angle map) were generated.

Following the above-cited scatterometry-approach, a two-phase technique was applied. Specifically, the LG-Mod algorithm was used for wind direction retrieval from wind-aligned patterns onto single Sentinel-1 amplitudes. This algorithm mainly consists of the following steps (Rana *et al*., 2016):

• *Image Smoothing and Decimation.* Smoothing and decimation operations are carried out on each calibrated SAR amplitude image with the aim at both reducing the SAR speckle noise and enhancing the wind rows visibility.

• *Local Gradients Computation.* Local Gradients (LGs) are pixel-by-pixel computed by means of optimised 3x3 Sobel operators (Koch, 2004) applied to the resized SAR amplitude image. LG values that correspond to "unusable points" (Koch, 2004), such as land pixels or pixels affected by non-wind features (i.e., SAR signatures and artefacts not caused by the wind), are discarded and not used for estimation.

• *Main Wind Directions Estimation.* The resized LG directions image is divided into sub-images (or ROIs), according to the spatial grid on which the wind is requested. A confidence interval, with a confidence level $(1-\alpha)$ fixed, is then associated to the main direction $\langle\beta^{ROI}\rangle$ estimated within each ROI, as follow:

$$\langle\beta^{ROI}\rangle \pm ME_{\alpha}^{ROI}\ [°]\ (1)$$

where ME_{α}^{ROI} is the marginal error corresponding to the directional estimate $\langle\beta^{ROI}\rangle$, and it is defined by the semi-width of the assigned confidence interval (eq. (1)). Ranging from 0° to 45°, the parameter ME_{α}^{ROI} represents an inverse measure of the directional accuracy of its related estimate. The smaller the marginal error, the better the accuracy of the directional estimate.

The orthogonal to the main directional estimate $\langle\beta^{ROI}\rangle$ provides the 180°-ambiguous main wind direction for each ROI (Koch, 2004). The latter ambiguity can be removed from the comparison with the reference NWP model direction.

• *Reliable Wind Directions Selection.* A suitable threshold of reliability, i.e. a maximum marginal error ME^{TH}, is finally applied to all LG-Mod wind direction estimates:

$$\{ROI_{rel}^{TH}\} = \{ROI|ME_{\alpha}^{ROI} \leq ME^{TH}\}\ (2)$$

This thresholding (eq. (2)) allows an automate discarding of those directional estimates that are considered not reliable enough by the user. The number of reliable wind directions progressively reduces, in accordance with a decreasing threshold.

Once reliable main wind directions estimated by the LG-Mod algorithm, according to user requirements (i.e., ME^{TH} and α), the corresponding wind speeds were inferred by inverting the CMOD5.N (Hersbach, 2010) GMF.

RESULTS

Tables 1 and 2 report the Root Mean Square Error (RMSE) and Mean Bias Error (MBE) obtained for all the ROIs analysed in the retrieval of SSW fields by means of (1) the LG-Mod algorithm (direction) followed by the CMOD5.N inversion (speed) and (2) the available NWP model (direction and speed).

Directional estimates from the LG-Mod were derived applying the standard reliability threshold for directions ME^{TH}*=10°* (and *α=0.05*, in eq. (2) and eq. (3)). Only the ROIs satisfying the selected threshold were considered in comparing different direction and speed values.

Summary results were obtained for both EW and IW images from comparisons with both the global ECMWF and the regional SKIRON models at their own output spatial resolutions, i.e. at 12.5 km (Table 1) and 5 km (Table 2) grid, respectively.

From tabled statistics, wind direction RMSE values at medium resolution (Table 1) are quite comparable for both EW and IW subsets (18.2° and 18.8°, respectively), although with different estimation percentages (84.9% and 99.8%, respectively). At high resolution (Table 2), the RMSE value (15.0°) for IW images indicates instead a close agreement between the LG-Mod and the SKIRON directional estimation. On the contrary, a greater RMSE value (20.2°) is obtained for EW images. This finding suggests a less agreement of the two compared methodologies, which is probably caused by the lower native resolution of EW images than the one of IW images. Albeit both types of Sentinel-1 data are reduced to the same pixel size, the directional content of EW ROIs is minor than that from IW ones, as confirmed by very different estimation percentages (24.2% and 87.2%, respectively).

In addition, findings from estimation percentages suggest, on the one hand, that the exploitation of Sentinel-1 IW images should be recommended for retrieving high resolution SSW fields in coastal areas, such as the Camargue. On the other, both IW and EW images could be used for medium resolution SSW field retrievals.

With respect to wind speed statistics, the use of Sentinel-1 NRCS for CMOD5.N wind speed retrieval provides values higher than the ones obtained either from ECMWF (Table 1) or SKIRON (Table 2), with smaller RMSE and MBE values when the latter NWP model is assumed as reference.

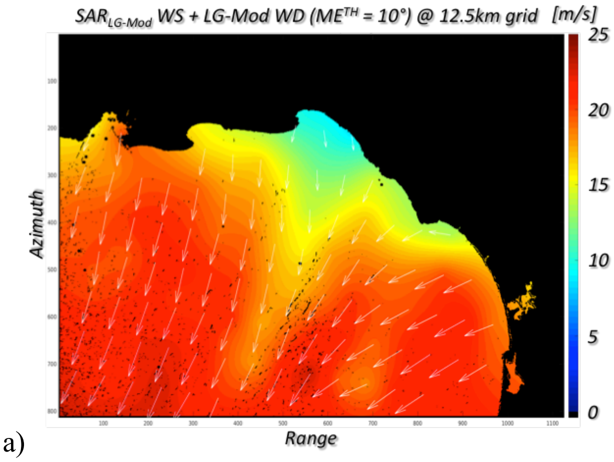
Table 1. Statistics from SAR LG-Mod wind directions (ME^{TH}=10° and α=0.05) and related CMOD5.N-derived wind speeds compared with ECMWF wind data. Spatial Grid ~ 12.5 km. Max Time Delay (SAR-ECMWF) ~ -16 min

Reference: ECMWF	*SAR LG-Mod Wind Directions*		*SAR_{LG-Mod} Wind Speeds*		*Sample Number*
	RMSE [°]	MBE [°]	RMSE [m/s]	MBE [m/s]	
EW Images	18.2	-7.6	6.3	4.7	1280/1508 (84.9%)
IW Images	18.8	6.6	6.0	4.6	551/552 (99.8%)

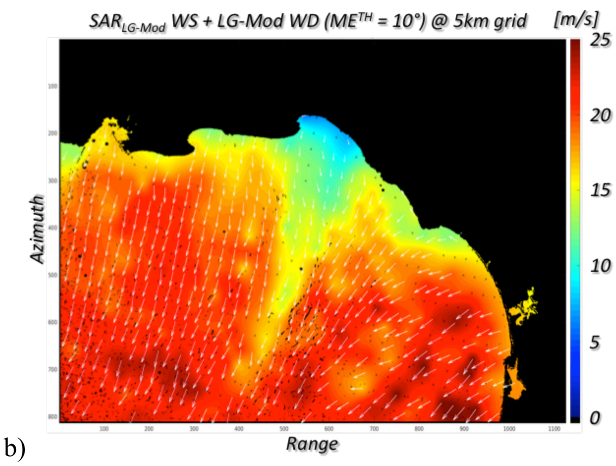
Table 2. Statistics from SAR LG-Mod wind directions (ME^{TH}=10° and α=0.05) and related CMOD5.N-derived wind speeds compared with SKIRON wind data. Spatial Grid ~ 5 km. Max Time Delay (SAR-SKIRON) ~ -16 min

Reference: SKIRON	*SAR LG-Mod Wind Directions*		*SAR_{LG-Mod} Wind Speeds*		*Sample Number*
	RMSE [°]	MBE [°]	RMSE [m/s]	MBE [m/s]	
EW Images	20.2	-7.2	4.9	2.5	2373/9811 (24.2%)
IW Images	15.0	-5.1	3.6	2.8	3308/3792 (87.2%)

Figure 1 illustrates Sentinel-1 derived SSW fields obtained at both output resolutions, i.e. 12.5 km (Figure 1a) and 5 km (Figure 1b). White arrows represent the LG-Mod wind directions and the coloured background is the interpolation of the related CMOD5.N wind speeds obtained from a Sentinel-1 IW image (5th Feb, 2015). Figure 2 shows the SSW fields provided by ECMWF and SKIRON, at 12.5 km (Figure 2a) and 5 km (Figure 2b) grid, respectively. Black arrows are the NWP model wind directions while the coloured background is obtained interpolating its wind speeds over the same geometry of the Sentinel-1 IW image in Figure 1.



a)

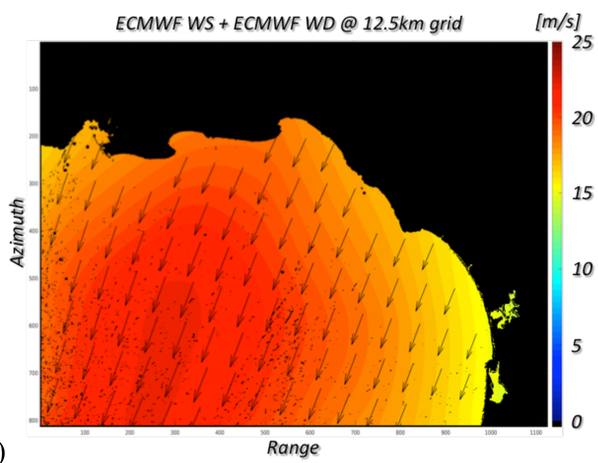


b)

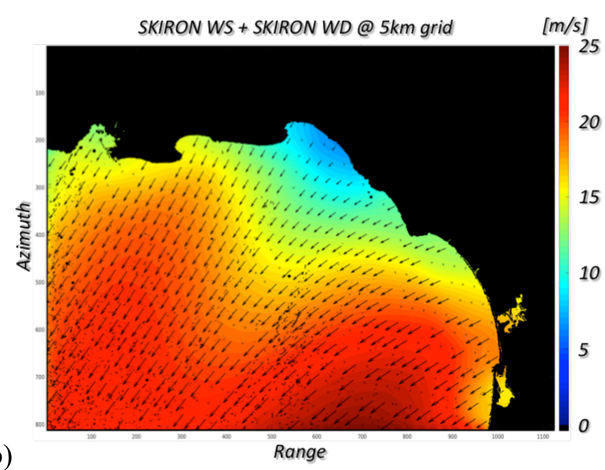
Figure 1. SAR LG-Mod wind directions (white arrows) and corresponding CMOD5.N wind speeds (coloured background) from a Sentinel-1 IW image, 5th Feb 2015, at (a) 12.5 km and (b) 5 km grid. Reliability threshold for directions selection ME^{TH}=10° (and α=0.05). Unusable pixels masked in black

As shown in Figure 2a, the global medium resolution ECMWF model provides a uniform average wind direction and a very smooth wind speed. Thus, the model appears not able to detail local wind spatial variability for both direction and speed. The regional high resolution SKIRON model exhibits instead the capability to sense two dominant wind flow patterns and shows a less smoothed wind speed pattern, as observed in Figure 2b. Wind field from SKIRON manifests a higher spatial variability than the one from ECMWF. This fact may be due to the different spatial and temporal resolutions of the two NWP models: wind data are gathered at 5 km grid every hour for SKIRON, and at 12.5km grid every 6 hours for ECMWF.

Furthermore, wind patterns obtained through the LG-Mod followed by the CMOD5.N inversion, at both medium (Figure 1a) and high (Figure 1b) output resolution, exhibit similar characteristics of the wind field provided by SKIRON (Figure 2b). The two above-cited wind flow patterns are clearly evidenced by the LG-Mod wind direction field at both medium and especially high resolution, thus showing an area where a wind front seems to be generated by the two colliding wind flows. These flows have the direction of the tramontane and the mistral (shown in SAR descending geometry), which are the prevailing winds in Camargue region. The local wind speed variability is also well detailed, especially at the smaller 5 km grid (Figure 1b) with respect to the larger 12.5 km grid (Figure 1a).



a)



b)

Figure 2. (a) ECMWF and (b) SKIRON wind directions (black arrows) and wind speeds (coloured background) at 12.5 km and 5 km grid, respectively. Each SSW from NWP models refers to the geometry of the Sentinel-1 IW image in Figure 1. Unusable pixels masked in black

Lastly, Sentinel-1 derived (Figures 1a and 1b) as well as SKIRON (Figure 2b) winds result consistent with both the surrounding orography of the Gulf of Lions and the prevailing North-Westerly winds, which usually strike the basin. It seems that SAR-derived and SKIRON wind fields cross-validate each other, thus resulting reliable in the complex area of the Camargue.

CONCLUSIONS

The investigations of local winds in the Camargue coastal area, characterized by a marked orography, yielded fruitful indications on the use of Sentinel-1 data for SSW field retrieval as well as of NWP model wind data in such area.

Sentinel-1 NRCS proved to be exploitable to both derive a reliable wind direction (when wind rows are present) and infer a wind speed that well reproduces the spatial characteristics of local wind, at both high and medium output resolutions.

SSW fields derived from Sentinel-1 IW images evidenced a better agreement both in direction and speed with the regional model SKIRON rather than with the global ECMWF. This result may be due to the better spatial and temporal resolution of SKIRON with respect to ECMWF as well as to the fact that SKIRON is a model optimised for the Mediterranean Sea.

The analysis carried out through the LG-Mod algorithm on Sentinel-1 EW and IW data, at different output spatial resolutions, showed that IW images appear very suitable for high resolution SSW field retrieval in coastal areas. The use of IW images may guarantee good LG-Mod performance in terms of both overall directional accuracy and percentage of reliable estimation, at medium and especially at high resolution. The findings showed also that EW images could be usefully exploited only in cases of medium resolution processing.

The assessment analysis in this work was limited by the lack of available coastal in situ measurements.

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BELHARMONY PROJECT: HARMONIZATION OF TIME SERIES ON WATER TARGET BY VICARIOUS CALIBRATION

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***Keywords*:** Earth Observation, coastal water, atmospheric radiative transfer model, vicarious calibration, aerosol

INTRODUCTION

The new generation of Earth Observation sensors providing free, full and open data with moderate-higher spatial resolution are becoming a fully operational service for space-based studies and monitoring of natural and anthropogenic ecosystems in land, water and coastal environment.
This aim is achieved especially by combined *Sentinel*-2A (and B), and *Landsat*-8 and Proba-V *missions*. The joint use is suitable to overcome both the low revisit time of each sensor and the frequent cloud coverage *by the harmonization of the remote sensing data. These data are calibrated by a different team of calibration and validation (cal/val) experts which use their own methods. Therefore, although these sensors are all calibrated within their absolute radiometric accuracy requirements (typically between 3 to 5%) cross-sensor radiometric biases might exist. Furthermore due to instrument response non-linearity effects the nominal calibration coefficients might not be applicable for low sensor signals observed over water targets.*
Within this framework the CNR-IIA will work on the harmonization of remote sensing data in case of coastal water, as international partner of the Belharmony project (Harmonization of multi-mission high resolution time series: application to BELAIR, https://belharmony.vito.be) (2018-2020) financed by the Belgian Science Policy office (BELSPO) in the frame of the Stereo III programme. The CNR-IIA activities will be based on the simulation of synthetic low radiance acquired by different instruments: MSI on board Sentinel-2 mission (MSI/S2), OLI on board Landsat 8 mission (OLI/L8), Vegetation instrument on board Proba-V mission (PV) and Deimos-1. The synthetic satellite observations will be generated by using the 6SV atmospheric radiative transfer model taking into account specific atmospheric and water parameters provided by the *ocean color* component of the ground–based Aerosol Robotic *Network* (*AERONET-OC*). The standardized *AERONET-OC* products of atmosphere (direct and inverse) and water (normalized water-leaving radiance) are the crucial elements for cal/val program of remote sensing data. The requirement to use this ground data for general calibration purposes and for the CNR-IIA activities, is the availability of ground data at the time of the *satellite* overpass (synchronous) or almost simultaneously (*quasi-synchronous*).
Finally, the synthetic radiance will be used to update the currently available radiometric gain coefficients to achieve an operational vicarious calibration in the case of water target.

DATA & METHODS

The synthetic low radiance (*REF*) will be simulated by using the 6SV vector atmospheric radiative transfer model (Kotchenova *et al*., 2008, 2007, 2006; Vermote *et al*., 1997) at the time of the available products of the AERONET-OC station adjusting the methodology described in Bassani *et al*. 2012 to the case of water target.
The Figure 1 shows the global distribution of the 27 AERONET-OC stations in which autonomous photometers operate on fixed platforms in coastal regions. The AERONET-OC products will be used as input of the 6SV code for the synthetic *REF* generation.
The spectral AERONET-OC products are provided in limited number of spectral channels (412, 441, 491, 530, 551, 667, 869, 1020nm at nominal wavelength). This weakness for calibration purposes is overcome defining the analytic function fitting the values within the spectral domain of the photometer channels and following the approach described in Pahlevan *et al*. (2014) for the extrapolation of the spectral behaviour of the products outside the photometer spectral domain.
In the Belharmony project, this interpolation procedure is applied for the retrieval of the spectral products at the 20 wavelengths (350.0, 400.0, 412.0, 443.0, 470.0, 488.0, 515.0, 550.0, 590.0, 633.0,

670.0, 694.0, 760.0, 860.0, 1240.0, 1536.0, 1650.0, 1950.0, 2250.0, 3750.0nm) required for the 6SV running.

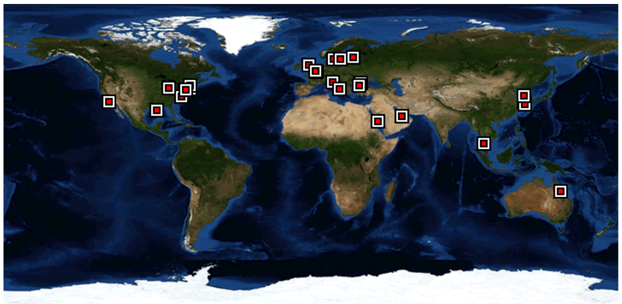

Figure 1. World map of AERONET-OC stations (red square)

The direct atmospheric products used to run 6SV model are the columnar content of water vapor and ozone, and the aerosol optical depth at 550nm retrieved by applying the power law considering the aerosol optical depth in the boundaries AERONET channels at λ = 440nm and λ = 870nm. The inverse atmospheric products are the micro-physical properties of the aerosol, i.e. size distribution and interpolated refractive index interpolated at the twenty 6SV wavelengths.

In order to achieve an accurate simulation of the *REF* signal, the specular reflection of the water surface will be considered by introducing as input the speed and directions of the wind provided by a meteorological station and/or ECMWF (*European* Centre for Medium-Range Weather Forecasts).

Furthermore, the interpolated AERONET-OC water-leaving reflectance will be included as input by modifying the source code of the 6SV model. Contextually to this step, the polarization of the radiation by the water-leaving reflectance as measured at the AERONET-OC station will be investigated.

For the simulation of the *REF* signal by 6SV model also the configuration of the sun-target-sensor geometry defined with solar (and view) zenith and azimuth angles has to be defined. In the Belharmony case the acquisition mode of the selected OLI/L8, MSI/S2, PV and Deimos-1 images will be considered.

Finally, the synthetic radiance will be simulated over the entire spectral domain. The simulated satellite observation (*REF*) of OLI/L8, MSI/S2, PV and Deimos-1 will be find once the convolution on the spectral sensor channels is applied to the spectral synthetic radiance. In the Figure 2, the relative spectral response (RSR) of the MSI/Sentinel-2 (left) and OLI/Landsat 8 (right) sensors sampling at 2.5nm used for *REF* retrieval by the convolution of the 6SV output.

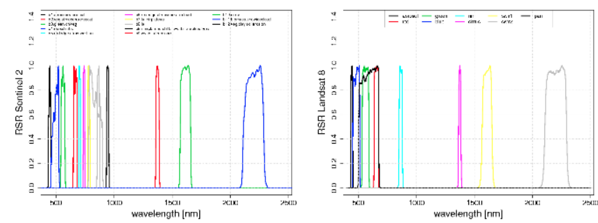

Figure 2. Relative spectral response (RSR) of MSI/Sentinel-2 (left) and OLI/Landsat 8 (right)

The achievement of an accurate *REF* strongly depends on the meteorological conditions. If the in-situ data acquired in clear-sky conditions are not available, an update of the scheduled time will be needed accordingly with an extra-time.

The *REF* calculations will be done for match-ups with the different satellite instruments. Strict criteria on time differences, cloud coverages, wind speed etc. will be applied in the match-up selection.

For each match-up set of *REF* and *MEAS*, where *MEAS* stands for the radiance acquired by OLI/L8, MSI/S2, PV and Deimos-1, the gain will be calculated as the ratio of *REF*/*MEAS*. The time-averaged gain is obtained through averaging over all valid observations, i.e. after removal of the outliers at a 2σ confidence interval. Here, it is essential that this averaging can be done over a sufficient number of observations in order to reduce the uncertainty in the final gain retrieval. Under the assumption that the uncertainties on the *REF* simulations are not correlated in time and are not systematic, the uncertainty is reduced with sqrt(N).

FINDINGS

The on-going CNR-IIA activities have been in place since December 2017. The findings of the initial work packages are here reported.

Initially, the AERONET-OC data considered in Belharmony project were the Lisco and Venise stations. In order to improve the amount of available data for the gain retrieval, all the AERONET-OC stations were taken into consideration.

Thus, the products of the 27 AERONET-OC stations were analyzed to find the data synchronous or almost simultaneously (*quasi-synchronous*) to the OLI/L8, MSI/S2, PV and Deimos-1 acquisition.

The selected satellite images of all available over the AERONET-OC stations were those with low cloud contamination by fixed a threshold of 6.0 for the scene cloud cover (SCC) parameter representing the cloud cover percentage. Consequently, the clear-sky condition required for accurate *REF* simulation by 6SV model was ensured.

The Table 1 reported the total amount of MSI/S2 and OLI/L8 images acquired over the *AERONET-OC* stations. The column *'P1'* reported the images with priority 1 that is the amount in case *of* quasi-synchronous acquisition (30min) with the water and atmospheric (direct and inverse) *AERONET-OC* products. The P2 contains the amount of images without quasi-synchronous inverse atmospheric products while the lower priority, P3, only the water products are quasi-synchronous with the satellite data. The Belharmony project will work on the P1 data which, compared to P2 and P3 datasets, provides a more comprehensive characterization of the atmosphere/water coupled system for signal simulation.

Table 1. Dataset for Belharmony activities for the MSI/S2 and OLI/L8 sensors. Columns: 'data' are the amount of images quasi-synchronous to AERONET-OC products (water); 'P1' amount of images quasi-synchronous to AERONET-OC products (water, atmospheric direct and inverse); 'P2' amount of images quasi-synchronous to AERONET-OC products (water, atmospheric direct); 'P3' amount of images quasi-synchronous to AERONET-OC products (water)

sensor	*data*	*P1*	*P2*	*P3*
MSI/S2	332	33	52	2
OLI/L8	445	29	82	2

The interpolation method was applied to the AERONET-OC water products for the retrieval of the spectral water-leaving radiance that will be a new input of the 6SV model as objective of Belharmony project.

The Figure 3 shows an example of the AERONET-OC products (black points) and the blue line is the final water-leaving radiance within the spectral domain defined by the boundaries of the RSR of the Figure 2. By this interpolation method, the AERONET-OC products are suitable for cal/val program of space data by their convolution on the sensor channels.

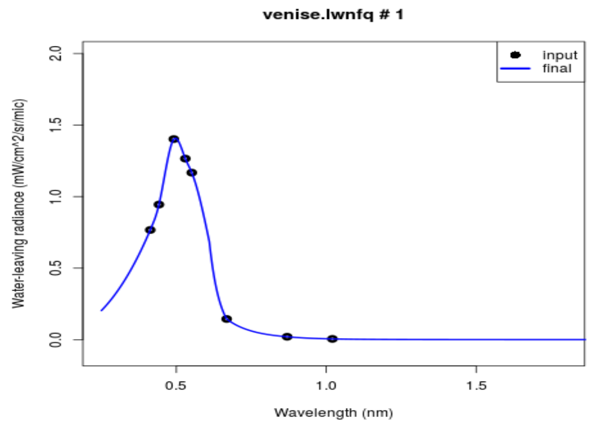

Figure 3. Water-leaving radiance. The black points are the AERONET-OC products; the blue line is the interpolated spectral water-leaving radiance within the selected spectral domain

The activity of the first task of Belharmony project is completed; in the next task the *REF* will be simulated by 6SV model following the method previously explained. The P1 dataset (Table 1) will be used to take into consideration all the parameters which play a crucial role on the radiative transfer modelling.

In addition to the interaction water-radiation, also the extinction due to the aerosol will be considered during the simulation by the inverse AERONET-OC atmospheric products. As explained in Bassani *et al.* 2012, the aerosol properties influence the *REF* signal especially in dark surface (water target).

As example, the Figure 4 of Bassani *et al.* (2012) shows the sensitivity analysis of the synthetic low radiance to the aerosol type varying the aerosol loading.

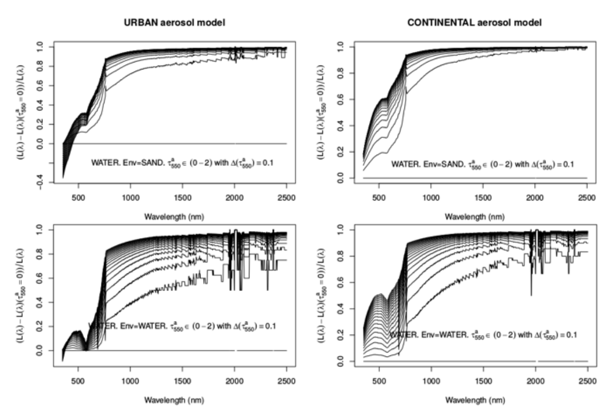

Figure 4. δL = (L(λ) − L 0 (λ))/L(λ) with τ 550 ∈ 1500 0.0, 2.0 2000 with 1τ 2500 column) 2000 and continental (second column) 550 = 0.1 using the urban (first Wavelength (nm) ws Wavelength (nm) ww aerosol models to view water surrounded by sand, δL (λ) (first row) and water, δL a (λ) (second row) (Bassani *et al.*, 2012)

CONCLUSIONS

At the end of the Belharmony project, harmonization of time series for the S2/L8/PROBA-V/DEIMOS-1 sensors over the selected BELAIR sites is expected.

Furthermore, the international remote sensing community will benefit from the Belharmony project results. The set of vicariously derived gains, both for aquatic and land application could be made available to the user as an option within this iCOR-SNAP plug-in (De Keukelaere *et al*,, 2018) and/or within the Mission Exploitation Platform which allows for a customized processing of PROBA-V time series.

ACKNOWLEDGEMENT

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A MODEL FOR SEASONAL FORECAST AT SUB-REGIONAL SCALE OVER ITALY AS A TOOL FOR LONG-RANGE ASSESSMENT OF AIR QUALITY

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Keywords: Seasonal Forecast, Neural Network, Downscaling, Air quality

INTRODUCTION

Nowadays the need for an extension of the weather predictability range beyond 10 days is a strong demand by our society. In the same way air quality is a matter of concern especially for urban environment. Thus, the idea at the basis of this work is to improve seasonal forecast performances at local scale (in particular over Italy) in order to gain information on future atmospheric states which impact on air quality.

Seasonal forecast is a hot topic for several meteorological centres worldwide. Unlike to the "conventional" (deterministic) weather forecasts, seasonal ones are based on a probabilistic approach that give an information about the mean state of the atmosphere for future months. Long-range predictability derives from components of climate system that present a slow variability in time (as ocean sea surface temperature, or cryosphere).

Typically, we obtain probabilistic forecast for meteorological parameters of interest for the next quarter. For example, the European Centre for Medium-range Weather Forecast (ECMWF) with the new System5 (available from last November 2017: S5 user guide) or the Met Office Glosea 5 (MacLachlan *et al*., 2015) provides good projections for the probabilities of 2m mean temperature especially for tropical areas. Instead, performances for European middle latitudes are quite reliable only for particular seasons (summer) and shows also a certain spatial variability (Weisheimer and Palmer, 2014). Italian peninsula shows the worst skill-score values for the winter season in the Euro-Atlantic scenario. Using seasonal forecast to obtain information about winter time air quality over Italy appears to be a heavy challenge.

In order to improve reliability at sub-regional scale some downscaling methods are used, both dynamical and statistical. The latter shows good performances despite of their relative simplicity in comparison to dynamical ones (Benestad *et al*., 2008).

In this framework, a statistical model for downscaling of seasonal forecast over Italy was developed (Amendola *et al*., 2017). The model is based on a neural network (NN) analysis applied to couples of historical output of ECMWF model (forcing field) and E-OBS dataset (response field).

The latter is constructed from observational station data at a resolution of 0.25°x0.25°, for 2m mean temperature or for cumulated rainfall over Italy (Haylock *et al*., 2008).

This model presents some innovative features that will be described in the next session and highlighted in conclusions. By using NNs a statistical (non-linear) relationship is built between the field at the largest spatial scale and that at the lowest one. Here we report results for a system configuration in which the NN analysis is performed by making use of both 2m mean temperature and 500hPa geopotential height output of ECMWF model as forcing. The result is a model that shows an overall improvement of skill scores for 2m mean temperature in all periods of the year, in particular for winter season. Then, the downscaling model permits to obtain information about the expected mean weather conditions for the winter season from which we can infer information on air quality.

As well known, air quality is a matter of concern of great relevance. High pressure conditions during winter season lead to stagnation of pollutants in the boundary layer, a condition that involves mostly big cities. Also, the danger of summer season should not be underestimated. In particular Ozone formation in very hot urban environments during heat waves leads to serious health problems.

After this introduction, a description of the downscaling model is provided in the next section. Successively, results and some future perspectives will be shown.

SYSTEM DESCRIPTION

The idea at the basis of our model is to improve seasonal forecast reliability using a data-driven model. Thanks to NN analysis we search for a statistical relationship between the parameter of interest at the largest spatial scale (ECMWF model outputs) and the same parameter at the lowest scale over Italy (E-OBS dataset). In addition, our model permits to use other fields (as the 500hPa geopotential field over the Euro-Atlantic scenario) in order to add physical information about the general circulation. For both time series we use data starting from 1981 up to 2010. For ECMWF we use System4 (S4) data. S4 presents a latitude-longitude spatial resolution of 0.75°x0.75°. Reforecast are available starting from 1981 with 15 ensemble members.

Pre-Processing

Before applying the NN analysis, some pre-processing steps are performed on both datasets (Wilks, 2011). One can choose to select (or not) these steps in the model.

The first step consists in a cluster analysis performed in order to identify and select zones with different climatic behaviour. So the Italian region is divided in several sub-areas (typically 4-5) for each period and parameter of interest. The partition is obtained on the basis of the linkage between forcing and response fields (Amendola *et al.*, 2017; Calmanti *et al.*, 2015).

The next problem is the choice of the domain of the forcing fields at the largest scale. It is an open problem for this kind of models (Radanovics *et al.*, 2013). Sometimes the choice is taken "a posteriori" but this is not a good solution for an operational system. Thus, our model permits to select between two methods of selection or a "manual" selection: see Amendola *et al.* (2017) for more details.

Once these two preliminary steps are made, some statistical analysis is performed on forcing and response fields in order to fix the predictor and target couple for NN analysis. In particular the two statistical tools of empirical orthogonal function (EOF) analysis and canonical correlation analysis (CCA) are applied on both large and small scale fields (Peixoto and Oort, 1992; Benestad *et al.*, 2008; Wilks, 2011).

The information content is filtered by EOF, separately, for each field. The observed (time and space) variability is summarized in some (typically 3-4) principal patterns, each of which has its related time series (Principal Components, PCs) that represent the observed temporal variability.

The datasets are cross-correlated by CCA. Again, the information content is summarized in some principal pattern and the associated time series (called Canonical Variates, CVs).

So, CV of forcing fields are the predictors, while PCs of response field are the target of NN analysis. In particular two CVs are considered for each forcing field, while the number of PCs of the response field is selected by the so-called *knee method* (Wilks, 2011).

Neural Network analysis

NN is the core of our system. The choice of NN is related to the possibility for searching any – even small – non-linear relationship between predictors and target. A different NN structure is trained for each PC separately.

The NN is a feedforward multilayer perceptron, with one hidden layer. The number of neurons of the hidden layer is equal to the number of inputs. A hyperbolic tangent is the transfer function at the hidden layer.

The overfitting problem is taken into account by selecting a small number of hidden neurons and using a training technique based on Bayes theorem (Bayesian regularization). This permits to calculate the weights of NN by minimizing an objective function. Thus, available data are exploiting at best to train the NN.

In order to evaluate the "real" error associated to each NN and for calculating the skill-score performances a particular approach is adopted. Bayesian regularization is performed excluding one year at a time, so this one is used as a "forecast year". In this way skill-scores can be evaluated over all the training period. This procedure is iterated 100 times for each year and PC with a different (random) choice of the initial weights (Nguyen and Widrow, 1990). In this way the search for the minimum of the objective function is done at best.

More details about NN structure and training are in Pasini *et al.* (2018), Amendola *et al.* (2017) and references therein.

The probabilistic forecast

We definitely obtain an ensemble of 100 NNs for each PC of the response field. Probabilistic forecast is calculated using the NN ensemble.

A Probability Density Function (PDF) for each PC is calculated as a Gaussian Mixture (GM) of each ensemble member, each of which is weighted in relation to the associated error. Making use of GM distributions allows us to take possible multimodal

behaviour of our meteorological parameters into account.
Then we return to the space of observations by a convolution between the PDFs of the PCs: see again Amendola *et al*. (2017). The procedure is iterated for all grid points over the Italian area. Finally, by comparison with the 1981-2010 E-OBS climatology we obtain the probabilistic forecast. The products that can be obtained are listed in Table 1.

Table 1. List of maps available for our downscaling model

Type	*Description*
Median	Probability for the parameter of interest to be over the 50° percentile of reference climatology
Upper Tercile	Probability for the parameter of interest to be over the 66° percentile of reference climatology
Lower Tercile	Probability for the parameter of interest to be under the 33° percentile of reference climatology
Middle tercile	Probability for the parameter of interest to be between the 33° and 66° percentile of reference climatology
Highest 20%	Probability for the parameter of interest to be over the 80° percentile of reference climatology
Lowest 20%	Probability for the parameter of interest to be under the 20° percentile of reference climatology
Mean Anomaly	Anomaly for the parameter of interest respect to reference climatology

RESULTS

Now we illustrate some results of the downscaling model together with a discussion about the support for air quality assessment. As a case study we report the statistics for winter season (December January February, DJF).
Skill-scores are calculated using each year of the period 1981-2010 as a "forecast year", as described in the *Neural Network analysis* section. In order to permit a comparison with ECMWF model the same skill-score tools for the evaluation of our NN model are used.
A detailed description of these statistical tools can be find in an ECMWF technical memorandum (ECMWF-memorandum), see also Amendola *et al*. (2017) for a deeper analysis of model results.
As cited in the introduction, seasonal forecast shows bad performance for middle latitudes. In Figure1 we show Spearman correlation for our downscaling system and for S4 over the Italian peninsula. Correlation is calculated using each data as a "forecast year". Results for 2m mean temperature over the winter season for 1981-2010 period are shown.

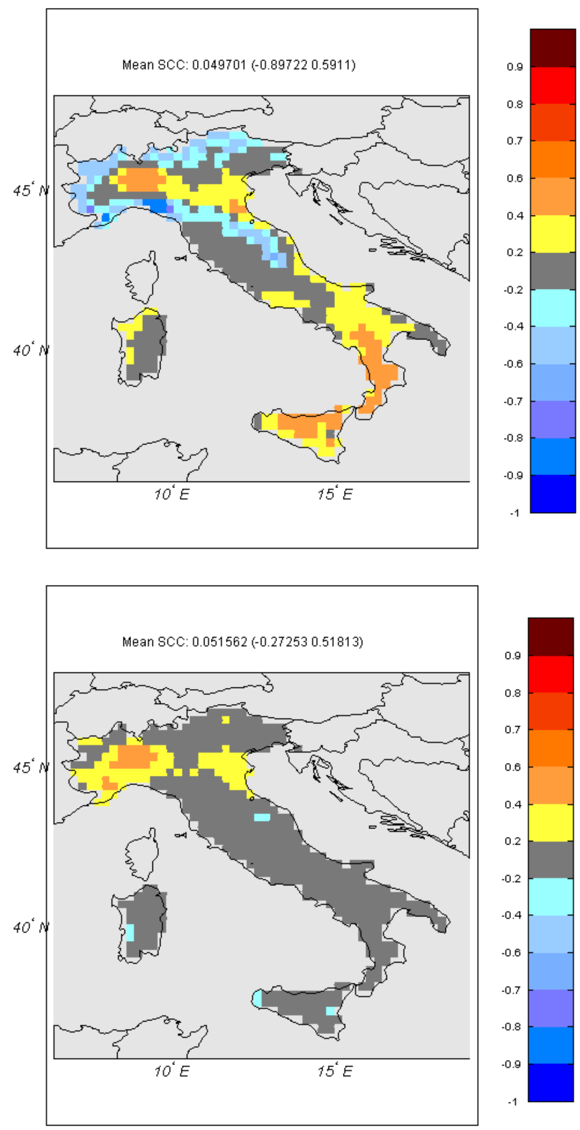

Figure 1. Spearman correlation over the period DJF 1981-2010 for 2m mean temperature for: NN downscaling system (top); ECMWF System4 (bottom)

As cited above, the winter season is the most critical one for the Italian peninsula. In the lower part of Figure 1 the correlation for ECMWF S4 is shown. No correlation at all is present for winter season with the exception of part of Po valley. In the upper part of Figure 1, an overall improvement is present with the exception of mountain areas. Probably complex topography of these areas is badly captured by E-OBS dataset, so that we have even negative correlation.
Figure 2 shows Brier Skill Score (BSS) over Italy. BSS give the accuracy of a forecast set related to an assigned reference forecast. Positive values mean

better performances in comparison to the reference, negative values mean the opposite.

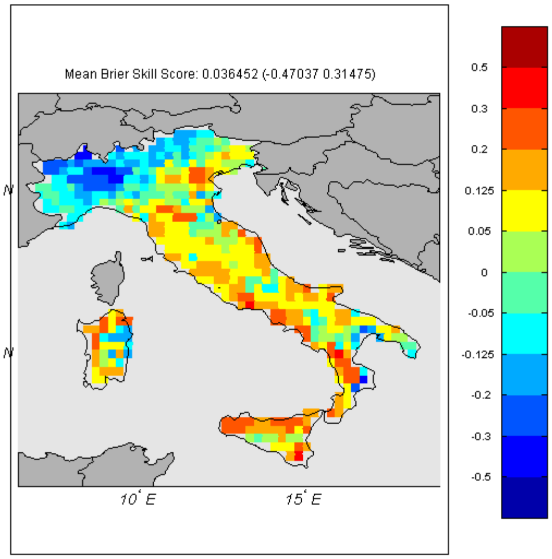

Figure 2. Brier Skill Score over the period DFJ 1981-2010 for 2m mean temperature upper tercile: downscaling VS ECMWF

In Figure 2 BSS for downscaling system in comparison to ECMWF is shown (for upper tercile forecast).

We can see that an overall improvement in comparison to System4 is present. Our model permits to obtain more reliable seasonal forecast for 2m mean temperature over Italy for winter season. These results hold, with even better performances, also for summer season (not shown).

It should appear clear that an improvement of seasonal forecast performances open very interesting perspectives for air quality assessment. From seasonal forecast projections we have probabilistic information about mean conditions for some meteorological parameters of interest. Thus, we can forecast meteorological mean conditions for the future quarter, and this strongly influences air quality. For example, a forecast of higher than normal temperatures together with drier conditions leads to think of frequent high pressure conditions, with consequent predisposition to rise in pollutants values.

In the same way, for summer season, the presence of a signal for higher than normal temperatures leads to infer for frequent heat wave conditions, the ideal ones for the development of a secondary pollutants such as Ozone in urban areas.

A more comprehensive treatment about climate change impacts on air quality can be found in Pasini *et al*. (2018).

CONCLUSIONS AND FUTURE PERSPECTIVES

Air quality assessments over long-range period can be achieved by consideration of reliable seasonal forecasts. This abstract shows that these forecasts are not an impossible goal thanks to downscaling models.

In particular, the statistical downscaling model here presented has some peculiar and innovative characteristic features that permit to look with interest to the sector of local area seasonal forecasts.

The absolute generality of our system could permit its application to different (possibly better) observational dataset, so that the real potentialities of the model are not even fully explored. Furthermore, also the application to station data must to be evaluated, for example for an urban meteorological station, in order to obtain a “point” air quality assessment.

Furthermore, also theoretical aspects of the model can be improved. Definitely, the scenario of local area seasonal forecasts can be considered at the stage of its growth phase.

Finally, the possibility of increasingly reliable seasonal forecasts opens new points of view for predictions of our urban environments and their air quality.

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OPTICAL ALTERATION OF THE SPECTRAL BEHAVIOUR OF COMPONENTS IN HVAC SYSTEMS

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Keywords**:** Vis-NIR, Dust, mold, yelds, HVAC

INTRODUCTION

The air quality in indoor environments is strictly related to the maintanance of Heating, ventilation and air conditioning (HVAC) systems. The outdoor air is usually conditioned to appropriate temperature, humidity and purity (low particle concentration, non-odorous) in order to support comfortable indoor conditions for occupants and to guarantee safe air conditions for any working or manufacturing process (Maus *et al*, 2001). The potential aerosol components that impact on the indoor environments are dust, volatile organic compounds (VOCs) and bioaerosol (molds, yeasts, pollens and patogenous bacteria) and there are several Environmental control practices (ECPs) aimed to reduce exposure to indoor allergens or nonallergic triggers (Sublett, 2011). From this perspective, the efficiency of the air filtration components constituting the HVAC systems and their maintenance are critical issues. The monitoring of the different HVAC components can represent an ECP since it can improve the timing and the localization of critical condition in the system. Furthermore, the efficiency of the system can also reduce the energetic consumption required for the air treatment and ventilation. This issue is very important if we consider that just an efficient filtering of air can impact on at least the 10% of the energy required by a HVAC system (Stephens *et al*., 2010).
The aim of this project is the development of a monitoring protocol aimed to alert tempestively the maintenance responsible of a HVAC system (we are considering only large-scale systems operating at hospitals and business buildings) and to restrict the critical parts of the system where maintenance is required. This activity is funded by CIANA srl, that is a small-medium enterprise leader in Central Italy on HVAC maintenance, and this feasibility study is an ongoing research focused on defining a protocol based on the optical alteration of materials. This approach offers the opportunity to improve practices on HVAC systems combining low-cost hardware and continuous monitoring of critical parts of the system.

The presence of altering materials on metallic surfaces present in the HVAC system can be easily detected considering that a low-reflecting material such as metals can be optically altered by the different aerosol components. All of the outdoor air components have a different spectral behaviour compared with metals (Berdahl *et al*, 2008) and the variance of the spectral behaviour of HVAC components can be an efficient trigger for intervention and maintenance.

METHODOLOGY

The research activity is composed by different phases: laboratory simulations; pilot sudy; and business analysis. The first phase is focused on defining the optimal setup for detecting the alteration of the optical properties of HVAC components in relation to the growth of molds and yelds and to the deposition of dust. Experiments are carried out under controlled conditions (concentration, temperature and humidity) in order to define the best alert levels. These experiments requires the use of matrices for the cultivation of biological materials and we are completing this phase moving from inhoculation on agar samples to incubation on metalllic surfaces. We have performed the first part of experiments under fixed T and RH conditions using five levels of concentration. We have used an AcquaAria impactor where petri dishes were exposed for different sampling times to the air. The final volume of sampled air varied from 0.2 to 1 m^3. The next step will consist in testing different thickness of agar over the metallic surface in order to obtain the most realistic simulation of HVAC conditions. The optical alteration of samples will be defined combining the online acquisition of visible images and the final spectral characterization of samples using a full-range spectroradiometer (Fieldspec 3, Analytical Spectral Device Inc.).
All of these information will contribute to the development of a prototypal device that will installed in a pilot HVAC system.

Figure 1. Evolution of a simulated sample with a sampled volume of 1m^3

The device will be firstly tested using commercial components, considering how to reduce costs and how to avoid interfences to the air flowing in the system. Furthermore, this pilot experiments will be carried out under real operating conditions of HVAC system and the impact of the selected alert levels will be analysed in terms of energetic consumption of the system.
The final phase of this project will consist on exploring the most substainable business model. This analysis will be performed considering the hardware costs, the reduction of personnel costs for the maintanance provider and the energetic savings for customers.

FINDINGS

The first set of experiments are very promising since the experimental setup can detect the formation of molds and yealds with a size resolution close to 1 mm^2. The growing rate of biological material was of course controlled by the sampling length, and consequently by the concentration. The fastest growing rate was detected for the highest concentration (1 m^3) and the complete coverage of the exposed surface was obtained after 5 days (Figure1). This set of experiments are still under analysis and different type of biological materials were dectected. Further information are expected after a more detailed investigation of the visible colour components.
While the experimental phase is going on, also the pilot phase has been started contacting potential customers that can provide “real” HVAC systems for the deployment of prototypal devices. This device has already been configured and a first instrument has been prepared for being installed and tested under real air flowing conditions (up to 10000 m^3 h^{-1}).

CONCLUSIONS

The maintenance of HVAC systems impacts heavily on health and the improvement of the supply air quality is typically achieved with air filters that consist of fibrous filter media. The efficiency of these systems can be optimazied acting on them tempestively. The presented research activity, started recently, is aimed to improve the effectivenes of HVAC maintenance using monitoring devices based on the optical alteration of materials. Experiments conducted under laboratory conditions are defining the optimal alert levels for scheduling intervantion on HVAC systems. Pilot experience will be scheduked for the identifycation of the impact of those levels to the energetic yeld of HVAC systems. The final business analysis will define the best trade-off between costs for maintenance provider and customer savings.

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SATELLITE REMOTE SENSING FOR ASBESTOS-CEMENT SURFACES MAPPING

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Keywords: Asbestos, remote sensing, satellite, spectral data

INTRODUCTION

The World Health Organization estimates that 100 thousand people in the world die every year from asbestos-related cancers and more than 300 thousand European citizens are expected to die from asbestos-related mesothelioma by 2030. Both the European and the Italian legislations have banned the manufacture, importation, processing and distribution in commerce of asbestos-containing products and have recommended action plans for the safe removal of asbestos from public and private buildings (Frassi *et al*., 2014).
In fact, asbestos has been used for decades in the construction industry for thermal and fire insulation. Moreover, the fibers were often mixed with cement (asbestos-cement) into prefabricated elements, corrugated roofing sheets or tiles.
In this context, Italy banned the production and use of asbestos in 1992 with the Law 257/92 (VV.AA., 1992) and provided guidelines to map areas containing asbestos fibers with the National Decree 101/2003 (VV.AA., 2003), in accordance with the European recommendations to support action plans for the safe removal of asbestos from public and private buildings.
In the past, remote sensing technologies were tested for the detection of asbestos-containing materials in asbestos-cement roofing. Several research activities were carried out using the Multispectral Infrared and Visible Imaging Spectrometer (MIVIS) for mapping asbestos-cement roofs (Basile *et al*., 2012) and for monitoring its deterioration status (Bassani *et al*., 2007).
In the last twenty years of CNR-IIA remote sensing activity, by the use of MIVIS sensor about 7 km^2 (of 45.000 km^2 analysed surface) of asbestos roofing have been detected.
With the introduction of a new generation of satellite sensors, operating in the VIS-NIR and SWIR spectral ranges with medium/high spatial resolution, it is possible to hypothesize their use in the distinction of the different roofs. This paper describes new potential to map asbestos-cement roofing with Worlview-3 remote sensed data.

METHODOLOGY

The advent of the Worldview-3 satellite sensor, that containing short wave infrared spectral bands, allows to evaluate a new approach in the field of asbestos-cement mapping.
The WorldView-3 sensor, launched in orbit in 2014, operates at an altitude of 617 km and is able to have revisitation period of the order of 1-2 days and to acquire areas of 680,000 km^2 per day.
The sensor provides a variable resolution depending on the spectral range considered: overall resolutions (at nadir) are: 31 cm in the panchromatic, 1.24 m in the multispectral, 3.7 m in SWIR (delivered at 7.5 m) and 30 m in CAVIS.
The image was provided by *Planetek Italia srl* and falls near Bergamo city (Lombardia). By applying the procedures experimented for MIVIS imagery, we tried to extract asbestos-cement roofs from the satellite image.
The procedure is based on the use of the spectral signature of a single pixel extracted from a asbestos-cement roofing. On the basis of this spectral signature the Spectral Angle Mapper (SAM) algorithm is applied. It discriminate the image pixels according to the degree of similarity between their spectral behavior and the reference spectra.

FINDINGS

The accuracy of the classification of asbestos-cement roofs using hyperspectral airborne data was evaluated at about 93%. In any case, only chemical analyses of the materials can confirm the presence or absence of asbestos inside the structures surveyed.
The WorldView-3 images provided an accuracy of 80-85%. This data is not reliable: in fact, it was not possible to carry out inspections in the study area and the data arises just from photointerpretation using high spatial resolution images.

To exclude materials that can generate spectral confusion and therefore lead to incorrect classifications of the “asbestos-cement” data, it was agreed the need to create a spectral signature library of all anthropogenic cover materials.
In this perspective, an initial field campaign was started in the Municipality of Montopoli di Sabina (RI) .
Four medium-sized covers were selected on which spectroradiometric, thermographic and multispectral measurements were performed.
During the field investigations, radiometric data were acquired by means of a Fieldspec 3 portable spectroradiometer of Analytical Spectral Devices (Inc. Boulder, CO, USA), in the range 350-2500 nm. Spectoradiometric data were acquired on 16/03/2017, during the hours of maximum insolation and in conditions of stable insolations.
Finally, for each data, a digital photo was taken taking care to reproduce the same conditions of illumination and geometry.
The four roofing materials investigated are: asbestos-cement, fiberglass, sheet metal and tiles.
Having a spectral library allows therefore to increase the accuracy of the classification of the coverings, and especially those in asbestos-cement. Furthermore, the availability of this field data is an useful tool for carrying out additional validation tests of the procedure for the extraction of asbestos-cement roofing.
In particular, in the asbestos-cement samples the characteristic absorption peak at 2327 nm is clearly identifiable. This peak is less evident in the investigated surfaces where the fibers are not exposed, or less so: this is due to the presence of superficial alterations such as oxidation crusts or the presence of lichens, while it is totally absent in the other types of roofing.
The SWIR band 8 of the WorldView3 sensor, fully fully describes this peak and would appear to be suitable for detection of cement-asbestos roofing.

CONCLUSIONS

The progress of remote sensing techniques has allowed to develop precise instruments for the monitoring of the territory and the use of images acquired by remote sensors has made it possible to reduce the time and costs of the census of asbestos-cement roofing.

In this context, the application of hyperspectral airborne data transformation techniques with high spatial and spectral resolution allows to discriminate asbestos-cement surfaces and other types of materials present in the territory. The use of WorldView-3 satellite images, however, allowed the mapping of surfaces containing asbestos.
WorldView-3 satellite images are useful for future monitoring of previously detected roofs with hyperspectral sensors, allowing to identify situations in which, after some time, asbestos-cement roofing has been removed (change detection of results).

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OBSERVING SYSTEMS AT GLOBAL AND REGIONAL SCALE: FROM DATA QUALITY TO KNOWLEDGE

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***Keywords*:** network, standard procedure, data-quality management, QA/QC protocols, cyberinfrastructure

INTRODUCTION

Air pollution has become an important global environmental issue during the past decades. In addition, air pollution prevention and reduction is an economic burden to a person and to a nation on a global scale; therefore, it is extremely important to understand its fundamental sources, causes, and health effects (Wagner *et al*., 2013; Ciucci *et al*., 2016; Sharma *et al*., 2017). To address these issues, various international agreements have been designed and specifically adopted to overcome the problems faced by each air pollution categories. Worthy of note are the UNECE Convention on Long-range Transboundary Air Pollution; the Minamata Convention for mercury; the Paris Agreement for greenhouse gases, and many others, all claiming for major monitoring efforts on data acquisition. For air pollution monitoring, the priorities include expanding the existing data collection networks and establishing new coordinated measurements of atmospheric pollutants (Pirrone *et al*., 2013). A lot of efforts have been recently made in building monitoring networks which integrate ground-based stations at global and at regional scale. Once realized these widespread observing systems, the real difficulty then consist in collecting the huge volume of data, produced from the network it-self, and producing a unique as well comparable database from which it is possible to extract information and knowledge. In the notable process of the hierarchy of data, information and knowledge, computations with elaborate algorithms play a major role in the initial processing of data to information, but computations with good reference databases become more important in the following processing to compile knowledge. In this regard, Harmonized Standard Operating Procedures (SOPs) and Quality Assurance/Quality Control (QA/QC) protocols for monitoring ambient concentrations of various air pollutants are extremely essential in order to assure a full comparability of site specific observing datasets with those obtained inside and outside existing monitoring networks. SOPs and QA/QC protocols should be also in accordance with measurement practice adopted in well-established monitoring networks and based on the most recent literature.

In this general context we extended valuable know-how about data quality collection and management within various international and regional networks, in which our Institute of Atmospheric Pollution Research, Section of Rende, has been involved. These specific projects are: the Global Mercury Observation System (GMOS), the Italian Special Network for air quality, and the High-altitude Climatic Observation System and Climate Station Network (NextDATA).

In order to ensure data reliability and comparability within the GMOS network, our scientific and research team in Rende made significant efforts to implement a centralized system, which is designed to quality assure and quality control atmospheric mercury datasets. Within the network, special attention was firstly paid to the harmonization of measurements in order to ensure full comparability between data from all the monitoring sites. To achieve this, Standard Operating Procedures (SOPs) were developed during the planning and implementation stage of the GMOS network (Munthe *et al*., 2011). This was done in accordance with best practice on measurements adopted in well-established regional monitoring networks, and based on the most recent literature (Brown *et al*., 2010; Steffen *et al*. 2012; Gay *et al*., 2013). Taking this in mind, an ad-hoc system named GMOS-Data Quality Management (G-DQM), was designed by using a web-based approach with real-time adaptive monitoring procedures aimed at preventing the production of poor-quality data.

The experience gained in managing atmospheric mercury data collected during the first-five years of the on-going GMOS network, gave us the advantage to have a benchmark and an opportunity to propose, with the appropriate changes, the innovative approach in managing and validating data produced within others regional projects as those concerning the Italian networks of Reti Speciali and NextDATA.

METHODOLOGY

The GMOS network, through the GEO-Flagship GOS^{4}M (Global Observation System for Mercury) in the framework of the GEO Strategic Plan (2016-2025), aims to support the goals of GEOSS and other on-going international programs, such as the UNEP Mercury Program. In order to ensure data reliability and comparability, a significant effort has been made to implement a centralized system, which is designed to quality assure and quality control atmospheric mercury datasets. The G-DQM system is plugged on a cyberinfrastructure (CI) and deployed as a service, which supports both routine and alert notifications to ensure proper instrument maintenance. G-DQM is a service that starts working after data are stored in the GMOS databases.

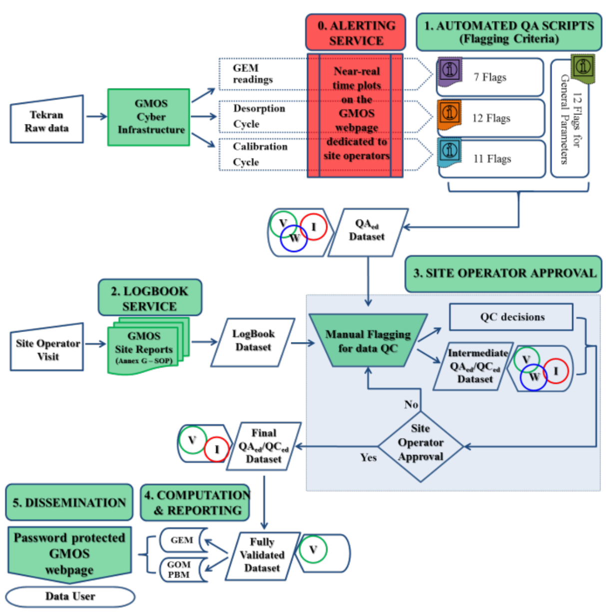

Figure 1. G-DQM workflow with the main step processes on which it is based

The data integration process is held by a software agent plugged on the GMOS-CI. This component acquires data coming from stations managed by the GMOS partners: it reads data shared by each partner using File Transfer Protocol (FTP), even though many other different protocols are supported. G-DQM essentially takes Tekran raw data as the input while the output is a flagged dataset with information on data validation. After data acquisition, datasets are processed for quality assurance using the workflow described elsewhere (D'Amore *et al.*, 2015) and reported in Figure 1. As an additional service, the G-DQM system is also able to provide an alerting system (0) by which it is possible to visualize the near real-time Tekran output parameters. This helps site operators to identify any questionable events and take quick corrective actions in order to prevent the production of poor-quality data.

The final full validated datasets are finally accessible upon request at the GMOS web portal (www.gmos.eu) for dissemination purposes. The GMOS database set by the CNR-IIA, section of Rende, is thus able to support advanced data acquisition, storage, quality management, integration, mining and visualization.

FINDINGS

The web-based system is able to fulfil the demands of processing monitoring data in near real-time, verifying if instruments adhere to standard procedures, and rapidly identifying non-representative measurements. Its application to five years of data allowed a very detailed analysis for each Tekran analyser used in the network. This centralized tool gave a fast and general overview of the analyser behaviour, and a rapid check of data quality. The flags adopted to tag values within datasets allowed us to understand issues occurring frequently and noticeably affecting data quality. The results obtained provide an important first assessment of the mercury data acquired with the on-going GMOS stations and give important feedback for future instrument management and maintenance guidelines that could be taken into account in further development of mercury-oriented monitoring networks (Bencardino *et al.*, 2017). In addition, the service allowed to compare and analyse together the atmospheric mercury datasets we acquired from stations widespread around the world. The scientific discussion resulting from this work is reported in Sprovieri *et al.*, 2016 and it represent a comprehensive overview of the state of the art on the global atmospheric mercury data that is going to well support the policy makers within the Minamata Convention implementation (Arts. 19 and 22).

Apart from mercury, the amount of environmental data in general is expected to increase rapidly in the coming years, thus there is an increasing need for automated, platform-based methods to check and correct data to ensure that datasets provided to various end-users are of highest quality. To this end, and similarly to what done with G-DQM, we are now working on the implementation of an adaptive system able to manage others air quality parameters produced in the context of the Italian Reti Speciali project (Pirrone *et al.*, 2017). The pertinent workflow, reported in Figure 2, show that we are expected to produce a unique and comparable database consisting of quality assured and controlled datasets coming from all the designed monitoring stations of this Italian network, and reporting specifically on Ozone and its precursors, Particulate Matter and its chemical species, Polycyclic Aromatic Hydrocarbons (PAHs), Heavy Metals (As, Cd, Ni, Hg).

In the context of data-quality managing we are also working on the definition a common approach for the data validation (data flagging) and for the format of the data that will be submitted to NextDATA archives and to the related reference international programs/projects, such as the World Data Centre for Greenhouse Gases (WDCGG) for greenhouse gases. The NextDATA project will specifically aim at creating a climate observing network in mountain and remote areas, based on climate observatories for the monitoring of meteo-climatic conditions and atmospheric composition. The network for monitoring the background atmospheric composition comprises five high-mountain atmospheric observatories among which the Monte Curcio station (CUR, Southern Apennines, WMO/GAW regional station; 1796 m) managed by the IIA-CNR, Section of Rende, is included.

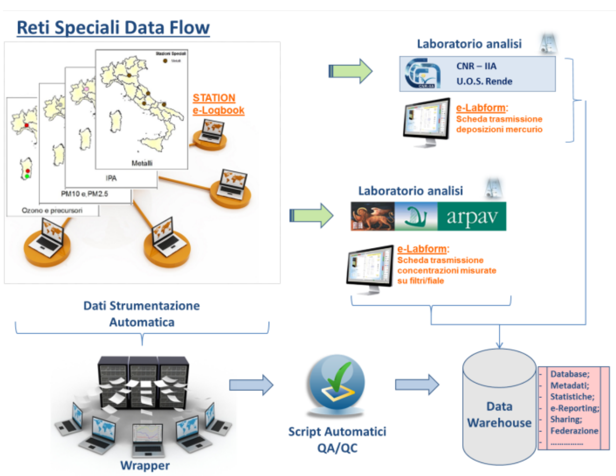

Figure 2. Data managing workflow within the Italian Reti Speciali project

CONCLUSIONS

Advances in monitoring and sensor networks now provide enormous quantities of data, even in near real-time. Dedicated Information Technology (IT) frameworks make it possible to deliver ever larger datasets to the end-users. In the coming years, improvements in sensor network technologies will provide researchers with more robust frameworks for data collection and management. Sensor network technologies enter many fields of modern life as they offer the opportunity to observe a wealth of environmental variables. Therefore, the problem is no longer how much data we have, but what kind of data we have, and above all its quality. Sensor networks are still subject to inevitable faults that may cause loss of data or poor quality and it is imperative to have a system in place to minimise data loss and alert operators to non-standard sensor performance. A first approach to obtain good quality data from raw datasets may include a post-processing performed individually and often manually by each station manager. This approach is, nevertheless, unsuitable when data are coming in near-real time from sensor networks. To deal with this scenario, QA/QC algorithms should run within an IT platform (i.e. a cyberinfrastructure) so that process optimization and data handling become more efficient. Even though it is almost necessary to have a level of human intervention and inspection in QA/QC, the use of automated common checks represents an improvement because it ensures consistency and reduces human bias thus avoiding misinterpretation and inappropriate data use. Widening the observing system, both at global and at regional scale, with new stations that comply with such system would instil larger confidence in atmospheric quality data and would ultimately improve the future research and policy efforts in getting a comprehensive assessment and knowledge in the atmosphere on the global scale.

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A WORD IS NOT ENOUGH: TERMINOLOGY TOOLS FOR EO AND CRYOSPHERE

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Keywords: terminology, thesaurus, ontology, earth observation, snow

INTRODUCTION

The huge amount of data and information made accessible by the Internet is no more a novelty, still remains the need to come to terms with a sort of "information deluge" and the risk of losing meaningful information in the background noise.
This statement is true in all information areas and scientific data are no exception to this rule, where Big Data and their interoperability (Nativi 2017) are an issue not only in terms of size, but also because the 95% of big data are unstructured (Gandomi 2015). Moreover Earth Observation (EO) and remote sensing activities produces "Big Data from Space" as ESA says: "the massive spatio-temporal Earth and Space observation data collected by space-borne and ground based sensors, and to synergetic use of data coming from other sources and communities."
A research infrastructure for data management should be to enable efficient data discovery and integration of heterogeneous data (Karam 2016). Terminological tools such as thesauri and ontologies could be useful in an "ocean" of data to help semantic searches and data retrieval, both for human purpose and use (metadatation, translation, concept understanding, data sharing, monitoring reporting) and machine to machine interactions. More specifically some specific environmental domains such as cryosphere (Schöner 2016) need semantic tools, to discover, access and share data and information more effectively than before.
In the framework of the i-CUPE project (integrative and Comprehensive Understanding on Polar Environments, strand 4 of ERAPLANET) that targets to provide novel insights and observational data on global grand challenges with a polar focus, the IIA-CNR EOSterm and Snowterm thesauri will be revised and updated with needed new terminology. Glossaries and two domain ontologies on earth observation and snow will integrate and complete the set of terminological tools.

METHODOLOGY

A thesaurus is a controlled vocabulary formally organized so that existing relationships between concepts are made explicit. The IIA-CNR thesauri EOSterm and Snowterm make no exception and follow the international standards (ISO 25964-1:2011 and ISO 25964-2:2013), they are arranged hierarchically by facets (top terms: ATTRIBUTES; DIMENSIONS; DYNAMIC ASPECTS; ENTITIES) and the terms are reciprocally linked with three types of relationships (Moreira 2018): hierarchical, equivalency or associative. Hierarchical relationships are used to indicate terms which are narrower and broader in scope. A "Broader Term" (BT) or hyperonym is a more general term, e.g. "satellite" is a generalization of "geostationary satellite". Reciprocally, a Narrower Term (NT) or hyponym is a more specific term, e.g. "along-track scanning" is a specialization of "scanning". The equivalency relationship is used primarily to connect synonyms and near-synonyms. Use (USE) and Used For (UF) indicators are used when an authorized term is to be used for another, unauthorized, term; for example, the entry for the authorized term "Frequency" could have the indicator "UF Pitch". Reciprocally, the entry for the unauthorized term "Pitch" would have the indicator "USE Frequency".
The thesauri are managed by "TemaTres: controlled vocabulary server", a web application for the management of thesauri, developed by Diego Ferreyra (CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina).
Ontologies are used to encode science concepts, in a machine operational format, their associated properties, and their relationships to terms in related disciplines, thereby supporting interdisciplinary data integration. The EO and snow ontologies are being built using the Protégé software, developed by Stanford University, with a specific, custom made model and in OWL (Web Ontology Language) as requested by W3C standard. For the ontology

development we utilised a modular approach (considered as a best-practice in the semantic web methodology community) with classes and sub-classes (Krishna Sinha 2013).

FINDINGS AND CONCLUSIONS

Although our work is still in progress and will be developed during the i-CUPE project development, practical studies and comparison in other scientific and non scientific domains reveal that terminological tools integrated in a knowledge management system, help a virtuous data circle for users and providers. For example in the case of The Unified Astronomy Thesaurus (UAT) attempts to provide a highly structured controlled vocabulary has been proved relevant and useful across the entire discipline, regardless of content or platform (Accomazzi 2013). As for ontologies where: "standard ontologies and encodings can be used directly for science data, or can provide a bridge to specialized domain ontologies." (Richards 2017).
The growing need for sharing, discovering and retrieving satellite images and datasets for the study of the cryosphere will benefit from these tools which, if integrated into a system, will allow both the metadation of new data sets and objects and the use of objects and information in the different products as well. These tools will be useful also to create a conceptual "map" of a specific domain that will support the recovery of the data and the link to other existing ontologies such as the NASA SWEET ontology. Moreover the collaboration with the computer scientists will allow the creation of automatic and semi automatic systems that will be in favour of both of the discovery and of the interoperability of data and objects.

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IIA-CNR. Thesaurus Snowterm: http://vocabularyserver.com/cnr/ml/snowterm/en/index.php

100 YEARS LATER WWI: GEODATABASE AND GIS ON TOPONYMS ALONG THE ITALIAN FRONT

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Keywords: First World War, GIS, online GIS, geographical terminology, geodatabase

INTRODUCTION

The memory of historical events and the geographical knowledge linked to those events is quite often connected only to the most relevant among them and there is still a sort of uncertainty to fill (Baker 2003); year after year a lot of information vanishes leaving only a trace of the most meaningful places, the so called "places of memory". During the First World War (WWI) commemorations a renewed interest arose for places where WWI was fought from May 1915 until November 1918 by the Italian Army. Only a limited number of places have been raised to national symbols, while most of the others simply disappeared from the collective memory.

Geo-information role to preserve memories and to improve historical knowledge by means of geographical information is well acknowledged (Gregory, Healey, 2007). It could also enhance the comprehension of strategy, tactics and logistics helping to follow the trend of war events.

Traditionally WWI historical-geographical studies are performed accessing texts and maps with a limited use of computer technology. A validation of geographical content appears mandatory, in order to identify a specific place and its name on the modern official cartography.

It is commonly acknowledged in the geographical domain that the position of one place corresponds to a couple of coordinates.

This is certainly true in the majority of cases, but sometimes it occurs that the correspondence between a couple of geographical coordinates and one name is not univocal. Geographical searches are usually performed automatically making use of alpha-numerical (names) or numerical (geographical coordinates) input, and the conversion of a generic place name into geographic coordinates (geocoding) is a regular procedure (Melo *et al*. 2016). It is therefore mandatory to ascertain the direct correspondence between one name and one place.

Even if modern times brought new techniques for the production of maps, global positioning systems, geolocalisation, geodatabases, GIS and online GIS, etc. quite often there is a lack of connection with other technologies for the dissemination of historical-geographical information. All those tools and techniques represent undoubtedly an advantage even if the complete automatisation could create the risk to lose information. In wider terms, dealing with geographical information like searching for historical places is still a complex task, especially taking into consideration the chronological distance from the facts and the heterogeneity of the textual and cartographic sources, as well as not having a proper digital corpus or a local gazetteer (geographical dictionary) that can be accessed and searched on-line and is a valuable resource for the automatic search of toponyms (Goodchild & Hill 2008, Zhu *et al*. 2016).

In this perspective a research project was carried on aiming at developing a Geographic Information System to collect and preserve information about places where the Italian Army was involved in WWI events, making available this set of information to the public and for further uses.

After having analysed the historical information and extracted the geographical information from documents and maps, the system is designed to handle it in different layers taking into account the multi-temporal perspective.

Lacking a specific gazetteer, the search of correspondence between place names extracted directly from text and old maps, and their positioning on the territory was one of the major issues that arose during this study. In many cases the situation was particularly challenging due to the difficulty to find in present maps any trace of places destroyed, renamed or nowadays located in different nations.

METHODOLOGY

The WWI geographical information was manually extracted from more than 300 printed and online documents presenting a very abundant even if heterogeneous content.

In order to be able to compare the present situation with the former land setup, the 1:100000 Italian national territorial representation (1876-1900) has been used. Those maps referred to the Bessel ellipsoid oriented to the Navy Hydrographic Institute in Genua were compiled according to a polycentric natural Samson-Flamsteed projection.
Another useful set of maps is represented by the 1:100000 sheets of the "Grande Carta della Guerra Italiana", edited by the Italian Touring Club in 1915 and based on the cartographic products of the Italian Military Geographic Institute.
The Austro-Hungarian 1:75000 cartography, the *Spezialkarte der Österreichisch-Ungarischen Monarchie*, adopting a polyhedral projection referred to Bessel ellipsoid was also used.
Furthermore, approximately four hundred maps drawings and sketches edited during and after the war period to present times were collected and made use of.
Once converted into digital format to made it usable into the GIS this material created very often difficulties due to lacking information concerning scales, projection and North position. Therefore a specific work in order to harmonise different coordinate reference systems and scales, referring the whole dataset to the GIS project's reference WGS84 system was carried out.
The cartographic base adopted for the Italian territory by the official cartography WGS84/UTM of the Italian Military Geographic Institute (I.G.M.), scale 1:25000 and for the Slovenian territory by the official Slovenian cartography ETRS89 D96/TM in scale 1:50000, rescaled.
Within the GIS both official Italian and Slovenian maps together with other useful material such as aerial photos of the Italian territory were accessed through Web Map Service (WMS) from the Italian National Geo-portal. This approach allowed to dynamically display raster maps coherent with the adopted projection system.
In order to handle the collected WWI geographical data, a Geographical Information System (GIS) was implemented to guarantee an accurate positioning of every site, in each and every case. The project made use of open sources tools such as QGIS, MapServer and p.mapper.
The national administrative borders database (http://www.gadm.org/country) was downloaded as well as the OpenStreetMap database of places (Haklay, M. 2008) (http://download.geofabrik.de/). The resulting raw geodatabase contained around 70,000 records. Data were organised mainly in point layers even if a limited use of line and polygon layers have been represented into the system following the need to draw changes of the front lines during the war, drainage basins and national, regional and municipal borders.
The geodatabase was modified in order to handle all relevant information, both geographical and historical dealing with WWI place names (Jordan, 2009) retrieved from texts. In particular some additional columns were created dealing with administrative geography (province, region, state), physical geography (altitude) and history (name of the place during the war, typology and occurrence into official documents).
In addition, the different terminological occurrences of WWI place names and their linguistic equivalents in French, German and Slovenian and other languages were collected to ease the queries.
At the end of this process the correct name and its terminological variants were inserted in the geodatabase.
This approach made also possible to highlight the terminological aspects related to different forms of geographical names such as use, language, translation, and meaning. Identification of different terminological variants is crucial to guarantee accuracy, a key factors to obtain a fully searchable and acceptable geographic information.

FINDINGS

The geodatabase contains at present 10200 identified WWI toponyms, the majority of them spread within an area covering more than 50000 km^2 in the Italian, Slovenian, Austrian and, to a limited extent, French, Albanian and Macedonian territory. Toponyms are categorized in order to distinguish their typology related to physical or human geography and to civilian and military infrastructures.

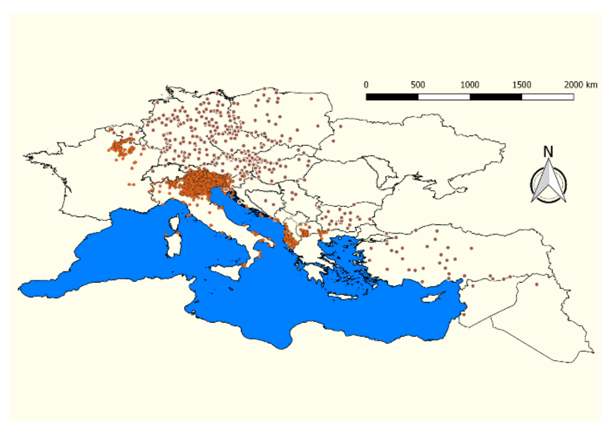

Figure 1. Area of study and the identified toponyms

Out of these identified places more than 3200 present at least one and up to six different variants (lexical, formal, linguistic, synonyms) totalling more than 16700 geographical alternative place names.
Lexical variants were subsequently organised as follows:

- Orthographic variants
    - Spacing and punctuation variants
    - Spelling variants
    - Omitted components
    - Orthographic errors
- Dialectical variants
- Translation equivalents
- Other name (civilian and military)

According to these terminological categories it is possible to notice that 52% of total amount of modified WWI place names belong to the class of orthographic variants, 34% are names that underwent historical changes, civilian and military, 9% can be attributed to translation equivalents and other than Italian languages and only 5% to dialectical variants.
Concerning the orthographic variants, the most relevant situations lead to formal variants where both names could be considered correct, to transcription errors, or to the use of forms that differ from the official ones. Moreover partial inversions, replacement of one or more letters and partial transliterations occurred quite often.
When the variants are related to different languages it is important to consider the borders variation before and after the war. These changes caused the need of handling names into three languages(Italian, German and Slovenian). The places located along the border between the Italian Kingdom and the Austro-Hungarian Empire are now mainly belonging to the territory of Italy and Slovenia.
Within the high number of accessed documents some places were named in different ways, some of them not classifiable as proper terminological variants, but as changes occurred for historical reasons.
Some toponyms were renamed during the war, mainly as a dedication to soldiers died in that place.
Other toponyms not having a name before the war, were given a name due to a specific reason occurred during the events.
In other cases the names were modified as results of successful war events.
Finally some places, mainly towns, changed their name years after the war with no connection with WWI.
Many homonyms were found. Since in many areas the places could present the same physical and/or historical features and quite often place names come from the geographical features that make them distinguishable and unique in a specific area, a specific analysis was required to disambiguate those cases.
A specific mention is due to the actual transcription errors where the form found into a document is not acceptable as one of the abovementioned cases.

CONCLUSIONS

A research project dealing with the detailed identification of places linked to WWI events is pretty unique on the international scenario. The work has been conducted without institutional commitments and does not take the cue uniquely from official documents whereas it was conducted analysing an heterogeneous collection of texts.
While collecting the WWI place names, it has been realised that quite often the name of one place was not univocally linked to geographic coordinates and one name not always led to one place. The different combination between toponyms and their position were faced and solved through the typical terminology manual approach, since the lack of a local gazetteer and of an actual digital corpus prevented from using automatic or semi-automatic tools, not suitable for this specific work. In fact the semi-automatic text analysis tools appears as not efficient enough to distinguish the differences in the geographic domain where multiple occurrences could be very frequent.
The analysis of the terminological forms of toponyms represents a huge improvement leading to a better, easier and more effective geographical search. In this work variants usually representing an obstacle during the search since they produce a noise level incompatible with the commonest tools such as search engines, provide conversely an extra value and an additional element to achieve positive results, also in terms of lexical richness of geographical names that are strictly connected both with geographical features and history of places.
Only 2% of identified places are still lacking of coordinates. The geographical/terminological component enriched the system with valuable hard-to-found information, usually disaggregated into a myriad of different textual and cartographic sources.
The dual point of view geographical and terminological leading to an analysis of names' variations, produced as a result the development and maintenance of a local specific gazetteer, where the above mentioned terms are listed, uniquely geolocalised and made available on the web through an online GIS (http://webgis.iia.cnr.it/GGGIS/)

The place names in this gazetteer are linked to geographical information in such a way that to each name now corresponds one and only one place and the name itself could be used while performing queries providing univocal and unambiguous results. After a four-years' work the online GIS appears as an effective tool able to provide precise and geographically coherent results. If compared with the pre-existing situation, it represents a turning point, able to contain all the collected information organised in a normalised format and allowing a controlled but flexible use.
Each one of the places currently available is endowed with historical and geographic additional information. This number will surely increase in future but it is sufficient to demonstrate how the territory was affected by WWI even if in some cases the only remnant of a place is represented by its name.

NOTE

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HYPERSPECTRAL IMAGING ANALYSIS FOR PE AND PVC SEPARATION

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Keywords: polypropylene, polyethylene, hyperspectral analysis, plastics

INTRODUCTION

The appropriate design of a product life cycle may contribute to the optimization of material reuses and the reduction of waste environmental impacts. Recycling improves the life cycle of plastics via the production of secondary raw materials and the reduction of toxic compounds in incinerator ash or waste extensive landfills disposal.
According to the Report “Plastics – the Facts 2017” from *PlasticsEurope*, in 2016 335 Mtons of plastics were produced worldwide and 60 Mtons in Europe. From 2006 to 2016 the volume of collected plastic waste increased by +11%, recycling by +79%, energy recovery by +61% while landfill decreased by -43%.
Though a consistent decrease in delivery of plastic materials in landfill has been observed in the last years, improvements in plastic recovery are still needed to reduce the disposal rate down to the goal of zero plastic wastes in landfills by 2020 in Europe.
The major Europe plastics converter demand in 2016 is represented by polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC). PE and PVC polymers represent the 39.8% of the European plastics converter demand. These categories of plastics are included in the “hard plastic” family such as polyethylene terephthalate (PET) and solid polystyrene (PS).
Traditional systems for plastic separation employ material physical properties such as density. In fact, due to the small their variability, the output quality may not be adequate enough.
The separation step can be challenging due to the similarities in physical properties between several categories of plastic polymers so traditional methodologies can be ineffective for plastic separation.
Among wet processes, sink and float separation is the most fundamental and mainly used for separating heavier- and lighter-than-water plastics. Selective flotation of different kinds of plastics can be attained by changing surface properties of plastics. Liquid-fluidized beds are another wet process allowing the separation of mixed heavier-than-water particles based on their density and size.
The electrostatic separation of solid particles prescribes the solids to be separated are first electrostatically charged in a suitable charging device and then fed into an electric field separator. Different type of plastics can then be separated from each other if they show a significant difference in their electron work functions (Yanar & Kwetkus, 1995).
Sensing technologies based on hyperspectral imaging appear suitable to separate materials (Moroni *et al*. 2015, Masoumi *et al*. 2012) and increase the quality of recycled products, which have to comply with specific standards determined by industrial applications.
Hyperspectral imaging system is based on the utilization of an integrated hardware and software architecture able to digitally capture and handle spectra, as an image sequence. The spectral information is contained in a 3D dataset, the “hypercube” (Serranti *et al* 2010).
This paper presents results of hyperspectral imaging application for polyethylene (PE) and polyvinyl chloride (PVC) separation in different stages of their life cycle (raw materials, waste and regenerate conditions). This is accomplished by the use of a NIR spectrometer allowing the comparisons between the spectral response of plastic materials.

METHODOLOGY

The hyperspectral platform

The hyperspectral method represents an alternative methodology to separate both different types of plastic polymers and contaminants from plastic wastes. This technology combines spectral reflectance measurements and image processing technologies. It is a low cost, reliable and fast method that allows overcoming the typical problems of the most used separation methods.

The laboratory equipment used in this study is composed by a linear spectrometer to investigate the NIR range of wavelengths (from 900 to 1700 nm). The NIR Specim Imspector spectrometer is centred in the near infrared region (from 900 nm to 1700 nm) and mounted in front of an InGaAs Sensor Unlimited camera, 320× 356 pixel resolution; the images presented are acquired at 50 fps and the spectral resolution is 3 nm.

The spectrometer captures a line image of a target and disperses the light from each line image pixel into a spectrum. A 2D spectral image sequence can be formed by sequentially acquiring images of a moving target.

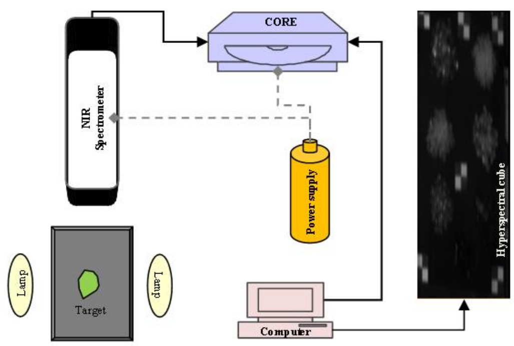

Figure 1. Diagram of the hyperspectral device

Tested samples

This paper presents the results of the analysis of 8 types of samples and the comparison of their spectral response measured via the platform based on hyperspectral imaging. For each sample 5 spectral signatures are extracted. Therefore, the dataset is composed by 50 samples. Those materials belong to different phases of a product life cycle and are represented as:

- Raw plastics in granules of virgin particles that represent the raw materials used to manufacture items.
- Plastic wastes in pieces and flakes from common post-consumer (urban and process) wastes.
- Secondary raw plastics of plastic waste partially recovered by simple steps such as washing and shredding.

FINDINGS

The characterization of the investigated materials requires several steps such as geometric and spectral calibration, imagery acquisition and processing, imagery enhancement quality, creation of hyperspectral cube, creation of spectral signature database.The reflectance (ρ) is therefore computed as: $\rho = (R-D)/(W-D)$, where R is the measured sample data, D is the dark current image and W is the white image captured from the Halon reference material. Figure 3, 4 and 5 shows the spectral responses of materials of different form and origin of the same base polymer.

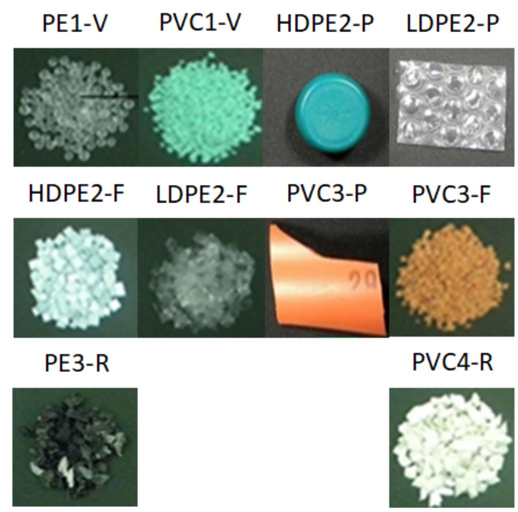

Figure 2. Plastics samples

Table 1. The plastic dataset

RAW PLASTICS IN GRANULES			
NAME	*DESCRIPTION*	*COLOR*	*DENSITY (g/cm^3)*
PE 1-V	Virgin particles	Transparent	0.93
PVC 1-V	Virgin particles	Green	1.37
PLASTIC WASTES IN FLAKES			
HDPE 2-F	Milk bottle	Grey	0.97
LDPE 2-F	Packaging film	Trasparent	0.88
PVC 2-F	Processing waste	Orange	1.61
PLASTIC WASTES IN PIECES			
HDPE 2-P	Milk bottle	Grey	0.97
LDPE 2P	Packaging film	Transparent	0.88
PVC 2-P	Processing waste	Orange	1.61
SECONDARY RAW PLASTICS IN FLAKES			
PE 3-R	recovered from waste	White/gray/bla ck	0.93
PVC 3-R	recovered from waste	White	1.44

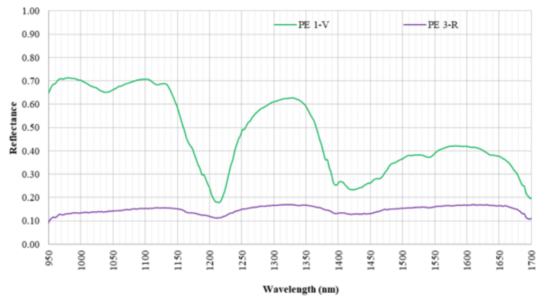

Figure 3. NIR spectral signatures of PE

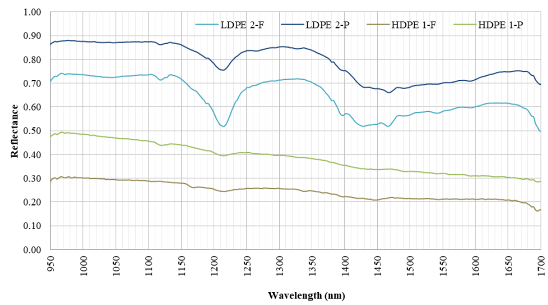

Figure 4. NIR spectral signatures of HDPE and LDPE

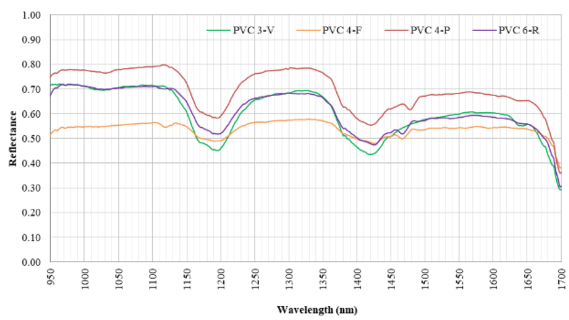

Figure 5. NIR spectral signatures of PVC

For each sample, spectral signatures are acquired in the wavelength range 900 nm - 1700 nm and results are shown in the figures reported below. The analysis shows the spectral responses of materials of different form and origin of the same base polymer.

The analysis of the spectral response shows several evidences. The spectral signature of virgin samples of PE shows evident absorption peaks at 1040nm, 1210-1220 nm, 1390-1400, 1420 nm and 1540nm. The regenerated material (secondary raw plastics) presents the same trend but peaks are less evident.

In order to study PE in flakes and pieces, samples are distinguished in LDPE and HDPE. LDPE shows evident peaks at 1120 nm, 1210-1220 nm, 1390-1400 nm and 1460-1470 nm. A slight peak at 1540 nm is observed for flakes. HDPE samples spectral signatures appear flat and show only a slight peak at 1220 nm. PVC virgin spectral signatures present absorption peaks at the wavelengths 1190-1200 nm, 1420 nm and 1640 nm. Flakes, pieces and regenerate plastics present, in addition to those mentioned above, a peak at 1120 nm and at 1470-1480 nm.

Analyzing the absorption peaks of the samples, peaks in the range 1190–1220 nm appear the most evident to characterize PE and PVC spectral signatures. The analysis of the shape of PE curves, in the range 1190 – 1210 nm reflectance values show decreasing values from 1220 nm to 1250 nm (peak at 1190 nm). Conversely, PVC signatures show decreasing values until 1190 nm while they increase until 1250 nm (peak at 1210 nm).

Using this different trend of the signatures, the spectral difference at R_{1190} and R_{1210} is applied to separate such polymers. By using this index, all samples of PE (included HDPE and LDPE) may be separated by PVC samples. In this process an accuracy of 100% is reached.

CONCLUSIONS

According to their spectral signature, the NIR region appears suitable to differentiate PE and PVC polymers.

The spectral difference from R_{1210} and R_{1190} makes it possible to optimize the differentiation of such polymers and could be used, also in combination with canonical system of plastic separation, to improve the efficiency of hard plastics separation.

In the next future the dataset will be implemented in order to investigate the efficiency of hyperspectral imaging.

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The Institute of Atmospheric Pollution Research of the CNR (Italy) held the Annual Conference on May 2018 in Montelibretti (Rome). The abstracts reported in this volume give an idea of how the Institute has evolved to meet the current challenges in atmospheric pollution research, the range of activities in which the Institute is involved, and demonstrate how these activities combine to produce research and innovation which is pertinent to current scientific questions, policy decisions and eventually the well-being of both the environment and society.

The Institute's involvement over the last ten years in European and International research programmes, its increasing role as a source of information and know-how to inform and advise on policy nationally and internationally is an evidence of the relevance of the Institute as a whole, and the quality and stature of the individuals whose daily efforts make it what it is.

__Nicola Pirrone__ has been Institute's Director of the CNR-IIA (www.iia.cnr.it) from October 2008 to June 2018. He is currently Research Director at the same institute and Adjunct Professor at the University of Michigan. During the last three decades he has been Principal Investigator of over 50 research projects funded by major European and international funding institutions (i.e., EC, USEPA, Italian Ministries of Research and Environment, World Bank, GEF, UNEP) and currently coordinates one of the leading European Programs on Earth Observation, the ERA-PLANET (www.era-planet.eu) that involves over 35 university and research institutions from 15 European Countries. During the last 25 years he had an active role as expert member / chair / head of Italian delegations in European, International and National programs and was part of European and international Task Forces related to different aspects of Earth Observation, Environmental Research, Environmental Policy development and Evaluation of research strategies in EU and abroad. He is currently the chair of the GEO Flagship "Global Observation System for Mercury – GOS4M" (www.gos4m.org), the GEO Principal of Italy (www.geoitaly.org), and Chair of the UNEP Global F&T Partnership. In 2017 he was designated by the Presidency of European Union as European Representative in the ad-hoc group on Effectiveness Evaluation of the Minamata Convention.

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