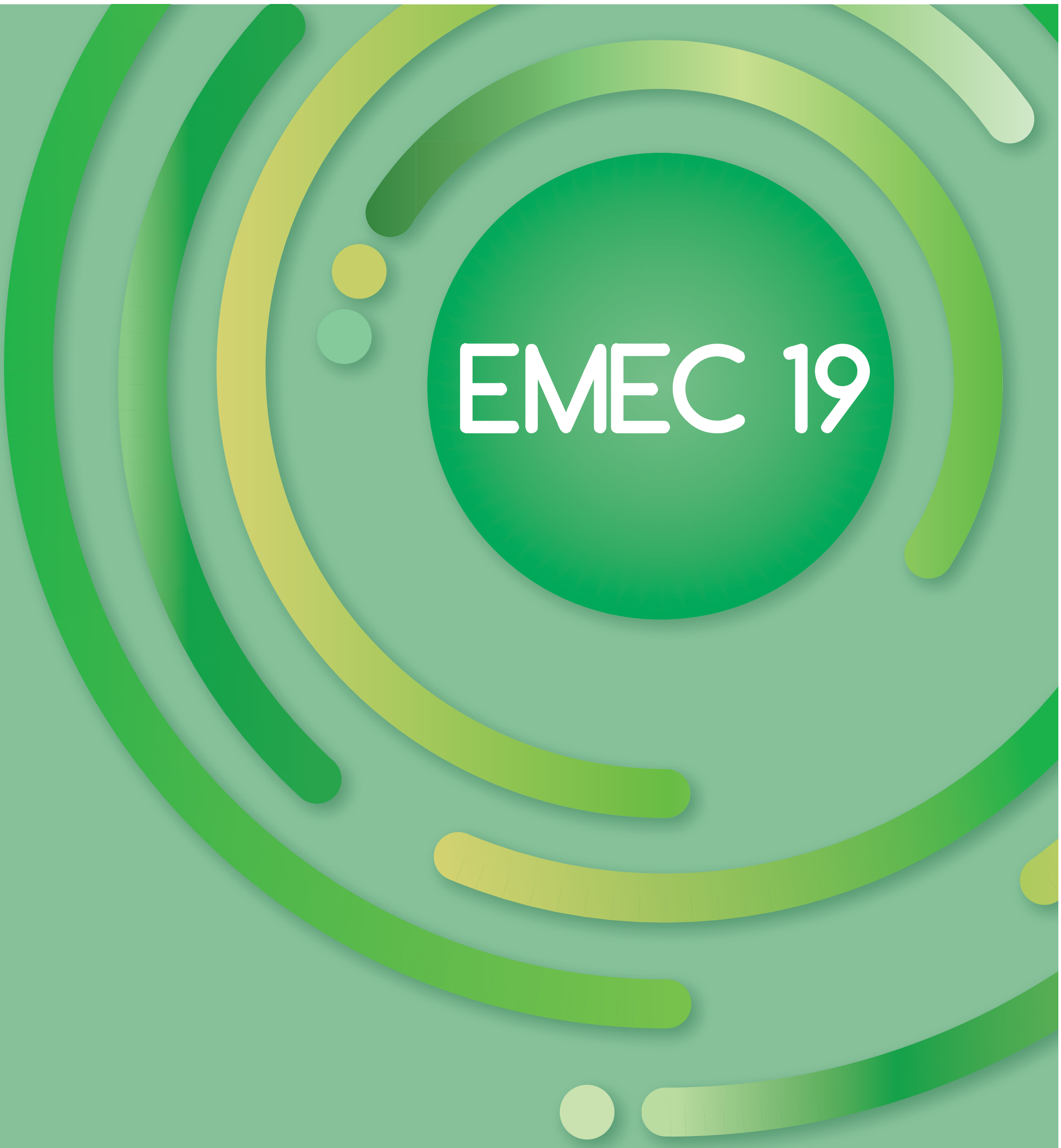

EMEC 19

PROGRAM BOOK

19th European Meeting on Environmental Chemistry

3-6 december 2018 Royat - France

Association of Chemistry and the Environment

Institut de Chimie de Clermont-Ferrand

Contents:

WELCOME

On the behalf of the organizing committee, it is my great pleasure to welcome you to Clermont-Ferrand/Royat in France for the 19th European Meeting on Environmental Chemistry (EMEC 19).
The conference is organized by the Institute of Chemistry of Clermont-Ferrand (ICCF) from the Clermont Auvergne University/CNRS/Sigma-Clermont, on behalf of the Association of Chemistry and the Environment (ACE).

The main objectives of this conference are to bring together scientists working in the field of environmental chemistry, to report the most advanced research progress in this research field, and to pave the way for future research and challenges.
EMEC 19 covers a broad range of topics within the field of environmental chemistry including:

- **Sustainable chemistry** (new compounds, green processes)
- **Environmental compartments** (atmosphere, soils, marine and surface waters) with a focus on **monitoring, processes** (biological and chemical), **remediation and ecotoxicology**
- **Methodology and modeling.**

In addition to the scientific program, a full **social program** has been organized: A guided tour will allow you to discover the rich history of Clermont-Ferrand. In parallel, we organize a short film presentation to pay tribute to Clermont-Ferrand as the host of the renowned annual International Short Film Festival. A gala dinner and a welcome party at the City Hall will complete this social program.

I wish you very pleasant and rich moments together.

Dr Anne-Marie Delort, Chair of the EMEC19 conference

COMMITEES

Organizing committee

Pierre AMATO, ICCF, Clermont-Ferrand, France
Karine BALLERAT, ICCF, Clermont-Ferrand, France
Angelica BIANCO, LaMP/OPGC, Clermont-Ferrand, France
Pascale BESSE-HOGGAN, ICCF, Clermont-Ferrand, France
Stéphanie BONNEFOY, ICCF, Clermont-Ferrand, France
Marcello BRIGANTE, ICCF, Clermont-Ferrand, France
Anne-Marie DELORT, ICCF, Clermont-Ferrand, France
Clément DESCARPENTRIES, ICCF, Clermont-Ferrand, France
Hani FARHAT, ICCF, Clermont-Ferrand, France
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Mohamad SLEIMAN, ICCF, Clermont-Ferrand, France
Aurélie VIOLETTE, ICCF, Clermont-Ferrand, France

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Margarida COSTA-GOMES, ICCF, Clermont-Ferrand, France
Anne-Marie DELORT, ICCF, Clermont-Ferrand, France
Barbara ERVENS, NOAA, USA, ICCF, Clermont-Ferrand, France
Claude FORANO, ICCF, Clermont-Ferrand, France
Albert LEBEDEV, Moscow University, Russia
Jan SCHWARZBAUER, Aachen University, Germany
Davide VIONE, University of Turin, Italy
Hans Christian Bruun HANSEN, Copenhaguen University, Denmark

ASSOCIATION OF
CHEMISTRY AND THE
ENVIRONMENT

The Association of Chemistry and the Environment (ACE) is a non-profit-making scientific association founded in October 2000 by a group of European scientists. We aim to promote global contact between scientists in academia and research institutes, the commercial sector and social representatives within governmental and regulatory bodies to address environmental problems and to promote education in this area.

We strongly welcome scientists from diverse fields such as atmosphere science, biology, geology, industrial chemistry, medicine, sociology, soil science, toxicology and water science to play an active role within the organisation.

http://www.europeanace.com/

Université Clermont Auvergne

Institut de Chimie de Clermont-Ferrand

The Institute of Chemistry of Clermont-Ferrand (ICCF, Université Clermont Auvergne, CNRS, SIGMA Clermont) brings together 250 people organized in six teams of disciplinary chemistry and five technical administrative and scientific platforms to form the basis of the academic research in chemistry of Clermont-Ferrand.

ICCF focuses its research efforts on the urgent issues that civil society poses to chemists. Its assets lie in the broad spectrum of its research activities such as inorganic materials, thermodynamics and molecular interactions, photochemistry, materials for health, biocatalysis and metabolism, and organic and medicinal chemistry.

ICCF is also organized in three transverse projects with high social impacts: “Chemistry and Environment”, “Chemistry and Life Sciences”, “Chemistry and Materials”.

In the field of environmental chemistry, interdisciplinary topics concern:

- **Sustainable chemistry (green processes)**
- **Bio-physico-chemistry of the atmosphere**
- **Fate of contaminants in the environment (soil, water, plants)**

Chemists in ICCF actively contribute to the activities of the Federation of Research in Environment (FRE) of Clermont-Ferrand.

Contacts : Director : Fabrice Leroux ; Vice-Director : Laurence Hecquet ;
tel : +33 - (0)473407125 ; web : http://iccf.univ-bpclermont.fr/

Federation of Research in Environment (FRE)

The FRE is a research structure that federates all Clermont-Ferrand researchers who develop research activities related to regional environmental and economic issues. Indeed, FRE brings together more than 500 people belonging to 16 research laboratories (all associated with CNRS, INRA or IRSTEA) with a large multidisciplinary research. FRE is labelled by the Ministry of Research and Higher Education, CNRS FR 3467 and INRA.

The research activities of FRE are all in connection with the general concept of sustainable development. In this context, the preservation and management of natural resources are the main concerns of environmental problematic of sustainable development. These preservation and management activities need a deep knowledge of fundamental processes which govern natural ecosystems and the agroecosystems functioning but also to estimate the answers of these systems in front of global changes and anthropic pressure.

The scientific objectives are focused around three questions. “What are the interactions between global change and functioning of these environmental systems? What processes of mitigation and of management of associated risks have to be set up? What will be the impacts on provided services and generated products by these environmental systems?

The research program is structured in three main themes in which were identified multidisciplinary research projects involving several teams. The various studied systems are gathered into two themes with different ends but highly complementary: (1) aquatic and atmospheric compartments with a purpose more specifically of management and protection and (2) the agro-ecosystems with a purpose centered on the sustainable production. The third theme is dedicated to the modelling of these systems until the production of scenarios integrating results obtained in the two first themes.

Contacts: Gilles MAILHOT (director) - gilles.mailhot@uca.fr, Tel 04 73 40 71 73 Jean-Louis JULIEN (vice-director) – j-louis.julien@uca.fr, Tel 04 73 40 79 24
Web site: http://www.recherche-environnement.univ-bpclermont.fr/wp/

The Clermont Auvergne project : I-Site CAP 20-25

The I-Site label: a mark of excellence

The I-Site label (**I**nitiative – **S**cience - **I**nnovation - **T**erritory - **E**conomy ») from the Investment for the Future program fosters the restructuring of French university sites through a dynamic of excellence: in all, only 18 universities have earned and retained a IDEX or I-SITE label since the establishment of the program in 2011.

The Clermont Auvergne Project: four key ambitions

➢ Scientific

The CAP 20-25 project aims to contribute in a significant way to scientific, technological, environmental and behavioral developments essential to designing "**models for sustainable production and living**". It identifies four main areas of research (so-called "Challenges") related to the region's scientific and economic strengths: **agriculture**, **industry**, **health** and **environment**. Each of these areas of research implements a multi-modal innovation strategy combining multidisciplinary approach, multi-stakeholder partnerships and multiple performances. Supporting cross-disciplinary programs such as **instrumental development and exploratory research** back these four topics.

➢ International

The CAP 20-25 project aims to create a research university with **high international visibility** in the western part of the Auvergne-Rhône-Alpes region, complementing university centers in Lyon and Grenoble. A dedicated program, “WOW! Wide Open to the World”, develops tailor-made tools in order to achieve this ambition.

➢ Regional

Thanks to the involvement of all regional stakeholders - higher education and research, local communities such as Clermont Auvergne Métropole and the Auvergne-Rhône-Alps region, as well as companies - CAP 20-25 promotes the **excellence of public research** in Clermont paired with the **best of private innovation** of major industrial partners, like Michelin and Limagrain, but also of the dynamic network of SMEs. Thus, the project participates in **expressing and strengthening the identity and attractiveness of Auvergne region**.

➢ Cross-cutting

Each challenge involves stakeholders of the socio-economic world in its work (public/private partnerships, shared structures, etc.). Cross-disciplinary measures such as the **Talent Policy**, **support for innovation**, **campus life**, **international promotion** and **teaching innovation** support this approach of scientific excellence by enhancing the site’s attractiveness.

http://cap2025.fr/en/

i_site_clermont

Prince Sultan Bin Abdulaziz International Prize for Water

Recognizing Innovation

Winners for the 8th Award (2018)

Creativity Prize

The Prize is awarded to two teams of researchers:

1) Dr. Andre Geim and Dr. Rahul Nair (National Graphene Institute, University of Manchester, UK)
for developing novel graphene oxide membranes that promise to enable energy-efficient and high-volume water filtration and desalination.

Dr. Andre Geim
Dr. Rahul Nair

2) Dr. Günter Blöschl (TU Wien, Austria) and Dr. Murugesu Sivapalan (University of Illinois at Urbana-Champaign, USA)
for developing the new field of Sociohydrology, a ground-breaking paradigm for water management and a new validated approach for studying the dynamic interactions and bi-directional feedbacks between water systems and people.

Dr. Günter Blöschl
Dr. Murugesu Sivapalan

Surface Water Prize

Dr. Wilfried Brutsaert (Cornell University, USA)
for developing, demonstrating, and validating a new theory that can generate unprecedented estimates of evaporation from the natural landscape.

Dr. Wilfried Brutsaert

Groundwater Prize

Dr. Martinus Th. van Genuchten (Federal University of Rio de Janeiro, Brazil)
for the development and application of key theoretical and software tools that describe water flow and contaminant transport in the subsurface.

Dr. Martinus van Genuchten

Alternative Water Resources Prize

Dr. Omar Yaghi (University of California, Berkeley, USA) and Dr. Evelyn Wang (Massachusetts Institute of Technology, USA)
for creating a solar-powered device that uses an innovative porous metal-organic framework (MOF) to capture water from the atmosphere.

Dr. Omar Yaghi
Dr. Evelyn Wang

Water Management and Protection Prize

Dr. Jim W. Hall and Dr. Edoardo Borgomeo (Environmental Change Institute, Oxford University, UK)
for developing and applying a new risk-based framework to assess water security and plan water supply infrastructure in times of climate change.

Dr. Jim W. Hall
Dr. Edoardo Borgomeo

Nominations are open for the 9th Award. Nominations can be made online until 31 December 2019.

www.psipw.org
email: info@psipw.org

valoriser & préserver

Since 1976, MS has been innovating and offering solutions to preserve water - the most consumed resource in the world after air - and sustain natural resources.

In the field of water treatment specifically, in collaboration with the CNRS and ICCF, MS has developed an innovative and single patented process for the treatment of chromium 6 and total chromium in wastewater, coming from concrete manufacturing units.

In addition to the equipment that remains essential, we provide bold and innovative solutions, highly service-oriented, at the right price, in order to contribute to sustainable constructions that always creates value. Tomorrow, we will build better !

Malvern Panalytical est l'un des principaux fournisseurs d'instrumentation scientifique pour la recherche et pour l'industrie.
Les technologies Malvern Panalytical sont utilisées par des scientifiques et des ingénieurs dans un large éventail d'industries et d'organisations pour résoudre les défis associés à l'optimisation de la productivité, au développement de produits de meilleure qualité. Notre objectif est de créer des solutions et des services innovants et orientés client afin d'améliorer l'efficacité et d'obtenir un impact économique tangible grâce à l'analyse physique, chimique et structurale des matériaux.

Nos technologies permettent de mesurer des paramètres tels que la forme, la taille et la concentration des particules, l'identité chimique, le potentiel zêta, la charge de protéines, le poids, la masse et la conformation moléculaire, les interactions et la stabilité biomoléculaires, les propriétés rhéologiques, les concentrations élémentaires et les structures cristallographiques. Il est fondamental de caractériser de façon pertinente et fiable ces propriétés pour prédire la façon dont un produit va se comporter pendant son utilisation, et pour optimiser ses performances et atteindre l'excellence en matière de fabrication.

La société Malvern Panalytical est née de la fusion de Malvern Instruments Limited et de PANalytical B.V. Elle dispose de sièges sociaux à Almelo (Pays-Bas) et à Malvern (Royaume-Uni) et emploie plus de 2 000 personnes dans le monde. Cette fusion fait de Malvern Panalytical un acteur important et novateur sur le marché de la caractérisation des matériaux et permet d'exploiter les forces de chaque entreprise sur leurs marchés finaux, allant des matériaux de construction aux produits pharmaceutiques en passant par les métaux, les produits miniers et les nanomatériaux. Forts de la présence de laboratoires d'applications et d'oganisations de vente et de service dans le monde entier soutenus par un important réseau de distributeurs, nous sommes en mesure d'offrir un support à la clientèle d'un niveau inégalé.

Malvern Panalytical fait partie de Spectris plc, fournisseur de dispositifs de contrôle et d'instruments visant à améliorer la productivité

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métropole

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Société Chimique de France
Le réseau des chimistes

MICHELIN

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Delivering the Right Results

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CEM

SHIMADZU

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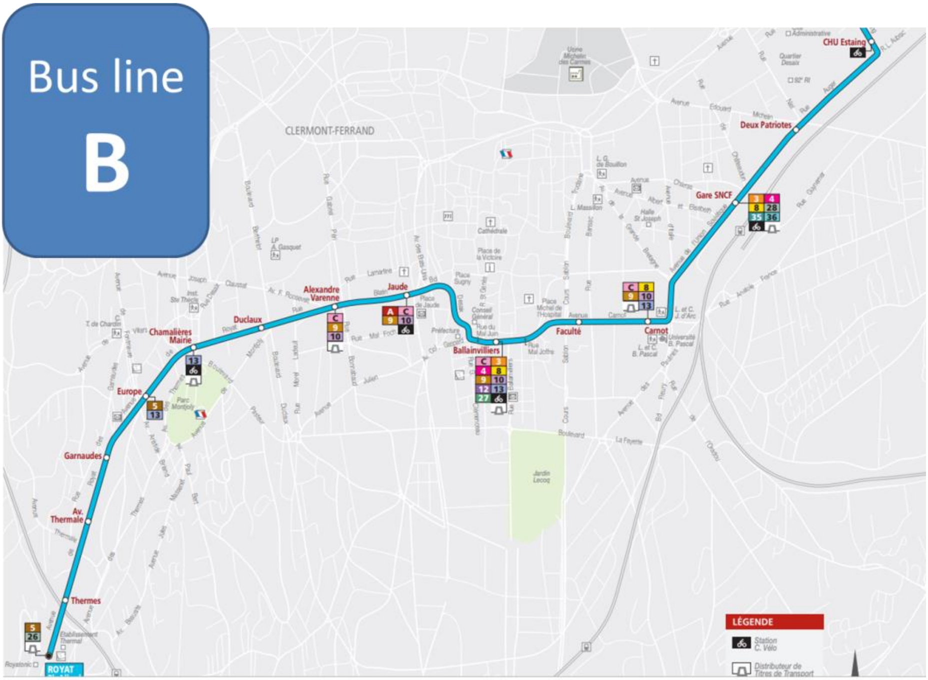
EAU MINÉRALE
NATURELLE

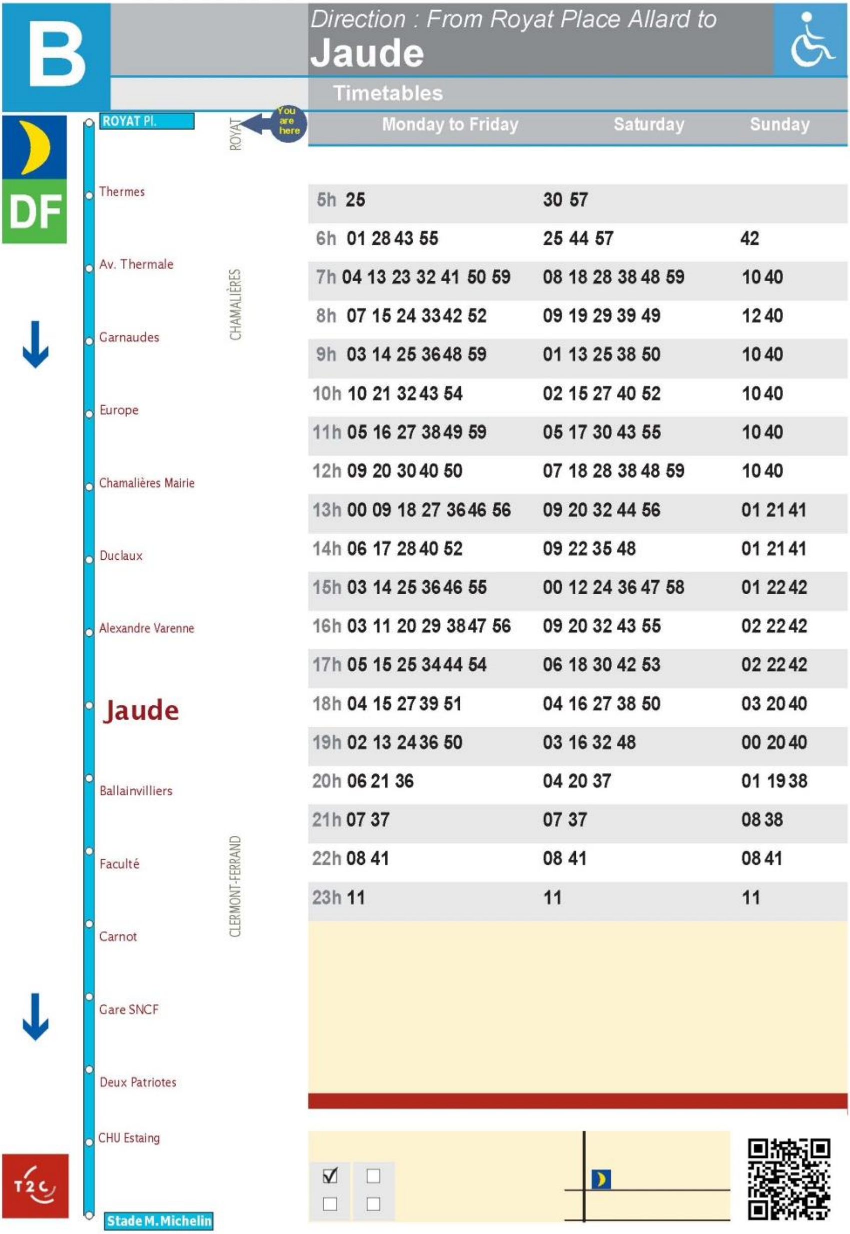
valoriser & préserver

Prince Sultan Bin Abdulaziz
International Prize for Water

Bus line B


Bus line
B
CLERMONT-FERRAND
CHU Estaing
Deux Patriotes
Gare SNCF
Carnot
Faculté
Ballainvilliers
Jaude
Alexandre Varenne
Duclaux
Chamalières Mairie
Europe
Garnaudes
Av. Thermale
Thermes
ROYAT
Jardin Lecoq
Parc Montjoly
LÉGENDE
Station C. Vélo
Distributeur de Titres de Transport

Bus schedule



Direction : From Royat Place Allard to
Jaude

Timetables

ROYAT Pl.
Thermes
Av. Thermale
Garnaudes
Europe
Chamalières Mairie
Duclaux
Alexandre Varenne
Jaude
Ballainvilliers
Faculté
Carnot
Gare SNCF
Deux Patriotes
CHU Estaing
Stade M.Michelin

	Monday to Friday	Saturday	Sunday
5h	25	30 57	
6h	01 28 43 55	25 44 57	42
7h	04 13 23 32 41 50 59	08 18 28 38 48 59	10 40
8h	07 15 24 33 42 52	09 19 29 39 49	12 40
9h	03 14 25 36 48 59	01 13 25 38 50	10 40
10h	10 21 32 43 54	02 15 27 40 52	10 40
11h	05 16 27 38 49 59	05 17 30 43 55	10 40
12h	09 20 30 40 50	07 18 28 38 48 59	10 40
13h	00 09 18 27 36 46 56	09 20 32 44 56	01 21 41
14h	06 17 28 40 52	09 22 35 48	01 21 41
15h	03 14 25 36 46 55	00 12 24 36 47 58	01 22 42
16h	03 11 20 29 38 47 56	09 20 32 43 55	02 22 42
17h	05 15 25 34 44 54	06 18 30 42 53	02 22 42
18h	04 15 27 39 51	04 16 27 38 50	03 20 40
19h	02 13 24 36 50	03 16 32 48	00 20 40
20h	06 21 36	04 20 37	01 19 38
21h	07 37	07 37	08 38
22h	08 41	08 41	08 41
23h	11	11	11

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☐ ☐

B

Direction : From Jaude

ROYAT Pl. Allard

Timetables

DF

Stade M. Michelin
CHU Estaing
Deux Patriotes
Gare SNCF
Carnot
Faculté
Ballainvilliers
Jaude ← You are here
Alexandre Varenne
Duclaux
CLERMONT-FERRAND

Chamalières Mairie
Europe
Garnaudes
Av. Thermale
Thermes
CHAMALIÈRES

ROYAT Pl.
ROYAT

	Monday to Friday	Saturday	Sunday
5h	46	41	
6h	14 27 38 47 57	10 29 42 52	49
7h	08 19 29 40 49 56	02 12 22 31 41 52	18 49
8h	05 14 24 34 44 55	01 11 21 32 44 55	21 52
9h	06 17 29 40 51	07 19 31 43 55	21 50
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11h	08 19 30 41 51	11 23 35 47 59	19 49
12h	01 11 20 28 38 48 57	10 19 29 39 49	19 44
13h	08 18 28 38 48 58	01 13 26 38 50	05 23 44
14h	07 16 26 34 44 55	03 16 29 41 53	05 25 44
15h	06 17 28 40 51	06 17 28 39 50	04 24 44
16h	00 09 18 27 36 46 56	01 13 24 35 46 58	04 24 44
17h	05 12 20 30 41 50 59	10 22 33 44 56	04 25 45
18h	08 19 31 43 54	07 19 30 41 52	04 23 43
19h	04 15 26 37 51	02 13 24 35 47	02 24 39 57
20h	05 17 30 48	01 14 29 48	22 48
21h	18 48	18 48	18 48
22h	18 51	18 51	18 51
23h	21	21	21

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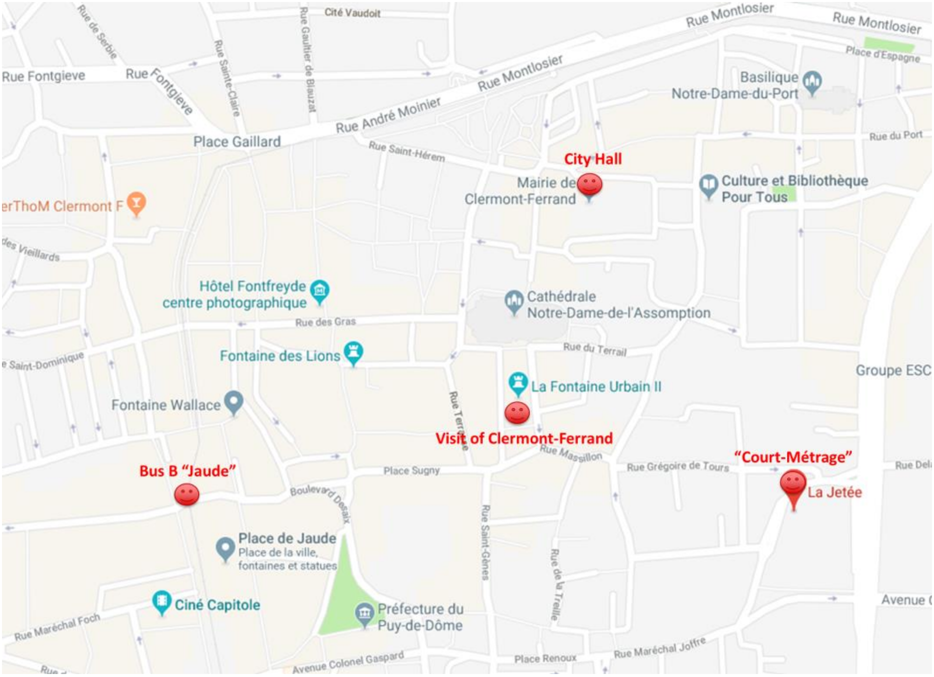
☑ ☐

City map


City Hall
Visit of Clermont-Ferrand
Bus B "Jaude"
"Court-Métrage"
La Jetée
Mairie de Clermont-Ferrand
Basilique Notre-Dame-du-Port
Culture et Bibliothèque Pour Tous
Cathédrale Notre-Dame-de-l'Assomption
Hôtel Fontfreyde centre photographique
Fontaine des Lions
Fontaine Wallace
La Fontaine Urbain II
Place de Jaude
Ciné Capitole
Préfecture du Puy-de-Dôme
Place Gaillard
Rue Montlosier
Rue André Moinier
Rue Fontgieve
Place Sugny
Groupe ESC

Car park

The "**Parking du Casino**" will be open.
For "**Parking St Victor**", you will have to take a ticket first, then you will be provided with a countercheck mark at the registration of the conference for gratuity.

Coordonnées GPS :Longitude 3.05766463 Latitude : 45.7678672
Arrivée de Paris-Bourges par la A71, sortie 15, direction Royat Chamalières.

Arrivée de Lyon / Saint-Etienne par la A72 ou Montpellier par la A75. Rejoindre la A71 (Paris) jusqu'à la sortie 15, direction Royat Chamalières.

Arrivée de Riom par RN9 : Direction Tulle-Bordeaux Chamalières-Royat.

Arrivée de Bordeaux / Tulle par la RN89 : Au lieu-dit "Les 4 routes de Nébouzat", prendre la direction "Puy de Dôme - Orcines" par le col de la Moreno, au lieu-dit "La Font de l'Arbre", prendre la direction de Royat-Chamalières.

Arrivée de Limoges / Aubusson par la D941 : Après le panneau Clermont-Ferrand, suivre la direction Royat (1ère à droite).

PROGRAM

➢ Monday December 3rd 2018: first day

17:00 – 20:00: *Welcome registration*

➢ Thursday December 4th 2018: second day

7:30 – 8:30: *Welcome - registration*
8:30 – 9:30: *Opening ceremony*

Session 1 Substainable chemistry (*Chairs: K.* ***De Oliveira-Vigier****, N.* ***Ratola)***

9:30 – 10:15: Plenary lecture (PL1):
Karine DE OLIVEIRA VIGIER **"Catalytic Conversion of Carbohydrates to Value Added Chemicals: Alternative Solvents and technologies**

10:15 – 10:45: *Coffee / Posters*

10:45 – 11:00: Oral presentation (O1):
V. Prévot*, R. Borges, F. Wypych, C. Forano*
Slow-released K/PO4 fertilizers based on mechanochemically activated clay minerals

11:00 – 11:15: Oral presentation (O2):
B. Eyheraguibel, ***M. Brissy****, B. Dieme, M. Leremboure, A-M. Delort*
Plastic biodegradation: Focus on the methodology to study this unknown process

11:15 – 11:30: Oral presentation (O3):
C. Bastos, S.F. Carvalho, A.B. Pereiro, ***J.M.M. Araújo***
The different faces of functionalized ionic liquids and deep eutectic solvents: From extraction/purification to drug development

11:30 – 11:45: Oral presentation (O4):
A. Amelio, ***A. Bianco Prevot****, P. Calza. M. Costamagna, G. Magnacca, M. Sangermano*
Use of hybrid material waste-derived organic substances/magnetite for sustainable water treatment: a Life Cycle Assessment case study

11:45 – 12:00:	Oral presentation (O5): *M. Doumas, A. Dupuis, M. Albouy-Llaty, N. Venisse, P.P. Eugene, M. Munier, P. Sibilia, P. Rodien, Y. Deceuninck, E. Bichon, B. Veyrand, P. Marchand, B. Le Bizec, V. Migeot,* ***P. Carato*** Synthesis and biological evaluation of halogenoBisphenol A derivatives
12:00 – 12:15:	Oral presentation (O6): ***N. Dulova****, B. Kaur, E. Kattel, M. Trapido* Activated persulfate processes for degradation of endocrine disrupting compound nonylphenol in aqueous matrices
12:15 – 12:30:	Oral presentation (O7): ***N. P.F Gonçalves****, M. Minella, D. Fabbri, P. Calza, A. Bianco Prevot* Humic acid coated magnetic nanoparticles as highly efficient heterogeneous photo-fenton materials for wastewater treatments
12:30 – 12:45:	Oral presentation (O8): ***S. Pap****, M.A. Taggart, S.W. Gibb, M. Turk Sekulic* Insights regarding the adsorption mechanism of pharmaceuticals onto phosphor doped carbonous material
13:00 – 14:00:	*Lunch*
14:00 – 14:15:	Oral presentation (O9): ***N. S. M. Vieira****, A. L. S. Oliveira, J. M. M. Araújo, L. P. N. Rebelo, A. B. Pereiro* Biocompatible fluorinated ionic liquid on the development of new "Green" tools for pharmaceutical industry
14:15 – 14:30:	Oral presentation (O10): ***D. Blanc****, O. Hammoud, M. Lupsea-Toader, M.L. Gonzalez, C. de Brauer* Technical and environmental assessment of reuse of Waste-to-Energy - Bottom Ash (WtE-BA) in construction products

14:30 – 14:45: Oral presentation (O11):
*M. Kania, **M. Gautier**, P. Jame, J. Liu, R. Guégan, R. Gourdon*
Use of analytical indicators to evaluate the quality of surface sludge deposits in vertical flow constructed wetlands treating wastewaters

14:45 – 15:00: Oral presentation (O12):
***L. F. Lepre**, D. Andre, A. Gautier,G. Mailhot, A. Padua, M. Costa Gomes*
Fluorinated ionic liquids for selectively absorbing refrigerant gases

15:00 – 15:15: Oral presentation (O13):
***M. Brumovský**, P. Andrýsková, T. Reichenauer, O. Sracek, J. Filip, R. Zbořil*
Controlled sulfidation of zero-valent iron nanoparticles prepared using hydrogen reduction: Towards enhanced TCE dechlorination on a large-scale

Session 2 Atmosphere *(Chairs: F. Keppler, A. Bianco)*

15:15 – 16:00: Plenary lecture (PL2):
Frank KEPPLER
"The global chloromethane cycle"

16:00 – 16:30: *Coffee / Posters*

16:30 – 16:45: Oral presentation (O14):
***P. Amato**, M. Sancelme, L. Deguillaume, A.-M. Delort*
Current knowledge about microbiological impacts on atmospheric chemistry

16:45 – 17:00: Oral presentation (O15):
***A. Bianco**, L. Deguillaume, M. Vaïtilingom, N. Chaumerliac, A-M. Delort, M. Bridoux*
Effect of endogenous microbiota on the molecular composition of cloud water: a study by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

17:00 – 17:15: Oral presentation (O16):
***J. Kammer**, C. Décuq, F. Lafouge, R. Ciuraru, V. Gros, B. Loubet*
Characterization of gaseous pollutant emissions from a typical French farm

17:15 – 17:30: Oral presentation (O17):
A.T. Lebedev*, O.V. Polyakova, V.B. Artaev, F. Cereceda, V. Vidal, K. Gonzalez Arancibia*
Chilean rain. Changes in composition and levels of emergency contaminants during fifteen years

17:30 – 17:45: Oral presentation (O18):
D. Mazur*, E. Detenchuk, A. Studenikina, A. Sarycheva, O. Polyakova, V. Artaev, A. Lebedev*
Distribution of semi volatile pollutants in the Moscow city area in the winter of 2018

19:30 *City Hall reception*

➢ Wednesday December 5th 2018: third day

8:00 – 8:30: *Registration*

Session 3 Soil and Sediments *(Chairs: A.E. Rosenbom, P. Besse-Hoggan)*

8:30 – 9:15: Plenary lecture (PL3):
Annette Elisabeth ROSENBOM
"Detailed pesticide fate descriptions and realistic hydrogeological settings applied in the pesticide leaching risk assessment for clay till fields"

9:15 – 9:30: Oral presentation (O19):
J.-Y. Cornu*, S. Randriamamonjy, M. Gutierez, K. Rocco, T. Lebeau*
Can the addition of bacterial siderophores help in the phytoextraction of Cu from vineyard topsoils?

9:30 – 9:45: Oral presentation (O20):
C. Forano*, M. Wang, L. Frezet, A. Bouakline, T. Alekseeva, D. Pinsky, M. Sancelme, P. Besse-Hoggan*
Effect of Cu^{2+}-contaminated soils on the biodegradation of the herbicide mesotrione by *bacillus megaterium* Mes11

9:45 – 10:00: Oral presentation (O21):
T. Grubar, D. Leštan, S. Gluhar, ***H. Prosen***
Monitoring of pesticide dissipation in remediated soil

10:00 – 10:15: Oral presentation (O22):
***N. Layglon**, N. Doumandji, S. D'onofrio, G. Durrieu, V. Lenoble, S. Mounier, B. Misson, D. Omanovic, C. Garnier*
Mobility of trace elements during laboratory resuspension experiment

10:15 – 10:45: *Coffee / Posters*

10:45 – 11:00: Oral presentation (O23):
***K. Mbusnum-Gweth**, L. Mailleret, P. Deschamps, I. Khabouchi, L. Asia, S. Lebarillier, G. Menot, Y. Garcin, R. Onguene, P. Doumenq*
Persisitent Organic Pollutants (POPs) in sediments from the Wouri Estuary Mangrove, Cameroon: Levels, patterns and ecotoxicological significance

11:00 – 11:15: Oral presentation (O24):
Y. Mishael
Micro-structural changes in soils induced by wetting and drying: Effects on herbicide mobility

11:15 – 11:30: Oral presentation (O25):
***J. Schwarzbauer**, L. Hagemann, M. Buchty-Lemke, A. Maas, H. Schüttrumpf, F. Lehmkuhl*
Geochemical footprints of human activity in low-order stream floodplains

11:30 – 11:45: Oral presentation (O26):
***Y. Tao**, H. Zhang, M. Brigante, G. Mailhot*
UVB activation of persulfate *vs* Hydrogen peroxide for soil washing effluent treatment: Efficiency, effect of various soil constituents and mechanism

12:00 – 13:00: *Lunch*

13:00 – 15:00: *Poster session / Photo*

Social events:
16:30 – 18:30: *Short films*
16:30 – 18:30: *Guided tour of Clermont-Ferrand*

20:00: *Gala diner*

➢ Thursday December 6th 2018: fourth day

Session 4 Waters *(Chairs: J.A. Sanchez-Perez, C. Richard)*

8:30 – 9:15: Plenary lecture (PL4):
José Antonio SANCHEZ PEREZ
"Solar photo-Fenton as a tertiary wastewater treatment. From mechanisms to reactor design"

9:15 – 9:30: ***D. Jalajel***
The Prince Sultan Bin Abdulaziz International Prize for Water: Recognizing Innovation

9:30 – 9:45: Oral presentation (O27):
L. Carena*, S. Berto, F. Valmacco, C. Barolo, E. Conca, D. Vione, R. Buscaino, M. Fiorito, C. Bussi, O. Abollino, M. Malandrino*
Acetaminophen monitoring in surface waters and assessment of its photochemical reactivity by an electrochemical sensor

9:45 – 10:00: Oral presentation (O28):
M. Godéré*, L. Malleret, A. Austruy, L. Asia, J. L. Boudenne, P. Doumenq*
Halogenated hydrophobic contaminants in a coastal industrialized area: Comparing passive samplers' accumulation to concentrations in waters, sediments and mussels

10:00 – 10:15: Oral presentation (O29):
V. Romanucci*, G. Di Fabio, G. Luongo, A. De Marco, A. Zarrelli*
Disinfection in wastewater treatment plants: isolation and characterization of tramadol parent by products and evaluation of their toxicity

10:15 – 10:45: *Coffee break*

10:45 – 11:00: Oral presentation (O30):
P. Trebše*, E.A. Detenchuk, S.A.Pokryshkin, O.V.Polyakova, V.B.Artaev, A.T.Lebedev*
The influence of inorganic salts on the formation of disinfection by-products during aquatic chlorination of UV-filter avobenzone

11:00 – 11:15: Oral presentation (O31):
***P. Venska**, M. Vavrova, M. Repkova*
Psychoactive pharmaceuticals in the aquatic environment

11:15 – 11:30: Oral presentation (O32):
M. Yassine, L. Fuster, M.-H. Dévier, E. Geneste, P. Pardon, A. Grélard, E. Dufourc, M. Al Iskandarani, S. Aït-Aïssa, J. Garric, H. Budzinski, P. Mazellier, A. ***S. Trivella***
Photodegradation of novel oral anticoagulants under sunlight irradiation in aqueous matrices

11:30 – 11:45: Oral presentation (O33):
M. Bavcon Kralj, A. Fortuna, E. Midžić, ***P. Trebše***
Biocide in waters after manual cleaning and its photodegradation in waters containing nitrate and humic acids

12:00 – 13:30: *Lunch*

13:30 – 14:00: *ACE General Assembly*

Session 5 Modeling and Methodologies *(Chairs: B. Ervens, J. Schwarzbauer)*

14:00 – 14:45: Plenary lecture (PL5):
Barbara ERVENS
"Modelling Chemical Processes in Clouds"

14:45 – 15:00: Oral presentation (O34):
***C. Gardia-Parege**, M.-H. Dévier, E. Geneste, S. Aït-Aïssa, H. Budzinski*
Untargeted chemical analysis for the assessment of the overall contamination and the identification of emerging pollutant in wastewater treatment plants

15:00 – 15:15: Oral presentation (O35):
***L. Pinto da Silva**, J.C.G. Esteves da Silva*
Modelling the absorption properties of brown carbon with DFT: The case study of PAHs in Seoul, South Korea

15:15 – 15:30: Oral presentation (O36):
***Z. Varga**, E. Nicol, Y. Xu, R. Grosshans, S. Bouchonnet, M. Lavielle*
A new software for the statistical treatment of high resolution mass spectra - Application for water contaminants

15:30 – 15:45:	Oral presentation (O37): ***V. Artaev***, *G. Tikhonov, D. Mazur, A. Lebedev* Complementarity of the different ionization techniques in GCxGC-HRMS for environmental analysis
15:45 – 16:15:	*Coffee break*
16:15 – 16:30:	Oral presentation (O38): ***D. Vione***, *B. Koehler, L. J. Tranvik, Marco Minella, C. Minero* Photochemistry modelling on a geographical basis: The case of swedish lakes
16:30 – 16:45:	Oral presentation (O39): ***D. Palma***, *M. Sleiman, C. Richard* Evidence of nitration and nitrosation of aromatic compounds upon irradiation of imidacloprid in water
16:45 – 17:00:	Oral presentation (O40): ***N. Hidayati***, *L. Asia, A. Piram, M. Picard, I. Widowati, A. Sabdono, A. Syakti, P. Doumenq* Pharmaceutical active compounds in shrimp farm aquatic environment: Method, development and validation
17:00 – 18:00:	*Award ceremony / Closing session*

PLENARY SPEAKERS

Session 1: Sustainable Chemistry

Karine DE OLIVEIRA VIGIER is a professor at the University of Poitiers, IC2MP (Institut de Chimie des Milieux et Matériaux de Poitiers), France. She received her PhD in catalytic conversion of vegetable oils in France (2002), then she moved to Canada for a postdoctoral position at the University of Sherbrooke for two years. She became an Associate Professor in 2004 in France and since 2017 she is a full Professor. Her main field of research consists in the development of unconventional media to assist the catalyst in the control of the selectivity for the conversion of biomass (carbohydrates, furanic derivatives, glycerol) to fine chemicals and fuels. She has received the young researcher price of the catalysis division of the French Chemical Society (2014) and she is a member of the editorial advisory board of the ACS Sust.Chem. & Eng. journal. She is the head of the chemistry department of the University of Poitiers and the co-supervisor of the team “catalysis and unconventional media” of IC2MP.

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Session 2: Atmosphere

Frank KEPPLER is a professor at Heidelberg University in Germany. He is head of the Biogeochemistry research group at the Institute of Earth Sciences. The research group addresses the formation of trace gases in the biosphere and studies the exchange and interactions of climatically important trace gases between the pedosphere, biosphere and atmosphere. These processes are studied by laboratory investigations and field measurements. The Biogeochemistry group has particular expertise in the application of analytical methods to identify and quantify volatile organic compounds and to determine their stable isotope composition.

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Session 3: Soil and sediments

Annette Elisabeth ROSENBOM is senior scientist at the Geological Survey of Denmark and Greenland (GEUS). With a background in civil engineering, she received her Industrial Ph.D. in *Preferential Flow and Transport in Variably Saturated Fractured Media* in 2005 from the Technical University of Denmark. Her emphasis through the past 20 years has been on introducing new field monitoring techniques and new numerical modelling concepts to measure and mathematically estimate preferential flow and solute transport through fractured soil/rock with particular focus on the variably-saturated zone and the effect of macropores (such as biopores and fractures). Being working in interdisciplinary research teams (e.g. microbiology, geochemistry, climatology, agronomy, geology, and hydrology) has led her to be the project leader of the Danish Pesticide Leaching Assessment Programme (PLAP; http://pesticidvarsling.dk/om_os_uk/index.html), which provides scientific guidance to the regulation of pesticides in Denmark based on high-quality field-scale monitoring data.

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Session 4: Waters

José Antonio SANCHEZ PEREZ is Professor at Department of Chemical Engineering, University of Almería. Degree in Chemical Engineering by the University of Granada (1988); PhD by the University of Granada (1992). Director of the Solar Energy Research Centre, CIESOL, joint centre between the University of Almería and the Plataforma Solar de Almería. He has been involved in 17 research projects (European and Spanish projects) and has leaded 9 of them. 12 Research contracts with private companies most of them related with the development of Solar Technologies applied to wastewater treatment. He has directed 14 PhD theses in different fields such as biotechnology of microalgae, filamentous fungi fermentation and wastewater treatment. Main research lines are solar photo-Fenton for microcontaminant removal and water disinfection. Co-authored 133 peer-reviewed international papers. H-index = 37 (Scopus).

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Session 5: Modeling and Methodologies

Barbara ERVENS was a research scientist at the Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, (USA), affiliated with the Chemical Sciences Division, Earth System Research Laboratory of the National Oceanic and Atmospheric Administration (NOAA), Boulder, Colorado (USA). She received her PhD in 2001 from the University of Leipzig (Germany) in chemistry on model development and experiments of atmospheric multiphase chemistry. She started a postdoc position at NOAA affiliated with Colorado State University, Fort Collins, Colorado (USA) in 2003. Her main research addresses the development and application of process models describing aerosol mass formation and modification in the atmospheric aqueous phase of clouds and aerosol particles. She is laureate of the Make Our Planet Great Again (MOPGA) french call and she is now at l'Institut de Chimie de Clermont-Ferrand for four years.

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Session 1: Sustainable Chemistry

Plenary lecture

Catalytic Conversion of Carbohydrates to Value Added Chemicals: Alternative Solvents and technologies

Plenary lecture PL1
(#**Sustainable chemistry**)

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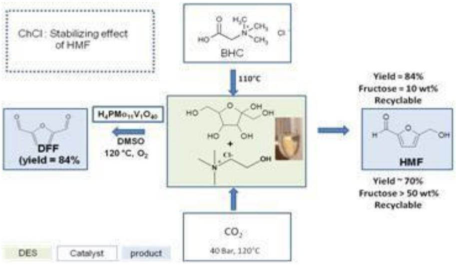
IC2MP, 1 rue Marcel Doré, Poitiers, France, karine.vigier@euniv-poitiers.fr.

The catalytic conversion of carbohydrates to value added chemicals or platform molecules is the topic of numerous researches. One of the challenges is the conversion of a highly concentrated solution of carbohydrates in an environmentally friendly process. To this aim, the nature of the catalyst, the solvent or an assisted catalyst [1] (i.e. combination of a catalyst and ball milling) can be investigated.

In a first part, the effect of the solvent nature will be presented. An interesting class of solvents is gaining more and more attention: Deep Eutectic Solvents (DES) [2] or Low Melting Mixtures (LMM). Formation of these solvents can be obtained by simply mixing together two safe components, (cheap, renewable and biodegradable) which are capable of forming an eutectic mixture or a low melting mixture. One of the most widespread components used for the formation of these solvents is choline chloride (ChCl). ChCl is a very cheap, biodegradable and non toxic quaternary ammonium salts which can be either extracted from biomass or readily synthesized from fossil reserves (million metric tons) through a very high atom economy process. In combination with safe hydrogen bond donors such as carbohydrates, ChCl is capable of rapidly forming a DES/LMM. We have studied several catalytic systems in the synthesis of furanic derivatives showing the benefit effect of these solvents in such reactions (Scheme 1) [3-5]. Some examples will be presented where ChCl can help to control the selectivity of the reaction by providing interactions with the furanic derivatives avoiding their degradation starting from highly concentrated solutions of carbohydrates. Some new insights of the mechanism will be provided.

In a second part, an example on a combination of a heterogeneous catalyst and a mechanical treatment will be demonstrated in the glycosylation reaction, showing that assisted catalysis is a promising sustainable route to obtain the desired product [6-7].



Scheme 1. Catalytic conversion of. carbohydrates to furanic derivatives in the presence of ChCl

Acknowledgements
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Session 1: Sustainable Chemistry

Oral presentations

Slow-released K/PO4 fertilizers based on mechanochemically activated clay minerals

ORAL O1
(#Sustainable chemistry)

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Concerning plant nutrition, new products or methods to improve the nutrients management have become more and more important for environmental resilience. Most inorganic fertilizers currently used in agricultural have high-solubility or are volatiles, which can pollute the environment and water resources, accumulating nutrients causing e.g. eutrophication of water resources. Such properties induce the use of large amounts of fertilizers to ensure the food production, so that the negative effects become increasingly pronounced. In the same scenario, economic losses are inserted with these non-sustainable nutrient supplies.

Sustainable slow-release fertilizers have been reported as environmentally friendly alternatives to highly soluble commercial products[1,2]. Their main advantages are that they dissolve and release nutrients into soils in a way that assures bioavailability of nutrients to plants over a long period of growth. In addition, novel formulations can reduce or eliminate environmental problems caused by excess use of conventional fertilizers, such as eutrophication and atmospheric pollution.

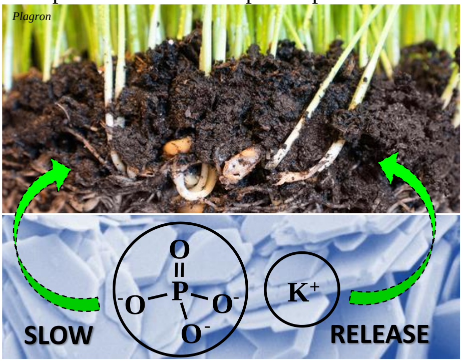

Fig.1: Slow-release of K/PO_4 fertilizers from SRF-clay minerals to soil.

In this study, the solid-state mechanochemical activation method was used to prepare slow-release fertilizers (SRF) by milling K_2HPO_4 and clay minerals. Montmorillonite (MMT), talc and calcined Layered Double Hydroxides (LDH: $Mg_2Al(OH)_6(CO_3).3H_2O$ and $Mg_2Fe(OH)_6(CO_3).\ 2.5H_2O$) were used as natural supports for K/PO_4 loading. Experimental conditions of milling and pre-thermal activations were screened for vaarious KH_2PO_4/Clay minerals in order to obtained the optimal release of K/PO_4 nutrients over the kinetic profile expected for SRFs, i.e. < 15% nutrient release in 24h and < 75% Nutrient release in 28 days and at least 75% Nutrient release according the American Plant Food Control Officials. Kinetic profiles were recorded for each systems over a 30 days period of time. In all cases, a minimum of 9h milling was necessary obtained SR properties.

In case of MMT and talc, even though K release behavior was similar for both systems, PO_4 release was slower for talc due to the formation of low soluble K-struvite ($MgKPO_4{\cdot}6H_2O$) formed during the milling activation. Calcination of LDHs was used before milling in order to activate the K_2HPO_4/LDH reaction and favour the slowest release. Best results were obtained for LDH calcined at 200°C for which amorphisation of both components was obtained.

All experiments were monitored using a full set of solid state characterization techniques (ICP, XRD, TGA, SEM and EDX). The complete kinetic and thermodynamic studies will be presented and discussed.

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Plastic biodegradation: focus on the methodology to study this unknown process

ORAL O2
(**#Sustainable chemistry**)

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Plastic pollution is a major ecological concern. Plastics have become essential for our everyday life, as a result, global plastic production reached 335 million tons in 2016 **[1]**. Plastic debris impact the environment, and create a new space of abiotic and biotic interactions: the plastisphere.

While the lifetime of plastic in environment is long, it is dynamic and constant transformation leads to the production of nanometric fragments, which are potentially biodegradable by the microbial flora.

Microbial species can colonize plastic fragments by forming biofilms enhancing biodegradation efficiency **[2]**. Although biodegradation of plastics is observed, biodegradation pathways remain largely unknown. As a consequence, the evaluation of the fate of these polymers in the environment is extremely difficult. The recent development of "metabolomics" methods opens new directions to understand the fate of plastics in environment. But currently, no study has been published using this approach. The objective of our work was thus to develop robust methods to study the metabolic pathways involved in biodegradation processes.

Our study focuses on a model system where polyethylene polymers are biodegraded by a bacterial strain, *Rhodococcus rhodochrous*, which is able to grow in this substrate as sole carbon source **[3]**. We have developed a metabolomic approach to characterize the extra-cellular and intra-cellular metabolism of *Rhodococcus rhodochrous*. The bacteria were incubated in minimum mineral media under two different conditions: 1) With plastic as sole carbon source, 2) with no carbon source. Three different extracts were generated from each sample (extracellular medium; polar and non polar extracts) and were analysed with LC-MS. The analytical data were cleaned and submitted to statistics treatments.

The results clearly show the difference between the profiles of the two conditions (with and without plastic) suggesting that *Rhodococcus rhodochrous* has a specific metabolism in the presence of plastic. Work is in progress to reconstruct the metabolic pathways involved in the biodegradation process.

Acknowledgements

This work was part of the research project OXOMAR (Abiotic and biotic degradation and toxicity of OXO-biodegradable plastics in marine waters), funded by Agence Nationale de la Recherche (ANR).

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The different faces of functionalized ionic liquids and deep eutectic solvents: From extraction/purification to drug development

ORAL O3 (**#Sustainable chemistry**)

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Nowadays, sustainability challenges have boosted the research in unconventional solvents, extraction techniques and drug development. Additionally, an emerging research field of interest is the use of ionic liquids (ILs) and deep eutectic solvents (DESs) in aqueous biphasic systems (ABS) and pharmaceutical applications.

ILs have emerged as one of the most attractive solutes for ABS, with outstanding performance in the extraction of targeted biomolecules [1]. Recently, we have proposed a benign route for ABS containing cholinium-based ILs [2] and disclosed novel ABS composed of fluorinated ILs (FILs) [3]. The superior extractive performance of IL-based ABS over conventional polymer-based systems results from the broad hydrophobic-hydrophilic range exhibited by the coexisting phases when ILs are employed [4]. Herein, new nature-inspired ILs and DESs (synthesized by natural primary metabolites, e.g. choline derivatives, carboxylic acids) and FILs were implemented to develop more versatile and amenable to be tuned ABS. To understand the phase formation process of these novel ABS and their potential as extractive platforms of biomolecules, the ternary phase diagrams, the polarity parameters of aqueous media in the coexisting phases, and the partition coefficients of biomolecules (from simple systems like amino acids (e.g. tryptophan) and peptides (e.g. tryptophan peptides) to complex systems as proteins (e.g. lysozyme)) were determined. Additionally, the standard batch (macroscale ABS extraction) was compared with flow-through processes (ABS in microfluidic setups), since ABS are particularly suitable for continuous operation in microfluidic devices, where the laminar regime and the low interfacial tension favour interface stabilization, a key requirement in ABS [5].

Likewise, the so-called third generation of ILs (API-ILs) has taken a further step in developing ILs that are themselves active pharmaceutical ingredients (APIs; strategy already implemented by us [6,7]). Some of the benefits of the ILs building-up platforms include the potential to modulate the water solubility of an API, and its membrane permeation properties. Tuning and controlling membrane transport is a key factor with impact on a variety of novel delivery methods. ILs and DESs constituents that are suitable for pharmaceutical use remain to be fully enumerated, but over 370 substances are listed as "Generally Regarded As Safe (GRAS)" by the FDA (U.S. Food and Drug Administration), including vitamins, food additives and other well-accepted substances. The presented results clearly demonstrate that, within the green chemistry framework, a nature-inspired ILs and DESs platform constitutes a viable alternative for enhancing the bioavailability of poorly water-soluble APIs.

Acknowledgements

The financial support from FCT/MCTES through the 2014 FCT Investigator (IF/00210/2014@ J.M.M.A.; IF/00190/2014@A.B.P.), grant PD/BD/135078/2017 (J.C.B.), and through projects PTDC/QEQ-FTT/3289/2014, PTDC/ QEQ-EPR/5841/2014, IF/00210/2014/CP1244/CT0003 is gratefully acknowledged. Also, this work was supported by the Associate Laboratory for Green Chemistry LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007265).

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Use of hybrid material waste-derived organic substances/magnetite for sustainable water treatment: a Life Cycle Assessment case study

ORAL O4
(**#Sustainable chemistry**)

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Sustainability has become increasingly relevant also in the context of environmental protection and research recently moved towards two main directions: the recycle and reuse of natural resources and materials to prevent waste, and the improvement of efficiency of air, waters and soils management, including remediation techniques. As for waters, there is a rising demand for exploring integrated water use and water treatment processes seeking for a transition to a more circular water management [**1**] as an alternative to traditional "linear" way of using water (extraction, disinfection, use, treatment processes, discharging).

Based on these premises we developed hybrid waste-derived organic substances/magnetite nanoparticles (HMNPs) for the heterogeneous photo Fenton caffeine degradation. Photo-Fenton is an Advanced Oxidation Process resulted very promising; it promotes the degradation of organic contaminants through the action of hydroxyl radicals (•OH) generated in situ from H_2O_2 decomposition catalysed by Fe(II) and accelerated by UV-VIS irradiation ($\lambda < 500$ nm) [**2**]. The heterogeneous approach was chosen because a critical step is the removal of the exhausted active materials from the liquid phase. Thus, the use of magnet-sensitive materials, in our case magnetite, represents a very promising solution. However, magnetite is sensitive to oxidation; in general, the addition of chelating organic anions or polymeric complexing agents during the formation of magnetite can enhance its stability. We studied the possibility of using waste-derived organic substances (bio-based substances, BBS) featuring like humic acids in order to protect magnetite from oxidation and to enhance the photo-Fenton activity. Indeed, it has been demonstrated that humic substances can enhance the photo-Fenton processes efficiency. Moreover, the valorization of urban and/or agricultural biowastes for BBS production (re-entering them into the economic cycle) could represent an adde value.

In this work HMNPs BBS/magnetite were applied to the heterogeneous photo-Fenton degradation of caffeine, chosen as representative contaminant of emerging concern.

The effect of several experimental parameters was investigated, i.e. pH, irradiation source, BBS loading, possibility to recover and re-use the HMNPs for more than one cycle. Very promising results have been obtained in term of caffeine abatement [**3**].

Nevertheless, in order to propose this material for sustainable water treatment it is important to define a suitable methodological tool to compare it with other process and/or other materials. Life Cycle Assessment (LCA) approach was therefore considered at this purpose.

The LCA analysis comprises four main steps according to the ISO standard 1040X: i) goal and scope, in which the definition of the object, functional units and the system boundaries are defined; ii) the life cycle inventory (LCI) analysis, in which all the materials and energies flows along with the emissions connected to the object of the analysis are calculated; iii) the life cycle impact assessment (LCIA), where the inventory data are assigned to each impact categories characterized using suitable LCIA models into common equivalence units (estimates) and finally summed to provide an overall impact; iv) life cycle interpretation, where the conclusions and the recommendation are set and the opportunities to reduce the environmental impacts are suggested.

In this specific case, it has been demonstrated that the most relevant contribution to the impact of the photo-Fenton process, run either in the traditional homogeneous way or with HMNPs, is related to the light sources. Indeed, with the same performance in term of caffeine abatement, the difference in impact can be seen passing from an artificial light source to solar radiation

This project has received funding from the European Union's Horizon 2020 research and innovative programme under the Marie Sklodowska-Curie grant agreement No 645551

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Synthesis and biological evaluation of halogenoBisphenol A derivatives

ORAL O5
(#**Sustainable Chemistry)**

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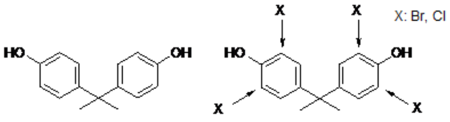

BPA

Cl_xBPA, Br_xBPA and BrxClxBPA

Endocrine-disrupting chemicals (EDCs) have been defined by the US Environmental Protection Agency as “exogenous substance that alters functions of the endocrine system and consequently causes adverse health effects in an intact organism”. EDCs, as Bisphenol A (BPA) can interfere with synthesis, secretion, transport, metabolism, binding actions, and mimic the occurrence of natural hormones [1]. Their use is so widespread that they can have serious deleterious effects, following exposure to even a low dose of BPA, inducing pathologies as developmental and reproductive toxicity [2], cancers [3], …

Given the fact that in most drinking water treatment plants, routine operations are carried out using a chlorination step, the formation of chlorinated derivatives of BPA (ClxBPA) (mono-, di-, tri- and tetra-chlorobisphenol A) in drinking water is to be expected [4-5]. In presence of bromine the formation of brominated derivatives of BPA (BrxBPA) is also expected. Indeed, bromine is formed by the oxidation of bromide, naturally dissolved in natural water, during the chlorination step [6]. Considering the electrophilic substitution reactions of chloration and bromation, mixed compounds Br_xCl_xBPA could also be found [5], but to date no detected in biological matrices or drinking water due to the lack of these derivatives commercially available as analytical standards.

Herein, in a first time, we described the synthesis of ClxBPA, BrxBPA and BrxClxBPA. For this purpose, reaction conditions were optimized with the modulation of solvents and the nature of the reagents. Compounds could be used as analytical standards in LC/MS/MS to quantify them in human biological fluids, drinking water, but also evaluated toward their biological profile.

Precedently, our team has collected, in a cohort of pregnant women (EDDS cohort), human biological fluids like urine, colostrum but also drinking water [7-8]. So, in a second time, we analyzed urine and colostrum through online solid-phase extraction coupled to ultra high-performance liquid chromatography tandem mass spectrometry (Xevo® TQS) to quantify BPA, Cl_xBPA. The detection frequency of BPA in colostrum and urine ranged from 45 to 71% and at least one Cl_xBPA was detected (57-93%). For both biological samples concentration ranged from 0.30 to 52.10 ng/mL and from 0.03 to 1.71 ng/mL for BPA and Cl_xBPA derivatives, respectively.

We also analyzed halogenated BPA in drinking water of EDDS cohort (340 samples) through gas chromatography tandem mass spectrometry. Monohalogeno-BPA and dichloro-BPA were the most often detected by-products (more than 30 % of the total sample number). Additional Br_xBPA, Cl_yBPA and Br_xCl_yBPA compounds were also quantified at lower frequencies (less than 12 % of the total sample number). All these halogenated by-products were quantified at the ng/L level, which stays significantly below the BPA concentration (median around 20 ng/L with a detection frequency of 74 %).

In final, BPA, ClxBPA and BrxBPA were evaluated *in vitro* on the Follitropin receptor (FSHR) function. It was showed that these derivatives acted as a negative allosteric modulator of FSHR.

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Activated persulfate processes for degradation of endocrine disrupting compound nonylphenol in aqueous matrices

ORAL O6 (#Sustainable chemistry)

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Among the various endocrine disrupting compounds, nonylphenol (NP) has been classified as a significant endocrine disrupter interfering with the hormonal system of numerous organisms and acting as an estrogen mimic. NP is mainly consumed in the production of nonylphenol ethoxylates (NPEs), effective non-ionic surfactants used in a wide range of industrial applications and products. Despite the fact that NPEs are highly treatable by conventional biological processes, effluent from wastewater treatment plants (WWTPs) is one of the main sources of NP, which is the main product of NPE biodegradation [1].

As a result, permanent NP occurrence in WWTPs effluents causes long-term concerns such as bioaccumulation and toxicity in the environment [2]. To prevent the release of NP into the aquatic environment or reduce the harmful effect, advanced oxidation technologies can be used as promising methods for effective water, groundwater and wastewater treatment.

Recently, a pioneering technology based on activated persulfate (PS) oxidation has been studied as an alternative to conventional hydroxyl radicals-based advanced oxidation processes for water matrices treatment [3]. The effectiveness of this technology relies on the formation of sulfate radicals through the activation of PS by heating, ultraviolet radiation, ultrasound, the addition of transition metal ions, alkali or peroxide [4].

Based on the above, this study aimed to explore the potential application of different activated persulfate systems for NP-contaminated ultrapure water and groundwater treatment. The activation methods studied included UV radiation, Fe2+, H2O2, and combinations thereof. The effects of the operating parameters and the impact of groundwater matrix on the treatment efficacy were investigated.

Photo-induced persulfate oxidation proved the most effective and particularly promising technique for NP degradation. For example, the efficiency of UV/PS/Fe2+ process was higher than that of the PS/Fe2+ system at the same NP/PS/Fe2+ molar ratio of 1/10/1, but indicated no improvement as compared to the UV/PS process. Whereas, the application of dual UV/H2O2 activation of PS showed some improvement in NP degradation as compared to the UV/PS process at the same oxidant concentration. Notably, irrespective of the applied treatment process, the efficacy of NP degradation was lower in groundwater as compared with ultrapure water trials.

The results obtained within this study provide valuable information for further in situ full-scale applications of UV-activated PS processes for the purification of water and groundwater.

Humic acid coated magnetic nanoparticles as highly efficient heterogeneous photo-fenton materials for wastewater treatments

ORAL O7
(**#Sustainable chemistry**)

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Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products, are increasingly being detected at low levels in surface water, and there is concern that these compounds may have an impact on aquatic life. Despite their low concentration, several CECs are a major health concern due to their toxicity [1]. Due to their incomplete removal in the traditional wastewater treatment plants, considerable efforts have been devoted to develop suitable purification methods capable to destroy these bio-recalcitrant organic contaminants. For this purpose, Advanced oxidation processes (AOPs) have been developed, since they are extremely efficient in the degradation/mineralization of a wide range of organic contaminants, including several CECs, through the action of highly oxidizing species, mainly hydroxyl radicals (•OH)[2].

Among AOPs there is increasing interest for heterogeneous Fenton, photo-Fenton and Fenton-like processes that can generate highly reactive species (mainly hydroxyl radicals and also superoxide iron species) through the reactions between recyclable iron (eventually immobilized in the form of heterogeneous catalyst) and H_2O_2 at acidic or even circumneutral pH. These processes can effectively remove CECs in water or soils and have become a promising environmentally friendly treatment technology. Due to the complex reaction system, the mechanism behind heterogeneous Fenton reactions has not been fully assessed, and it is worth to be studied in deeper details. Fe_3O_4 magnetic nanoparticles (MNPs) applied as iron-sources in Fenton and phot-Fenton processes have attracted significant interest due to their low cost, facile recovery and recycling. Recently, the potential application of Fe_3O_4 MNPs in heterogeneous Fenton and photo-Fenton for the removal of CECs has been investigated [3].

As demonstrated in the literature, the introduction of humic-like substances in both Fenton and photo-Fenton processes appears to significantly enhance the pollutant degradation capacity, even though the effective role played by humic-like substances in the oxidation mechanism is still not fully solved [4]. Additionally, in order to avoid the complete oxidation of magnetite/maghemite phases to hematite, the stabilization with an organic coating is usually carried out.

In this study, humic acid coated Fe_3O_4 magnetic nanoparticles (Fe_3O_4/HA) were prepared by co-precipitation method under controlled conditions using different amounts of humic acid, both in anoxic and oxygenated conditions. The Fe_3O_4/HA materials were tested in aqueous media using 4-chlorophenol (4CP) at different pH, in the presence of H_2O_2, in the dark and under sun-light irradiation. The very efficient process for 4CP degradation (0.2 mM) (used as a model pollutant) was evidenced by the complete abatement in less than 5 minutes, identifying the best degradation conditions using Fe_3O_4/0.5%HA prepared under anoxic conditions. Additionally, the best performing material was tested for the removal of a CECs mixture giving very promising results both in artificial and real wastewater samples.

Acknowledgements

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Insights regarding the adsorption mechanism of pharmaceuticals onto phosphor doped carbonous

ORAL O8 (**#Sustainable chemistry**)

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The presence of pharmaceuticals (PhCs) in freshwater and wastewater has been reported worldwide. PhCs can have adverse effects on non-target organisms and can potentially impact human health via the food chain [1]. Several treatment methods have been used to remove PhCs, such as adsorption, advanced oxidation and membrane filtration. Removal by adsorption is a very interesting solution due to its versatility and high efficiency [2] - yet, engineering a sustainable low-cost adsorbent is challenging.

Here, a highly effective adsorbent was designed using "acid catalyst" functionalization - whereby phosphate and phosphonate surface groups were introduced to the interface and bonded to a lignocellulosic structure [3]. The phosphorized microporous carbonous material (PPhA) was tested with three priority PhCs (sulfamethoxazole (SMX), carbamazepine (CBZ) and ketoprofen (KP)). Morphological, structural and physico-chemical properties were investigated by BET, pH_{zpc}, SEM, FTIR and XRD. Furthermore, EDX was used to confirm the thermochemical modification process. FTIR and EDX showed that phosphor was introduced in the form of condensed phosphate bound to the carbon matrix by C-O-P and C-P linkage. BET data (657.1 m^2/g and 0.315 cm^3/g) showed an obvious decrease in the specific surface area and total pore volume, confirming that pore filling with pore blocking was a key PhC adsorption mechanism. From FTIR spectra, we concluded that O- and P-containing functionalities (-OH, -COOH, C=O, P=OOH, P-OH, P-O-P) on the carbon surface played a significant role in PhC uptake. Adsorption occurred mainly through pseudo-second order and intraparticle diffusion processes, while Langmuir isotherms (with maximum adsorption capacity of 19.2, 21.5 and 19.7 mg/g for SMX, CBZ and KP, respectively) were suitable for describing the process. The results regarding pH influence, FTIR peak shifts and XDR patterns suggest strong H-bonds (both dipole-dipole and Yoshida type) along with n-π and π-π electron donor–acceptor interactions (EDA) might be key interactions (because of the high number of O- and P-containing functional groups at the material interface). Also, XDR diffraction peaks (after PhC uptake) became weak and wider, which may be due to surface adsorption. However, no shift in peak position was observed, which indicates that no phase transformation occurred. Also, the low adsorption enthalpy (ΔH < 10 kJ/mol) confirmed that the adsorption process was mostly physisorption. At the tested pH range, SMX and CBZ existed mainly in there zwitterionic forms, which influenced adsorption capacity. KP had the highest log K_{ow} coefficient and indeed the highest removal efficiency in multicomponent solution. It must however be emphasized that the PhC removal efficiency did not differ drastically - which indicated that hydrophobic interactions were not key among the adsorption mechanisms. The adsorption behaviour of these PhCs was not modified significantly by the presence of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. This is likely a consequence of different adsorption mechanisms being at play (for PhCs and metal ions). Thus, limited competition was observed.

Based on the observed affinity here, a well-organized microporous structure with O- and P-rich functional groups and a synthesized carbonous adsorbent is proposed as an excellent platform for PhC removal.

Acknowledgements

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Biocompatible fluorinated ionic liquid on the development of new “Green” tools for pharmaceutical industry

ORAL O9 (**#Sustainable chemistry**)

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Nowadays, more efforts and investments are made in the research and development sector of the pharmaceutical industries. These investments came along with an increasing purchase on safety standards and a need to not only show the therapeutic effect of new drugs but to also show that they offer a significant improvement in comparison to existing therapeutics [1]. The design of new “greener” and sustainable pharmaceuticals is expected to integrate lower environmental harmfulness of both products and processes as one of the screening criteria in drug development. for biomedical applications. Therapeutic proteins, which are natural products, make part of the most promising classes of biopharmaceuticals, mainly due to their biocompatibility, selective and efficacy against several and untreatable diseases [2]. However, there are some problems associated to the use of proteins, as their instability, short half-life in the bloodstream and the possibility to trigger immune responses [3]. To avoid these problems maintaining the therapeutic levels without side effects, the development of novel drug delivery systems (DDS) are being intensively studied.

Fluorinated ionic liquids (FILs), defined as ionic liquids (ILs) with fluorous tags equal to or longer than four carbon atoms pursue numerous intrinsic properties that make them very attractive for the design of DDS. These specific family of ILs combine the best properties of both fluorinated surfactants (such as their high surfactant power, their chemical and biological inertness) with the greatest properties of ionic liquids (such as their negligible vapour pressure, high thermal and electrochemical stability, high tuneability and null flammability) [4,5].

The main purpose of this work is to evaluate the use of FILs as DDSs for therapeutic proteins. The initial screening studies were performed to select the most biocompatible and ecofriendly FILs. With this goal in mind, the cytotoxicity of FILs in four different human cell lines (Caco-2, HepG2, Ea.hy926 and HaCaT) were performed. To evaluate the impact of these FILs after being released in the aquatic environment from the human body or from accidental industrial processes, ecotoxicity tests were performed in aquatic species with different levels of biological organization (*Vibrio fischeri*, *Daphnia magna* and *Lemna minor*).

After the initial screening, different studies were performed using lysozyme (the best characterized protein with antimicrobial activity against several pathogens), as a model to examine the interactions and influence of FILs in therapeutic proteins. Activity and stability assays were performed to probe the chemical inertness of these ionic liquids for lysozyme. Moreover, it was possible to evaluate the absence of modifications in the secondary structure of lysozyme in the presence of FILs using the circular dichroism technique. The encapsulation of the protein inside the micelle’s structures formed by these ionic liquids was supported by dynamic light scattering and microscopy studies. Finally, the encapsulation efficiency and the drug loading were also discussed, as well as the release profile under several physiological conditions.

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Technical and environmental assessment of reuse of Waste-to-Energy - Bottom Ash (WtE-BA) in construction products

ORAL O10 (**#Sustainable chemistry**)

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France produces about 37.6 million tons of non-hazardous household waste per year. 30% of this waste is valorised in Waste-to-Energy plants. The main by-product of incineration is the Waste-to-Energy – Bottom Ash (WtE-BA). In France, the valorisation of BA is currently limited to road materials. The French decree from 18/11/2011 fixed the thresholds to recover BA in road materials. However, BA shows physical and mechanical properties that could make it suitable as secondary raw material in construction, preventing, moreover, the use of natural aggregates and reducing the landfill materials.

The aim of this study is to investigate the feasibility and potential reuse of bottom ash in two kind of construction products: a Ready-Mix Concrete (RMC) and a Self-Compacting Material (SCM) formulations. The bottom ash used in this study were recovered from two energy enhancement unit located in the Auvergne-Rhône-Alpes region in France.

For the Ready-Mix Concrete application, three samples of BA with different granulometric fractions were used: a global fraction (0-31.5 mm), an intermediate fraction (3-6 mm) and a coarse fraction (6-31.5 mm). Next, three different substitution rates of natural aggregates were tested (10, 20 and 30 %). All the RMC formulations were defined with a constant water to cement ratio of 0.55. For the Self-Compacting Material application, a global granulometric fraction was used with a total substitution rate of natural aggregates.

The environmental behaviour and mechanical performance of RMC and SCM samples were compared to the results obtained for the control samples. The environmental assessment was performed on monolithic concrete samples, according to the dynamic surface leaching test CEN/TC351/TS-2. For both applications, the results show that the potential leaching of different heavy metals remained below the thresholds of the Dutch Building Decree (Soil Quality Decree from 22/11/2007), whatever the granulometric fraction and whatever the substitution rate.

In order to ensure the technical performances, the compressive strength was measured for RMC application after 7, 28 and 90 curing days. The results show that the compressive strength increased with time, whatever the substitution rate for the global granulometric fraction (0-31.5 mm). Smaller evolutions were observed for intermediate and coarse granulometric fractions. Moreover, the compressive strength of samples incorporating BA was twice as low as the compressive strength of control sample (e.g. 16 MPa towards 37 MPa, after 90 days curing, for 10 % substitution rate).

On the other hand, the technical assessment of SCM application was achieved, with a low compressive strength after 28 days, allowing for easy manual excavation.

In conclusion, the reuse of WtE-BA in construction products seems to be a promising solution for BA valorisation. Nevertheless, application and technical requirement must be adapted. BA preparation need to be improved. For example, the influence of pre-treatment methods (e.g. washing) on the environmental and technical performances need to be investigated.

Use of analytical indicators to evaluate the quality of surface sludge deposits in vertical flow constructed wetlands treating wastewaters

ORAL O11
(**#Sustainable chemistry**)

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One of the major issue in sustainable development is to protect natural ecosystems from anthropic activities. Wastewaters must therefore be treated so that water can be discharged to the environment in a safe manner, or reused if possible. Constructed wetlands are considered amongst the technologies best adapted to household wastewater or stormwater treatment. They became over the last decade the number-one technology used by small communities in France for the treatment of domestic wastewaters.

The design of French Vertical Flow Constructed Wetlands (VFCW) leads to the formation of a sludge layer at the surface of the first filters due to the retention of suspended solids from the percolation of unsettled wastewater. This phenomenon is often considered as a risk to reduce permeability and induce clogging, but it contributes also in the retention and/or degradation of pollutants, as a support media for organic matter accumulation and microbial growth [1]. However the nature, structure, composition and reactivity of the constitutive organic matter are still poorly known [2]. Yet, in order to maintain the treatment performance over the long term, the characteristics of the sludge deposits and their evolution have to be well described.

In this objective, a panel of sludge deposits from 14 VFCW sewage treatment plants with different treatment processes and number of years of implementation were characterized. In addition, suspended solids and sludge deposits sampled from two French VFCW plants were investigated by different methods in the objective to assess the evolution of particulate organic matter (POM) along the treatment chain and within the sludge layer, and identify relevant analytical indicators of these phenomena. The treatment chain included two successive stages of reed bed in all treatment plants. Some of them comprised additionally an aerobic trickling filter followed by $FeCl_3$ injection [3,4].

All samples were characterized by different methods of investigation: particle size, elemental analysis, biodegradability, fractionation of organic matter into humic and fulvic substances and thermogravimetric analyses coupled to differential scanning calorimetry. Some samples of particular interest were further analysed by Fourier transformed infrared spectroscopy, 3D fluorescence and carbon, hydrogen and nitrogen isotopic distributions of aqueous extracts [3,4,5].

The objectives were to better understand the evolution of the surface deposits, and more particularly the processes involved in the evolution of its constituent organic matter (OM) and to identify relevant analytical indicators in order to improve the monitoring and the evaluation of the treatment plants.

The results notably showed an evolution of the particulate organic matter with the age of the deposits: strong differences were observed over the first few years of operation, and appeared to diminish over time and the sludge deposits older than 3 years reached a similar state. The influence of the treatment chain such as additional treatments by trickling filter or ferric chloride addition was also highlighted.

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Fluorinated ionic liquids for selectively absorbing refrigerant gases

ORAL O12
(**#Sustainable Chemistry**)

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Hydrofluorocarbons (HFCs) are refrigeration gases that in the end of the 1980's replaced chlorofluorocarbons (CFCs) due to the harmful effects of CFCs for the atmospheric ozone layer. However, HFCs have a high global warming potential and a long atmospheric permanence. New technologies are then needed for recovering and recycling HFCs and thus closing the life cycle of these compounds in the sense of a circular economy (Fig. 1).[1,2] For that purpose, ionic liquids are promising absorbers for selectively recovering HFCs from disaffected refrigeration systems.

Fig.1.
Schematic representation of the concept of circular economy.

We have studied the capacity of different ionic liquids to absorb 1,1,1,2-tetrafluoroethane (R134a, Fig. 2) – one of the most used refrigerant gases. We have used five different ionic liquids – $[C_2C_1Im][NTf_2]$, $[C_8C_1Im][NTf_2]$, $[C_8H_4F_{13}C_1Im][NTf_2]$, $[C_8C_1Im][BETI]$ and $[C_8H_4F_{13}C_1Im][BETI]$ – containing fluorinated moieties both in the cation and in the anion (Fig.2) to investigate the effect of fluorination on the solubility of R134a.

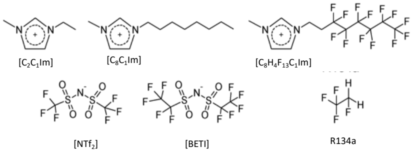

Fig.2. Structure of the R134a gas and of the cations and anions that constitute the ionic liquids.

The R134a solubility increases in the following order: $[C_2C_1Im][NTf_2] < [C_8C_1Im][NTf_2] < [C_8C_1Im][BETI] < [C_8H_4F_{13}C_1Im][NTf_2] < [C_8H_4F_{13}C_1Im][BETI]$. We can then conclude that the R134a absorption increases with the increase of the fluorination in the ionic liquid, the effect being more pronounced when larger fluorinated moieties are present in the alkyl side-chain of the imidazolium cation.

Even if R134a can stablish unique hydrogen bonds involving fluorine and hydrogen atoms (C-F-H),[1] its solubility increases from $[C_2C_1Im][NTf_2]$ to $[C_8C_1Im][NTf_2]$, an evidence of non-specific interactions between the gas and the ionic liquid.

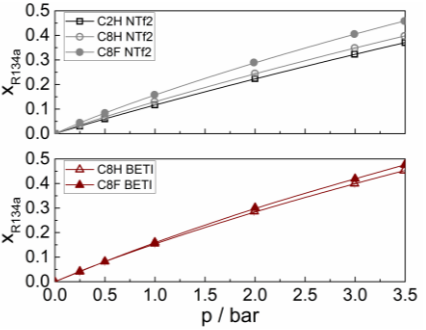

Fig. 3. R134a mole fraction solubility as a function of pressure in (☐) $[C_2C_1Im][NTf_2]$, (○)$[C_8C_1Im][NTf_2]$, (●) $[C_8H_4F_{13}C_1Im][NTf_2]$, (△)$[C_8C_1Im][BETI]$ and (▲)$[C_8H_4F_{13}C_1Im][BETI]$ ionic liquids at 303 K.

The ideal selectivity of R134a towards other gas impurities such as CO_2, N_2, C_2H_6 and C_2F_6 will be discussed. Moreover, NMR spectroscopy and molecular dynamics simulations were used to determine the most probable sites of solvation of R134a in both the hydrogenated and fluorinated ionic liquids.

Acknowledgements

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Controlled sulfidation of zero-valent iron nanoparticles prepared using hydrogen reduction: Towards enhanced TCE dechlorination on a large-scale

ORAL O13
(**#Sustainable chemistry**)

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Zero-valent iron nanoparticles treated by reduced sulfur compounds (S-nZVI) have attracted increased attention as promising materials for environmental remediation owing to the synergistic effect of sulfidation on faster contaminant removal and decreased iron corrosion in water [1-4]. However, the S-nZVI particle synthesis procedures investigated so far are suitable mainly for laboratory-scale preparation (e.g. using borohydride as reducing agent) with only a limited possibility of an easy and cost-effective large-scale production.

Herein, we present a novel approach to synthesize S-nZVI particles using a commercially available nZVI prepared by reduction of iron (hydr)oxide precursors that are subsequently treated by aqueous solution of sodium sulfide.

In order to provide the best description of the sulfidic shell and understand its role and transformations during reaction with trichloroethylene (TCE), a common groundwater pollutant, several complementary characterisation techniques such as XRD, XPS, HRTEM including elemental mapping, Mössbauer spectroscopy, surface area and SEA were used. Geochemical modelling was further employed to describe the nature of Fe-S phases that are likely to form during sulfidation treatment.

This novel synthesis approach resulted in particles with a core-shell structure where the core consists predominantly of zero-valent iron and the shell contains mostly amorphous iron sulfides and iron (hydr)oxides.

Up to 14-fold increase in TCE removal was observed after treatment of nZVI with sulphide in degradation experiments, depending on the amount of sulfide added. The rate of TCE removal increased with increasing sulfide dose up to S/Fe mass ratio of 0.05. The rate then plateaued and decreased when the sulfide loading exceeded a S/Fe mass ratio of 0.1. All sulphide-treated materials transformed TCE into fully dechlorinated hydrocarbons, i.e., no less chlorinated species (dichloroethylenes nor vinylchloride) were detected throughout degradation experiments. Nearly 100% chlorine balance was found at the end of experiments further confirming complete TCE degradation and the absence of chlorinated transformation products.

Acknowledgements

Financial support from the Czech Science Foundation (Grant Number GF17-33779L) and Technology Agency of the Czech Republic “Competence Centres” (TE01020218) is gratefully acknowledged.

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Session 2: Atmosphere

Plenary lecture

The global chloromethane cycle

Plenary lecture PL2
(**#Atmosphere**)

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Chloromethane (CH_3Cl, often named methyl chloride) is an important provider of chlorine to the stratosphere. It accounts for ~16% of the ozone-depleting halogens delivered to the stratosphere **[1]** and is predicted to grow in importance as the chlorine contribution to the stratosphere from anthropogenic chlorofluorocarbons decline. Today CH_3Cl originates mainly from natural sources with only a minor fraction considered to be of anthropogenic origin. However, until as recently as 2000 most of the CH_3Cl input to the atmosphere was considered to originate from the oceans, but investigations in recent years have clearly demonstrated that natural terrestrial sources such as biomass burning, wood-rotting fungi, salt marshes, tropical vegetation and soil organic matter degradation must dominate the atmospheric budgets of CH_3Cl **[2]**.

Anthropogenic CH_3Cl release to the atmosphere comes from the combustion of coal and biomass with minor emissions from cattle and humans. In addition, it has been reported that emissions from industrial sources might be much higher than previously assumed **[3]**.

The dominant sink for atmospheric CH_3Cl results from the reaction with photochemically- produced hydroxyl radicals **[1]**. Furthermore, in the marine boundary layer the reaction of CH_3Cl with chlorine radicals represents another sink. Microbial CH_3Cl degradation in soils may be a relevant additional global sink **[4]** but its impact on the global CH_3Cl budget is still highly uncertain. Moreover, small proportions of tropospheric CH_3Cl are lost to the stratosphere and to cold polar oceans though oceans in total are a net source **[1]**.

In summary many uncertainties still exist regarding strengths of both sources and sinks, as well as the mechanisms of formation and degradation of CH_3Cl. A better understanding of the atmospheric budget of CH_3Cl is therefore required for reliable prediction of future ozone depletion.

A potentially powerful tool in the investigation of the budget of volatile compounds in the atmosphere is the use of stable isotope ratios **[5].** Stable isotope analysis, when used in combination with CH_3Cl flux measurements, has the potential to better constrain the atmospheric CH_3Cl budget as suggested by **[6, 7]**. The isotopic composition of tropospheric CH_3Cl depends on the isotopic source signatures and the kinetic isotope effects (KIE) of the sinks.

In this presentation recent advances in our understanding of the origin and fate of CH_3Cl in the environment/atmosphere with particular emphasis on the applications of stable isotope techniques/tools including hydrogen, carbon and chlorine will be discussed.

Acknowledgements

The ORCAS group and the German Science Foundation (DFG) are greatly acknowledged.

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Session 2: Atmosphere

Oral presentations

Current knowledge about microbiological impacts on atmospheric chemistry

ORAL O14
(**#Atmosphere**)

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In the early 2000's, biological activity was detected in cloud water **[1]**. This raised the possibility that microorganisms participate to the complex chemical reactivity existing in cloud droplets. Since then multidisciplinary approaches have been deployed to investigate the influence of microbial activity on atmospheric chemical processes. Notably, a research consortium has been established in Clermont-Ferrand, France, gathering atmospheric physicists, chemists, and microbiologists. Sample collection and measurements are conducted at puy de Dôme Mountain's historical atmospheric station, and laboratory investigations are led in parallel in order to document the microbiological content in the atmosphere, its environmental features, and the extent to which microorganisms can be considered actors of atmospheric chemistry. The presentation at EMEC will consist of a review of the knowledge gained over these last 15 years, concerning the identified impacts of microorganisms on cloud chemical reactivity.

A large number (>1000) of microbial strains (bacteria, fungi, yeasts) have been isolated by culture of cloud water samples, which allowed fundamental laboratory experiments. Numerous isolates were able to develop at low temperatures relevant for activity in clouds, and to use organic compounds abundant in the atmosphere such as small chain carbon compounds (formate, formaldehyde, acetate, succinate, etc) **[2]**. These aspects directly supported the potential of microbial cells to interact with carbon compounds, notably, in clouds and participate to their transformation. Further developments of the sampling instruments made possible the access to larger sample volumes. Natural cloud water, including its own microbiota could thus finally be studied, in microcosms under laboratory controlled conditions, in specifically designed photo-bio-incubators. This clearly demonstrated some level of participation of microbial communities in the fate of organic compounds in natural clouds; these were quantified relatively to photochemical processes to be significant under these conditions. In addition, some impacts on the concentration of radicals and their precursors, considered as the main atmospheric chemistry catalysers, were observed and emphasized that biological activity probably has broader influence that previously thought **[3]**. In turn, the oxidant capacity of cloud water was observed to regulate the metabolic functioning of the microorganisms **[4]**, depicting a complex system whose functioning is driven by both biological and chemical features in interaction with each others. Further developments will consist in characterizing and quantifying metabolic activity *in situ*, using notably molecular biology tools and isotopic signatures, and implement atmospheric models to account for the presence of these biological catalysers.

Acknowledgements

In addition of the authors, this research involved many undergraduate and PhD, postdocs, and technical staff since 2003 in the corresponding affiliated laboratories. They are all warmly acknowledged for their contribution. Funding was obtained, for the most part, from international and national programs coordinated by ANR, CNRS or Auvergne Region.

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ORAL O15
(#**Atmosphere**)

Effect of endogenous microbiota on the molecular composition of cloud water: a study by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

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Cloud droplets contain dynamic and complex pools of highly heterogeneous organic matter, resulting from the dissolution of both water soluble organic carbon in atmospheric aerosol particles and gas-phase soluble species, and are constantly impacted by chemical, photochemical and biological transformations. Recently, the presence of microorganisms, as bacteria, fungi and yeasts, was highlighted in clouds: they are alive and metabolically active [1]. In this work, we studied the molecular composition of a cloud water sample collected at the puy de Dôme observatory (PUY), incubated with endogenous microbiota at two different temperatures (5 and 15°C). Control experiments were performed incubating filtered cloud water in the same conditions. Microbial metabolism can change the molecular composition of cloud water, as evidenced by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), previously used to characterize cloud waters at the PUY station [2].

The influence of endogenous microbiota was evaluated looking at oxygen to carbon and hydrogen to carbon ratios, double bond equivalents and other parameters. In addition, the formation and consumption of organic compounds was investigated using Venn diagram that shows all possible logical relations between data of different sets. Four fractions of compounds were identified: Yellow sector in Figure 1 represents compounds that are present at initial time (t_0) and in control experiment but not in the incubated sample because they are transformed by microbial activity. Green sector reports compounds that are not transformed during incubation. Blue sector shows compounds that are present in the control and in the incubated sample but not in t_0: they are produced by transformations of organic matter but, since they are present in the control experiment, they are produced by chemical reactions under dark condition (hydrolysis, Fenton reaction). Pink sector contains all the compounds that are only present in the incubated sample and that results from microbial transformations. Microorganisms consume 58% of the initial compounds and produce 266 new compounds. The impact of dark chemistry is clearly low (25 compounds formed).

Molecular formula assigned to these fractions have been analysed following the classification into in seven classes [2]: (1) lipids-like, (2) aliphatic/peptides-like, (3) carboxylic-rich alicyclic molecules (CRAMs-like structures), (4) carbohydrates-like, (5) unsaturated hydrocarbons, (6) aromatic structures and (7) highly oxygenated compounds (HOC).

Incubation at 5 and 15°C leads to the formation of different compounds: at 15°C the formation of oxidized compounds is shown whereas at 5° reduced compounds are also produced. We can observe that lipids-like and aliphatic/peptides-like are the most impacted by degradation.

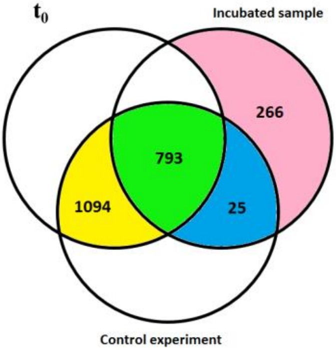

Figure 1

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Characterization of gaseous pollutant emissions from a typical French farm

ORAL O16
(**#Atmosphere**)

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Agricultural activities are one of the major source of pollutants in the atmosphere. Agricultural emissions can be both particulate and gaseous, that may affect the air quality as well as the climate. Farm buildings are recognized as significant ammonia emitters (1), and may emit many other compounds in the atmosphere, especially Volatile Organic Compounds (VOCs). Unravel atmospheric sources of VOCs is of particular importance as they are a source of secondary organic aerosols and ozone. Only a few studies proposed complete VOCs identification, despite considerable amounts of VOCs may be emitted from farm buildings. More studies about VOC emissions from agricultural activities are thus needed to better-constrained VOC emission inventories, still subject to large uncertainties.
A field measurement campaign was conducted to characterize the emissions from a typical agricultural farm in France. The experiments took place inside a sheepfold, inside a cowshed, and outside close to the buildings. Emitted VOCs have been characterized online using a PTR-Qi-TOF-MS, and off-line by GC-MS and GC-FID. To strengthen our analysis, identified VOCs from both off-line and on-line techniques have been confronted. This analysis provide a unique dataset of more than 3 hundred compounds that have been successfully identified in the cowshed and the sheepfold. Emitted compounds can be hydrocarbons, oxygenated VOCs, polycyclic aromatic hydrocarbons, amines and other nitrogen containing compounds, sulphur containing compounds and halogenated compounds. From all of them, ammonia is the most emitted compounds, reaching concentrations above the ppm level. Both the sheep house and the cowshed emit many of the identified compounds, but tracers for each farm building are proposed. Finally, emission factors from farm buildings have been estimated using the CO2 mass balance model. VOC emission factors were calculated for the first time for most of the identified VOCs. These new emission factors could now be implemented in future emission inventories for air quality and climate.

The authors acknowledge ANAEE France and ADEME (AgriMultipol program) for funding.

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Chilean rain. Changes in composition and levels of emergency contaminants during fifteen years

ORAL O17
(**#Atmosphere**)

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Air quality is a worldwide problem.

Thousands of chemicals may be found in the atmosphere from biogenic and anthropogenic sources as well as due to atmospheric reactions. However, only a small group of organic compounds is monitored on a regular basis throughout the world. Thus, an important task involves discovering the most important pollutants for particular cities and regions for regular monitoring in the future. Direct measurements of contaminants in the atmosphere are not always efficient as air represents an extremely dynamic medium. So, indirect methods by analysis of precipitations become often a method of choice in environmental analysis.

Rainwater samples collected in Valparaiso (Chile) were analyzed using modern GC/MS instrumentation. Our focus was on detecting and identifying as many as analytically possible organic pollutants and selecting the most relevant among them (priority and emerging pollutants). We were also planning to estimate the quantitative changes in pollutants levels over the studied period. In order to reach these aims we have to use the most powerful modern technique for sensitive analysis of complex mixtures - GCxGC-High-Resolution Mass Spectrometry. This is the first work dealing with comprehensive GC×GC-HRMS analysis of the rainwater in Chile. Earlier we have successfully used the same approach in the studies of Arctic snow, Moscow rain, French cloud water.

The samples were collected in the glass flasks during rain events every June in 2003-2017 in the Avenida Espana, Valparaiso, Chile (33o2'3.46"S; 71o35'42.84"W). The samples were then deep frozen for storage. The samples preparation was done in March 2018 according to the US EPA 8270 Method. Dichloromethane extracts of the samples at basic and acidic pH values were combined before the injection. The GC-HRT+ 4D and BT 4D (both LECO Corporation, USA) were used for the analysis.

Over 700 organic compounds belonging to the various classes of chemicals were identified. Here we report the nature and levels of over 200 priority pollutants and emerging contaminants belonging to the most relevant classes from the environmental point of view: polycyclic aromatic hydrocarbons, pesticides, dialkylphthalates, organosulfur compounds, alkylpyridines, organophosphates, and phenols. Phenols were the most representative class of pollutants. Besides priority phenols, where dominated were cresols, over fifty chlorinated (up to pentachloro) and nitro derivatives were detected. Bisphenol A and 13 isomers of bisphenol G were also identified. The concentration levels of phenols constitute 5 orders of magnitude depending on the species and a year. Principal PAHs and their numerous alkyl derivatives were also detected. However their levels were lower than we expected (low ng/l). Among 40 detected phthalates diethyl and dibutyl were the dominant species with their concentration at mkg/l levels. Sulfones and especially substituted thiophenes represented a majority of organosulfur compounds. Their levels are from 0.1 to 300 ng/l. The assortment of these compounds was very wide. Over 20 organophosphates were detected at quite different levels. They are actively used nowadays for replacing more toxic phthalates and polybrominated ethers as plasticizers and flame retardants, correspondingly. Dialkylformamides and substituted pyridines become more and more widespread pollutants all over the world. Quite a number of them were detected in our Chilean rain samples, although their levels were in very wide concentration range. Among novel pollutants it is worth to mention such compounds as simazine (in all samples) and lindane (in several samples). Besides those, benzothiazol, benzoic acid, benzyl alcohol, acetophenone, benzaldehyde, were determined at the levels of mkg/l. Surprisingly not a single PCBs class representative was detected in any of the samples.

As a result of the study the following chemicals may be considered as priority pollutants for the studied region: isomeric cresols, bisphenol A, simazine, diethylphthalate, dibutylphthalate. However there is no information about the toxicities of the majority of the detected compounds. The levels of majority of the detected compounds were increasing over the years, demonstrating the increase of the air contamination in the region. More thorough data review may definitely increase the number of detected priority pollutants which should be monitored at regular basis, while their sources should be identified.

Distribution of semi volatile pollutants in the Moscow city area in the winter of 2018

ORAL O18
(**#Atmosphere**)

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Moscow is one of the largest cities in the world with a population of over 12.5 million. Though the urbanisation process during last decades pushed out many factories and plants out of city limits, Moscow still remains an industrial center with many industrial and power plants, incinerators, landfills and refineries located near the residential areas and the city center. There are also 5.5 million cars and trucks registered in Moscow plus a lot of transit vehicles. All those create a significant level of the anthropogenic burden on the Moscow air. Thus, establishing the spread of the contaminants and pollution sources in the city air becomes an important issue for the public health policy.

Snow is having a very powerful adsorption ability and it is a useful matrix for long term storing volatile and semi volatile compounds, even the most unstable ones.

There is a large variety of different classes of organic compounds, which could be present in the polluted air. However, in this study, we have focussed on semi volatile organic compounds as representing the majority of the known hazardous pollutants, including the ones from the US EPA list of priority pollutants. Two-dimension gas chromatography coupled to high resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS) with electron ionisation (EI) nowadays is the most comprehensive, reliable and sensitive analytical method for analysis of volatile and semi volatile organic compounds. Retention indexes and EI mass spectral libraries together with accurate mass measurement allow identification of the known and even unknown compounds with high confidence. It was previously shown that application of HRTOFMS in case of analysis of unknown compounds in complex mixtures is the key for obtaining reliable results [1]. Previously we have studied spatial distribution of the polar organic pollutants with high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [2]. Herein we present the results of studying distribution of semi volatile pollutants in Moscow air during winter of 2018.

Nine snow samples were collected in February 2018 in the different locations in Moscow. After melting the snow samples at room themperature, the further sample preparation procedure was conducted according to US EPA 8270 method. The extracts and blanks were analysed using Pegasus GC-HRT+ 4D instrument (GCxGC-EI-HRTOFMS, LECO Corporation, USA). The identification of organic compounds was made using mass spectral library NIST14. Besides, all identification results were thoroughly annotated to avoid the false-positive results.

The majority of the identified compounds corresponded to petroleum hydrocarbons, fatty acids, phthalates, surfactants, flame retardants, dyes, solvents, UV-filter, cosmetic additivies and other. Among these classes several dozens of compounds are from the US EPA priority pollutant list. From the large list of the identified compounds special attention was payed to pyridine derivatives, mainly alkyl pyridines. These compounds have currently become widespread environmental pollutants in the highly populated areas. They were detected recently in some other types of environmental samples [3, 4].

To understand the similarities and differences of the air pollution between the sampling sites and spatial distribution of identified pollutants across the city, the principal component analysis (PCA) method was used. The analytical data were processed using a homebuilt software package. The obtained results were combined with traffic information, location of potentially main pollution sources and weather conditions during the winter of 2018. As a result of this study we have created a map of the city polution by priority contaminants.

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Session 3: Soil and sediments

Plenary lecture

Detailed pesticide fate descriptions and realistic hydrogeological settings applied in the pesticide leaching risk assessment for clay till fields

Plenary
lecture PL3
(**#Soil**)

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The use of pesticides is of environmental concern because of the many non-targeted side effects it generates. Numerous guidelines and models have been set up, to predict the general fate of pesticides, and more specifically, the risk of pesticide leaching from primarily agricultural soils, e.g. Council-directive-91/414/EEC (1991) [1]. These guidelines and models incorporate key fate processes like sorption and degradation and flow through the variably-saturated soil. None of these predictions, however, take into account the variation in space and time of the fate processes nor do they account for realistic hydrogeological settings.

Field-scale monitoring results collected within the Danish Pesticide Leaching Programme (http://pesticidvarsling.dk/om_os_uk/uk-forside.html) [2] reveal that some pesticides and/or their degradation products, contrary to the predictions, can leach through the variably-saturated zone to the groundwater. This is especially pronounced at the low-permeable clay till fields.

At these fields, wormholes linked to deeper fractures seem to facilitate rapid preferential transport of solutes to great depth. Low permeability mineralized layer, or coating, often exists at the interface between the matrix and the discontinuities (fractures or wormholes), i.e., a layer, which reduces matrix imbibition and thus promotes discontinuities-dominated flow as opposed to matrix dominated flow. Coatings varies from organic matter in the wormholes to heavy deposits of iron- and manganese oxides in the deeper part of the fractures. Such hydrogeological setting responds quickly to the climatic input resulting in yearly groundwater fluctuations of 3-4 meters or more.

Recent studies of the degradation and sorption potential of different domains in clay tills have revealed a huge spatial heterogeneity [3]. The largest and most homogeneous degradation potential is found in the upper app. 30 cm layer if not artificial build, whereas deeper layers may have domains of fast and slow and even no degradation. The active domains are often linked to the discontinuities in the soil matrix, which give rise to a higher water-soluble carbon concentration, larger bacterial densities and thus activities in the discontinuity compared to the adjacent soil matrix. This difference can be caused by the presence of a coating on the walls of the discontinuity having negligible porosity and hence disconnecting the two domains. This coating also seem to play a role in the sorption potential of compounds. Like degradation, sorption is generally most pronounced in the top layer having the highest organic matter, but also sorption to the coating in the discontinuities can play a role.

With the modelling tool COMSOL Multi- physics® the impact of such heterogeneity and hydrogeological setting on the leaching risk of MCPA [4], glyphosate and tebuconazole through clay till is evaluated based on extensive laboratory experiments on soil samples from each soil domain together with realistic coherent net precipitation and fluctuating groundwater table. The results indicate that a fluctuating groundwater table and the influence of domain specific sorption and degradation (also in regard to artificial soil layer) in many cases are imperative for assessing the pesticide leaching risk from clay tills.

Acknowledgements

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Session 3: Soil and sediments

Oral presentations

Can the addition of bacterial siderophores help in the phytoextraction of Cu from vineyard topsoils?

ORAL O19
(**#Soil**)

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The use of copper-based fungicides to control downy mildew in grapevine has led to a Cu contamination of vineyard topsoils. This copper contamination is suspected to be at the origin of harmful effects on grapevine leading to its decline. Extracting copper from vineyard soils using plants able to accumulate metals is an option whose effectiveness is often limited by the low phytoavailability of Cu in soil [1]. The addition of bacterial siderophores could help increase the phytoavailability of Cu since some of these molecules strongly complex Fe(III) but also divalent metals including Cu [2]. However, it is necessary to better understand how these molecules interact with the soil constituents and modulate the dynamics of Cu in contrasting pedogeochemical contexts.

The objective of this work is to evaluate the extent to which an addition of the siderophore pyoverdine (Pvd) modulates the mobility and the phytoavailability of Cu in vineyard soils. This work is based on a collection of eleven vineyard topsoils with the same total Cu content (120 ppm), on which extractions with 0.005 M CaCl2 were carried out. The concentration of total Cu and free ionic Cu in these extracts were used to assess, respectively, the mobility and the phytoavailability of Cu in these soils, in presence and absence of Pv

The first results show that Cu phytoavailability can vary by a factor of 1000 among soils with the same total Cu content. The phytoavailability of Cu seems to depend more on the speciation of Cu in solution than on its partitioning between the solid phase and the solution, as evidenced by the strong relationship observed between pCu and pH in CaCl2 extracts. Pyoverdine addition systematically increased the mobility of Cu as well as that of Fe and Al. The Cu mobilization factor varied from 1.4 to 16.5 depending on the soil, with no obvious relationship to its physico-chemical characteristics (pH, texture, organic matter content). However, Pvd addition systematically reduced the phytoavailability of Cu due to a significantly higher complexation of Cu, a priori to Pvd, in the extracts. All these data suggest that the participation of the Pvd-Cu complex to the root uptake is essential for Pvd addition to promote the phytoextraction of Cu in vineyard soils.

Effect of Cu^{2+}-contaminated soils on the biodegradation of the herbicide mesotrione by *bacillus megaterium* Mes11

ORAL
O20
(**#Soil**)

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Copper is one of the heavy metals most extensively used in agriculture and industries and consequently one of the most found in the soil compartment. Indeed, due to its fungicide activity, Cu^{2+} is intensively applied to tree cultivation and vineyards to prevent mildew disease leading to topsoil contamination up to 1g per kg of dry soil. This pollution does not only disturb the biogeochemical cycle of Cu but it also strongly affects the diversity, viability and activity of the soil bacteria and consequently impacts their biodegradation activity toward pesticides. Among the new pesticides that recently appear on the market, mesotrione, a pesticide from the triketone family, is increasingly applied either as individual or in cocktail form [1]. However, so far, there is still a great lack of understanding concerning the fate of mesotrione in soil, its biodegradation by the microbial community and the impact of heavy metals (Cu^{2+} particularly) on its dissemination.

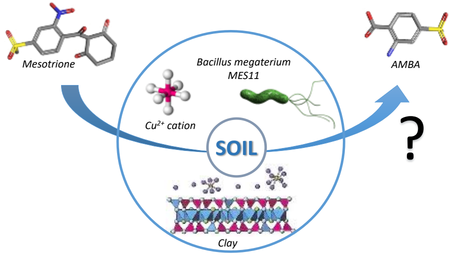

Fig.1: Combined effect of Cu^{2+} and soils on the dissemination of mesotrione

This study focus on the impact of Cu^{2+} contamination on the biodegradation of mesotrione by *Bacillus megaterium* Mes11 embedded in two natural soils and in clay mineral fractions (Fig. 1). As clay and organo-clay fractions are known to strongly interact with herbicide molecules, bacteria and heavy metals, our objective is also to address the joint effect of all components to the fate of mesotrione.

The complexation reactions of Cu^{2+} with mesotrione (1/1 stoichiometric ratio) were first highlighted using UV-Vis and fluorescence spectroscopies while no complexation was evidenced with other metallic cations (Cr^{3+}, Zn^{2+}, Pb^{2+}, Fe^{3+}). Two natural soils (a Vertisol from France: VS and a Red soil from Russia: RS), clay minerals (Montmorillonite, MMT; Layered Double Hydroxides, LDH) and organo-clay fractions (MMT-HA, LDH-HA) were contaminated with Cu^{2+}. The speciation of Cu^{2+} (precipitated-Cu^{2+}, exchanged-Cu^{2+}, coordinated-Cu^{2+}) was identified. Abiotic immobilization of mesotrione by Cu^{2+}-contaminated soils and clay minerals was quantified using adsorption isotherm experiments. The presence of Cu^{2+} and organic matter (Humic acid, HA) loaded on soils and clay minerals increased strongly mesotrione adsorption.

Kinetics of mesotrione biodegradation by *Bacillus megaterium* Mes11 in the presence of free Cu^{2+}, pure and Cu^{2+}-contaminated soils and clay minerals will be presented. Combining Cu^{2+} and clay minerals resulted in a complete inhibition of the mesotrione biodegradation. The competition between biotic and abiotic mesotrione processes will be presented and discussed.

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Monitoring of pesticide dissipation in remediated soil

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The amount of fertile soil available for agriculture world-wide is rapidly decreasing because of erosion, non-agricultural use and pollution. A very important group of soil pollutants are heavy metals. These were in many areas introduced into soil by the mining and metal industry up to the second half of 20th century, when the environmental concerns gradually changed the production in these industries, introducing cleaner processes. However, many areas surrounding (former) mining areas and industrial sites are still heavily polluted with certain metals: lead, chromium, arsenic, cadmium, copper, mercury, nickel, etc. These are problematic because some are highly toxic both to plants and animals. Agriculture on heavily polluted soil is not recommended because of uptake of metals into the crops. Metal ions can also leach into drinking water sources.

Several options are available to remediate the soil polluted with heavy metals. An acceptable method should be effective and economically acceptable due to the fact that huge amounts of soil are to be processed. Also, it should lead to normal functioning of the soil with minimal risks during and after remediation [1]. Phytoextraction and immobilization of metals in the soil are acceptable, but are not possible for some more problematic metals, e.g. lead; or raise concern due to the fact that metals are still present in the soil, respectively.

A very effective remediation technology of soil washing with EDTA solution, followed by EDTA recycling, has been developed and patented by D. Leštan and co-workers [2]. EDTA-remediated soil is then revitalized by fertilization and soil amendments [3].

In this study, we developed a reliable analytical method for the determination of four selected pesticides (bentazone, isoproturone, mecoprop, and metolachlor) in heavy-metal contaminated soil samples before and after the washing with EDTA and revitalization. The aim was to monitor the dissipation of these pesticides in the soil after the application. Dissipation can be caused by pesticide leaching, but is more often the result of abiotic and biotic degradation, the latter usually representing the major part. Therefore, pesticide dissipation gives a reliable measure of functioning of the soil microorganisms.

The main part of method development was optimization of the extraction of pesticides from the soil. Ultrasonic extraction was used, followed by solid phase extraction (SPE) for clean-up. Analytical determination was performed by HPLC-UV. Method validation was performed. Extraction method has shown satisfactory recoveries (61–97 %) and precision (RSD 0.6–22 %). Limits of detection were 5–10 µg/kg for all analytes.

The results of monitoring have shown that there is no difference in pesticide concentration after either two or three weeks in treated and untreated soil from two contaminated sites. This is a further confirmation of the efficacy of the applied soil remediation technology.

Acknowledgements

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Mobility of trace elements during laboratory resuspension experiment

ORAL O22
(**#Soil**)

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Dissolved trace metals can bind to a solid phase (sediments, colloids) according to three main mechanisms: adsorption and ion exchange, precipitation or co-precipitation [1]. Particles will eventually settle down to sediments, which turn into an important sink for trace metals [2-3]. Nevertheless, sediment can be resuspended due to numerous events (tides, waves, wind, dredging activities...) and become a major source of contamination. Indeed, sediment resuspension leads to an important release of metals in the dissolved phase (remobilisation), more important than the continuous flux due to metals' diffusion from sediments' porewater to the water column.

To understand the kinetics of dissolved trace metals release and/or removal, as well as their extent, a laboratory resuspension experiment was performed by mixing sediment (collected by a core-sampler) to seawater collected at the same sampling site [4-5]. The study area (La Spezia harbour, Italy) is semi-closed bay and undergoes strong anthropic pressures. Trace metals' concentration was analysed both by electrochemical technique (voltammetry) and HR ICP-MS.

The obtained results demonstrated that the remobilization kinetics and amplitude is depending on both the considered metal and the solid/liquid ratio.

For example, a decrease of dissolved Cu concentration occurred ever since the beginning of the resuspension experiment, followed by an increase after 1 day of the contact time, finishing with a higher concentration than in ambient seawater after 2 weeks of contact time. On the contrary Pb showed an important release from particles just after their addition with a maximum of release at 1 day of contact time before being re-adsorbed to drop down to the initial seawater concentration after 2 weeks. Furthermore, the higher the particle's quantity was, the more exacerbated the metal's behaviour, resulting in a more pronounced Cu decrease or increase after 1 or 2 weeks of contact time, respectively. Such observation could also be underlined for Pb kinetics. Poisoning seawater (with 50mM NaN3) also showed, at 1 day of contact time, a decrease of dissolved Cu suggesting that the behaviour of Cu can be related to micro-organisms, whereas no such trend was found for Pb, suggesting its abiotically-controlled behaviour.

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Persisitent Organic Pollutants (POPs) in sediments from the Wouri Estuary Mangrove, Cameroon: Levels, patterns and ecotoxicological significance

ORAL
O23
(#**Soil**)

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Mangroves are one of the most threatened tropical environments despite their numerous ecological and socio-economic services. Anthropogenic activities stand as a major factor inducing the degradation of these ecosystems. Previous studies revealed the presence of Persistent Organic Pollutants (POPs) in various mangrove compartments but to our knowledge, few such studies were performed in Africa and in Cameroon in particular [1,2]. The present work aims at carrying out an extensive geographical assessment of 22 Chlorinated Pesticides (CPs), 7 indicator Polychlorinated Biphenyls (PCBs) and 15 US EPA priority Polyaromatic Hydrocarbons (PAHs) in superficial sediments (0-5cm) sampled (November 2017) at 21 stations around the Wouri Estuary Mangrove (WEM) situated nearby the densely populated town of Douala.

The results indicate the presence of the 22-targeted pesticides, except endrin, in all stations. Most frequently found compounds are; 4,4' DDD, 4,4' DDE, 4,4' DDT, HCH, endosulfan and alachlor. Generally, the concentrations are very low (<100 $ng.kg^{-1}$), but can rise to some hundreds of $ng.kg^{-1}$ for DDT and metabolites, or even higher for endosulfan I and alachlor, which were detected in about 50% of samples at concentrations higher than 1 $\mu g.kg^{-1}$. Total pesticides content varied between 2.2 and 29.1 $\mu g.kg^{-1}$, with average and median values of 11.1 and 10.4 $\mu g.kg^{-1}$, respectively. The presence of these compounds in the study area could mainly be assigned to the use of pesticides related to disease vector control and to a lesser extend peri-urban agriculture.

PCB concentrations ranged from 1.7 to 31.6 $\mu g.kg^{-1}$. The major compounds were the congeners CB153, CB188, CB138 and CB180 accounting together for 86,57 % of the Σ7PCBs. Indeed, heavily chlorinated PCBs are more accumulative and persistent in sediments, whereas lightly chlorinated PCBs are more susceptible to losses through volatilisation and possibly microbial degradation [1]. Their presence could originate from the discharge of untreated industrial and municipal wastes in the mangrove area.

The concentrations of PAHs ranged from 83 to 544 $\mu g.kg^{-1}$. The dominance of high molecular weight over low molecular weight PAHs indicates a predominant pyrogenic origin. Furthermore, PAH ratios (Phe/Ant < 15, Fl/Pyr < 1 and B(a)Ant/Chry $\geq$ 0.5) show that PAHs originate from pyrogenic sources associated with used lubricants, combustion of gasoline, diesel, crude oil, fuel oil and emissions from automobiles and diesel trucks [3]. This is supported by dense traffic, intense industrial and harbour activities carried out in this area.

POPs concentrations were similar to others measured in mangrove sediments of African countries such as Senegal, Ghana, Congo and Nigeria [1,4,5]. Furthermore, to evaluate the ecotoxicological significance of sedimentary POPs levels, the findings of this study were compared to sediment quality guidelines.

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Micro-structural changes in soils induced by wetting and drying: Effects on herbicide mobility

ORAL O24
(#**Soil**)

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Wetting and drying, even at a daily scale, affects soil structure; however, this phenomenon has been addressed mainly at the macro-aggregate scale [1-2]. In the current study, the effect on soil micro-structure, aggregate packing and stability and subsequent effect on pesticide mobility, have been investigated. To reach a mechanistic understanding, structural changes as well as atrazine desorption and leaching from vertisol, sandy, and loess soils, subjected to wetting and drying, were quantified. Atrazine mobility from the vertisol was enhanced by a wetting and drying cycle, while mobility from the loess soil was suppressed. As expected, mobility of atrazine in the sandy soil remained unchanged. Micron scale alterations in soil packing, obtained by micro-CT imaging coupled with image processing, suggest that large vertisol aggregates disintegrate during the drying stage [3], while fine loess particles form larger aggregates. To quantify and reflect these observed changes in soil stability, an aggregate durability index was developed and validated, based on changes in soil particle size distribution [4]. Wetting and drying induced disaggregation of the vertisol structure at the micron scale; by contrast, wetting and drying stabilized the loess aggregates, an effect which may be due to CaCO3 cementation. These trends can explain atrazine mobility in the different soils. As atrazine is trapped within the vertisol aggregates, disaggregation leads to enhanced mobility of the pesticide, while stabilization of loess aggregates reduces its mobility. Finally, wetting and drying directly effects the soil micro-structure which has an immense indirect effect on pollutant mobility [5], with both potentially leading to soil degradation.

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Keywords: soil structure, herbicide mobility, micro, CT

Geochemical footprints of human activity in low-order stream floodplains

ORAL
O25
(#Soil)

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Purpose

This study evaluates the variability of the trace element and organic contaminant inventory and dispersion in a small-scale floodplain sediment transect at a reach of a typical Central European foothills to lowland river. By using threshold contents of pollution-sensitive trace elements and market introduction dates of organic xenobiotics, the sediment is assigned to phases of anthropogenic activities of the past 200 years, and sedimentation rates are estimated. The potential of a methodological combination of the research fields geomorphology, geochemistry, and fluvial morphology is evaluated.

Materials and methods

The study is based on a sediment core transect expanding approximately 60 m between the river bank and the wall of the valley. The sediment samples were analyzed for grain size composition, trace element inventory, and organic xenobiotics contents as important prerequisites for geochronological invetsigations [1]. The frequency and magnitude of floodplain inundation, as well as estimated flow velocities and volume of deposited sediments were numerically modeled. Changes in floodplain morphology were interpreted on basis of a Digital Elevation Model (1 m resolution), historical maps from 1865, and field surveys. The architecture of the alluvial sediments was investigated at the sediment cores taking the recent floodplain relief and possible subrecent settings into account.

Results and discussion

The investigated Fluvisols obtain a heterogeneous pattern of alluvial deposits, bearing trace element and organic compound gradients that allow the distinction between pre-industrial, industrial, and post-industrial sediments [2]. Cu, Zn, and Pb – as trace elements that are representative for the industrial activity in the catchment – show different depth profiles that are independent from grain size composition and organic content. The Zn content, for example, varies within a range of 130–1700 mg kg^{-1}. On basis of the determined local empirical threshold values, sedimentation rates were estimated and verified by means of the historical development of the urban areas in the headwater. The estimated sedimentation rates vary between the three applied methods within a range of 0.1–0.7 cm a^{-1}.

Conclusions

The investigation of the anthropogenic impact benefits from an interdisciplinary, complementary approach that combines common methods from geomorphology, organic chemistry, and fluvial morphology. An assessment of the pollution of floodplain sediments requires data from the surrounding area and should not rely on single bank profiles, since pollution patterns can vary on small scales. Horizontal and vertical changes of facies have to be taken into account. Low-order stream floodplains allow the detection of distinct signals that might be blurred in catchments of a larger scale.

Acknowledgements

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UVB activation of persulfate *vs* Hydrogen peroxide for soil washing effluent treatment: Efficiency, effect of various soil constituents and mechanism

ORAL
O26
(**#Soil**)

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Contamination of soils by toxic pollutants, especially by the persistent organic compounds has been a serious concern worldwide. Hydrophobic organic compounds (HOCs) represented by polycyclic aromatic hydrocarbons (PAHs) are known to induce high environmental risks due to their long-term persistence resulted from their characters of low solubility in water, and high ecotoxicity (mutagenic, carcinogenic and teratogenic) [1-2]. Surfactant enhanced soil washing has been proposed as a valid, efficient and relatively inexpensive alternative for soil remediation of PAHs contaminants. However, a large amount of soil washing effluent produced during the processes of soil washing must be further treated to avoid discharge of wastewater containing toxic substances.

Advanced oxidation processes (AOPs) based on generation of hydroxyl radical ($HO^{\bullet}$) or sulfate radical ($SO_4^{\bullet-}$), using hydrogen peroxide (H_2O_2) or persulfate ($S_2O_8^{2-}$) as species precursors, have been investigate as efficient and environmental friendly techniques for treatment of water soluble contaminants under UV irradiation [3-4]. UVB based oxidation has great potential due to i) possible use of LED ii) reduced operating cost compared to UVC and iii) higher efficiency than UVA. To the best of our knowledge, there are only few studies systematically using UVB activation of PS comparing with H_2O_2 for soil washing effluent treatment.

The current work focus on $HO^{\bullet}$ based versus $SO_4^{\bullet-}$ based AOPs for treatment of simulated phenanthrene (PHE) contaminated soil washing effluent using non-ionic surfactant polyoxyethylene-(20)-sorbitan monooleate (Tween 80) to improve the solubility of PHE. The performance of UVB based homogenous oxidation processes, *i.e.* UVB/$S_2O_8^{2-}$ and UV/H_2O_2 and using UV irradiation alone as a control is studied in this paper. Comparison of key factors efficiency, such as oxidant concentrations, pH, and presence of commonly found inorganic anions (Cl^-, HCO_3^-/CO_3^{2-}, NO_3^-), on the PHE degradation efficiency using the two precursors are evaluated. Main photoproducts generated during the oxidation process are identified.

The results suggest that pH has no significant effect on PHE degradation for the $S_2O_8^{2-}$ system while, slight effect can be observed in the presence of H_2O_2. The presence of Cl^- shows opposite influence on PHE degradation with the two radical precursors. The addition of HCO_3^- exhibit different effect on PHE degradation. A degradation mechanism of PHE involving different radical species is also suggested.

Acknowledgements

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Session 4: Waters

Plenary lecture

Solar photo-Fenton as a tertiary wastewater treatment. From mechanisms to reactor design

Plenary lecture PL4 (#**Water**)

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The challenge facing global water scarcity is to reduce water contamination. Nowadays, conventional wastewater treatment plants (WWTPs) are not able to remove certain organic compounds such as pesticides, pharmaceuticals and hormones. Although these compounds, called micropollutants, are found in secondary wasterwater effluents at very low concentrations (ng L^{-1} - ug L^{-1}), they have a toxic effect on

organisms and environment [1]. Among Advanced Oxidation Processes (AOPs), the photo-Fenton process has been reported as an environment friendly treatment for micropollutant removal. It involves the oxidation of organic matter with the hydroxyl radicals generated by a redox cycle between iron and hydrogen peroxide accelerated by UV radiation.

The photo-Fenton process is carried out at mild oxidative conditions for micropollutant removal, around 5 mg L^{-1} of Fe and some tens of mg L^{-1} of H_2O_2. At acidic pH, 2.8, and low concentration of the light absorbing species (Fe^{3+}), an excess of photon availability is observed when using reactors with short light path length. As a consequence, the use of raceway pond reactors (RPR) was proposed [2]. RPR consists of open channels in which the light path length can be varied by changing the liquid depth.

A simplified kinetic model predicting photo-Fenton kinetics as a function of environmental (irradiance and temperature), geometrical (light path length) and operating variables (reactant concentration) has been developed. Additionally, it tracks the saturation of ferric iron photoreduction at high values of the volumetric rate of photon absorption (VRPA), above 866 µE m^{-3} s^{-1} [3].

The use of the iron chelator, ethylenediamine disuccinic acid (EDDS), has been proposed to run the photo-Fenton process at the natural pH of water, and hence to reduce operating costs [4]. Micropollutant removal in RPR at neutral pH using the Fe^{3+}-EDDS complex has been studied and the main reactions taking place have been characterized. Again, an excess of light at short light path length was observed and photosaturation was reached at a VRPA of 1550 µE m^{-3} s^{-1}, higher than that corresponding to Fe^{3+} at acidic pH due to the higher absorptivity of the complex. Although the Fe^{3+}-EDDS complex decomposes with light, and consequently iron precipitates, high micropollutant removal rates can be achieved at short reaction times [5]. In line with this, a mechanistic model of the process has recently been proposed for the first time. Despite the complexity of the reaction system at neutral pH (iron precipitation and presence of species such as HCO^{-} /CO^{2-}ions), the model acceptably reproduces the kinetics of Fe^{3+}-EDDS reaction, iron precipitation, H_2O_2 consumption and micropollutant removal.

Finally, both the model at acidic pH and at neutral pH have been successfully validated outdoors with a change of scale from 0.35 to 360 L under solar UV radiation in winter and summer conditions. These models are, therefore, of great application for RPR design as well as for the control and optimization of the photo-Fenton process as a tertiary treatment in WWTPs.

Acknowledgements

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Session 4: Waters

Oral presentations

Acetaminophen monitoring in surface waters and assessment of its photochemical reactivity by an electrochemical sensor

ORAL O27
(**#Water**)

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he use of huge amounts of water by human beings and their activities, such as industry and agriculture, causes contamination of water bodies. Pharmaceuticals and personal-care products (PPCPs), pesticides and nanoparticles are often detected in surface waters at low but potentially harmful concentrations. The presence of these emerging contaminants (ECs) in water bodies is of high environmental concern because they have not yet a legal regulation and could cause potential toxic effects on aquatic ecosystems and human health [1]. The wastewater produced by municipalities and industrial activities is often a source of water pollution, because traditional Waste Water Treatment Plants (WWTPs) are usually unable to remove water-soluble and biorecalcitrant ECs from wastewater. Consequently, ECs are often released in surface water bodies [2] where they can undergo transformation by both abiotic (mainly, chemical and photochemical reactions) and biotic processes. Although these transformation pathways can degrade ECs, they can also produce by-products of higher environmental concern than the parent compounds. Therefore, the monitoring of ECs (and of their by-products) in both WWTPs influents/effluents and surface waters is an important tool to assess the human impact on aquatic environments. In particular, there is a lack of fast and cheap screening techniques to assess potential hot spots within a widespread environmental occurrence of ECs.

In this work, the Differential Pulse Voltammetry (DPV) was used to detect the widely used analgesic drug acetaminophen (also known as paracetamol, hereafter APAP) in surface water samples [3]. An electro-activated glassy-carbon electrode (aGCE) was adopted as electrochemical sensor. With a Design of Experiments approach, the DPV parameters were optimised to provide the best electroanalytical response. The linearity range, the limit of detection (LoD) and that of quantification (LoQ) were determined in both synthetic solutions and real samples by using different pulse-time (t_{pulse}) values. In synthetic solutions, measurements with t_{pulse} = 8 ms provided lower LoD and LoQ (1.8 and 5.5 µg L^{-1}, respectively) but a quite short linearity range (5.5-33 µg L^{-1}). By increasing t_{pulse} to 16 ms, the linearity range increased (8.9-290 µg L^{-1}) but the LoD and LoQ got worse. Furthermore, APAP concentrations >4.4 µg L^{-1} and >0.2 µg L^{-1} could be detected in real-water samples, respectively untreated and pre-treated with solid phase extraction. The electrochemical sensor was then used to monitor APAP in the Po river basin near the city of Turin (Piedmont, NW Italy). Moreover, to verify the reliability of the electrochemical response, the DPV-based results were compared with those obtained by liquid chromatography coupled with High Resolution Mass Spectrometry (HPLC-HRMS), commonly used for pharmaceuticals quantification.

Finally, an aGCE-DPV-based technique was also implemented in an electrochemical set-up to carry out real-time monitoring of the photochemical degradation of APAP in the presence of nitrate and UVB light. It was thus possible to obtain a reliable assessment of the second-order rate constant of the reaction between APAP and $HO^{\bullet}$ radicals [4].

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Halogenated hydrophobic contaminants in a coastal industrialized area: Comparing passive samplers' accumulation to concentrations in waters, sediments and mussels

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Water becomes a scarce resource subjected to numerous anthropogenic pressures and is particularly threatened by chemical pollution. The identification and quantification of the responsible compounds is a prerequisite for remediation and to protect aquatic ecosystems and human life. In this line, the Water Framework Directive (WFD, 2000/60/EC) and the Marine Strategy Framework Directive (MSFD, 2008/56/EC) involve intense monitoring of the water bodies. Highly hydrophobic compounds are particularly troublesome because of their persistence and their specific tendency to bioaccumulate. Nonetheless, their monitoring in water constitute an analytical challenge due to their presence in aqueous dissolved phase at ultratrace levels – ng. L-1 or even less [1]. One solution is to determine them in other aquatic related matrices, such as sediments or biota. However, the heterogeneity of these matrices and the partition coefficients applied to derive aqueous concentrations are huge sources of variability and errors [2]. Alternatively, passive sampling of water has gained increasing interest over the past decade [3]. Particularly, it enables to overcome the difficulty in the ultra-trace analysis of hydrophobic contaminants through direct in situ preconcentration of compounds.

Among the passive sampling devices applied for hydrophobic contaminants, silicone rubbers have been selected because of the availability of detailed guidelines for use and field deployment. Moreover, sampler-water partition constants have been determined for classical contaminants, such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) [4]. But laboratory and field research are still needed for emerging halogenated pollutants.

In this work, occurrence of PCB and two classes of emerging halogenated hydrophobic pollutants, namely polybrominated diphenyl ethers (BDE) and chlorinated paraffins (CP), were investigated in a marine coastal area located in the Gulf of Fos (South-East of France) and surrounded by numerous industries. Nine coastal stations were monitored by collecting spot and passive water samples, sediments and mussels (Mytilus galloprovincialis). The performance reference compound approach [5] was used to analyse the influence of site conditions – i.e. water turbulence and biofouling – on compound accumulation by the silicone rubbers.

Main findings show that CP were omnipresent in the passive samplers, whereas they cannot be detected in almost all spot samples. This class of compounds was also consistently evidenced in sediment samples, but the chromatographic patterns were not necessarily similar to those found in silicone rubbers. BDE were also detected in all matrices, except spot water, at some specific stations. This kind of pollution can be well justified by historical industrial activities, and by potential contribution of the Rhône River. As far as we know, this is the first time that the field applicability of silicone rubbers has been demonstrated for the monitoring of CP in water.

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Disinfection in wastewater treatment plants: isolation and characterization of tramadol parent by products and evaluation of their toxicity

ORAL O29
(**Water**)

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During the last years, the widespread occurrence of personal care products, pesticides and stimulating drugs in water has gained much attention, especially for the evaluation of the environmental risk based on the calculation of the Predicted Environmental Concentrations (PEC) obtained from consumption data [1]. Data on the occurrence of these emerging pollutants were reported by Xing et al. (2018) in sewage treatment plant influents, effluents and sludge in many countries of the world, where they were found until to hundreds ng/L concentrations [2]. Often the products obtained by disinfection treatment could be more toxic than parent compounds especially using the chlorination process [3]. Moreover, the potential risk posed by these pollutants could be increased by their susceptibility to produce photo-transformation products [4]. Tramadol is a synthetic, centrally acting analgesic agent used for the relief of acute and chronic pain, which has been used in both human and veterinary medicine. Recent papers have reported a study on the increasing tramadol utilization associated to the mortality over the past 15 years in the UK, highlighting the high toxicity of this drug [5].

Our research is focused on the evaluation of the environmental effects of tramadol and its transformation products, mimicking the most common experimental conditions in wastewater treatment plants. After disinfection treatment, the main transformation products have been isolated and characterized by NMR and ESI-MS analyses. Furthermore, in order to evaluate the environmental effects of products, aquatic acute and chronic toxicity have been tested on Brachionus calyciflorus and Ceriodaphnia dubia as well as their mutagenesis and genotoxicity tested on bacterial strains.

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The influence of inorganic salts on the formation of disinfection by-products during aquatic chlorination of UV-filter avobenzone

ORAL O30
(#**Water**)

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Disinfection is an important step in the purification of drinking and swimming pool water. The most common procedure involves chlorination, which efficiently eliminates microorganisms. However, the reaction of active chlorine with dissolved organic matter produces numerous organochlorine compounds posing a hazard to the environment and human health. The UV filters is the emerging class of contaminants, as their application to skin for protection from UV irradiation becomes increasingly popular all over the world. Certain components of UV filters were detected in swimming pools and result in the emergence of new ecotoxicants. Earlier we have reported the formation of disinfection by-products of the most popular UV-filter, avobenzone, in conditions of aqueous chlorination in fresh [1] and sea [2] water. However it was also interesting to understand the influence of the common inorganic ions often present in the natural water and swimming pool water. Thus, in the present study, 32 compounds, including numerous brominated and two iodinated derivatives, which result from the chlorination of avobenzone in water with addition of Br^-, I^-, Cu^{2+} and Fe^{3+} ions, were identified by gas chromatography – high resolution mass spectrometry (GC-HRMS).

Aquatic solution of avobenzone reacted with sodium hypochlorite solution at neutral pH. Solutions of potassium bromide and iodide, copper chloride and iron chloride were added to the corresponding reaction mixtures. The ratio of the active chlorine/avobenzone/inorganic ions was 20/1/1. Aliquotes of reaction mixtures were taken at the time intervals from 1 hour to 4 days. Dichloromethane was used to extract semivolatile compounds from the mixture. Purge-and-trap system was used to control the formation of the volatile by-products. Perdeuterated polycyclic aromatic hydrocarbons were used to estimate the levels of the by-products. The Pegasus 4D and GC-HRT 4D (LECO Corp., USA) GC-MS systems were used for the analysis. Identification was done by matching abtained mass spectal data with NIST library and the LECO accurate mass library AML 1.1. The novel by-products were tentatively identified using the known pathways of fragmentation of organic compounds in electron ionization conditions.

Thirty two disinfection by-products were detected in the reaction mixtures. The most wide assortment of by-products was found after performing reaction for 96 hours. The reaction starts with the substitution of the methylene hydrogen atoms for chlorine (bromine). Mono and dibrominated avobenzones were identified in presence of bromine, although the corresponding iodinated avobenzones were not detected. Nevertheless α-iodoacetophenones with metoxy and *tert*-butyl substitutes were detected. This fact is worth special mentioning as iodinated compounds are usually much more toxic than the corresponding chlorinated and even brominated compounds with the same structures. Besides that the acetophenones constitute the most dangerous group of avobenzone chlorination by-products. Due to its reducing properties iodine causes significant increase of unsubstituted tert-butyl- and methoxy-acetophenones among the reaction products. Addition of Br^- highly increases the assortment of by-products due to the formation of various organobromines. Addition of copper and iron salts does not cause formation of additional by-products, although the ratios of the forming products may differ significantly. Interesting that not a single volatile product including chloroform was detected.

The presence of inorganic salts in the swimming pools may bring to the notable increase of the assortment and levels of the disinfection by-products of such popular UV-filter as avobenzone. Brominated and iodinated products are of special concern. The assortment of the products increases with the reaction time. It should be taken into account especially in the swimming pools, where water is not changed often.

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Psychoactive pharmaceuticals in the aquatic environment

ORAL O31
(**#Water**)

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The concern of presence of pharmaceuticals in the environment is still current topic of number of studies. Pharmaceuticals in the wastewater are not completely removed in today's conventional WWTP. Although this problem was first highlighted in 1970s and the knowledge on environmental contamination significantly grew in mid-90s these is still no unambiguous solution [1,2].

Psychoactive pharmaceuticals represent group of medicaments that presence in aquatic ecosystems could possibly bring about some serious environmental and health consequences. Increased consumption of antidepressants, anxiolytics and hypnotics leads to higher environmental exposure and risks [3].

The connection between presence of certain group of antidepressants (selected serotonin reuptake inhibitors – SSRIs) in water and changes in Na/K-ATPase activity in brook trout nerve system has already been proven. Changes in fish behaviour after exposure of environmentally relevant concentrations of SSRIs were also observed [4].

The very fact that these chemicals are designed to make changes in human nerve system and the way of thinking points to the possibility of highly negative effects on living organisms. The possible link of environmental contamination with SSRIs and development of autistic spectra disorders in children is alarming [5].

The research focuses on AOPs (Advanced Oxidation Processes) removal with emphasis on the most prescribed psychoactive pharmaceuticals in the Czech Republic (representatives of anxiolytics, hypnotics and antidepressants). The interaction of these chemicals with activated sludge in municipal sewage treatment plant is also investigated.

Screening tests show that AOPs could be considered as reasonable method to remove target substances from wastewater.

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Photodegradation of novel oral anticoagulants under sunlight irradiation in aqueous matrices

ORAL O32
(**#Water**)

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The Food and Drug Administration (FDA) recently approved the use of three novel oral anticoagulants (NOACs), namely dabigatran etexilate (2010), rivaroxaban (2011), and apixaban (2012) [1]. These three compounds are also increasingly used in Europe. In particular, these NOACs currently represent 30% of ingested anticoagulants in France with an increase in their consumption by a factor of 10 between the second trimester 2012 and the third trimester 2013 [2]. The main limitation for their use was the absence of antidote. In 2015, the FDA approved the idarucizumab as dabigatran antidote while rivaroxaban and apixaban antidote (andexanet alfa) is about to be validated [3, 4]. Thus, their prescriptions are expected to continue to rise in the near future.

To our knowledge, information reported in the literature about the occurrence of NOACs in the aquatic compartment, their fates, and their toxicity and those about their degradation products are very scarce [5-7]. This is especially worrying since human metabolism studies show that NOACs are eliminated in urines as unchanged forms at levels between 27 and 85% of the delivered dose [8]. In fact, organic pollutants are known to undergo degradation processes which must be taken into consideration. Photolysis can be one of the major ways of degradation for pharmaceutical compounds absorbing solar light as well as for those degraded by photosensitization. The presented work has for objective to bring information on the environmental fate of NOACs and especially on the direct and indirect photolysis reactions that they may undergo into the aquatic compartment.

Kinetics of photodegradation of NOACs were studied under simulated solar light irradiation in purified, mineral, and river waters. Dabigatran and rivaroxaban underwent direct photolysis with polychromatic quantum yields of 2.2×10^{-4} and 4.4×10^{-2}, respectively. The direct photodegradation of apixaban was not observed after 19 hours of irradiation. Kinetics of degradation of rivaroxaban was not impacted by the nature of the aqueous matrix while photosensitization from nitrate ions was observed for dabigatran and apixaban dissolved in a mineral water. The photosensitized reactions were limited in the tested river water (Isle River, Périgueux, France) certainly due to the hydroxyl radical scavenging effect of the dissolved organic matter.

The study of photoproduct structures allowed to identify two compounds for dabigatran. One of them is the 4-aminobenzamidine while the second one is a cyclisation product. In the case of rivaroxaban, as studied by very high field NMR, only one photoproduct was observed *i.e.* a photoisomer. Finally, seven photoproducts were clearly identified from the degradation of apixaban under simulated solar light.

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Biocide in waters after manual cleaning and its photodegradation in waters containing nitrate and humic acids

ORAL O33
(**#Water**)

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Cleaning dishes is a daily activity in every household, which does not receive special attention by most people. Only a few of them actually read the instructions before using the detergent and usually people do not dose it. In such cases, the misusage of the cleaning agent could lead to elevated amounts of residues on the dishes, that could have some harmful effects on our health and environment.

The purpose of our research was to determine residues of a biocide usually added in detergents for manual dishwashing. The model biocide was 1,2-benzisothiazol-3(2*H*)-one (BIT). Its residues were monitored on five different materials after manual dishwashing, in waters from kitchen sink after manual cleaning and after photocatalytic degradation of water samples from household containing detergent with BIT in the presence of nitrate and humic acids.

To determine the amount of residue of BIT in water samples solid phase extraction on C18 was used for preconcentration. The extracts were then analysed employing high performance liquid chromatography (Agilent 1100) with DAD detector (254 nm). The roughness of materials (pots and plates) used for the experiment was determined by atomic force microscope. After determining the residues of BIT on plates, pots, cleaning waters from kitchen sink, and waters from photoreactor, the assessment of toxicity was done by measuring the inhibition of the luminescent *Vibrio fischeri* bacteria on LUMIstox instrument. The photocatalytic degradation of BIT was done in the photoreactor (6 polychromatic fluorescent UVA lamps) with TiO_2 as a catalyst and the addition of humic acid and nitrates in deionized water.

The results of residues on five different materials and two type of dishes, showed that the residues of BIT are higher on pots compared to plates. The concentration of the remaining BIT, however depends on the material (glass < stainless steel <ceramics < plastics < wood) and its roughness. In fact the correlation coefficient (R^2) correlating the amount of BIT residues to the material roughness is 0.84 for pots and even higher 0.91 for plates. The average residues of BIT found on pots and plates (from 0.07 – 0.08 ppm) caused 7,1 % to 11,5 % inhibition of tested bacteria; whereas almost all bacteria (99%) were killed by concentrations of BIT residues in waters from kitchen sink after manual cleaning.

The waters containing BIT where then additionally analysed after photocatalytic degradation using TiO_2. In deionised water the amount of BIT decreased to 32.7 %, while when nitrates were added to 36.0 and humic acids to 37.0% of the initial value. The results suggest that the degradation of BIT is not affected by the presence of common sensitizers.

The toxicity assessment of samples containing BIT exposed to the photocatalytic degradation process showed that even in the case, when the amount of BIT was reduced to around one third of the initial value (25 ppm of BIT, commonly found in kitchen sink) a complete inhibited of the *Vibrio fischeri* bacteria was observed. This is in accordance with the measured value for BIT, which has a low IC_{50} value – 0.31 ppm.

Due to higher detergent and biocide residues in case of rougher materials and deeper dishes, it is suggested that higher volumes of water should be used for the final washing procedure, since this will remove a larger portion of the cleaning agent from the surface of the dish. On the other hand, the problem of chemicals' release is not adequately addressed by the dilution. The key element is also the dosing of the detergent which should be done according to the instructions and following the rule "that less is sometimes more". Only in this way, some side harmful effects on public health and environment from dishwashing could be avoided.

Acknowledgements

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Session 5: Modeling and Methodologies

Plenary lecture

Modelling Chemical Processes in Clouds

Plenary lecture PL5
(#**Modelling**)

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Water plays an important role in the atmosphere in form of cloud, fog or rain droplets and associated with aerosol particles. In this aqueous phase, unique chemical reactions occur that often lead to different products and take place on different time scales than in the surrounding air [1]. Examples include the oxidation of sulfur dioxide (SO_2) to sulfate (SO $^{2-}$), the major contributor to 'acid rain' or the formation of secondary organic aerosol$_4$in water (aqSOA). Implementing chemical aqueous phase processes in models is a great challenge as often the resolution of models is much coarser than the size of individual clouds and/or the small spatial and temporal scales, on which particle composition and water content change, cannot be resolved. Thus, computationally efficient parameterizations are needed to allow the description of such processes in large scale models.

There is general agreement that in-cloud formation is globally the major sulfate source. However, the implementation of sulfate formation processes among models greatly differs in complexity and accuracy. I will briefly discuss different approaches as included in global and regional models.

Organic mass is another significant contributor to atmospheric particle loading. Most organic aerosol is secondary, i.e. formed from gases in the atmosphere. Traditionally, secondary organic aerosol (SOA) has been described as condensation of low volatility gases on pre-existing particles. Over the past 15 years, evidence from model, laboratory and field studies has shown that secondary organic aerosol can be also formed in the aqueous phase of clouds and particles (aqSOA) [2]. I will highlight process model studies that demonstrate the ability of models to explain the presence of aqSOA compounds in clouds. Oxalate can often be considered a tracer compounds for such processes; I will contrast scenarios where this assumption is valid to those where aqueous processing is occurring, but oxalate cannot be detected.

The representation of aqSOA formation in deliquesced aerosol particles is much more complex and difficult as the aqueous phase is not dilute and, thus, approaches for ideal solutions, such as Henry's law, do not apply. I will give an overview of current assumptions and approaches that are used in models that describe aqSOA formation in aerosol water. In addition, I will discuss chemical mechanisms in aerosol particles that lead to products that have a higher molecular weight than the initial reactants. Such accretion or oligomerisation reactions are unique to aerosol water where high organic concentrations are present.

Many of the organic reactions in the atmospheric aqueous phase are initiated by the OH radical. Thus, an understanding of OH concentrations, sources and sinks in the aqueous phase is important to accurately model aqSOA formation. The direct uptake of OH from the gas phase is a major OH source in the aqueous phase. Since OH is only moderately soluble but highly reactive in the aqueous phase, its reaction rates show an apparent dependence on the drop surface [3]. As the implementation of cloud droplet distributions in models is often not feasible due to model resolution and/or lack of observational input data, a simplified approach is needed that both represent the size-resolved OH concentrations, and consequently, aqSOA formation rates, but is sufficiently simple for models. I will show how a limited set of microphysical parameters can be used to parameterize OH concentrations in clouds and thus to improve the representation of aqSOA formation [4].

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Session 5: Modeling and Methodologies

Oral presentations

Untargeted chemical analysis for the assessment of the overall contamination and the identification of emerging pollutant in wastewater treatment plants

ORAL O34
(**#Modelling**)

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The occurrence of known emerging organic pollutants in aquatic ecosystem was intensively studied in recent years due to the improvement of target analytical methods. To date, the challenge is to characterize environmental complex mixtures and to identify unknown compounds such as transformation products. Once in the environment, each compound undergoes structural transformations by biotic and/or abiotic processes which could affect their toxicity and it has already been reported that several transformation products could be even more toxic than the corresponding parent compound. Based only on target analysis, the current usual monitoring of environmental pollution allows only partial assessment of the overall chemical contamination of ecosystems. High Resolution Mass Spectrometry (HRMS) allows compensating this problem by tracking all detectable known and unknown compounds in environmental samples and identifying them. A complete identification of all chemicals detected in a complex mixture is nevertheless not possible and due to the complexity of the acquired signals, such analytical approach requires strategies to prioritize the way to treat data and to identify relevant compound.

In this study, HRMS was applied to several wastewater treatment plant (WWTPs) samples to establish an overall contamination diagnostic and to identify major contaminants that could be released in environment. Indeed, all compounds used in everyday life as well as natural molecules are collected in wastewaters and are released for a part after treatment in the aquatic environment. Thus, effluents of WWTPs represent a major pathway of introduction of organic pollutants into the aquatic environment. A part of the contamination of aquatic ecosystems such as rivers and groundwaters is also due to the water ingress and water runoff on farm plot after land application of sludge. It is therefore important to assess the environmental impact of WWTPs. This requires an efficient characterization of the presence and the identification of compounds, especially transformation products, in both wastewaters and sludges in order to predict their potential occurrence in natural waters and finally the associated risks for wildlife. In this context, we have analysed by LC-QTOF, influents and effluents but also sludges from WWTPs. The non-target screening performed on wastewaters allowed detecting more than 7000 and 4000 features in influent and effluent extracts of WWTP, respectively. Based on the reprocessing of non-target screening data, 83% of features were removed from the dissolved phase in effluent suggesting either some degradation phenomena or compound transfer to sludge and biofilter. To address this hypothesis, further investigations are under progress on sludge and first results will be presented. Concerning other detected features in the effluent, we found that 70% of entities were detected only in effluent suggesting that the treatment process produced transformation products. To identify compounds of interest, we have conducted a step-wise prioritization based on biological effects for molecular elucidation. We implemented effect-directed analysis methodology as a tool to target active compounds in relation with selected biological activity [1]. For this purpose, the crude wastewater extracts were fractionated by HPLC and biologically active fractions (estrogenic, androgenic and glucocorticoid activities based on in vitro bioassays) were isolated for further chemical identification. The molecular identification performed on active fractions allowed establishing a list of compounds including natural compounds, pesticides and several drugs and their transformation products, (e.g. O-desmethyl venlafaxine, O-desmethyl tramadol) which were then systematically detected in several wastewaters.

Acknowledgements

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Modelling the absorption properties of brown carbon with DFT: The case study of PAHs in Seoul, South Korea

ORAL O35
(**#Modelling**)

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While the effect of light-absorbing atmospheric particles on climate forcing has been integrated into climate models, the absence of Brown Carbon (BrC) has led to significant differences between model predictions and measured data on radiative forcing. Thus, the study of BrC is essential for the development of more adequate models. However, making quantitative predictions of the contribution of BrC has been a challenging task for experimental approaches, resulting in high uncertainties regarding predicting and mitigating the climate effects of BrC.

Given this, our goal is to demonstrate the potential of computational chemistry-based modelling in the determination of the absorption properties of BrC, with focus on Density Functional Theory (DFT) calculations. DFT has become a reliable and essential tool in environmental chemistry, providing detailed information regarding reaction mechanisms, energetics and absorption properties [1-3]. This is achieved with efficiency gains towards experimental approaches, as there is no need for a high number of steps such as chemical synthesis, separation and purification, and characterization processes.

Herein, we have applied DFT calculations to create a model for the „real-life" absorption of BrC, namely of polycyclic aromatic hydrocarbons (PAHs) over Seoul, South Korea (taking into account the experimentally observed distribution of organic compounds in PM10 particulates [4]). More specifically, we modelled not only the absorption properties of different PAHs but also their combined absorption spectrum, considering their seasonal concentration in the atmosphere.

Our modelling efforts allowed us to identify the more relevant UV and visible regions for the light absorption spectrum of the PAHs, and to decomposed these relevant bands to contributions attributable to individual molecules. It allowed us also to determine and understand changes in the combined absorption spectrum of PAHs due to the seasonal variation of their concentration, helping to identify the most problematic season of the year for climate forcing.

This type of information is essential for developing global models able to predict and mitigate the climate effects of BrC. Therefore, this study demonstrates the advantages that DFT calculations can bring to the study of the effects of light-absorption atmospheric particles on climate forcing.

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A new software for the statistical treatment of high resolution mass spectra - Application for water contaminants

ORAL O36
(**#Modelling**)

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There is a scarcity in the methods used for extracting information from the large data files obtained from direct infusion high-resolution mass spectrometry analysis. A new software is being developed for the analysis of HR-MS data with the aim of (1) suppressing operator subjectivity in handling such big data, (2) taking into account variability and measurement uncertainties inherent to experimental approaches, (3) gaining much time and confidence in results interpretation.

The current primary applications of this statistical tool are in the field of analysis of contaminants of emerging concern and their photodegradation products in water samples. The mathematical background is based on the detection of the small variability of all m/z intensities in mass spectra, within a set of samples, and concluding whether the changes are statistically relevant or not. The software also aims to track the evolution in time of molecules under different degradation procedures. Kinetic modeling of the progression of each molecule is realized, to elucidate the photodegradation mechanisms and to optimize reaction parameters.

It is essential to understand the photodegradation mechanism of pollutants since some photoproducts often exhibit higher toxicity than the parent compound [1]. The software was applied to analyze pesticides in ultrapure water and lake water samples. Benzisothiazolinone, a biocide which can cause dermatitis in humans and is toxic to fish, was selected as a first test compound[2]. The software was successfully employed to detect a wide range of photodegradation products of Benzisothiazolinone in water and to model their change during photodegradation reaction (Fig.1).

Although it is a powerful technique, it has to be used as a complementary method, with hyphenated techniques, since it cannot currently differentiate isomeric molecules. The software gives a great insight into the degradation kinetics of various molecules. Many features will be implemented in the software, to allow the analysis of complex mixtures and assess kinetics models.

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Complementarity of the different ionization techniques in GCxGC-HRMS for environmental analysis

ORAL O37
(**#Modelling**)

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Good science starts with good reliable data. The untargeted screening of environmental samples presents significant challenges in reliable identification of the detected compounds. First, the commonly used separation techniques, such as gas chromatography (GC) or liquid chromatography (LC), cannot guarantee complete separation of hundreds or thousands of components present in the samples. Peaks coelution and interferences from the background could dramatically affect identification to the point of not detecting important analytes or misidentifying compounds which were detected. Wide variety in chemical properties and structures of compounds of interest makes it also difficult to select a single analysis method. Analysing same samples at the different instruments is not always practical, and aligning the data is a challenge.

Chromatographic peak coelutions can be addressed by implementing comprehensive multidimensional separation techniques, such as GCxGC [1]. It also has its own challenges but they were successfully addressed in commercial products. When coupled to time-of-flight mass spectrometry (TOFMS), the GCxGC is widely used in variety of applications dealing with complex samples (flavour, fragrances, petroleomics). Using TOFMS as the GCxGC detectors also allows reliable and efficient deconvolution in cases when even multidimensional separation still makes some peaks partially overlap. Electron impact (EI) ionisation is the most common ionization method for GC-MS as the resulted mass spectra can be compared with available standard mass spectral libraries (NIST, WILEY) and as it provides fragmentation pattern which is well understood for the majority of organic compounds [2], which makes analytes assignment quite reliable most of the time. Application of high resolution mass spectrometry significantly improves the probability of correct identification based on confirmation of elemental compositions of all ions in the spectrum [3]. However, many organic compounds do not form molecular ion under the standard EI conditions, and thus their molecular formula cannot be confirmed, making analytes assignment less reliable. Hence, application of soft ionisation methods significantly helps in providing additional information for identification.

Here we present results of analysis of environmental samples (snow samples collected in the different locations across the city), while using GCxGC coupled to a high resolution TOFMS (HRTOFMS) (GC-HRT+ 4D, LECO Corp. USA), equipped with the experimental ion source capable of running in three ionization modes: electron impact (EI), positive ions chemical ionization (PCI) and negative ions chemical ionization (NCI). By using three ionization techniques on each sample we can obtain additional analytes information, which can be used for more reliable analytes assignment and improve sample coverage. The signal response of some compounds can be higher in certain ionization processes; hence we can improve detection limit and dynamic range of identification for related classes of compounds. And all that is done on the same instrument, at the same chromatographic conditions and with automatic workflow regarding instrument operation and data processing. In many instances CI and NCI data have confirmed the results obtained with EI (about 80% of all peaks were identified with EI). But sometimes EI mass spectrum helps only with defining the compound class, while soft ionization methods complement these data with molecular formula. Thus the identity of at least 50% of unknown peaks in EI was clarified only by using CI and NCI spectra. Moreover due to increased sensitivity of negative ion mass spectrometry towards polyaromatic and polyhalogenated structures the minor, but environmentally very significant components hardly detected in EI mode were easily detected and quantified in NCI mode.

Thus, it was demonstrated that the number of reliably identified compounds could be significantly increased by using both EI and soft ionisation methods at the same GC conditions.

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Photochemistry modelling on a geographical basis: The case of swedish lakes

ORAL O38
(**#Modelling**)

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Photochemical processes in surface waters are important because they are involved in the oxidation/mineralisation of dissolved organic matter (DOM) and in the degradation of pollutants [1]. These processes are triggered by sunlight, which is absorbed either directly by the molecules involved in transformation, or indirectly by other species called photosensitisers. The main photosensitisers in surface waters are nitrate, nitrite and the chromophoric moieties of dissolved organic matter (CDOM). The absorption of sunlight by these photosensitisers yields reactive transient species such as the hydroxyl ($^{\bullet}$OH) and carbonate radicals ($CO_3^{\bullet-}$), singlet oxygen ($^1O_2$) and CDOM triplet states (^{3}CDOM*). These transients are involved in the transformation of dissolved compounds, including the pollutants [2].

It has recently been possible to model the photochemical reactions taking place in surface freshwaters, by taking into account water-body features such as chemical composition, absorption spectrum, depth and sunlight irradiance [3,4]. In this way one can assess the photochemical processes that are operational in a particular water body, and address their possible time trend [5]. Up to now, however, no studies have addressed the geographical distribution of the transient steady-state concentrations.

In the case of Sweden, a wide dataset is available concerning water chemistry, sunlight irradiance and water depth of over one thousand lakes distributed throughout the country. This large database was the starting point of our study, because it allowed for the first modelling ever to be carried out of transient steady-state concentrations over a large geographic region. The available water chemistry data were derived from samplings carried out around the fall equinox, thus the used sunlight irradiance was here referred to the equinox as well.

Photochemical modelling allowed us to obtain detailed photochemical maps of Sweden, reporting the steady-state concentrations of $^{\bullet}$OH, $CO_3^{\bullet-}$, $^1O_2$ and ^{3}CDOM* under equinox irradiation conditions, adjusted for the latitude of each lake. Compared to temperate lakes, those in Sweden are characterised by a much higher DOM content and, as a consequence, they have on average higher [$^1O_2$] and [^{3}CDOM*] and lower [$^{\bullet}$OH] and [$CO_3^{\bullet-}$]. Moreover, climate change is leading to a gradual increase in DOM content in lake-water in the whole Scandinavian region [3], thus it is foreseeable that these peculiar features of Swedish lakes will increase even more in the future.

On this basis, it was also possible to assess the potential for Swedish lake waters to induce pollutant photodegradation. Sulfadiazine (SDZ) was chosen as model pollutant, because it is the only sulfonamide antibiotic for which photochemical modelling is possible [1], and because sulfonamides are quite common in Swedish freshwaters. SDZ undergoes an acid-base equilibrium, but the photochemical behaviour of both forms is known in detail [1].

The results of model calculations showed that, due to a combination of DOM content, water pH and average depths, the potential of Swedish lake waters to induce SDZ photodegradation is very variable. Very effective degradation would be observed in the northern part of the country, where low population density would make SDZ occurrence quite unlikely. In contrast, the least effective SDZ photodegradation is expected to be operational in the populated Stockholm area, where water pollution by pharmaceuticals is often non-negligible.

Acknowledgements

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Evidence of nitration and nitrosation of aromatic compounds upon irradiation of imidacloprid in water

ORAL O39
(**#Modelling**)

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A lot of micropollutants undergo phototransformation in sunlit surface waters with two consequences. This abiotic process leads to micropollutants degradation, which can be viewed as a positive phenomenon, but also to the formation of new molecules, the toxicity of which might be higher than that of the starting compound. Research to better know these new molecules are therefore necessary. Two types of reactions can take place in surface waters: photochemical transformations induced by light absorption by the micropollutant itself, and photosensitized reactions due to the presence of natural chromophoric molecules able to generate reactive species. Numerous examples of these reactions are reported in the literature [1].

Another possibility poorly considered to our knowledge is the photodegrading effect of two micropollutants on each other. In this case, a micropollutant undergoing photolysis could be able to induce the degradation of another micropollutant. Such situation is illustrated in the present work by the mixture of imidacloprid, a neonicotenoid insecticide, and phenol, a molecule representative of a large class of pollutants.

The irradiation of imidacloprid within the wavelength range 300-450 nm mainly led to the elimination of the NO2 group with formation of an imine identified by HPLC-HRMS analysis. To get a better view of the reaction, imidacloprid was irradiated in a hermetic chamber and NOx formations were monitored in the gaseous phase using a specific detector. NO and NO2 were detected in deoxygenated medium while NO2 alone in oxygenated medium. These results show that the NO2 elimination proceeds in two steps: release of O followed by the release of NO. This makes oxidation and nitrosation of surrounding chemicals possible.

To check this, we irradiated imidacloprid in the presence of phenol. Phenol significantly increased the rate of imidacloprid disappearance in the absence of oxygen, while imidacloprid increased the rate of phenol disappearence whatever the oxygen concentration in the solution. The formation of hydroquinone was detected whatever the oxygen concentration, that of nitrosophenol was observed in deoxygenated medium and that of nitro and dinitrophenol in oxygen-saturated medium.

These results confirm that NO is released in the medium upon irradiation of imidacloprid and is able to react with aromatic compounds. The aromatic targets could be the other chemicals surrounding imidacloprid or more generally natural organic matter due to its abundance in aromatic moieties. Considering the potential toxicity of nitroso and nitro derivatives, the photoreactivity of aqueous imidacloprid is an issue that should deserve more attention.

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Pharmaceutical active compounds in shrimp farm aquatic environment: Method, development and validation

ORAL O40
(**#Modelling**)

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Today, the presence of pharmaceuticals in aquatic environments has become an important environmental concern that might deteriorate the water quality and have an adverse impact on the aquatic environment. Because of their presence at trace levels, sensitive and reliable analytical methods must be developed for their detection and quantification. Thus, the aim of the present work was to develop and validate a method for the analysis of human and veterinary pharmaceuticals (sulfamethoxazole, SMX; oxytetracycline, OTC; acetaminophen, ACM; trimethoprim, TMP; and erythromycin, ERY), occurring in the shrimp farm aquatic environment.

The performance of the method was evaluated in terms of linearity, method detection limits (MDL), method quantification limits (MQL), recoveries of extraction (RE), and matrix effects. The method validation was performed using an artificial brackish water sample. The method is based on solid phase extraction (SPE) followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. Linearity of the method was settled for each compound by analyzing spiked water samples over a range of concentrations of 2-5000 ng ml−1. MDL and MQL were determined as the minimum amount of analyte detectable with a signal-to-noise ratio of 3 and 10, respectively. RE of target analytes was determined using water samples spiked at three different levels while the matrix effects were evaluated by comparing the analytical signals obtained with water sample extract spiked with a standard mixture solution containing all the target compounds.

The developed analytical methodology displayed MDL and MQL in the range of nanograms per liter. The RE (%) of the target compounds obtained during recovery tests were between 79.7±8.1 and 97.2±5.1. In this study, we also evaluated two of the common acidic modifiers (acetic acid and formic acid) of the mobile phase, and the stability of target compounds in those solutions with varied pH from 0 to 1 for 480 minutes.

The results indicated that there were no significant differences between acetic acid and formic acid in the chromatographic peak shapes. The degradation of OTC was obtained in the absence of acid, while ERY was degraded in the presence of acid. Generally, the optimum stability of all the target compounds (except ERY) was determined at pH 0.5. The matrix effect study showed a signal enhancement for OTC, while suppression of the signal was obtained for SMX, TMP, ACM and the surrogate standards (TMP-d3 and SMX-d4).

Finally, the developed method can be applied simultaneously for the whole targeted compounds excepting for ERY due to its stability response toward acidity.

Acknowledgements

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Session 1: Sustainable Chemistry

Poster presentations

[3,3]-Sigmatropic oxo-rearrangement of substituted allylic carbamates under microwave conditions: Scope and limitations

POSTER P1
(#Sustainable chemistry)

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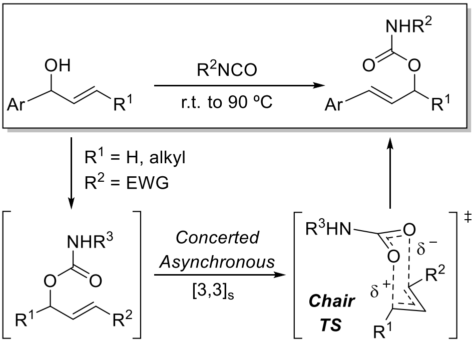
[3,3]-sigmatropic rearrangements have long been used in organic chemistry due to the fact that they allow regio- and stereoselective carbon-carbon or carbon-heteroatom bond formation with relative ease [1]. Among the carbon-oxygen bond forming reactions, the sigmatropic oxo-rearrangement of allylic carbamate is not highly investigated. In fact, the scarce examples described in literature require using metal-catalysed methods based on palladium or mercury salts [2,3]. However an unexpected [3,3]-sigmatropic oxo-rearrangement occurred when we tried to investigate an allyl cyanate/isocyanate rearrangement on aryl substituted allylic carbamates.



Thus, several linear allyl carbamates were prepared via a "one-pot" process starting from allylic alcohols. The rate of the rearrangement is highly dependent on the electron density of the aryl ring and on the nature of isocyanate used. This work is under process for publication in the journal of organic chemistry.

Since molecules bearing a carbamate group play an important role as synthetic intermediates as well as in modern drug discovery and medicinal chemistry [4,5], we decided to further explore the substrate scope and to try to overcome the limitations of the process through a microwave-assisted method. In fact this latter has become a popular theme in organic chemistry. Microwave heating has turn out to be a very efficient method to reduce reactions time and to increase products yields. Thus, the use of this technology has become a very useful tool for the medicinal chemistry community for whom reaction speed play a crucial role for drug discovery [6].

Acknowledgements

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A natural approach to reduce soil and water contamination by pesticides: Bioprophylaxis

POSTER P2
(**#Sustainable chemistry**)

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One of the major problems with pesticides is linked to the non-negligible proportion of the active ingredient quantity spread that does not reach its intended target. Consequently, they can be transported/transferred in(to) the surrounding compartments and widely contaminate the environment. Nowadays, pesticides are detected everywhere and this issue became priority society concerns due to potential risks on the environment (biodiversity, ecosystemic services) and human health. Another strategic issue concerns uncontaminated water resources which are getting scarce. Therefore to insure a good water quality costs more and more, as specific heavy treatments are required to remove these compounds and to obtain drinkable water.

One well-developed approach consists in the decontamination / remediation of polluted sites using different chemical and/or biological treatments [1,2]. Another approach would be to limit the pesticide dispersal and to act preventively.

We developed a bioprophylactic process based on simultaneous application of pesticide and pesticide-degrading microorganisms, providing optimal conditions for microbial degradation of pesticides after their specific action and before their transport to environmental compartments. To date, studies related to bioprophylaxis focused more on non-agricultural uses of pesticides [3, 4].

The aim of our study was to determine the suitability of this concept in agriculture, with a model herbicide (2,4-dichlorophenoxyacetic acid = 2,4-D) and one of its bacterial degrading-strains (*Cupriavidus necator* JMP134).

The biodegradation of 2,4-D was studied in soil microcosms planted with sensitive (mustard) and insensitive (wheat) plants. Simultaneous application of 2,4-D in a commercial formulation (DAM) at agricultural recommended doses with the JMP134 strain showed that the herbicidal effect was conserved and the 2,4-D concentration decreased by 99% within seven days, while only 35% reduction was observed in the un-inoculated control. The 2,4-D was 1/3 as persistent in the studied inoculated soil (OCDE 5M, Lufa Speyer, Germany) compared with the same soil for which no mineralizing-bacterium was added ($T_{1/2}$ = 2.3 and 7.4 days, respectively, Tukey test, $P < 0.05$).

The bioprophylaxis treatment significantly increased the abundance of the 2,4-D degrading communities and their *tfd*A gene but without impacting the α- and β- diversity of the soil microbial communities.

Using realistic conditions as close as possible to those of the field (*i.e.* the recommended field dose of pesticide, commercial formulation), this study constitutes the first basis for the development of bioprophylaxis as a means to reduce environmental contamination by agricultural pesticides. Experiments with other soils having contrasting pedological properties but also with a formulated bacterial strain are in progress.

Acknowledgements

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Shaping and thermal resistance of geopolymers based on different aluminosilicate sources

POSTER P3
(**#Sustainable chemistry**)

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Geopolymers are innovative materials and an alternative to the ordinary Portland cement, due to their high working properties, low energy consumption and environmental impact. They can be defined as a low temperature hardening materials, with an amorphous three-dimensional network, resulting from the alkali-activation of an aluminosilicate source. Other natural resources or industries by-products were also proven to be suitable to produce alkali-activated materials. This work aims to highlight the influence of the raw materials, and the incorporated mineral fillers, on the shaping properties and the thermal behaviour of geopolymers. For this, the behavior of various aluminosilicates in presence of potassium or mix of potassium and sodium based alkaline solutions was investigated. Two deferent fillers were also used: sand and wollastonite. Different shapes such as cylinders and sheets of all compositions were successfully obtained. The results show a persistence or an increase, of mechanical strength after thermal treatment of geopolymers containing calcium. This result was explained by the differences of chemical composition of the used raw materials influencing the formed phases by solid state reactions after thermal treatment.

Catalytic properties of Co/Mn LDH phases for the redox transformation of H_2O_2 "Structural, morphological and electrochemical characterizations"

POSTER P4
(**#Sustainable chemistry**)

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Hydrogen peroxide is a large scale chemical with a world production over 2.2 Mton/year [1], mainly employed as bleaching agent in textile and paper industry [2] or for the treatment of waste water and contaminated soil to remove organic impurities [3], but also in pharmaceutical and medical applications [4]. In pathological context more and more evidences have demonstrated that excess level of H_2O_2 will affect the functions of intracellular signaling transduction and thus trigger many chronic diseases including Alzheimer, diabetes, cancer diseases [5]. Therefore, development of novel methods for the rapid and sensitive determination of the exact level of H_2O_2 is very important. Electrochemical method using modified electrode is proved to be a powerful and effective technique due to the electrochemical redox activity of H_2O_2. Various modified electrodes based on Layered Double Hydroxides (LDH) have been reported in the literature for an amperometric detection of hydrogen peroxide [6]. Among the different LDH, the CoMn-LDH appears to be particularly interesting [7].

Considering the requirements on the construction of CoMn-LDH with excellent catalytic activity for H_2O_2, this phase was successfully fabricated in this work. A series of Co_xMn were prepared by co-precipitation method with different ratios Co/Mn ($2 \le x \le 5$) in a basic medium and optimizing the synthesis parameters to avoid the formation of thermodynamically favorable oxide and hydroxide phases (MnO_2, Mn_3O_4, β-$Co(OH)_2$). The formation of the LDH phase is confirmed by X-ray diffraction and Infra-Red spectroscopy. Particle sizes and surface charges were determined by dynamic light scattering and scanning electron microscopy. According to our work, the best ratio of metal ions in LDH is 3:1 which displays the purest crystal phase and the best electrochemical properties. The X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectrum (EDX), and elemental mapping analysis were used to analyze elements compositions of the sample as well as to detect the atomic ratios of Co/Mn in the obtained CoMn-LDH. The electrocatalytic performances of the Co_3Mn-LDH in the oxidation of H_2O_2 were investigated; the results are shown in (Figure 1).

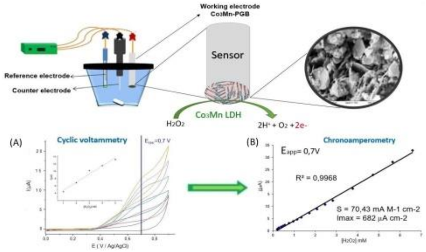

Figure 1: Electrochemical detection of H_2O_2 by Co_3Mn-HDL.

The LDH was deposited as thin films on the surface of pyrographitic carbon electrode (PGB). The deposits are characterized by cyclic voltammetry in basic medium to study the redox signal of the 3d-Metal cations in the LDH layers, then in a neutral medium (Tris-HCl buffer pH 7) in the presence of increasing concentrations of H_2O_2 (Figure 1A). Calibration curves were then established by chronoamperometry (Figure 1B). The CoMn-LDH modified electrode exhibits high sensitivity S = 70.43 mA M^{-1} Cm^{-2}, and an excellent linearity between 0.2 and 7 mM.

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UTILIZING IRON-BASED NANO CATALYSTS FOR ACTIVATION OF PERSULFATE: IMPLICATIONS FOR THE DEGRADATION OF SULFALENE

POSTER P5
(**#Sustainable chemistry**)

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The increased growth of mankind, society, technology, and science led to the higher consumption of fresh water and consequently higher production of wastewater. Recently, the inappropriate discharge of the hospital waste and pharmaceutical industries to the water have seriously affected the human life. Many pharmaceutical compounds are non-biodegradable, and have great resistance to the natural degradation processes. Therefore, advanced oxidation processes (AOPs) such as ozonation, Fenton reaction, sonocatalytic degradation, and photocatalytic processes have gain great attention for the removal of various toxic compounds from the contaminated water. AOPs are the promising processes which produce reactive species to attack organic pollutants and make deep changes in the chemical structure. In recent years, AOPs based on persulfate activation have developed into a promising alternative system. Persulfate has been widely concerned because of its ability of producing sulfate radical ($SO_4^{\bullet-}$). Sulfate radicals have a longer half-life and a same oxidation potential than that of $HO^{\bullet}$ radicals. However, non-activated persulfate exhibits very low oxidation potential to organic pollutants. Various activation processes such as UV, base, heat, or transition metals were used for generation of $SO_4^{\bullet-}$. In this context, the researchers have synthesized many metal-containing catalysts such as reduced graphene oxide–elemental silver/magnetite nanohybrids, copper-doped iron metal-organic framework and BiOI/Fe_3O_4 [1, 2]. Among the synthesized catalysts magnetic catalysts have attracted a great attention due to the higher separation efficiency in aqueous solution which enables their application in the industrial scopes.

Furthermore, metal doped magnetite serving as heterogeneous catalyst to effectively activate oxidants, using the synergistic effect of metal and ultraviolet light to achieve the purpose of pollutants degradation [3].

Present study reports the effect of metal doped magnetite as the separable iron-based photocatalyst for the activation of persulfate and evaluating the degradation efficiency of pharmaceutical compounds from contaminated water. Accordingly, the sample catalysts were synthesized with a co-precipitation method. Then, the physico-chemical characteristics of the so-synthesized samples were determined using XRD, FT-IR, SEM, EDX, and BET analysis. Afterwards, the impact of different operational conditions was evaluated on photocatalytic degradation performance of synthesized catalysts for the removal of proposed pollutant. Then the optimal condition such as pH, pollutant concentration, catalyst dosage, oxidant concentration, and concentration of reactive species, was used for comparing the obtained results with the removal efficiency of Fe_3O_4, and doped magnetite nanocatalysts. A mechanistic approach was adopted in order to evaluate the main oxidative species involved during photo-assisted degradation. Finally, the catalyst reusability and stability were evaluated.

Acknowledgements

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Novel BPA-free Epoxy-Silica Resins Enriched With Ce Doped TiO_2 As Advanced Materials For The Preservation Of Stone

POSTER P6
(#**Sustainable chemistry**)

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Advanced materials are designed and developed for the preservation of built heritage with the aim of being chemically, physically, and mechanically compatible with stone. In this sense, hybrid organic-inorganic materials have increasingly attracted great attention due to their properties deriving from the combination of the different building blocks. Accordingly, their properties can be modified modulating the functionality or the segment size of each component. In such systems, polymer blocks lead to good adhesion, hydrophobicity, flexibility and ease of processing, whereas inorganic domains improve the physical properties such as abrasion resistance, optical transparency and heat resistance. At the same time, the presence of Si-OH groups in inorganic additives should lead to durable interactions to the stone [1].

The latest studies are focused on epoxy resins, due to their well-known performances, properly modified by sol-gel technology, that may easily incorporate silica-based products to become hybrids. However, the most common monomers used for this purpose are the diglycidyl- Bisphenol-A (BPA-DGE) derivatives since they transfer to the resins specific features such as adhesive properties, great chemical resistance and good thermal stability, thanks to the epoxy and hydroxyl groups and to the presence of ether bonds, respectively [2].

On the other hand, innovative solutions for stone conservation should result in increased sustainability and reduced environmental impact so that several alternatives are being investigated to develop promising eco-sustainable multifunctional materials to be successfully employed in the field of built heritage preservation.

In this context, the challenge of this research pursues the development of new BPA-free epoxy-silica resins that, while retaining the consolidating and mechanical properties typical of epoxy resins, could also display biocidal and self-cleaning properties by their nano-reinforcement [1, 3].

With this goal, different materials were synthesized using an epoxy precursor, 1,4-cyclohexanedimethanol diglycidyl ether (CHDM-DGE), by reaction with 1,8-diamineoctane (DAO) as epoxy hardener, in the presence of different siloxane precursors, i.e. glycidoxypropylmethyldiethoxysilane (GPTMS), tetraethyl orthosilicate (TEOS) and isobutyltrimethosysilane (iBuTMS). Furthermore, TiO_2 and Cerium-doped TiO_2 nanoparticles (NPs), in the anatase form, were also synthetized and added into the reaction mixtures.

After the selection of the most performing samples, the curing temperature, the interpenetration of the organic and inorganic networks as well as the homogeneity of the NPs distribution into the hybrid matrixes were successfully studied by a combination of SEM-EDS and Imaging Raman spectroscopy analysis. Moreover, the thermal behaviour and water repellence capability of the most promising samples were investigated by means of TGA, DSC, DMA and contact angles measurements.

Acknowledgements

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Save application methods for stone treatment: slow release systems

POSTER P7
(**#Sustainable chemistry**)

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Nowadays, there are large varieties of commercial products, in liquid form, for stone treatment. Most of them are aplicated with a spray or brush and the main inconvenience of such procedures is that the application of the product is not always located, selective or even, save for workers. Agar gels have demostrate to be a suitable ecofriendly alternative acting as slow release application systems since, these hydrogels act as reservoires of the treatment liquid [1-2]. Agar gel is prepared in the selected liquid medium at 1-3 % of agar, to get the wanted rigidness for the poultice that will ensure a selective application of the treatment. Another application possibility is the use of microcapsules of the active principle. Calcium alginate microcapsules have been used as storage systems with preservation purposes [3]. However, the microcapsules can be enveded on different materials (i.e restoring mortars) to add new properties.

In the stone conservation field, EDTA has been succesfully applied to remove stains of different nature as black crusts [1] or iron oxide stains [2] due to its complexing capacity, but its biocide capacity is also wellknown. On the other hand, specific synthetic biocides products of wide biological spectrum are comercially available. Among them, quaternary amines are recommended due to their desinfectant and tensioactive properties and effectiveness for biopatina removing from alcaline stone materials [4].

In this work, the biocide capacity of two comercial biocide products (Preventol RI 80, and New-Des 50), EDTA and eugenol (as a green alternative) has been tested when applied as poultices on biofilms of different nature located in exposed architectural elements of the Punta Begoña Galeries of Getxo (Biscay). Concretelly, agar gels of the active principles were prepared at 1-3 agar % to test both horizontal (6 cm diameter semi rigid poultices) and vertical applications. Besides, eugenol was selected in orther to test the performance of calcium alginate microcapsules with biocide aims.

The results confirm the biocide capacity of the agar preparations regardless the active principle, but the tensioactive properties of Preventol prevent the gel formation at low % of agar. However, the low rigidness of the poultices at such agar contents allowed their vertical application even in areas with present of thick biopatinas. In addition, the greenest alternatives (EDTA and eugenol) showed to be as effective as the tested commercial products.

Moreover, eugenol filled calcium alginate microcapsules were also successfully produced, which, although did not show a good adherence as to be vertically applied, showed to have a biocide capacity similar to the agar gel.

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CO_2 chemisorption in ionic liquids having imidazolic gemini cations

POSTER P8
(#**Sustainable chemistry**)

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The negligible vapor pressure of ionic liquids at ordinary temperatures and pressures grant them the potential to replace volatile solvents used in industrial processes.[1] Moreover, their dual ionic and organic nature [2] offers an enourmous synthetic versatility to tune their physicochemical properties by changing moieties of the cation or the anion structure.

Concerning their use in gas separation processes, 1-alkyl-3-methylimidazolium acetate ionic liquids are known to absorb high amounts of CO_2 due to a 2:1 chemical reaction between the imidazolium cation and the CO_2.[3]

This work presents an investigation of the CO_2 absorption capacity and the physicochemical properties of newly synthesized ionic liquids composed of bromide (Br^-) or acetate (OAc^-) anions and imidazolium gemini cations having alkyl or ether chains (Fig 1).

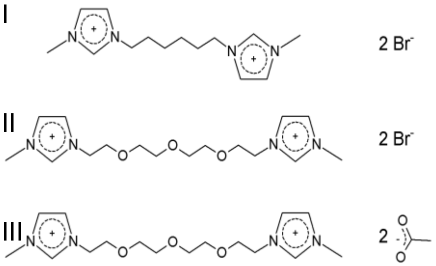

Fig. 1. Structure of the dicationic ionic liquids studied.

The ionic liquid composed of the alkyl chain gemini cation (structure **I** in Fig. 1) is a white powder solid at room temperature while the ionic liquid having the oxygenated chain (structure **II** in Fig. 1) is a highly viscous liquid whose viscosity at 343 K is higher than 10 kPa.s. The replacement of Br^- with the OAc^- in the ionic liquid composed by the oxygenated chains (structure **III** in Fig. 1) increases the fluidity of the liquid reducing its viscosity to 0.48 Pa.s at 343 K.

Since the viscosity of the solvent is of major importance for the mass transport and reaction kinetics of CO_2 and the absorbing fluid, the less viscous ionic liquid **III** was studied in more detail.

The characterization of the reaction products between CO_2 and the ionic liquid **III** was realized in the same manner as in our previous work with the 1-butyl-3-methylimidazolium acetate, $[C_4C_1Im][OAc]$ by using ^1H and ^{13}C NMR spectroscopy.[4] Fig. 2 shows that the zwiterionic reaction product observed with $[C_4C_1Im][OAc]$ ionic liquid is also formed in the much more viscous gemini ionic liquid **III**.

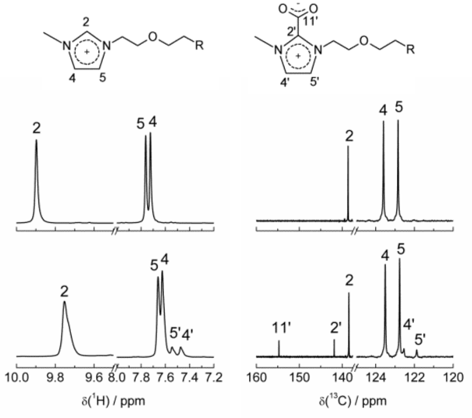

Fig. 2. ^1H (left) and ^{13}C (right) NMR spectra of ionic liquid **III** at 343 K under vacuum (top) and at 10 bar of CO_2 (bottom). On the top, the chemical structure of the ring moiety of the imidazolic gemini cation before (left) and after (right) the reaction with CO_2.

Following the characterization of the chemical species formed after CO_2 absorption as well as the measurement of CO_2 absorption capacity by the ionic liquid **III**, the CO_2 absorption mechanism will be analysed and discussed.

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New biosources solvents for co2 capture process optimization

POSTER P9
(#**Sustainable chemistry**)

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The large emission of anthropic greenhouse gases, especially carbon dioxide (CO2), caused an increase of Earth's temperature (1 °C since 1910), of oceanic level (16 cm in 100 years), lead to irreversible changes of the climate. To face the global warming, hundreds of countries have established the Kyoto Protocol in 1997, with the objective of reducing the emission of such gases. The European Union then decided to reduce its emissions by 8% [1]. During the COP21 in 2015 in Paris, all the countries committed that Earth's temperature should not increase more than 2 °C by 2100, to avoid environmental disasters.

Capture, utilization and sequestration of CO2 (CCUS) is one of the option. One strategy consists in capturing CO2 in post-combustion industrial fumes by using selective absorption in a chemical solvent. The solvents commonly used are aqueous systems containing alkanolamine. There is a reversible acid-base reaction between the CO2 and the amine: in the first step of the process, the CO2 is selectively absorbed in the solvent, and in the second step, the mixture is heated to release the pure CO2 for valorization or sequestration. This requires significant regeneration energy, which makes the process less economical [1].

A new approach based on solvents presenting a Low Critical Solution Temperature (LCST) is studied, especially aqueous solutions of demixing amines. These amines show a partial miscibility with water, under specific temperature conditions and gas loading charges. A phase separation is induced after acid gas absorption by increasing the temperature, leading to the treatment of only the CO2 rich phase [2]. The major problem of this process is the adjustment of the demixing temperature.

The addition of a physical solvent in aqueous solutions of amines was considered to optimize some steps of the process. Coulier et al. studied a system based on aqueous solutions of N-methylpiperidine with triethylene glycol as physical solvent. This new system shows several advantages as the decrease of the specific heat capacity of the absorbent and the control of demixing temperature [3]. However this solution has to be improved especially considering the respective quantity of gas dissolved in each phase.

A new solvent family, named Deep Eutectic Solvents (DES), has been discovered in 2003 by Abbott et al. [4]. A DES is a mixture of several compounds, charged or neutral, whose melting temperature is lower than the pure compounds. These solvents are attractive because of their easy preparation, their low cost and their specific properties [5]. Furthermore, some DES in presence of water presents a LCST.

The aim of this work is to combine an aqueous solution of demixing amine with a DES to modulate the temperature of the phase separation. First, a screening with systems based on water, DES and demixing amine is realized. To analyze these systems, the quantity of CO2 absorbed is determined by weight and the demixing temperature is obtained by heating the samples. Then, one promising system issued from the screening is studied by Differential Scanning Calorimetry, infrared spectroscopy and by optical microscope. These methods allow a better understanding of the behavior of the mixture and a precise characterization of the phase separation due to the gas loadings.

Acknowledgements

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Toxicity of different types of Quantum Dots for selected model plants

POSTER P10
(#**Sustainable chemistry**)

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The quantum dots (QDs) are fluorescent semiconductor nanocrystals which are being extensively developed because of their unique size-dependent optical and photophysical properties. Unfortunately, several disadvantages in the using of QDs occurred. Especially, the leach of free Cd ions from core Cd-based QDs in the contact with aqueous media is their biggest drawback. However, it is believed that the encapsulation of nanoparticles should reduce their toxicity and increase their stability in different environments. We report on the toxicity and bioaccumulation of different types of Cd-based QDs for a selected model plant organism. After a certain exposure, we monitored the growth of roots and dry biomass of roots as a macroscopic toxicity end-point. Then we determined the total Cd content in different plant parts by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Consequently, the plant roots were inspected by the fluorescence microscopy to determine if Cd-based QDs are adsorbed on the root surface and how it depends on the QD type. Selected QDs showed different toxicity in correspondence with different Cd bioaccumulation patterns. We discussed possible hazardous effects of Cd-based QDs for selected plant as well as the environmental implications of the exposure to Cd-based QDs.

Environmental impact of fluorinated ionic liquids to be used in pharmaceutical industry

POSTER P11
(**#Sustainable Chemistry**)

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In the pharmaceutical industry it is as important to show the efficacy of new drugs as well as an improvement in comparison with the existing therapeutics [1]. However, besides this development policies, there are still many therapeutics, novel and existing, with several issues to be solved. Poor solubility in water and pharmacokinetics, requires delivery to the target site, which implicates the help of carriers. Drug delivery systems (DDS) used as carriers are combined with drugs and have being intensely studied to fulfill the needs of the industry to improve issues of solubility, stability, distribution and pharmacokinetics while controlling and decreasing the side effects associated with some therapies [2].

Fluorinated ionic liquids (FILs), a specific class of Ionic Liquids (ILs), are considered non-conventional solvents, composed entirely by anions and cations, being considered a green solvent. These compounds combine the best characteristics of traditional ILs (*i.e.*, tuneable properties, thermal and hydrolytically stability) with the unique properties of common perfluorinated compounds (*i.e.*, high surfactant power, chemical and biological inertness). There is an increasing interest on FILs due to their tuneable origin which allow the manipulation of properties by the different ions conjugation. Based on these tunable properties and surfactant behavior FILs started to be studied as a powerful tool for the design of new "green" and biocompatible DDS for therapeutic proteins [3,4].

The application of FILs as drug delivery systems can overcome the problems in this field because they are capable of developing structures that protect, through encapsulation [5], various biomolecules from enzymatic degradation during their biodistribution. This will consent in an increasing of the therapeutic effect due to the higher bioavailability at the target site.

The main purpose of this work is to evaluate the risk these compounds pose for the environment and human health. Focusing on a "Green Pharmacy" development, different acute ecotoxicity tests were performed in both aquatic and terrestrial species. The aquatic species used in the tests represent different levels of biological organization. A luminescence inhibition test with the marine bacterium *Vibrio fischeri;* an immobilization test with freshwater crustacean *Daphnia magna;* and a sub-chronic growth inhibition test with *Lemna minor* were performed to evaluate the impact of the pure compounds in the aquatic environment. Relatively to the terrestrial species, the soil bacterium *Pseudomonas stutzeri* was used to determine the toxicity of FILs towards the determination of the Minimum Inhibitory Concentration (MIC). Following the ecotoxicity tests, also the ready biodegradability of the FILs were evaluated using a manometric respirometry test for 28 days.

The results from this environmental assessment provide the necessary knowledge to select the compound with greater impact in the environment to be used in the pharmaceutical industry.

Acknowledgements

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Fluorinated ionic liquids for the fluorinated gases separation

POSTER P12
(#Sustainable chemistry)

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Fluorinated gases ('F-gases') are a family of synthetic gases used in a large range of industrial applications. They are often used as substitutes for ozone-depleting substances because they do not damage the atmospheric ozone layer. However, F-gases are powerful greenhouse gases with a global warming effect up to 23 000 times greater than carbon dioxide, and their emissions are rising strongly. In European Union (EU), fluorinated gases emissions have increased up to 60% since 1990, in contrast to all other greenhouse gases whose emissions have been reduced.

Due to their utility, economic value and industrial application, the worldwide production of fluorinated gases is expected to increase for the foreseeable future. Then, hydrofluorocarbon emissions are projected to grow by nearly 140% between 2005 and 2020, mainly in air conditioning and refrigeration systems.

Hence, their use has been controlled since 2006 with different legislations aiming to combat their effect into the atmosphere. The new EU regulation (No 517/2014) targets to cut the emissions of these gases by 2/3 by 2030, compared to the levels of 2014. Although there are technologies under development to avoid the growth of these emissions, they may not be successful in finding the right compound with the required properties for some specific applications. Therefore, actions to reduce these emissions are needed, including the capture of these gases and the development of environmentally benign solvents to recovery and recycle these greenhouse gases.

Ionic liquids are salts in the liquid state with negligible vapor pressure at room temperature. Although publications dealing with IL have been growing exponentially, there are still numerous unexplored subjects, such as the family of fluorinated ionic liquids (FILs) [1]. FILs are defined as ionic liquids that contain fluorinated tags greater than or equal to 4 carbon atoms [2]. These neoteric compounds can be designed to be more suitable for each of the desired applications and have enhanced properties such as low surface tension, high thermal stability, high electrical conductivity, non-flammable [1,2]. Furthermore, FILs can be used as "*3 in 1*" solvents due to the formation of three nanosegregated domains (the fluorinated, polar and hydrogenated nanosegregated domains) [2]. Playing with the interactions and the size of different domains will allow the development of solvents designed for separation of fluorinated greenhouse gases.

The objective of this work is to develop climate-friendly processes based on fluorinated ionic liquids. The most appropriate solvent will be custom designed and evaluated for separation of fluorinated greenhouse gases. The fluorinated gases usually used in air conditioning and commercial refrigeration equipment (such as R-134a (1,1,1,2-tetrafluoroethan), R-32 (difluoromethane) and R-125 (pentafluoroethane)) will be studied. In order to evaluate the performance of FILs in this application, sorption equilibrium isotherms will be measured using an ISOSORP 2000 high-pressure magnetic-suspension microbalance (Rubotherm GmbH, Bochum, Germany). Supported porous materials will be used because they will increase the mass transfer between the gas and the ionic fluids that will be studied. This work will deliver both fundamental understanding of the behaviour of these new alternative solvents and the skills to manipulate their behaviour to process development and scale-up.

Acknowledgements

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Fluorinated ionic liquids as a tool to improve carbon dioxide, oxygen and nitrogen solubility

POSTER P13
(**#Sustainable chemistry**)

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Fluorinated Ionic Liquids (FILs) is a unique family of Ionic Liquids (ILs) which are distinguished by their fully or partially fluorination, attaining remarkable properties. The ILs members of this family are flawless candidates to be used in applications where perfluorocarbons (PFCs) find an important role [1]. The fluorinated alkyl chains enable an improvement of the surfactant properties of these compounds and the formation of a 3rd nanosegregated domain that upgrade their tuneability power [2]. Moreover, the increased solubility of gases, the decreased polarity and increased rigidity, conferred by the carbon-fluorine bonds of these FILs make them a potential tool to improve the solubility of these gases. They have a lower surface tension and weak interactions with organic compounds, obtaining chemical and biological inert compounds. Their power of self-assembling in aqueous solutions makes these novel compounds also useful to be applied in the solubilization of respiratory gases [3].

A combined theoretical-experimental approach has been used to characterize these compounds considering their thermodynamic behaviour in the presence of respiratory gases (oxygen, nitrogen and carbon dioxide). The ILs used in this work are based on perfluorobutanesulfonate, perfluoropentanoate, trifluoromethanesulfonate and trifluoroacetate anions, conjugated with imidazolium and pyridinium cations. The soft-SAFT (Statistical Associating Fluids Theory) molecular based equation of state (EoS) [4,5] was used to calculate the solubility behaviour of respiratory gases in the selected ILs. Taking advantage of the physical ground of the EoS, the molecular parameters from the model of $[C_nC_1Im][C_4F_9SO_3]$ FILs [6] family were transferred and optimized for these novel FILs. Then, to have insights in the solubility of respiratory gases in these ILs, the vapour-liquid equilibria was calculated. The solubility of respiratory gases in these ionic liquids was experimentally determined and compared with the calculated results in order to validate the models.

This approach ensures the built of a new, efficient and predictive molecular model for FILs, describing the behaviour of these complex systems in a fast and reliable manner, compared to classical models or molecular simulations. This approach will enable the future transferability of this model to other FILs families, allowing an enlarge study of their thermodynamic properties. This methodology will enable the discovery of the best candidate to replace harmful PFCs that are used in the process of solubilize these gases, in a faster and accurate way.

Acknowledgements

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Membrane technology applied to the separation and recovery of fluorinated gases used as refrigerants

POSTER P14
(**#Sustainable chemistry**)

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The use of hydrofluorocarbons gases (HFCs) has drastically increased in recent years, especially in the refrigeration sector, as they are a good alternative for ozone-depleting substances (CFCs and HCFCs) that phased out under the Montreal's Protocol (1987). Despite being energetically efficient, ozone-friendly and safe for users, with low levels of flammability and toxicity, HFCs are powerful greenhouse gases, with a global warming potential (GWP) up to 23 000 times greater than that of carbon dioxide. For this reason, HFCs emissions to the atmosphere must be reduced according to the Kigali Amendment to Montreal Protocol (2016) and the new European regulation [1], which search an 85% reduction in the production and consumption of HFCs by 2047 through the development of new separation technologies that enable the reuse and recycling of these compounds. Therefore, research efforts should be placed on the development of novel alternatives that contribute to the reduction of HFCs emissions.

In this context, this work focuses on the separation and recovery of HFCs using membrane-based gas separation processes. Membrane technology offers a cost-effective alternative compared to conventional gas separation technologies such as cryogenic distillation or pressure swing adsorption (PSA) [2]. However, there is a lack of research data regarding the permeability of HFCs through conventional polymeric membrane materials.

Thus, in this work, the permeation properties of some of the currently most employed fluorinated gases in the refrigerant industry, namely, R32, R134a and R1234yf, are assessed for the first time. The gas permeability of these compounds through several polymers, both rubbery and glassy, is determined as a function of pressure and several temperatures using an experimental setup that allows for continuous permeation of single and mixed gases [3]. Also, the permeation properties of these gases are compared to that of their hydrocarbon analogues (methane, ethane and propylene, respectively) in order to gain a deeper understanding of the effect of fluorine substitution in hydrocarbon molecules on the gas permeation properties.

Results show that the permeability of all gases linearly increases with pressure, which is the typical behavior of organic vapors and condensable gases. In addition, the permeation properties are highly dependant on the polymer used to cast the membrane, consequently significant differences can be found in HFCs gas pair selectivities.

Based on this results, the membrane that shows the best performance in terms of permeate flux and gas selectivity will be selected for further work aimed at enhancing the membrane performance by synthesising composite polymer ionic liquid membranes [4].

Acknowledgements

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Design of new environmentally-friendly eutectic mixtures for CO2 absorption

POSTER P15
(**#Sustainable chemistry**)

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Acetate-based ionic liquids are capable of chemically absorb large quantities of carbon dioxide. The reaction mechanism involves a proton transfer between the imidazolium cation and the acetate anion with the formation of a highly reactive intermediate capable of chemically binding CO2. The carbon dioxide absorption is reversible and the regeneration of the ionic liquid is energetically more favourable than that of conventional absorbers like aqueous solutions of amines [1]. However, the use of imidazolium-based ionic liquids is still relatively expensive and presents environmental concerns linked with the toxicity of these cations [2]. The design of alternative solvents, also based on acetate salts, can lead to cheaper and greener CO2 absorbers. In this work, we have studied three eutectic mixtures reasonably cheap, biodegradable and easily prepared from readily available precursors. They were prepared by mixing choline acetate (ChAc) salts, with urea or with different carboxylic acids – glycolic acid and diglycolic acid – at mole ratios of 1:2 and 1:1, respectively (see Figure 1).

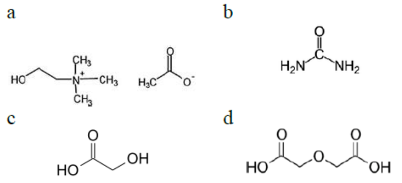

Figure 1: Precursors used for the preparation of the eutectic mixtures: a. choline acetate; b. urea; c. glycolic acid; d. diglycolic acid

The eutectic mixtures were characterised by measuring their density, viscosity and water content. The eutectic mixtures are denser and more viscous than alkyl-imidazolium acetate ionic liquids with short alkyl side-chains [3].

Carbon dioxide absorption was determined using a thoroughly tested isochoric technique at different temperatures. The mole fraction absorption of CO2 at normal pressure is 3×10-3 at 313 K in ChAc:Diglycolic acid and 9×10-2 in ChAc:Urea at 323 K. We found that CO2 absorption is twice as low in ChAc:Urea when compared to two acetate-based ILs [4] (Figure 2). The selectivity towards CH4, on the other hand, is considerably higher for the ChAc:Urea mixture making it a promising competitor to be used on an industrial scale.

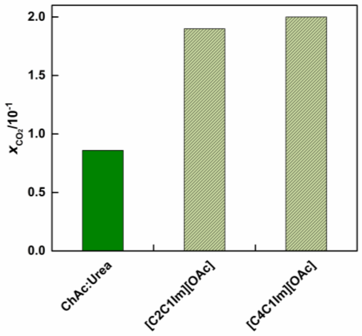

Figure 2: Absorption of CO_2 at 1 bar, 323 K in ChAc:Urea (this work) and 2 acetate-based ILs([4])

Acknowledgements

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The study of electron transport and photovoltaic parameters in DSSCs based on TiO_2 nanoparticles-nanotubes with mixed phase

POSTER P16
(**Sustainable chemistry**)

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Dye-sensitized solar cells (DSSCs) have become a promising alternative to conventional solar cells due to the merit of their low cost and high energy conversion efficiency, easy fabrication process and simple fabrication equipment. The use of titanium dioxide (TiO_2) based photoanode is mainly dependent on their morphology and size. In this study, DSSCs based on TiO_2 nanoparticles (NPs) and nanotubes (NTs) with different weight ratios and phase compositions were studied. NPs with anatase and rutile main phases were obtained by Sol-Gel reflux synthesis and anatase NTs were obtained by hydrothermal route. The obtained nanostructures were investigated using XRD, SEM, TEM/HRTEM and UV–Vis Spectroscopy. Electron transport and photovoltaic performance of DSSCs were investigated by Current-Voltage measurements (I-V) and electrochemical impedance spectroscopy (EIS). An increase of 14% in cell efficiency was achieved by introducing 10 wt% NTs (NP90 cell). In this configuration, high dye loading is ensured and substantial improvement of electron transport efficiency is achieved by a more effective stack of the particles. Moreover, 21 wt% rutile content in NP90 cell is beneficial to the overall solar energy conversion by prompting high efficient electron migration from rutile conduction band to anatase trapping sites. When 20 to 100% NTs are incorporated in the structure, the photocurrent and thus the cell efficiency decrease, due to a less amount of adsorbed dye and the decrease of electron life time.

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Session 2: Atmosphere

Poster presentations

Sub-aerial bacterial adhesion to materials used in solar panels

POSTER P17
(**#Atmosphere**)

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Currently, more than 4000 km2 of areas around the world are covered by photovoltaic panels, and solar photovoltaic energy has demonstrated the highest growth rate in the world, namely 37.3%, amongst renewables from 1990 to 2016 [1,2]. Recent studies have found sub-aerial biofilms (SABs), comprised of highly diverse microbial communities (phototrophic algae, cyanobacteria, heterotrophic bacteria and fungi) colonising solar photovoltaic panels, which can reduce the amount of light reaching the photoelectrically active layer by up to 70% and can lead to significant power reductions [1,3,4]. Different materials used in photovoltaic or photothermic application for the construction of solar absorbers are expected to affect the attachment of microbial populations differently. Amongst others, substrate characteristics, such as hydrophobicity, play an important role in microbial adhesion [5].

The aim of this study was to determine the adhesion of aerosolised Bacillus subtilis culture to a surface of hydrophilic and hydrophobic high solar absorptivity absorber (HSA) coatings used for concentrated solar power plants. Inorganic silicon-based coatings were made on Inconel 617 substrate, where on hydrophobic coatings additional polydimethylsilsesquioxane layer was applied in order to add hydrophobic behaviour to inorganic coating cured at 600 °C. A homemade glass aerosol flow chamber as a benchtop model simulating atmospheric aerosolic deposition onto surfaces was constructed and optimised for this purpose. At the inlet of the chamber, an ultrasonic nebulizer (Medikoel) vaporising a suspension of bacterial spores was placed. At the outlet, an air sampler MAS-100 (Merck) was used to sample the bacterial aerosols onto the target materials. Three techniques for the transfer of the attached B. subtilis spores onto the agar medium were tested for efficiency, (1) submerging the HSA plate into a saline solution and spread plating a sample onto an agar medium, (2) pressing the HSA plate onto an agar medium, and (3) flooding the HSA plate with a molten agar – double agar layer method. All plates were then incubated overnight at 36 °C and the number of colonies counted.

Of the three tested methods, method (2) proved to be the most representative, giving the most consistent results. Moreover, the adhesion of B. subtilis spores was found to be greater on hydrophobic HSA plates as compared to the hydrophilic HSA plates. This, however, is yet to be confirmed with SEM imaging.

The preliminary results of this study indicate that the microbial sub-aerial adhesion is likely to happen on the surface of HSA panels and hence decrease the light absorption. The adhesion will also largely depend on the physical characteristics of the material or coating used in the construction of HSA panels.

Acknowledgements

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Phototrophic organisms in clouds and rain in the area of puy de Dôme, Central France

POSTER P18
(**#Atmosphere**)

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The atmosphere contains diverse microbial assemblages, of which the heterotrophic population has been the most studied. Some heterotrophs maintain activity in clouds[1] and in air[2]. The activity of other modes of metabolism in the atmosphere, such as phototrophy, has not been heavily investigated. Previous work has detailed the presence of phototrophs, but it is unknown what potential role they could have in the atmosphere and if they are active[3,4]. Culture-independent and dependent methods were used to examine the presence and diversity of phototrophic microorganisms in clouds and rain collected at or around puy de Dôme, France. DNA was extracted from cloud water collected at the puy de Dôme meteorological station (1465 m a.s.l., France) and the metagenome was analyzed for the presence of phototrophic microorganisms[5]. Data from Amato *et al.* 2017[1] was re-analyzed for phototrophic microorganisms and, based upon the *16S* and *18S* RNA/DNA ratios, phototrophic microorganisms were active in clouds. Additionally, phototrophic microorganisms were enriched by culture from two cloud event samples. These grew at cloud-relevant temperatures (4°C and 15°C). Sequencing of a portion of the *16S rRNA* and *18S rRNA* genes of these cultures indicated that *Cyanobacterium spp.* and *Chloroidium saccharophilum* were the dominant phototrophic prokaryote and eukaryote, respectively. Isolation of these microorganisms is ongoing. Furthermore, the presence, abundance, and diversity of phototrophic microorganisms in rain is being studied. Rain samples were collected at Opme, France. The flux of chlorophyll-a containing phototrophs from the atmosphere was quantified and cultures were established. An investigation of the diversity of these phototrophs is ongoing. Overall, diverse phototrophs are present in the atmosphere and have the potential to interact with physicochemical processes in the atmosphere.

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Effect of agricultural practices on Biogenic Volatile Organic Compound (BVOC) emissions from winter wheat

POSTER P19
(**#Atmosphere**)

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Vegetative ecosystems emit large amounts of biogenic volatile organic compounds (BVOCs), estimated to reach around 760 Tg C each year (1), which largely exceed those from anthropogenic origin. Several studies have shown that most of BVOCs react with atmospheric oxidants (mainly OH, O3, NO3), promoting the formation of secondary pollutants such as O3 or secondary organic aerosols (SOAs). According to the Food and Agriculture Organization of the United Nations (FAO), agricultural crops cover around 35% of the Earth land surface. Like all vegetative ecosystems, agricultural crops emit significant amounts of BVOCs. Despite their important land cover, studies regarding BVOC emissions from agricultural ecosystems remain very sparse. Karle t al. (2009) (2) pointed out that the agricultural crops could be a major source of BVOCs, but remain highly uncertain due to a lack of investigations.

The global aim of the present study is to reinforce our knowledge on BVOC emissions from agricultural crops. Among all the crops, wheat is the most cultivated one at the global scale (in area harvested, according to the FAO). However, wheat BVOC emissions remain poorly characterized, especially from field experiments. Moreover, there is no study dealing with the effects of the different agricultural practices (e.g. the use- of organic fertilizer or pesticides) on BVOC emissions.

Within the framework of the ADEME-project AgriMultiPol (2017-2020), a field campaign was carried out at a measurement station located at Grignon (France), 40 km southwest from Paris. The field site consisted in a 17 ha agricultural stand of winter wheat (Triticulum aestivum L., variety boregar), over a silt loam soil. The site is also integrated to the ICOS European network (Integrated Carbon Observation System, FR-GRI-ICOS site). The goal of the study is i) to quantify BVOC fluxes over a wheat stand and ii) to evaluate the effect of agricultural practices. The experimental set-up consists in measuring eddy covariance fluxes of momentum, latent and sensible heat, CO2 and BVOCs (with a PTR-TOF-Qi-MS (national instrument within the ANAEE-France framework)). NH3 concentration, particle number size distribution and aerosol chemical composition are also characterized. Nitrogen oxides (NOx) and O3 concentrations are routinely monitored, as well as meteorological parameters (air temperature, relative humidity, solar radiation, wind speed and direction).

Results presented here will highlight the identification and quantification of the major emitted BVOCs. A special attention will be given to the effect of agricultural practices on BVOC fluxes. Finally, potential relation between BVOC emissions and SOA/new particle formation will be discussed.

Potential for phenol biodegradation in cloud waters

POSTER P20
(**#Atmosphere**)

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Phenol is toxic and can be found in many environments, in particular in the atmosphere due to its high volatility. It can be emitted directly from manufacturing processes or natural sources, and it can also result from benzene oxidation. Although phenol biodegradation by microorganisms has been studied in many environments, the cloud medium has not been investigated yet as the discovery of active microorganisms in cloud is rather recent.

The main objective of this work was to evaluate the potential degradation of phenol by cloud microorganisms. Phenol concentrations were measured by GC-MS on two cloud samples collected at the PUY station (summit of puy de Dôme, 1465 m a.s.l., France): they ranged from 0.15 to 0.21 $\mu g.L^{-1}$ [1].

The strategy for investigating its potential biodegradation involved a metatranscriptomic analysis and metabolic screening of bacterial strains from cloud water collected at the PUY station for phenol degradation capabilities (from the 145 tested strains, 33 were isolated for this work).

Among prokaryotic messenger RNA enriched metatranscriptomes obtained from 3 cloud water samples, different from those used for phenol quantification, we detected transcripts of genes coding for enzymes involved in phenol degradation (phenol monooxygenases and phenol hydroxylases) and its main degradation product, catechol (catechol 1.2-dioxygenases). These enzymes were likely from Gamma-Proteobacteria, a dominant class in clouds, more specifically the genera *Acinetobacter* and *Pseudomonas*.

Bacterial isolates from cloud water samples (*Pseudomonas* spp., *Rhodococcus* spp. and strains from the Moraxellaceae family) were screened for their ability to degrade phenol: 93% of the 145 strains tested were positive. These findings highlight the possibility of phenol degradation by microorganisms in clouds [2].

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Photosensitized reduction of nitrogen dioxide on corn leaves as a souce of nitrous acid

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Nitrous acid (HONO) is of considerable interest in atmospheric chemistry as it is an important precursor of hydroxyl radicals (OH) (up to 34% of OH production during measurements in Milan [1]). Moreover, nitrous acid can form nitrosamines in the atmosphere which are carcinogenic compounds. It is therefore crucial to identify and quantify HONO sources and sinks in order to model and predict its concentrations.

Most atmospheric models show discrepancies with experimental measurements. HONO concentrations are underestimated suggesting a missing source [2]. This source has been shown to be maximum at midday, suggesting a photochemical pathway. Additional sources as nitric acid (HNO3) photolysis and heterogeneous reaction of HNO3 on soils have been proposed but these formations were discredited in atmospheric conditions [3, 4].

As NO2 is known to undergo heterogeneous reactions on different surfaces (soil, soot...) and higher concentrations of HONO have been reported above the canopy than aboveground [4], we can hypothesize that one production pathway is the photosensitized reduction of NO2 on leaves. If this is confirmed, these reactions could have a significate impact on HONO concentrations in rural regions, considering the available surface.

The aim of this study is to investigate the production of HONO on corn leaves via photoreduction of NO2. Corn plants are used as a model as their large leaves enable to work with the laboratory system and it represents about 9% of the agricultural areas in France. Experiments are carried out in a flow tube reactor in which a corn leaf is placed around a glass plate. The reactant gas (NO2) is introduced with a mobile injector at different positions with a constant flow. The contact time between the reactant and the leaf is therefore controlled and enables to work out the kinetics of the reaction. HONO and NO formation, as well as NO2 consumption are studied under several conditions of temperature, relative humidity and light intensity. An Ecophysics model (CLD88p) associated with a photolytic converter (PLC860) is used for NOx detection while HONO is recorded with a LOng Path Absorption Photometer (LOPAP). The reactor is irradiated with fluorescent lamps (340-400nm).

The results obtained show a slight increase of HONO emission with temperature (the emission is multiplied by 5 between 288K and 313K). Relative humidity seems to increase HONO emissions after 60% while it does not show any dependence on light intensity in the range tested between 5 and 20 W.m-2.

For all experiments, NO2 consumed is transformed either in HONO or NO, meaning that no HNO3 is formed or its production is below the uncertainties.

For each condition tested, HONO formation is occurring on corn leaves. Due to the large surface available, it could therefore represent an interesting source in rural regions. Modeling studies would be useful to assess the real impact of these surface reactions.

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Air/droplet partitioning of volatile organic compounds (VOCs) in the cloudy atmosphere of the puy de Dôme station in France

POSTER P22
(**#Atmosphere**)

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VOC precursors play a key role on air quality and climate by contributing to ozone production and by modifying the physicochemical properties of aerosols, one of the main agents of Earth's radiative forcing. Among VOCs, oxygenated VOC (OVOC) and biogenic VOC (BVOC) are of particular interest due to their high reactivity. Meanwhile, the cloud system represents a multiphase medium (gas, aerosol, water) for transformations of OVOC[1]. However, the speciation and concentrations of organic matter in the gaseous phase (interstitial air) and atmospheric liquid phase (cloud droplets) is still poorly described[2].

A new analytical approach has been optimized (ie. linearity, repeatability, sensitivity and relative humidity) to explore VOCs in both gas and liquid phases by taking into account real cloud conditions. First, a new gas sampler AEROVOCC collects gaseous VOCs/OVOCs (–C=O and –OH functional groups) simultaneously by deploying three types of Tenax TA sorbent tubes pre-coated with different derivatisation reagents[3]. Simultaneously, cloud sampling is performed by using a dynamic one stage cloud collector. Then, OVOC concentrations in the cloud water samples are evaluated by using direct liquid derivatization and extraction by Stir Bar Sorptive Extraction (SBSE)[4]. Finally, collected samples are analysed by TD-GC-MS at the laboratory. The whole set-up has been deployed on the field to study the partitioning of VOCs; this experimental partitioning is evaluated towards the theoretical one described by the Henry's Law constants. The result shows that experimental concentrations of VOCs are significate and supersaturated by a factor of 100-10000, which means that they have a tendency to get into cloud phase. Larger and less soluble carbonyl compounds were found to be supersaturated by a factor of 100−1000 in orographic clouds in other studies[5].

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Metal pollution of road dust in the vicinity of thermal power plants

POSTER P23
(**#Atmosphere**)

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Road dust are particles deposited on the road that originate from interactions of gaseous, liquid and solid materials from different sources. Road dust receives metal inputs from different sources including traffic, industrial plants, power plants, construction, resuspension of surrounding soil, etc. Therefore, the study of road dust can help us determine the origin, distribution and levels of metals in the environment [1].

Road dust samples were collected from inhabited villages in a 15 km radius surrounding two coal fired thermal power plants. Two samples were collected in the near vicinity of each power plants, Kostolac and Drmno, one sample half way between the power plants, Stari Kostolac, one to the east of power plants, Klicevac, one to the west, Petka, and one across the Danube river to the north, Gaj.

Samples were collected in September of 2015. All samples were sieved through a 63 µm nylon mesh.

Weight 3.0 g of road dust sample and 0.6 g of wax were pressed into 32-mm diamater pellet under 15 t pressure. The concentrations of Al, Ba, Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, P, Rb, S, Si, Sr, Ti, V, Y and Zn were measured using ARL™ PERFORM'X Sequential wavelength dispersive X-ray fluorescence spectrometer (Thermo Scientific, Switzerland).

The normality of the data was assessed using Kolmogorov-Smirnov test. The results were processed using one way analysis of variance (ANOVA) followed by Tukey's HSD multiple comparison test. Enrichment factor (EF) of an element in the studied samples was based on the standardization of a measured element against a reference element, in this case Fe, using the formula: $EF=(C/Fe)_{dust}/(C/Fe)_{crust}$. EF were interpreted so that: $EF < 2$ states deficiency to minimal enrichment, $EF = 2–5$ moderate enrichment, $EF = 5–20$ significant enrichment, $EF = 20–40$ very high enrichment and $EF > 40$ extremely high enrichment [2]

Gaj is the location that had significantly higher concentrations of Al, Fe, K, Rb, S, Sr, and Y, while at the same time having significantly lower concentrations of Cr, Mn and Si compared to all other locations. Significantly lower concentrations compared to most of the other locations were observed for Al, Ba, Co, Cu, Fe, Ni, Rb, S, V and Zn in location Klicevac. This could be explained by dominant wind directions that blow from southeast to northwest.

To differentiate natural origin from anthropogenic sources of metals in road dust EF can be used. The average EF showed moderate enrichment for Ca, Co, Cr, S, Zn and Zr. Ca, Co, Pb and Zn were moderately enriched in all locations.

Although Gaj had the most number of analysed elements with highest concentrations it was shown that it had the least number of enriched elements (Ca, Co, Pb, and Zn). This shows that high concentrations of these elements in Gaj are most likely of natural origin.

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Session 3: Soil and sediments

Poster presentations

Composition and distribution of saturated hydrocarbons in the vicinity of a heating plant in New Belgrade - alluvial sediments of the Sava River, Serbia

POSTER
P24
(**#Soil**)

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The aim of our present research was to investigate the composition and distribution of saturated hydrocarbons in alluvial sediments of the Sava River in the vicinity of a heating plant in New Belgrade, Serbia.

The heating plant in New Belgrade is one of the largest heating plants in Belgrade, the capital of Serbia. During the months of May and June 2015 a detailed investigation of the pollution of the soil and sediments in the vicinity of this heating plant was conducted.

The soil and sediments were sampled from 20 micro locations at 5 different depths.

The pedologic analysis indicated that the lithologic profile at this location was represented by alternating layers of sand and clay. Moreover, most of the layers in the soil profile were characterized by low content of organic matter. According to these data, low adsorption capacity and reduced retention of oil pollutants at this location can be expected.

From the soil and sediment samples, extractable organic matter was isolated with dichloromethane using a Soxhlet apparatus. The extracts were fractionated using column chromatography into fractions of: saturated hydrocarbons (Fraction I), aromatic hydrocarbons (Fraction II), and polar compounds (alcohols and keto compounds - Fraction III) The analytical procedure employed was described in our previous papers [1].

The results showed that in most of the extracts isolated polar compounds (Fraction III) were most abundant while saturated hydrocarbons (Fraction I) were least represented. This ratio between the fractions remained almost unaltered in different soil profiles in this area and at different depts.

Saturated hydrocarbons were analyzed by gas chromatography – mass spectrometry (GC-MS) techniques.

The analyses of *n*-alkanes ($m/z = 71$) and isoprenoids ($m/z = 183$) revealed presence of oil pollutant in almost all of the samples analyzed. GC-MS analysis indicated that the soil/sediment samples investigated contained diesel and/or a heavy oil fuel which have been used for decades in this heating plant.

The analyses of steranes ($m/z = 217$) and terpanes ($m/z = 191$) showed that, at some locations, different diesel and different heavy oil fuel were present. These results suggested that multiple discharges of these pollutants to the surrounding soil occurred over the years.

The distribution of the *n*-alkanes in the $m/z = 71$ GC-MS chromatograms revealed that most of the samples contained a mixture of an oil pollutant and a native organic matter. Their ratio varied depending on the distance from the heating plant, which was the only suspected source of oil pollution in this area.

According to all of these results it can be concluded that the saturated hydrocarbons in the soil and the sediments at the investigated location represent a mixture of an oil pollutant and a native organic matter. The oil pollutant's saturated hydrocarbons originate from multiple discharges of diesel and/or a heavy oil fuel. At some microlocations, these pollutants leaked through the sediment profile almost unaltered, most probably due to the low adsorption capacity of the surrounding sediments.

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects 176006 and III 43004) for supporting this research..

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Organic matter turnover in the organic and in the mineral soil layers across a chronosequence of stone pine forest on mount vesuvius

POSTER
P25
(**#Soil**)

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Forest ecosystems act as a substantial carbon sink and store about 20% of all soil C. The amount of organic matter sequestered in the soil is dependent on the quantity of plant litter delivered to the soil as well as to the extent of litter decomposition. Stone pine forests are common in the Mediterranean areas of southern Italy, were this tree has been largely used for afforestation of volcanic substrates on Mount Vesuvius. Nevertheless, very little is known about carbon accumulation in Stone pine soil as well as about soil organic matter turnover in the organic and in the mineral soil layers.

The aim of this study was to assess, along the whole soil profile, the organic matter turnover across a chronosequence encompassing a 40y, a 70y and a 100y old Stone pine forest within the National Park of Vesuvius. The chronosequence allows to estimate the changes with forest age in C and N concentration and the allocation of organic matter below-ground. The amount and the activity of microbial community at different depth along the soil profile are an indicator of the organic matter turn-over.

The forest stands had been implanted on the same type of parent material, i.e. on lava. The sandy mineral soil was less deep in the youngest forest as compared to the two older forests. Litter fall steadily increased from the youngest to the oldest forest stand (3828, 6144 and 7831 Kg/ha/y, respectively) and was positively related to tree basal area.

C and N concentration in the organic soil layers (litter and humus) of the three stands did not change remarkably with forest age. In contrast, in the mineral layer, C and N concentrations were about threefold higher in the 70y old compared to the 40y old forest stand. A further increase was observed in the 100y old compared to the 70y old forest stand. Differences in organic components in litter and humus of the three forests as well as in the water soluble fraction of organic and mineral layers were shown by 13C CPMAS NMR and 1H NMR spectra respectively.

The amount of microorganisms was related mainly to soil water content and was highest in the humus layer. The 40y old forest showed the highest fungal biomass (mg/g d.w.) and respiration values (mg CO2 g d.w.-1 h-1) compared to the others forests, both in organic layers and mineral soil at depth of 40 cm. When referred to soil organic matter, microbial biomass and fungal mycelium were most abundant in the mineral soil layers as compared to the soil organic layers. This suggests that organic matter turnover is more active in the upper mineral soil layers and decreases with depth and forest age favouring a major accumulation in the deepest layers of the oldest forest stand.

Effect of pesticide formulation on the microbial biodegradation of the active substance

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Pesticides are applied as commercially-available formulations, containing one or several active substances and other ingredients. These supplementary ingredients, described as adjuvants, co-formulants or inerts - as they are supposed to be biologically inactive -, are added to stabilize and to enhance the efficiency of the active substance. Although surfactants and solvents make up the largest group of adjuvants [1], the chemical families used can be diverse. The adjuvants are present as mixtures and the exact composition of a given formulation belong to the industrial secret.

Whilst many studies on adjuvants and formulations are focused on the field efficiency enhancement, only a few papers report on their environmental fate, impact on the active substance behaviour and (eco)toxicity [2,3]. Nevertheless, up to date, the potential effects of these mixtures of molecules are rarely taken into account for a global and correct environmental risk assessment (ERA) of the pesticide.

The aim of our research work was to study the effect of the adjuvants on the active substance biodegradation by pure cultures of different Gram-positive (*Bacillus* sp.) and Gram-negative (*E. coli*, *Pantoea* sp.) bacterial strains. The strains were selected for their ability to biotransform mesotrione {2-(4-methyl-sulfonyl-2-nitrobenzoyl)-1,3-cyclohexanedione}, a selective triketone herbicide commonly used on maize crops [4]. The biotransformations of pure and commercially-formulated mesotrione (Callisto®, Syngenta Crop Protection, 100 g.L^{-1} mesotrione) were compared at different initial concentrations of the active substance (from 0.1 to 1 mM), in terms of kinetics and metabolic pathway.

Interestingly, the results showed that the adjuvants present in the commercial preparation induced two opposite effects on the biotransforming-capability of the strains studied, depending on their type. In the presence of an increasing concentration of Callisto®, the mesotrione biotransformation was more and more strongly inhibited in the case of the Gram-positive bacteria and was more and more stimulated in the case of Gram-negative. Nevertheless, the biotransformation pathway of mesotrione remains the same in all cases. The monitoring of the global adjuvant concentrations by ^{1}H NMR during all these incubations showed a strong decrease for some of them, suggesting a degradation of these molecules. This could explain either a competition towards the substrates (negative impact on the active ingredient biodegradation) or a co-metabolism phenomenon (positive effect). Further research will investigate the biodegradation of the known adjuvants present in Callisto® (octanol and PEO 10-6) and formation of potentially toxic metabolites.

Nevertheless, all these results show the complexity of the chemical mixture interactions but emphasize the necessity to study formulated pesticides in order to assess their real eco-toxicological and environmental behaviour profiles.

Acknowledgements

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Sewage sludge as a secondary source of phosphorus

POSTER P27
(**#Soil**)

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Phosphorus (P) is an essential non-renewable element used predominantly in agriculture (80 %). The main source of P is mineral apatite Ca3(PO4)2. The world deposits are es- timated at around 100 years but these estimates are very inaccurate. The impulse for the beginning of discovering methods of phosphorus recycling was the rapid price increase several years ago { from the original price about 50 US$/t to 430 US$/t [1].

The most important secondary source of phosphorus is sewage sludge. During wastewater treatment up to 90 % of P passes into sludge and this pool could be recovered by several ways in di_erent forms. Potential options (Fig. 1) are digester supernatant, sewage sludge or sewage sludge ash with respect of recycling rate, removing of pollutants, environmental impact and, last but not least, cost. The highest recovery is achieved by recycling methods from ash because up to 90 % of phosphorus passes into ash during thermal processes. The disadvantage of these methods is low bioavailability of the _nal product (mainly iron and calcium phosphate) [2].

In the Czech Republic, phosphorus contained in sludge is the most used by direct appli- cation to agriculture land. The method of phosphorus recycling by direct application to agricultural land will probably be banned due to national legislation after implementation of European legislation already since 2020 if microbiological criteria and heavy metal content are not met [3]. In addition, sewage sludge contains a number of persistent organic contaminants such as personal care product, pharmaceuticals, hormones, etc. that are introduced into the environment through sewage sludge [4].

Methods for phosphorus recovery have been tested on a large scale but their application on an industrial scale is limited by high price of the _nal product, which is not competitive with the price of phosphorus obtained in the common way.

Potential methods with acceptable results of recovery are AirPrex, MEPHREC, AshDec, EcoPhos [5].

The aim of our research project is to analyze the sewage sludge potential as a secondary source of phosphorus and to optimize its recycling technology during material and energy use. The component of interest is ash. The WWTPs were selected according size (more than 10.000 EP), technology and location in the Czech Republic. The screening test shows that the phosphorus content in sewage sludge ranges from 12.000 mg/kg to 60.000 mg/kg.

Keywords: phosphorus, sewage sludge, WWTP

Phototransformation of myrigalone, a natural herbicide, in water and on leaves

POSTER P28
(**#Soil**)

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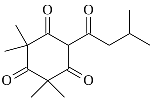
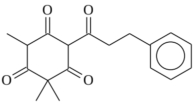
Increasing food production without increasing the use of synthetic pesticides is becoming a challenge. In this context, biopesticides are attractive pest management tools due to their low toxicity and generally fast degradation in the enviroment. β-Triketones herbicides, in particular, are interesting molecules [1]. In 1977, the allelopathic properties of *Callistenum citrinus* were discovered: no weed seeds were able to germinate around the plant. The main constituent of this plant, leptospermone, was extracted and found to prevent seeds germination and to be herbicidal. This discovery led to the design of a series of synthetic β-triketones herbicides.


Leptospermone


Myrigalone A

Myrigalone is another natural triketonic compound showing interesting properties. It is produced by *Myrica Gale* on the surface of leaves and fruits and constitutes about 40% of the excudate. It was demonstrated to show herbicidal properties and to be potentially allelochemical [2]. The presence of this compound in a so big amount in the excudate let us to consider whether its herbicidal and allelochemical properties are related with solar exposure and with the formation of photoproducts. Indeed, this molecule aborbs solar light until 400 nm and should be able to undergo photolysis as leptospermone [3].

The objective of the work was to investigate the photolysis of myrigalone and determine what are the photoproducts and if they are volatile. Experiments were performed on pure synthetic myrigalone A as well as on natural extracts from leaves containing a mixture of myrigalones.

The photoreaction was studied in aqueous phase and on solid mimicking the surface of leaves. Photoproducts generated in solution and evolved in the gazeous phase were analyzed by HPLC-HRMS and GC-MS.

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Determination of a scalable methodology for soil spiking with organic compounds

POSTER P29
(#**Soil**)

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Soil pollution has become a matter of concern in the last decades and a variety of techniques had been researched to its treatment for contaminant elimination. Anyway, due to the presence of different polluting species and the heterogeneity of the soil, its physicochemical properties are anisotropic and, thus, very complex.

In order to simplify the system for research purposes, soil spiking has been widely investigated. This way, the number of variables to take in account during the study is lower, the interactions between diverse variables are diminished and the detection of the effect of one specific variable on the characteristics of a pollutant becomes more reliable [5].

However, the need of a proper soil spiking methodology is still there. Some attempts on determining the procedure to follow in order to introduce a pollutant into a clean soil matrix had been made, but they are mainly focused on spiking low amounts of soil, variability on procedures has been found between papers and most of them were developed some years ago[3, 6].

This work is included on a soil remediation project that seeks to eliminate the pollutants from soil through ultrasonic washing. As the main goal is to be able to focus on the soil remediation processes at large scale, the spiking method must provide a simple way to spike large amounts of soils, in order to simulate the remediation process with industrial equipment.

So, different spiking methodologies [1,2,4] had been taken as basis in order to develop a scalable and straightforward spiking procedure able to handle larger amounts of soil. While the previous work on this topic has been focused on developing a pollutant specific method for spiking, the method developed in this work is believed to be suitable for a wider range of compounds.

In order to successfully determine the required methodology, the spiking conditions need to be adapted so the method becomes more suited to the process and more sustainable and eco-friendly.

Two different lots of soil had been spiked for this work. The first of them more fitted to laboratory scale work (1 kg) and the second, focused on a larger scale work (50 kg). Both soil lots were spiked in order to reach 50000 ppm content in diesel fuel.

Given the amount of soil involved in the process and fearing some lack of homogeneity, a study of the sampling effects and the analysis reproducibility was carried out. It was seen that the homogeneity of the spiked soil lots was more than satisfactory. Through the analysis of the soils, a proper spiking was identified, with the same organic compound distribution that can be found on diesel fuel.

Afterwards, to validate the method for the remediation process, the soil lots were treated through ultrasonic washing. Both lots showed a similar behaviour during the washing process, achieving, in both cases, a diesel recovery of around 20%.

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Migration and transformation of toxic rocket fuel 1,1-Dimethylhydrazine in the peaty soil

POSTER P30
(**#Soil**)

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Various types of carrier rockets use highly toxic fuels based on 1,1-dimethylhydrazine (UDMH). In addition to its high toxicity [1] and the ability to produce a wide range of hazardous transformation products (TP) [2], there is an acute problem of their migration when rocket fuel released into the soil. The only one published work on this topic is devoted to the study of the distribution of 1-methyl-*1H*-1,2,4-triazole (MT) in the sandy soil profile at the crash place of Proton carrier rocket near the Baikonur cosmodrome in Kazakhstan [3]. So far, there are no any data on the distribution of UDMH and its most important transformation products in numerous fall places of spent rocket stages in European North of Russia which are characterized by very complex and difficult to study peat bog soil.

The objects of this study were more than 100 soil samples with organic matter content of >95% taken at the impact place of the first stage of the “Cyclone” vehicle (launched more than 10 years ago) in Arkhangelsk region of the Russian Federation. Sampling was done at depths 0–150 cm at a distances of up to 10 m from the crater in the directions of the four cardinal points.

The contents of hydrazine, methylhydrazine and 1,1-dimethylhydrazine were determined by the high-performance liquid chromatography with amperometric detection [4]. The seven most important TP (dimethylhydrazones of formaldehyde (DMHF), acetaldehyde (DMHA) and 2-furaldehyde, 1,1,4,4-tetramethyl-2-tetrazene (TMT), MT, nitrosodimethylamine (NDMA), and formic acid dimethylhydrazide (DMHFA)) were determined by the developed recently gas chromatography / tandem mass spectrometry method combined with pressurised solvent extraction by subcritical acetonitrile [5].

It has been established that the maximum concentrations of unsymmetrical dimethylhydrazine are found in the epicenter and reach values of 150-180 mg kg^{-1} of soil, which corresponds to a 1000-fold excess of the maximum permissible concentration. In the soil profile, the maximum content of highly toxic rocket fuel is reached at a depth of 20-80 cm. At a distance of 10 meters or more from the epicenter the concentration of UDMH is below the detection limits, which indicates the local pattern of pollution.

The content of hydrazine and methylhydrazine is lower by 1 and 2 orders of magnitude, respectively, when compared with 1,1-dimethylhydrazine and their distribution completely correlates with UDMH.

Among the products of transformation, five of the seven analytes studied were found. The TMT and dimethyl hydrazone 2-furaldehyde were not detected, which can be caused by their low stability. The content of the studied transformation products varies in the range from a few to several tens of mg kg^{-1}, reaching a maximum in the epicenter. At a distance of 10 meters from the crater only trace amounts of MT and DMHF were detected.

Thus, peat extremely strongly binds hydrazines and their transformation products, which leads to long-term preservation of pollution - high concentrations of hazardous compounds remain for decades. The binding process is reversible, a small amounts of TP were found in the crater water, which indicates the possibility of release of pollutants under certain conditions.

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Transport and deposition of silver nanoparticles through saturated sand columns

POSTER P31
(#**Soil**)

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Engineered nanoparticles are widely used in various application fields, such as drug delivery, electronics, cosmetics, textiles, and detergents, and their annual production is gradually increasing. Among them, silver nanoparticles are one of the most commonly used engineered nanomaterials. In this study, the influences of physical and chemical factors (e.g., ionic strength, pH, and flow rate) on the transport and despotion of citrate-coated silver nanoparticles (Cit-AgNPs) were investigated through saturated sand columns. For the transport behavior of Cit-AgNPs under various conditions, retardation was confirmed with increasing ionic strength while early elution developed with increasing pH and flow rate. These transport experiment outcomes were simulated through Hydrus-1D, and the observed breakthrough curves were confirmed to have a significant correlation with the fitted results. Interestingly, the Cit-AgNPs and quartz sand showed a negative charge in the experimental conditions studed. The surface roughness of sand grains was considered to be a major factor in the deposition of Cit-AgNPs onto the sand surface under the unfavorable conditions. This hypothesis was supported by the zone of influence calculation in accordance with IS, the interpretation results of the fractional sand surface coverage in accordance with concentration changes of Cit-AgNPs, and series column tests. Our study provides a more complete understanding of the effect of surface roughness on the transport and deposition of nanoparticle in environment systems.

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Microclimatic conditions, vegetation cover and human impact as drivers of soil quality

POSTER P32
(#**Soil**)

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Soil quality can be defined as "the capacity of the soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain biological productivity, promote the quality of air and water and maintain plant, animal, and human health"(Karlen et al., 1997). Nowadays, natural parks have been established in order to preserve the environmental quality, to maintain high the biodiversity but also to enhance recreation and tourism (Korkanç, 2014). Unfortunately, in these areas, recreational and touristic activities have various negative impacts on soil properties (Cakir et al., 2010). In fact, atmospheric pollutants can move over long distances from the emission sources (car, touristic bus, motocycle) and can reach the soils through wet and dry depositions (Pan and Wang, 2015). Thus can, in turns, modify the geochemical background (Memoli et al., 2018), endure the edaphic community and cause loss of soil quality and consequently had an indirect effect on ecosystems health. The aim of the research was to identify which environmental factors (microclimatic conditions, vegetation cover, human impact) mainly affect soil physical-chemical characteristics (pH, water and organic matter contents, C, N and heavy metal concentrations) as well as biological ones (microbial activity, fungal and microbial biomasses) and which environmental factor can be considered the driver of soil quality.

The research was performed at the Vesuvius National Park (Southern Italy), an example of a peculiar volcanic system of great naturalistic interest, surrounded by a densely populated area and subjected to an intense touristic impact inside the park. This area is characterized by diversified landscapes can be defined by the spatial pattern of elements of topography, vegetation and soil. The Vesuvius National Park is greatly impacted by human activities in fact, it attracts numerous tourists a year (600 thousand visitors in a year). In order to highlight probable differences according the touristic flow and microclimatic conditions, surface soils (0-10 cm) were collected along two roads, leading to the cone: Ercolano road, characterized by continuous and various traffic, and Matrone road, crossed by a limited period and only by touristic bus that transport people to the crater from April to October. The soils were collected, in 2015, 2016 and 2017, at the end of the touristic season (autumn) and at the beginning of the next one (spring) at approximately 600 m and 900 m of altitudes. For reach the aim an NMDS analysis was performed to evaluate the effects of environmental factors on soil properties. In addition, the confidence ellipses for seasonality, altitudes, plant cover and human impact were superimposed on the NMDS in order to evaluate their effects on parameters distribution inside the national park.

The results showed the fundamental role of temporal and spatial climatic variations in defining soil characteristics inside the Vesuvius National Park In particular that the soils distinguished according different seasons or altitudes, both site-specific characteristics strongly controlled by climatic factors. The different microclimatic conditions that occurred along the altitudinal transect regulated the plant cover inside this area. Also, the soil physic-chemical parameters were mainly influenced by altitudes and human impact. The biological parameters were more influenced by seasonality and altitude. In this study, altitude and human impact seemed to be the main drivers of soil quality.

Assessing the levels of siloxanes and musks in sewage sludges for a sustainable and safe use in soils

POSTER P33
(**#Soil**)

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Municipal wastewater treatment has increased in recent years in European countries, resulting in an estimated amount of 10 million tons of sewage sludge (dry matter) every year [1]. As this number tends to increase, the disposal management of sludge is a problem that has been raising concerns.

Currently, the reuse of sewage sludge for rectification of soils for agricultural purposes is the most preferred way to reduce the amount of sludge directed to landfill disposal sustainably [2], a practice regulated by the Council Directive 86/278/EEC [3]. However, treatment approaches in wastewater treatment plants (WWTPs) do not target a broad range of emergent compounds (used at trace levels in household and personal care products by millions of people) that end up in municipal wastewaters. Volatile methylsiloxanes (VMSs) and synthetic musk compounds (SMCs) are examples of emergent pollutants that are not treated in WWTPs and, due to their low water solubility, tendency to adsorb to organic matter and limited degradability, accumulate in the sludge, turning it a vector of contamination to different environmental compartments [2]. Regarding the potential harmful and toxic effects of some of these compounds, both to the environment or to crops grown in sludge-amended soils (and therefore for animal and human health), the knowledge on this topic should be increased, aiming for a better understanding of the risks and possible drawbacks of this practice.

Therefore, this study intends to assess the safe fertilizer potential of sludge from municipal WWTPs for agricultural purposes, in terms of organic matter, pH, and macro and micro nutrients, as well as to evaluate the levels of VMSs and SMCs in final sewage sludge reported in studies available from the past 10 years. Despite the sewage sludge composition may vary greatly, depending on the type and origin of the waste streams received by a WWTP, among other sociodemographic and spatiotemporal parameters, as well as other facility operating factors, the results showed a clear presence of the target pollutants in sludge. From the VMSs family, the cyclic congeners D5 and D4 are those usually reported at higher concentrations, as well as long linear VMSs, while galaxolide (HHCB) and tonalide (AHTN) are the most frequently detected SMCs and at higher levels. An estimation of risks associated to the use of such sludge in soils was then calculated based on agricultural parameters and appropriate soil conditions. Concentrations in the sludge-receiving medium were predicted (PEC), following the methodology described in the EU Technical Guidance Document [4]. Those values were compared to no-effect concentrations (PNECs, determined using previously published toxicological data) and hazard quotients (HQ) were estimated.

Acknowledgements

This work was financially supported by the projects: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) and (ii) AGRONAUT, POCI-01-0145-FEDER-029425, funded by European Regional Development Fund (ERDF) through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (PIDDAC) through FCT – Fundação para a Ciência e a Tecnologia/MCTES, and (iii) "LEPABE-2-ECO-INNOVATION" – NORTE-01-0145-FEDER-000005, supported by North Portugal Regional Operational Programme (NORTE2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and (iv) Contract IF/01101/2014 (Nuno Ratola).

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Photochemistry of agrochemicals on plant surfaces: key parameters affecting reaction rate, pathways and products

POSTER
P34
(**#Soil**)

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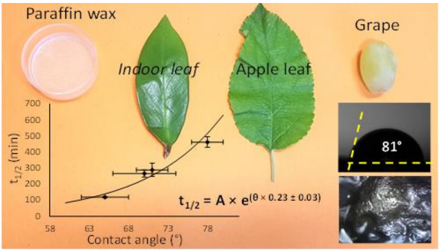
Estimating the half-life ($t_{1/2}$) of pesticides due to photodegradation on plant surfaces is challenging. Due to the difficulties to handle leaves, recent studies have attempted to use isolated cuticles or paraffin wax(1). This model surface is easy to handle and resistant to long-term irradiation. However, is it a good model? and how can we extrapolate data to plant surfaces?

In this study, we investigated the photodegradation kinetics of six widely used pesticides (azoxystrobin, acibenzolar S-methyl, pyrimethanil and thiophanate methyl, α-cypermethrin and imidacloprid). Experiments were performed on model and natural surfaces (glass, paraffin wax, grape skin, apple leaves and indoor plant leaves) in the laboratory and under sunlight exposure. Formation of surface and gaseous photoproducts was investigated using high resolution LC-ESI-Orbitrap-MS and an online thermal desorption system coupled to GC-MS, respectively. Furthermore, the effects of solvent, formulation and concentration of active ingredients were examined. The influence of deposit spreading and homogeneity on the photodegradation was evaluated using contact angle measurements and microscopic analyses.

The results showed that the photodegradation rate varies in the order: paraffin wax << glass < apple leaves & grape. Depending on the support used, the photodegradation half-life was found to vary by a factor of 2 to 200 for pyrimethanil. The influence of other parameters such as composition and concentration of pesticide was less pronounced. This suggests that studies using model surfaces can over- or under-estimate the dissipation of pesticide photodegradation on plant surfaces. This drastic difference in photoreactivity was attributed to the nature and spreading of deposit, as influenced by surfactant and surface characteristics. Abiotic stress of irradiated apple leaf was also shown to produce OH radicals which might contribute to the enhanced photodegradability. The spreading can be represented by the contact angle formed by the pesticide droplets and the surface.

A correlation was developed based on the use of the contact angle (θ) and paraffin wax as surrogate. The correlation ($t_{1/2} = A\ e^{(0.24 \pm 0.03 \times \theta)}$) was validated for azoxystrobin and thiophanate methyl. This correlation could be used to extrapolate kinetic data from model to plant surface, facilitating the estimation of half-life on plants, and allowing to improve environmental fate and risk assessment models. The developed experimental approach can provide valuable insights on the heterogeneous photoreactivity of other sprayed agrochemicals and could help improve dissipation models leading to a better risk assessment.



Acknowledgements

This project was funded by the European Regional Development Fund of the European Union and by the Region Auvergne Rhône Alpes under the Program "Nouveau Chercheur" (AV0004494).

Mercury distribution in the brown coal and in different coal combustion process by-products

POSTER P35
(**#Soil**)

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Mercury contamination is a seriously threatening for human health and all compartments of the environment. The Global Mercury Assessment Report by UNEP revealed that the combustion of fossil fuels is one of the major sources of mercury emission into the air. It is assessed that in 2012 in Poland about 90% of energy came from combustion in the public electricity and heat production sector. The mercury emission steadily decreases for the last several years in Poland, however it remains still at an unsatisfactory level. Based on the information delivered by the National Centre for Balancing and Management of Emissions about 10 tons of mercury and its compounds were emitted into the atmosphere in 2015 from the area of Poland. Starting from the 16 August 2017, mercury emission standards from fuel combustion plants are regulated by The Minamata Convention - a global treaty to protect human health and the environment from the adverse effects of mercury. It is recognized that the policy on the reduction of mercury emissions into air from coal-combustion power plants is one of the most important strategies to reduce mercury emissions, which may require a development of technologies that will allow efficient reduction of mercury emissions from this sector.

According to the Best Available Techniques (BAT) conclusions for large combustion plants adopted in July 2017 under the 2010/75/EU Industrial Emissions Directive (Commission Implementing Decision (EU) 2017/1142), all new installations have to reduce emissions of mercury to below 3 micrograms per normal cubic metre (µg/Nm3). Monitoring of mercury emissions to air must be carried out once every three months in plants with a thermal output under 300 MWth (megawatts thermal), or continuously in plants with output higher than this value. Since the mercury content varies greatly depending upon the coal used, the monitoring of the mercury in the fuel and its further distribution into combustion products seems to be necessary [1-5].

This work was dedicated to establish an extent and type of the interrelations between the mercury content in brown coal and its levels in the coal combustion process by-products such as ash (different size fractions) and slag. For comparison purposes the content of mercury was determined as well in the limestone (sorbent) and in gypsum produced as a consequence of a wet flue-gas desulfurization. The mercury content was measured by the cold vapour atomic absorption spectrometry technique (CVAAS) with the use of an automatic Mercury Analyzer MA-3000 (Nippon Instruments Corporation). The correctness of the proposed method was confirmed by the analyse of the reference materials with the certified Hg content (fly ash BCR-038, coal fly ash NIST-1633c, coal NIST-1632d, soil NCS ZC 73001, lake sediment IAEA-SL-1) and an acceptable agreement was achieved between certified values and gathered results.

Based on the obtained results it can be stated that mercury content in the gas stream emitted into the atmosphere is strongly influenced by the individual purification processes. The fly ashes removal in electrostatic precipitators plays here a crucial role. It was proven that the more brown coal contains mercury the more is removed together with the smallest fraction of fly ashes, and consequently less polluted by mercury is the gypsum by-product. In addition, no correlation was observed between the amount of mercury in the slag and the mercury content in the coal. The gathered Hg levels in studied samples were directly compared with literature data and stayed within the found limits.

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Bio-physicochemical reactivity of marine sediments after dredging

POSTER P36
(#**Soil**)

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50 Mm^3 and 200 Mm^3 of sediment are annually dredged in French and European harbors respectively [1], to ensure the development of commercial and tourist activities, and also to allow navigation. They could be contaminated by heavy metals at different levels and their management is therefore strictly controlled. Storage on land is then often used because those sediments cannot be returned to immersion. However, when removed from water, these matrices could be very reactive with the oxydoreduction potential change. Therefore, their geochemical behavior must be understood in order to avoid dispersion of contaminated leachates in the surrounding ecosystems.

This reactivity is the result of both physicochemical and biological effects. These mechanisms will influence the release or trapping of inorganic contaminants such as trace metals and sulfur that can be tightly bound to sulfide contained in the sediment [2]. Some trace metals (Cu, Zn etc.) are also bound to organic matters, hence the potential release of trace metals into the environment following the degradation of organic matter.

This study is a part of the SEDITERRA project, a European INTERREG program for the valorization of marine and fluvial sediments (http://www.sediterra.eu/). As part of the objectives set out in the Europe 2020 strategy, the project promotes the eco-innovation in the management of polluted or unpolluted sediments. One of the objectives is to supplement knowledge on the biological and physicochemical mechanisms that occur during the exposure of sediments with air in the situation of valorization in landscape.

The present work is focused on the physicochemical characteristics that lead to a potential biological and physicochemical evolution in contact with oxygen. Three marine sediments around the Mediterranean basin have been selected and studied. Their biological and chemical reactivity are the key point of the mobility of contaminants, which has been studied finely with several tests under controlled conditions with air.

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Session 4: Waters

Poster presentations

Finding the best fitting solutions for wastewater management in Baltic Sea Region villages (VillageWaters)

POSTER P37
(**#Waters**)

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Wastewater Solutions Information Tool

Let us help you select best wastewater treatment solution for your needs

Choose the country

Choose from location list

See which wastewater treatment systems are available in particular country and conform with local rules and regulations.

VillageWaters project (2016-2019) funded by Interreg Baltic Sea Region programme brings together sparsely populated areas households and village communities, local authorities, small and medium-sized enterprises as well as research institutes. The project team consists of 13 partners from five countries that are Estonia, Finland, Latvia, Lithuania and Poland. The main challenge of this project is to develop practical tool for selection of the most feasible, cost-effective and environmentally friendly wastewater treatment solutions for the scattered dwelling households not connected to centralized sewage collecting systems in order to decrease wastewater emissions into the Baltic Sea.

During the project lifetime, the available technological, social, economic and environmental data collection and assessments is done. The data is also gained from pilot villages located in all partner countries where, within the framework of this project, optimal technological solutions for households were applied. Based on the results obtained the Information Tool, a practical e-service system, was created to help find the most feasible and environmentally friendly wastewater treatment solutions for homeowners in sparsely populated areas.

The tool considers the topic of wastewater treatment from a technological, environmental, economic and social point of view. It will also include discussion and communication forums through which it connects and brings the target groups together to discuss, exchange data and ideas, assess and commit planning, implementation and management of wastewater treatment systems

The Information Tool is already available as a prototype starting in spring 2018 and will be fully developed by the end of the project. The project results are also actively disseminated among all target groups at seminars, trainings, workshops and materials, using social media and digital solution (project website https://villagewaters.eu/, Facebook, Q&A-forum, etc.).

It is proposed that the outcomes of project will help households avoid unnecessary investments and operating costs when shifting to improved wastewater treatment solutions, and thus to encourage them to implement the new treatment systems. Therefore, the results of VillageWaters project will help to improve the state of the local receiving water bodies and the Baltic Sea in such a way that total environmental impact would not increase.

Acknowledgements

The financial support provided by Interreg Baltic Sea Region Programme (project VillageWaters, #R014) is gratefully acknowledged. The authors would like to thank all project partners from Estonia, Finland, Latvia, Lithuania and Poland for collecting and processing data.

Variation of particulate trace metals in two small rivers discharging in Toulon Bay: Raw and net fluxes

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The Toulon bay (N-W Mediterranean Sea, France) is a semi enclosed bay submitted to severe nautical activities (ferries, commercial harbours, 1st Navy harbour) and is closed to an urbanised zone of 0.45M inhabitants. Previous studies showed that the surface water exhibits an important gradient of contamination for most of dissolved trace metals (as example Cd, Zn, Cu, Pb, Hg) from enclosed parts to open sea **[1]**. Potential sources of trace metals are (1) well established: the sediment multi-contamination [2], or (2) to be more studied: harbour (antifouling paints), waste water treatment plant output, atmospheric deposits and rivers (Eygoutier river in the large bay, Las river in the small bay).

This study is part of the METFLUX project (evaluation of trace metals fluxes in a coastal zone – case study of Toulon bay, 2016-2019) supported by the French water agency Rhône-Méditerranée –Corse.

In this study we focused on the transport of trace metals in particles by the rivers with discrete and integrated sampling device. A one-year monitoring was conducted by collecting discrete samples during base flow each month for analyses of particulate trace metals (including mercury), particulate organic carbon and nitrogen. In addition to discrete samples collection, a particle sampler device [3] was installed to collect composite sample during the same period, corresponding to base flow or flood event. Basic physico-chemical parameters were monitored during the study (temperature, specific conductivity, turbidity). The obtained results show that Las river is less contaminated than Eygoutier river, with the average content of Cu, Pb an Zn higher than the Rhône river. The data are also used to calculate particulate trace metals fluxes and discussed in comparison with meteorological data from Météo France.

Moreover, a batch remobilisation experiment was conducted in laboratory. It consists in mixing river flood deposits with different river water / seawater ratio at different times (15min, 1h, 6h and 24h). This experiment allows to better understand the process occurring in the salinity gradient (adsorption or desorption) and finally determine a net flux for each trace metal.

The trace metals fluxes determined for these two rivers would finally be compared to other sources to determine the most important source leading to the gradient observed in the Toulon Bay.

Eco-geochemical characterisation of downstream flow of the Tamis River (Serbia)

POSTER P39
(**#Waters**)

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The Tamis is a 340 km long river, springs in Romania, and a 118 km of this river flows through northern Serbia and flows into the Danube near Pancevo city (Serbia). Within this study for the first time sediments from the Tamis river were investigated with the aim of eco-geological characterization. A detailed study includes the entire flow, and here are presented the results of the its downstream flow near the confluence of the Tamis and Danube river and its flow through Pancevo city, which is a large industrial city.

In the downstream flow, the samples were taken from 8 sampling points to a depth of 1 m in the period September-November 2017. Then the sediment core was divided into 4 samples. The grain size analysis was done by laser diffraction and by sieving, X-ray diffraction (XRD) was used for mineral identification, the content of macro- and microelements was determined by X-ray fluorescence (XRF).

The obtained results of grain size analysis show that investigated samples consists mainly of sandy, with variable content of clay and silt.

XRD analysis shows that main mineral part of analysed samples is composed of quartz, folowed by feldspar, carbonate and clay (most commonly represented by chlorite) minerals. The content of macroelements confirms determined mineral composition.

Potentially toxic elements in the investigated samples have a uniform trend, only Cr, Cu, Co, Ni and Zn have significant variation of concentration in certain sampling points.

The ratio of Ni and Co in investigated samples shows good correlations with the ratio of these elements in the Timok river. This can be explained by the fact that the Timok and Tamiš rivers flow through the Carpathian - Balkan Mountain Wreath and draining the same geological base [1].

In order to determine the intensity of anthropogenic impacts on contemporary sediments the Enrichment Factor (EF) was calculated for elements that have shown significant variation in concentration in certain sampling points [2].

The Incidence Factor (Cif), Risk Factor (Eif) and the Ecological Risk Index (RI) were calculated for the same elements to assess the environmental risk [3].

The EF shows that majority of analysed samples have small anthropogenic influence, only Cu and Zn have moderate to moderately increased anthropogenic influence in some locations.

Based on values of Cif, Cr, Co, Ni and Zn have a low to moderate degree of pollution, while Cu has a significant degree of pollution in some locations. Values of Eif and RI indicate low ecological risk of sediments from all sampling points.

Investigated samples of all locations of downsteam flow show low ecological risk, singled out only certain sites near Pancevo city with increased concentration of Cu and Zn for which further and more detailed analysis is needed.

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Mechanism of photochemical degradation of Fe (III)-EDDS complex

POSTER P40
(#waters)

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In the last few years, one of the most popular ways of treating water is the approach of AOPs (Advanced Oxidation Processes). These technologies (AOPs), generate in situ very reactive radical species, mainly hydroxyl radicals ($HO^\bullet$), which is a strong oxidant (E_0 = 2.8 V), have an extremely short life time (≈ 10^{-9} s) and can instantaneously oxidize most organic compounds in water **[1]** .

One of the most famous, used and efficient AOPs is based on the Fenton process. However, this process has a strong drawback due to the pH limitation. Indeed, Fenton process is efficient for pHs close to 3.0 and at pH higher than 4.5 the efficiency of such process is very low due to the precipitation of iron in this domain of pH. To overcome this drawback, polycarboxylates and aminopolycarboxylates are added to form stable complexes with Fe (III) which absorb light in the near-UV and visible regions and undergo photoredox process through a ligand-to-metal charge transfer (LMCT) generating Fe(II) ions and oxidized ligand **[2].** Ethylenediamine-N,N'-disuccinic acid (EDDS) is one of the most popular ligand because is a safe and environmentally benign compound, is a strong complexing agent of iron and Fe(III)-EDDS, 1:1 complex, is photochemically efficient until pH 9.0 **[3].** So, nowadays Fe(III)-EDDS complex can be considered as one of the most used complex in the different AOPs **[4].** However, no target study on the photo-transformation of this complex and more particularly the mechanism of the organic part (EDDS) degradation has been performed. The fate of EDDS during the photochemical process is essential to know the organic compounds formed and their potential role on the iron chemistry and more generally on the aquatic compartment. So, the main objective of our work is to identify the main primary by-products of the EDDS degradation and to propose a general mechanism of the complex Fe(III)-EDDS degradation under light irradiation.

To reach our main goal, analyses of the irradiated solutions, at λ > 280 nm, are performed with UHPLC-MS system in various modes: positive and negative, in order to detect and qualify the main by-products. With the use of Xcalibur software, most of the products following this mechanism were identified and a photodegradation mechanism of this complex is proposed until the formation of the first by-products. The first part is presented in **Figure 1.**

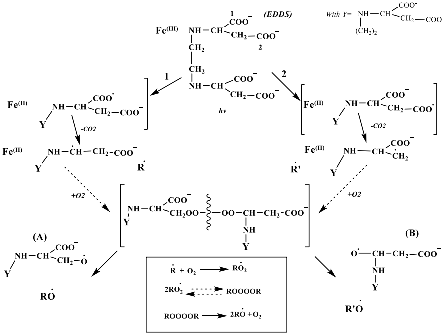

*Figure 1***: *First part of the mechanism of FeEDDS complex photodegradation.***

The identification of the main organic products generated from the oxidation of EDDS allows understanding and identifying what are the main pathways for the degradation of such organic ligand complexing iron. This is essential for the use of iron complexes in water treatments.

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Plastic contaminants in streams: new substrates for microbial activity?

POSTER P41
(**#waters**)

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Plastic contamination in freshwaters is an emerging problem due to its ecological consequences that include non-exhaustively ingestion by aquatic organisms and subsequent trophic transfer, release of chemicals by leaching and transport to oceans [1]. Aquatic microorganisms are also impacted by the presence of these man-made substrates that select and promote the growth of communities to the detriment of others [2]. In streams where microorganisms play a key role in carbon and nutrient cycling, changes in the nature and quantity of benthic substrates where they develop may alter the functioning of this ecosystem [3].

The objective of our study was to assess functional consequences of plastic contamination in streams by the comparison of microbial colonization and enzymatic activities on naturally occurring substrates (leaves, sediments), on inert substrate (glass slides) and on two possible plastic substrates contamination [low density polyethylene (LD-PE), biodegradable bioplastic (BDBP)]. All substrates were immerged for 4 weeks in two contrasted sites of the Artière river (Auvergne-Rhône-Alpes region, France): one less polluted site (Upstream) and one more polluted site (Downstream), the latter being subjected to strong chemical pollution and where plastic fragments were frequently observable on river banks.
Bacterial, fungal, and photosynthetic organisms quantification, enzymatic activities (β-D-glucosidase (GLU), N-acetyl glucosaminidase (NAG) and phosphatase (PHO)) and mass loss were determined weekly on each substrate as well as water physico-chemical parameters. A deeper insight in substrate colonization was established after 3 weeks on the polluted site by prokaryotes and eukaryotes sequencing (16S and 18S genes respectively).

First results showed that all substrates were colonized by microorganisms but at different rates, leaves and sediments being the first colonized by bacteria while LD-PE and glass were the last, especially in the unpolluted site. After 4 weeks immerged on stream water, bacterial density were the lowest on LD-PE and BDBP on the upstream site while BDBP bacterial concentration were higher and equivalent to those of glass and sediments in the downstream site.
Diversity analyses highlighted low richness on both studied plastics compared with leaves and sediments for prokaryotes, and with leaves for eukaryotes. LD-PE and BDBP diversity profiles were close to each other with 31% of amplicon sequence variants (ASV) shared and were more similar to that of leaves than that of glass or sediments.
While the highest activities were recorded on leaves and sediments, activities on BDBP and LD-PE were non-negligible compared to those measured in natural substrates, in particular in the polluted site. Modelling enzymatic activities as a function of BDBP/LD-PE coverage on benthic surface suggested that presence of plastic contamination could increase GLU, NAG and PHO activities but also favour C-cycling over N- and P-cycling.

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Investigation of transformation products of 1,1-Dimethylhydrazine and development of technology for neutralizing industrial sewage containing 1,1-Dimethylhydrazine and its transformation products

POSTER
P42
(#waters)

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1,1-Dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) is a component of a widely used rocket fuel. Along with significant advantages over other fuels, UDMH is a toxic substance with mutagenic and carcinogenic activity. UDMH pollutes the environment during the fall of the used rocket stages, filling and discharge of fuel tanks as well as emergency spills. The danger of UDMH consists in its high reactivity and a large number of possible transformation products. Some of them, namely N-nitrosodimethylamine, tetramethyltetrazene, are highly toxic and carcinogenic compounds. There are also risks of getting UDMH into the environment when storing and transporting the fuel as well as during washing the fuel tanks. One of the technologies for the neutralization of UDMH storage tanks and refilling equipment is their treatment with water. In this case, it is assumed that the waste water after collection through the industrial sewage system will be neutralized by afterburning in a special apparatus using the combustion of aqueous solutions in a mixture with kerosene. At the same time, the operation of such afterburners is characterized by cyclicity, due to the fact that a considerable amount of fuel is needed to start and stop its engine. That is why afterburning is carried out when a significant amount of waste water containing UDMH is accumulated. The storage of such wastes (in the case of the leak in the storage tanks) often leads to the formation of high-molecular nitrogen-containing products, traditionally called "black tar", because visually in the volume and on the walls of the reservoirs, a dark, mazut-like compounds are formed. There are lists of known products of UDMH transformation, products with unconfirmed formula, products that are assigned with different structures and products with a completely unknown structure. At the present time, several research groups are conducting a large-scale investigation of the previously unknown products of UDMH transformation. Chromatography and mass spectrometry are widely used to determine UDMH and its transformation products.

In this research, we studied the sample of the oxidised mixture of 1,1-dimethylhydrazine which is a water solution of the contents of the storage tank where the washing water with UDMH was stored. In order to detect UDMH transformation products, HPLC-MC/MC and MALDI-MC methods were used. A comparison of different methods of mass spectrometry analysis of sample preparation was made. The compounds m/z in the range of 100-300 Da were detected. Settings for the chromatographic separation were picked and we succeeded to isolate isomeric substances from a mixture of UDMH transformation products. A series of chromatography-mass spectrometric analysis was carried out to study the structure of the explored compounds.

Fractions corresponding to ions with m/z 154 and 224 Da were isolated for carrying out of cytotoxicity measurements. Fractions with concentrations up to 0.05 mg/ml were obtained. The concentrations were evaluated by UV and MS calibration curves for the closely related triazole derivatives. The test compounds exhibited dose-dependent cytotoxicity for HeLa cells in the 0.05 mg/ml - 0.35 μg/ml concentration range with a 72-hour incubation. A line of sample toxicity relatively HeLa cells was deduced.

There are different technologies for the UDMH neutralization, but using oxidizers (chloric lime and potassium permanganate), halogenated alkanes and ground burning - do not meet modern requirements for environmental safety. In this regard, the use of natural sorbents to neutralize objects contaminated with UDMH is an alternative solution. That is why it was decided to analyze the sorption ability of a natural material, shungite, which is used as one of the ways for the UDMH neutralization, for its transformation products. It was obtained that shungite sorbs part of the high-molecular components. At this moment we are trying to modify this sorbent for increasing its sorption activity and develop a new technology for neutralizing both UDMH spills and products of its transformation based on shungite material.

Removal of trichloroethylene from groundwater using sulfidated nanoscale zero valent iron: Laboratory versus field experience

POSTER P43
(#waters)

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Chlorinated hydrocarbons (especially perchloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC)) are common environmental contaminants frequently found in groundwater and soils. These substances are dangerous due to their persistence, toxicity, potential carcinogenicity and the ability to accumulate in biological systems and food chain [1, 2]. Removal of these organic pollutants is an important challenge in the field of advanced water treatment.

Last fifteen years, the nanoscale zero-valent iron particles (nZVI) have been often used for abiotic reductive in-situ remediation methods. However the high reactivity of nZVI leads to inefficient treatment due to competition with various natural reductant demand processes [3]. nZVI modified in the presence of reduced sulphur compounds have been shown to degrade TCE at significantly higher rates than original nZVI [4]. The selectivity of sulfidated nZVI for reductive dechlorination of TCE was reported in many scientific papers [3, 4, 5, 6].

This poster presents laboratory analysis results of groundwater (sampled from two different anonymous localities, Czech Republic; labelled as locality B and F) containing above-limit VC, cis-DCE, TCE and PCE and their treatment by original iron nanoparticles (nZVI) and the sulfidated counterpart (S-nZVI). Decrease of chlorinated ethenes was measured using HS-GC/MS technique. nZVI and S-nZVI were applied at concentrations 1 g/L, 4 g/L, 5 g/L and 10 g/L for 3 and/or 7 days depending on pollutants concentration.

The dominant contaminants for groundwater taken from locality B were PCE and cis-1,2-DCE.

The concentration of PCE, cis-1,2-DCE and TCE was ten mg/L. Concentration of VC was thousands μg/L. The significant removal was observed only for TCE 47 and 82 % after application 1 g/L and 4 g/L S-nZVI respectively. The removal of other pollutants in this case was negligible. Finally 10 kg of S-nZVI was applied in concentration 4 g/L in October 2017 on the locality B.

The major pollutants for groundwater taken from locality F were cis-1,2-DCE and TCE. Concentration of cis-1,2-DCE and TCE was around ten mg/L. Concentration of VC was around unit mg/L. In this case, selectivity of S-nZVI for TCE removal was proved again. Application of S-nZVI at concentration of 5 g/L removed 93 % of TCE after 3 days. Original nZVI removed only 67 % of TCE at the same conditions. Finally 150 kg of S-nZVI was applied at concentration of 2 g/L in August 2018 on locality F.

S-nZVI was selected for perspective pilot applications based on successful laboratory test results. Increase of less chlorinated compounds (namely of VC) was not observed during the long-term monitoring of both sites.

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New concept for the electrochemical detection of the herbicide Mesotrione involving Nitroreductase/Layered Double Hydroxide biohybrid

POSTER
P44
(#Waters)

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Mesotrione,2-(4-methylsulfonyl-2-nitrobenzyl) cyclohexane-1,3-dione, is a selective herbicide belonging to the triketone family. This nitro aromatic derivative was marketed in 2001 by Zeneca, under the brand name Callisto®, as a new pre- and post-emergence selective weed control in maize. As many other pesticides, mesotrione may be washed off from soil or leaves by rain and reach surface water and groundwater. Therefore, this molecule has been found in all these compartments of environment and justify the development of fast and inexpensive biosensors, as possible alternatives to the conventional analytical methods, namely liquid chromatography coupled with UV-Vis or fluorescence **[1]**.

The present work deals with the first use of nitroreductase ($NfrA_2$), isolated by Carles *et al.* **[2]**, for mesotrione detection. For the biosensor design, $NfrA_2$ was immobilized by adsorption on nanoparticles of Mg_2Al-NO_3 layered double hydroxides (LDH-NPs), coated on a glassy carbon electrode **[3]**. The amperometric transduction process was based on the competitive enzymatic reduction by NfrA2 of both substrates, i.e. $Fe(CN)_6^{3-}$ and mesotrione. Indeed in the presence of enzyme cofactor, NADH, $Fe(CN)_6^{3-}$ was enzymatically reduced and the released $Fe(CN)_6^{4-}$ was then oxidized at 0.375 V/SCE. When mesotrione was added into the electrolyte solution, a competitive enzymatic reaction takes place at the $NfrA_2$/LDH-NPs modified electrode leading to a decrease of the anodic current. Mesotrione can thus be quantified by chronoamperometry with a sensitivity of 18.4 mA M^{-1} cm^{-2} over a linear concentration range between 5 and 60 µM ($R^2 = 0.998$) and a detection limit of 3 µM.

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Enhanced adsorption of Phosphate from water using activated Chitin-Calcium based sorbent: A mechanism study

POSTER P45
(#Waters)

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Phosphorous (P) is an essential macroelement, but its excessive presence as phosphate (PO_4^{3-}) in aquatic ecosystems can lead to deterioration of water quality due to eutrophication [1]. Human activities such as the discharge of industrial, domestic and agricultural wastewater are often responsible for the enrichment of surface waters with phosphate [2]. P recovery from wastewater streams, through the adsorption of P onto natural, solid waste material may provide one solution. Ideally, this would be a low-cost solution that would create a P-rich material (low in other adsorbed contaminants) for direct use in agriculture as a fertilizer [3]. Crab carapace, a waste by-product from the seafood industry, is generated in millions of tons annually and large quantities are simply discarded as waste (i.e., to landfill). Therefore, a feasible approach may be valorisation of this solid waste into a high value-added product. Additionally, to improve the competitiveness of a sorbent on the commercial market, three main criteria need to be fulfilled: low production cost, high product yield and high removal efficiency.

Chitin-calcium based sorbent from crab carapace was modified thermochemically with KOH to improve surface chemistry and pore structure. The raw material was milled and sieved to a particle size <100 µm, mixed with a KOH solution, then the impregnated material (CCM) was heated. Low temperature activation showed good results with a removal efficiency up to 80% (200 mg of CCM in 50 mL of solution, rotation speed 150 rpm, initial concentration 20 mg/L, and contact time 120 min at 22 ± 1°C). The influence of solution pH on phosphate adsorption was investigated at pH 2.0 to 12.0. During phosphate sorption a change in pH ($\Delta pH = pH_e - pH_{ini}$) was detected, which indicates that inner-sphere complexation and precipitation mechanisms were involved in the sorption process. The point of zero charge (pH_{pzc}) of the CCM was found to be 8.78, which is indicative of protonation of surface charge and transformation to a more positively charged surface at pH 4.0, resulting in a higher adsorption performance than that at pH 6.0 and 8.0. The activation energy of the adsorption process (E_a; kJ/mol) can be predicted with the Arrhenius equation. The positive E_a value (26.191 kJ/mol) implied that the adsorption is an endodermic reaction; and the low E_a value also signified that the adsorption process was governed predominantly by diffusion transport and physical adsorption. The maximum monolayer adsorption capacities (q_{max}) exhibited the following order: 42 > 32 > 22 °C or 24.85 > 23.88 > 21.36 mg/g, respectively. The positive ΔH^o values reflected the endothermic nature of the adsorption process. Instrumental techniques, such as BET analysis, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and TGA/DTG analysis were also used to determine the characteristics of the sorbent and explore the main adsorption mechanisms.

CCM displayed a high sorption ability for phosphate. Also, low temperature activation was innovative, effective and a low cost way to prepare crab carapace for phosphate removal.

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Degradation of artificial sweeteners in wastewater using AOP processes

POSTER P46
(**#Waters**)

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Artificial sweeteners are used as sugar substitutes in remarkable amounts in food and drinks but also in drugsand sanitary products. Replacement sweeteners, together with other substances, are recognized as a new class of water contaminants. This was mainly due to the proven or potentially adverse effects on human health and aquatic ecosystems. Recent studies have documented the widespread occurrence of these chemicals in the aquatic environment and four of them (namely acesulfame, saccharin, cyclamate, sucralose) have been detected in municipal wastewater [1].

Physical-chemical separation methods (microfiltration, ultrafiltration, reverse osmosis, sand filtration, adsorption on activated carbon) are for the elimination of some groups biologically of non-degradable organic substances are ineffective. Consequently, Advanced Oxidation Processes (AOPs) have been proposed as an alternative method to degrade artificial sweeteners effectively [2,3].

The aim of this work is the determination of two selected artificial sweeteners (saccharin, sucralose) in wastewater from wastewater treatment plant (WWTP) in the Czech Republic and the subsequent degradation of the thus obtained concentrations in model water using advanced oxidation processes.

An analytical method for the determination of the artificial sweeteners in wastewater has been developed. On sampling, wastewater samples were treated with Solid Phase Extraction (SPE) and then evaluated by HPLC/MS (High Performance Liquid Chromatography). The concentrations of artificial sweeteners found in samples from WWTP were spiked to model water and then treated by three AOPs: O_3 / UV, H_2O_2 / UV and O_3 / H_2O_2 methods. For each of these methods, the efficiency of the degradation of sucralose and saccharin was investigated. From the evaluated data it was found that the most efficient way of AOP processes for the removal of artificial sweeteners from water is the O_3 / H_2O_2 method, where the degradation efficiency was almost 100 % [4]. The results show the possibility of using AOPs in the operation of a conventional wastewater treatment plant.

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Electrochemical degradation of a textile dye on pbo₂ electrode of a lead-acid battery

POSTER P47
(#Waters)

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The advanced oxidation processes are currently expanding in the field of environmental technologies to improve existing municipal and industrial wastewater treatment systems, or to replace conventional technologies that are found low efficiency for the removal of refractory organic pollutants. This work presents a feasibility study for removing of a textile dye by electrochemical oxidation on PbO_2 electrode of a lead-acid battery. The various characterization techniques (SEM, EDS and XRD) showed that the positive electrode of the lead-acid battery used as an anode in the electro-oxidation consists essentially of crystals in the form of pyramid attributed to β-PbO_2. Results indicated that lead-acid battery electrode is effective for removing color and chemical oxygen demand (COD). The effect of certain operating factors on electro-oxidation performance has been studied. It is found that current density, the stirring speed, and the supporting electrolyte concentration have a positive effect on decolorization and mineralization, and no significant effect of the distance between the electrodes on methylene blue degradation and COD removal was observed. By contrast, the percentage of color and COD removal decreases with increasing of pH. Kinetic analysis of the results revealed that the COD removal follows a pseudo-first-order kinetics

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Molecular transport of pesticides in water : measurements and estimations

POSTER P48
(**#Waters**)

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In the present work, our aim was (1) to propose a precise determination method of the diffusion coefficient in water for selected pesticides either experimentally or by means of existing correlations (including a group contribution method in the present work) and (2) to evaluate the impact of the diffusion coefficient on the estimation, using a fugacity model, of the environmental fate of the pesticide.

Diffusion coefficients of six common pesticides in water were measured as a function of temperature from 5 to 50°C using the Taylor dispersion technique [1]. For that purpose, six pesticides (cyromazine, chlorotoluron, pirimicarb, metazachlor, tebuconazole and sulcotrione) were studied. They were selected because they are among the ones approved for use and known to be used in European countries especially in France: two of them are insecticides (cyromazine and pirimicarb), three of them are herbicides (chlorotoluron, metazachlor and sulcotrione) and the last one, tebuconazole is a fungicide. Each measurement was triplicated and the results were averaged. Uncertainty of diffusion coefficient, calculated by error propagation taking into account the various parameters of the experiment, is less than 3%. At room temperature (25°C), the lower diffusivity, 0.35×10^{-9} $m^2.s^{-1}$, is obtained for tebuconazole. For the other studied pesticides, diffusivities are higher, varying at 25°C from 0.59×10^{-9} $m^2.s^{-1}$ for pirimicarb to 0.73×10^{-9} $m^2.s^{-1}$ for cyromazine.

Three empirical models and a group contribution method was developed to estimate diffusivity of these compounds in water. The estimated molecular diffusion coefficients are unsatisfactory for tebuconazole and sulcotrione, the two heaviest pesticides considered (average relative deviations between 25 and 36%). This may be explained by a molar volume not correctly estimated for example because no temperature dependency is considered and because of the absence of some functional groups present in pesticides (in particular aromatic cycles) in the Le Bas additivity constants [2]. The GCM developed here can be used for pesticides leading to a precision of the diffusion coefficients of 15%. Alternatively, correlation equations lead to precisions of typically less than 10% but are not equally efficient for all the pesticides considered.

Diffusion coefficients were then incorporated in a prediction scheme of the fate of persistent pollutants in the environment (fugacity soil model) [3]. The only process affected by the diffusivity in water is the volatilization rate that is evaluated from the diffusion in water and air (present in the soil) and from the diffusion at the interface water-air. The precision obtained with the Group Contribution Model was proved to be sufficient for use in this environmental.

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Assessment of solar photo-fenton in raceway pond reactors at neutral pH with Fe(III)-EDDS for micropollutant removal in municipal wastewater treatment plant effluents of different composition

POSTER
P49
(#Waters)

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The aim of this research was to study the effect of the composition variation of real effluents from municipal wastewater treatment plants (MWWTP) on the micropollutant removal by the photo-Fenton process at neutral pH with Fe(III)-EDDS.

Contaminants such as antibiotics, biocides and pesticides are persistent to the treatments in conventional MWWTPs. Although they are detected at very low concentrations (ng/L - µg/L), the legislation is becoming stricter with its discharge [1]. As a solution, the photo-Fenton process, one of the most efficient advanced oxidation processes, is being studied as a tertiary treatment. Currently, the studies are focused on reducing operating costs. In line with this, the use of the biodegradable Fe(III)-EDDS complex, to maintain iron dissolved, and raceway pond reactors (RPRs) as low cost systems have been proposed [2].

The experimentation was conducted outdoors in a 19L-RPR with 5 cm liquid depth under global UV radiations close to 30 W/m^2, using 0.1 mM Fe(III)-EDDS at 1:1 molar ratio and 0.88 mM hydrogen peroxide. Five effluents from MWWTPs located in different areas of Spain more than 1000 km away were used, and they were classified according to its chloride and sulphate salinity. Prior to the experiments, the inorganic carbon was reduced to 15 mg/L.

Around 45 microcontaminants were detected and quantified by direct injection coupled to ultra-high-performance liquid chromatography quadrupole-linear ion trap analyser (UHPLC-QqLIT-MS/MS). In all the effluents, the non-biodegradable metabolites of dipyrone represented around 40% of the total micropollutant load. The pharmaceuticals such as gabapentin and venlafaxine were also detected at high concentrations.

No effect of MWWTP effluent composition on the photo-decomposition of the complex was observed, since the profiles were similar in all effluents under similar UV radiation conditions, in agreement with the reaction mechanism recently reported [3]. During the first minutes of reaction a high hydrogen peroxide consumption took place. This also agrees with the mechanism reported, since the high light absorptivity of the complex allows its fast photoactivation, and therefore its fast reaction with hydrogen peroxide.

Concerning the effect of anions and organic matter concentration on micropollutant removal, no linear relationship was found. Nonetheless, the results showed that the type of organic matter could affect the process significantly. In addition to acting as HO$^\cdot$ scavenger, it could form non-photoactive complex with the iron remaining after Fe(III)-EDDS decomposition with light, avoiding its reaction with hydrogen peroxide, and consequently the micropollutant oxidation. According to a pseudo-first order kinetics, a fast removal was obtained in the effluent with the highest initial pollutant load.

The average total pollutant load removal in the five effluents was higher than 80% after 15 min of the reaction, which highlights the efficiency of the low cost RRPs to treat MWWTP effluents by photo-Fenton at neutral pH taking into account the variability in their composition. Furthermore, the phenomena observed in real effluents can be explained based on the reaction mechanisms developed with synthetic effluents under controlled conditions. Future works could be focused on including the effect of organic matter composition on process mechanism.

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WWTP secondary effluents disinfection by solar photo-fenton process in continuous mode at neutral pH

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Although chlorination is one of the most widely applied disinfection methods to inactivate microorganisms in wastewater, the generation of toxic disinfection by-products has forced the investigation on alternative disinfection methods such as Advanced Oxidation Processes (AOPs). In this regard, the efficiency of the photo-Fenton process for real wastewater disinfection has been demonstrated lately [1]. However, the high costs associated with the installation of the most popular used photoreactors for microorganism inactivation, the Compound Parabolic Collectors (CPC), is one of the main shortcomings in scaling up the process. However, the successful application of low cost reactors such as raceway pond reactors (RPRs), has been recently demonstrated, not only in micropollutant removal [2] but also in pathogen microorganism inactivation [3]. Nevertheless, to achieve the photo-Fenton process implementation at large-scale in RPRs, the continuous operation of the reactor is also required to improve productivity and treatment capacity. As far as the authors know, only the feasibility of the continuous operation of the solar photo-Fenton process for micropollutant removal has been successfully investigated at acidic pH [4]. As such, this work was aimed to study the operational viability of the solar photo-Fenton process for wastewater disinfection in RPR at neutral pH at 5 cm liquid depth. The effect of hydraulic residence time (HRT) on pathogen microorganism inactivation was studied.

Firstly, three HRTs (15, 30 and 60 min) were tested at lab scale to establish the best operational conditions. These assays were carried out in a solar simulator at 30 W/m^2 with a 5 cm deep cylindrical reactor, monitoring wild total coliforms (TC), *Escherichia coli* (*E. coli*) and *Enterococcus sp.* as faecal contamination indicators. The concentrations of iron and hydrogen peroxide used were 20 mg Fe/L and 50 mg H_2O_2/L. The results demonstrated that total effluent disinfection was achieved for the three microbiological groups at steady state at 60 and 30 min of HRT. Taking into account these results, the next experimental sets were conducted in 18-L raceway pond reactors with 5 cm of liquid depth at 30 and 60 min of HRT. The experiments were performed on three consecutive days in outdoor conditions. All experiments were carried out with real secondary effluents of the WWTP of Almeria city (Spain). Iron concentration was 20 mg/L in the experiments operated in both batch and continuous flow. Nevertheless the hydrogen peroxide concentration was 50 mg/L at the start of batch mode operation and 30 mg/L in the continuous mode. The experiments showed excellent results during the process for the three microbiological groups selected. At the end of the batch stage the TC concentration, *E. coli* and *Enterococcus* dropped to 1-log, 1.5-log and 0.5-log, respectively. However, the *E. coli* inactivation below the detection limit (1 CFU/mL) required for the Spanish legislation (RD 1620/2007) for water reuse was achieved in continuous flow in all days. The 3.5-log of TC and 2.5 log for *Enterococcus* sp. were also inactivated in continuous operation.

Acknowledgements.
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Arsenic removal from acid mining drainage by green synthetized Fe_3O_4-nanoparticles entrapped in Calcium Alginate beads

POSTER
P51
(#Waters)

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The mining activities in Huelva province (SW Spain) are continuously releasing great quantities of metals mostly in the form of acid mine drainage (AMD) [1]. These acid mine waste waters have caused severe pollution of the Odiel and Tinto rivers with transference of large amounts of acidity, dissolved metals and arsenic. In our laboratory, we are developing a research project with the aim of using these waters as a source of valuable metals, but the presence of arsenic makes difficult the task. For this reason, a method to eliminate arsenic before the use of AMD in extracting metals is investigated.

In this study, Fe_3O_4 nanoparticles (Fe_3O_4-NPs) synthetized by a green method with plant extracts, have been used for the sorption of As from AMD. In order to apply the Fe_3O_4-NPs as sorbent, the NPs synthetized were entrapped in calcium alginate beads. In this way, it is avoided the nanoparticles mobility, iron precipitation and the subsequent contamination of the aqueous solution.

The synthesis method of magnetite nanoparticles (Fe_3O_4-NPs) was based on the co-precipitation of Fe^{2+} and Fe^{3+} ions by NaOH in an aqueous solution using grape stalks extract as capping agent to stabilize the nanoparticles. The experimental conditions were optimized in a previous study [2]: 20 mL of 0.02 mM Fe^{3+} /0.01 mM Fe^{2+}, 22 mL of extract from grape stalks and 2.8 mL of NaOH 1M at 80ºC. The colloidal suspension formed was, first separated from the pellet by double centrifugation of 10 min at 5000 rpm and then, characterized.

The resulted NPs suspension of 11% (w/v) NPs content was used to prepare a 3% (w/v) sodium alginate solution. The resulting suspension was disposed, drop by drop, to a 1 M calcium chloride solution, in a continuous stirring, for beads formation.

Once the sorbent beads were synthetized they were mixed with arsenic synthetic solutions to perform the sorption process. The effect of pH, contact time and initial concentration on arsenic have been studied, in batch mode, to optimize arsenic sorption conditions.

The results reveal that sorption was favoured at pH range 4-8, equilibrium was achieved after 5h, and sorption increases as initial arsenic concentration increases. The presence of high concentration of Na^+ (higher than 100 mg/L) resulted in the partial release of NPs to the solution due to the dissolution /destruction of the hydrogel.

Finally, the Fe_3O_4-NPs beads were used to remove arsenic from three AMD water samples that contains arsenic at a concentration range within 1 and 120 mg/L. The results showed that the presence of other metals and the low pH of AMD strongly influenced arsenic removal by Fe_3O_4-NPs beads. Nevertheless, Fe_3O_4-NPs entrapped in calcium alginate showed a promising potential for arsenic sorption from AMD.

Acknowledgements

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Session 5: Modeling and methodologies

Poster presentations

Compositional characterization of brake pads: ICP-AES method development

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Automotive brake pads are composite materials and for their formulation many aspects must be taken into account: performance, thermal and mechanical resistance, noise, corrosion. Friction materials are not homogeneous in chemical composition and can contain different classes of substances, including abrasives, friction modifiers, fillers, reinforcements and binder materials. More than 2000 raw materials are currently used in the friction manufacturing and for this reason the complete characterization is challenging.

The inorganic compositional analysis is essential even for an environmental point of view because brake pads are considered, with tyre and road wear, non-exhaust emission source of particulate matter (PM). In this context, representatives of the U.S. Environmental Protection Agencies (EPA and ECOS) and motor vehicle industry associations recently signed a *Memorandum of Understanding* (MOU) with the purpose to reduce copper, asbestiform fibers, cadmium, chromium (VI), lead, mercury and their compounds in motor vehicle brake pad friction materials (C*opper-free Brake Initiative*) [1]. In this document is suggested to determine the metal content using ICP-AES analysis following SAE J2975 norm (*Measurement of Copper and Other Elements in Brake Friction Materials*) [2].

The ICP-AES technique, however, requires the use of liquid samples, and the biggest obstacle is to extract from the matrices the analytes of interest. The procedure of microwave acid digestion suggested by the norm is the EPA3052 [3]. If a complete dissolution for both the individual raw materials and the final mixes has to be reached, this procedure should be optimized.

The aim of this study is to enhance the EPA3052 procedure developing a more efficient methodology of sample preparation.

In a previous work the dependence of sample recoveries by microwave digestion parameters has been evaluated using a One-Factor-At-A-Time approach [4]. In order to evaluate these parameters simultaneously, we applied a Design Of Experiments (DOE): we considered, in particular, the effect of temperature, time and amount of sample on the recoveries. To reduce the uncertainty on the results we applied the DOE on a certified material, zirconium silicate, often used in brake pad formulations. This silicate is one of the most refractory materials used as friction material ingredient. The response surface of DOE suggested the best test conditions and these parameters have been applied on different raw materials and friction material mixes commonly used.

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Modelling of trace metals capacity into a high organic sludge deposit

POSTER P53
(**#Modelling**)

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Human activities generate wastewater, solids waste etc. that needs to be managed. A major challenge for the sector is to improve and develop new treatments process for recovering interest elements composing these matrices (trace metals, phosphorus...). Some rainwater and domestic water treatments generate deposits that can be assimilated to sediment and sometimes to “neosoil”. Vertical Flow Constructed Wetlands (VFCW) can treat rainwaters and domestics water of small communities. Sludge deposits accumulated at the surface of VFCW is composed of organic, but also inorganic constituents [1]. They also contain significant amounts of nutrients such as nitrogen and phosphorus [2], but also pollutants such as trace metals and organic micropollutants [3].

Geochemical modelling is widely used on mineral materials. However, the interactions of inorganic constituents with particulate and soluble organic matter has been less extensively studied. Speciation of these pollutants inside a matrix determines their potential impact on the environment. The use of a geochemical model can help to predict the leaching of pollutants within these matrices but also the degree of oxidation of some elements.

The definition as precisely as possible of an organo-mineral assemblage representative to the chemical behaviour of the sludge deposits of VFCW will allow to better predict the behaviour of different molecules within the matrix. In this type of highly organic matrix, the competition between organics (humic substances) and minerals (oxy-hydroxides, clays, etc.) binding sites for metallic elements is particularly complex to model. Both sorption sites influence the release of elements during leaching phenomena. Different scenarios could be tested to improve on-site management to limit the risk of pollution but also to consider new ways of reuse after dredging. The influence of changes in redox conditions (alternate of immersion and dry periods) or pH could be easily tested.

Matrix have been characterized using several techniques. To optimize modelling, aliquote fractions of sludge deposits were also submitted to Acid and Base Neutralization Capacity tests (ANC-BNC) following the European standards CENTS/TS 14429. The matrix faces different pH and after equilibrium (reached after 48 hours) solutions are filtered at 0.45 µm giving two different fractions: the leachable fraction and the non-leachable one. Elements in the leaching fraction was then analysis by ICP-AES and ionic chromatography. Because of the high organic content, additional analysis were done such as Dissolved Organic Carbon (DOC), specific index of UV absorbance (SUVA) and Volatile fatty acid [3]. The modelling work is based on the combined use of two softwares: (i) PHREEQC, a software dedicated for chemical speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, and (ii) WHAM, which has been built to model the chemical (sorption/complexation) binding of metals to humic substances. Humic substances can bind mineral elements via two mechanisms: (1) specific bounds on carboxylic and phenolic sites and (2) non-specific bonds. The use of chemical constants (equilibrium constant, acidic dissociation constant, electrostatic charge...) of fulvic and humic substances allowed to integrate specific binding sites. A total of 50 binding sites have been considered and integrated in PHREEQC code via a method developed by [4].

First modelling results showed a good concordance between ANC-BNC results and model predictions. Major elements but also trace metals have been investigated. Mineral dissolution models were not sufficient to explain the behaviour of all elements, showing the importance of taking in account the adsorption by organic matter in this matrix. For example a strong affinity between copper and organic matter was clearly highlighted by the model.

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Screening organic contaminants in the cloudy atmosphere by Q-HRMS Orbitrap®: from cloud droplet to precipitation

POSTER P54
(**#Modelling**)

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The chemical composition of the atmosphere modulates its impacts on the global climate, regional air pollution, human health and ecosystems [1]. Organic matter (OM), a key component of this composition, is ubiquitous within all atmospheric compartments: gas, aerosol and cloud. Clouds act as a potential vector of the OM between gases and particulates, which, by various processes (dissolution, rain-out, wash-out), can be transferred to other environmental compartments like soils or underground waters. Rain deposition also affects the agricultural productivity. Quantifying this multiphasic distribution of OM will definitely improve our understanding and characterization of its impacts. Given it complexity and the high number of molecules involved, this characterization is still challenging. Only 20% of OM in cloud water have been identified so far by traditional analytical techniques [2]. As an alternative, non-targeted advanced techniques based on high resolution mass spectrometry have recently shown their ability in exploring the unknown organic fraction [2].

This new project focuses on a comprehensive exploration of organic matter composition in the cloudy atmosphere by GC-Q-HRMS Orbitrap ®, an extremely promising technique which already proved its efficiency for the untargeted analysis of pollutants (Hollender et al., 2017).

Here, analysis was applied to cloud and rain water samples collected at the puy de Dôme observatory (1465m - GAW network) and at the Cournon station (Auverwatch hydrological network, SNO H+) located 15 km downwind of the puy de Dôme station under westerly wind regimes. Efforts have been paid on the extraction step of target chemical markers from the cloud water before analysis by solid phase sorption (here SPME). First, we confirmed the feasibility of the detection of water contaminants including PCBs, PAHs and pesticides by GC-Q-HRMS Orbitrap ®. Second, we provide first insights on their potential transfer from the atmosphere to the continental surface during advection, wash-out and rain-out processes.

Acknowledgements

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Efficient facilitated transport of lead and cadmium across a plasticized cellulose triacetate and polymer membranes mediated by crown-ethers

POSTER P55
(**#Modelling**)

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Polymer inclusion membranes (PIM) used for selective transport and separation of metallic ions has emerged in recent times. Their expansion depends on the method of preparation and their structure.

This paper reports on the synthesis of a novel class of polymer inclusion membranes based on two polymers cellulose among which triacetate (CTA) plasticized by 2-Nitrophenyl pentyl-ether (NPPE) and doped with crown ethers incorporated into the polymer as a metal ion carrier. All the membranes were characterized by several techniques as well as Fourier Transform Infra - Red (FTIR), X-ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). As application, transport of Pb(II) and Cd(II) ions in polymeric membranes (PIM) was studied. Overall, our results showed that the addition of plasticizer with two polymers resulted in homogeneous and hydrophobic membranes whose physical properties, such as density, thickness, and hydrophobicity, were modified. All membranes were thermally stable up to nearly 200 ◦C. The study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using NPPE as carrier

Influence of the molecular structure of fluorinated ionic liquids on their thermophysical properties. A molecular modelling approach

POSTER P56
(**#Modelling**)

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Fluorinated ionic liquids (FILs) have started to be attained a special attention in areas where highly fluorinated compounds (FCs) are used, as potential replacements for them. They can combine the best properties of highly FCs (inert compounds with extremely low surface tension and ability to rearrange into stable self-assembled supramolecular systems) with those of ILs (almost null vapour pressure, easiness in recovering and recycling, non-flammability and tuneable properties) [1]. FILs can form a new nanosegregated, fluorinated domain, asides from the polar and hydrogenated domains that occur in the traditional ILs, showing the highly complex behaviour of these systems [2].

One of the major drawbacks of the FILs investigation is the amount of resources and time to perform a fully characterization. In this direction, the soft Statistical Associating Fluid Theory equation of state (soft-SAFT EoS) [3,4], has been presented as a systematic theoretical tool to describe the thermodynamic behaviour of different ILs and their complex mixtures. Soft-SAFT has been able to predict the main physical features of these compounds, by accounting for the strong short-range directional forces, such as hydrogen bonding of these complex systems [5].

This work belongs to a long-term project to provide novel insights into the influence of the FILs structural features on the soft-SAFT transferability approach, on the robustness of the molecular models and on the macroscopic thermodynamic properties of FILs. A comparison between the parametrization of families based on different ILs families (pyridinium- and imidazolium- based ILs conjugated with different fluorinated anions such as bis(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, trifluoracetate, perfluorobutanesulfonate, and perfluoropentanoate) is performed. It is observed that all the ILs families preserve the same association scheme, demonstrating that three associating sites provide enough degrees of freedom to account for the interactions between the counterions and the charge delocalization by the presence of fluorine atoms. From the parameterization of each model, it was concluded that the five soft-SAFT parameters (chain length, volume and energy of the groups composing the molecules, and volume and energy of association) are mainly influenced by the anion and the fluorination features. The transferability approach developed in this work was applied by building models for FILs with parameters transferred from the studied ones. Two FILs from $[C_nC_1Im][N(C_2F_5SO_2)_2]$ ILs family (n = 2 and 4), and $[C_4C_1py][CF_3SO_3]$ were chosen and compared to experimental thermodynamic property data of the pure compounds and solubilities in carbon dioxide, methanol and water, providing excellent agreement with the available data. Overall, this work reinforces the robustness of the soft-SAFT equation for modelling ILs and will allow the assembling of reliable ILs models for new systems with high predictive capabilities in a more intuitive way regarding the process of parametrization.

Acknowledgements

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Development of networking for overcoming technical and social barriers in instrumental analytical chemistry education

POSTER P57
(**#Modelling**)

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Networking for Overcoming Technical and Social Barriers in Instrumental Analytical Chemistry Education (NETCHEM) Project [1] aims to decrease the gap between Serbian and Albanian higher education institutions (HEIs) and their peers in European countries regarding education level and technical capacities related to analytical instrumentation usage for environmental and food safety control (EFSC).

HEIs in these counties often suffer due to small number of instruments and lack of up-to-date equipment available. Their Study programs offer some courses in instrumental analytical methods which are mostly theoretical without enough active participation of students and development of their practical skills, with no sufficient equipment available for the students. That is the rationale to introduce Remote access to analytical instruments, consultation "in real-time" with an expert presenting the lecture of specific topic, while simultaneously performs the analysis using concept "Real analysis in the virtual lab". With this Project approach expensive instruments will be shared and opened for usage, furthermore access to disabled students will be provided.

NETCHEM Project tends to promote life-long learning opportunities for HEI teachers as well as employees in private and public enterprises, quick and reliable results comparisons between researcher groups, distance education and virtual mobility of students within universities, overcoming in this way the technical and social barriers between Serbian and Albanian and European Countries.

The Project will last for 36 months and gather 14 institutions including universities from France, UK and Czech Republic, prominent public EU research organization, 4 Serbian universities, 2 Albanian universities and 3 enterprises.

NETCHEM Project is establishing platform which will provide 3 main services:

1. To establish good use of Open Educational Resources (OER) in majority of courses that incorporate teaching of the use of analytical instrumentation.
2. To provide partners with web accessed remote instrumental analytical laboratories (WARIAL) which are essential for spreading of technology of enhanced learning environment between institutions of different countries. Use of WARIAL promotes cost-effective, expert level knowledge transfer, which is problem oriented. WARIAL enables higher education institutions to overcome barriers related to their limited capacity regarding analytical instrumentation usage for Environmental & Food Safety Control. Trans-boundary networking will also provide sharing of environmental and food safety risk practices.
3. To establish SQL (Structured Query Language) based system for data collection in the field of environmental and food safety control. Collection of environmental and food quality indicators and chemical data in SQL data base will also be used for increasing the public awareness about environmental and food problems, aimed to both the professional sector and general public.

Beside development of WARIAL, the Project will provide training for teachers regarding use of WARIAL and OER, as well as modernisation of MSc, PhD and CPD courses in Serbian and Albanian countries higher education institutions.

Acknowledgements

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Meta-metabolomics, what did you expect?

POSTER P58
(**#Modelling**)

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Currently, metabolomics use standardized procedures and workflows to ensure biomarkers' relevance and try to merge data with more mature "omics" (genomics, transcriptomics and proteomics). The outputs are promising, trying to reveal scientific and economic opportunities for personalized medicine, micro-scaled agronomy, up scaled biotechnologies, survey of global disturbances on animals, plants and microorganisms, ultimately environment. We know now that a honeybee is a superorganism, comprising many exogenous genes and exposed to xenobiotics. We also know, for a long time, that microorganisms are everywhere including in clouds. They compete for space and nutrients, from biofilms to cloud droplets, impacting health, fitness and communities' evolution.

In fact, looking at a global metabolic profile is like watching a forest, where nobody is capable to distinguish contributions of each, from the pillar to the toothpick. Nevertheless, an exhaustive evaluation of metabolic interplays between individuals (animals, plants or microbes) looks accessible and, sooner or later, mandatory. For achieving this properly, the design of relevant meta-metabolomics experiments is needed. However, we are not ready yet to perform such projects with enough chances of success. We need tools and protocols, gathering knowledge and skills, to maintain the richness of the metabolic information from the field to the bench, and from lab to silico. First assays are in progress, dealing with (simplified / labeled) models, developing wiser analytical-based tools and/or optimizing data management for multi-scaled information in order to synthesize the quintessence (relevance) into in silico ecosystems.

Then, meta-metabolomics is the opportunity to embrace the entire information available in every biological context of study. And if we want to succeed, international efforts have to be proposed, granted and available to everybody (from experimental design to result).

Oxidation of unsymmetrical Dimethylhydrazine with various oxidants: A Study by high-resolution orbitrap Mass Spectrometry

POSTER P59
(**#Modelling**)

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Unsymmetrical dimethylhydrazine, (UDMH) - is one of the most common rocket fuels and is used by various types of carrier rockets and missiles of the EU, Russia, India and China [1]. Being an extremely toxic substance with carcinogenic, mutagenic and teratogenic properties [2], UDMH poses a serious threat to natural ecosystems and human health [3]. Since UDMH is a strong reducing agent, the main method for detoxification of soils contaminated with rocket fuel involves the treatment with various oxidizing reagents.

The component composition of the UDMH transformation products formed in an aqueous solution by the action of air oxygen and various oxidizing reagents (potassium permanganate, aqueous chlorine, hydrogen peroxide in the presence of transition metal ions as catalysts) used to detoxify the spills of highly toxic rocket fuel was studied by high-resolution orbitrap mass spectrometry with positive mode electrospray ionization. It includes at least two hundred compounds of CHN and CHNO classes, among which heterocyclic structures predominate (methyl and amino substituted pyridines, pyrazoles, triazoles, imidazoles) and is similar for most of the oxidants studied, including air oxygen. A significant part of the compounds found was not previously described in the literature as products of rocket fuel transformation, and their toxicity is not characterized so far. The reagent based on hydrogen peroxide and iron (III) complexonate and currently used for detoxification of soils contaminated with rocket fuel, is distinguished by the greatest variety of formed products of UDMH oxidation. The minimum number of oxidation products is formed by interaction with air oxygen and aqueous chlorine. Moreover, for those reagents significant residual amounts of unreacted UDMH were detected (the relative intensity of the peak is 100% and 15%, respectively) in the reaction mixtures even after 40 days. During the oxidation of UDMH with $KMnO_4$, O_2 and also H_2O_2 in the presence of Na[Fe(EDTA)] the number of peaks of transformation products passes through a pronounced maximum, followed by a decrease. This effect has already been observed earlier in the study of the interaction of UDMH with hydrogen peroxide [4].

The peculiarities of the component compositions of the products formed under the action of various oxidants were revealed by the principal component analysis. It indicates the proximity of the oxidative transformation pathways of UDMH for most of the oxidants used and air oxygen, despite the significant differences in the reaction rates. The exceptions are HOCl, H_2O_2 + Cu^{2+} and, to the greatest extent, $KMnO_4$, giving sets of nitrogen-containing oxidation products that differ significantly from each other and from sample.

The results obtained are of great importance for understanding the processes of unsymmetrical dimethylhydrazine transformation in environment and improving the technologies for detoxification of sewages and soils contaminated with rocket fuel.

Acknowledgements

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Evaluation and calibration of the Chemcatcher® passive sampler for the monitoring of short-chain chlorinated paraffins in water

POSTER P60
(**#Modelling**)

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Following a major European concern about the deterioration of surface and groundwaters, the Water Framework Directive (WFD, 2000/60/EC) and the Marine Strategy Framework Directive (MSFD,2008/56/EC) were implemented in order to characterize, measure and limit the anthropological impacts on the aquatic environment. The monitoring of the water bodies requires burdensome water sampling campaigns and analyses. In order to obtain representative data of the water quality status, high-frequency sampling is necessary but very expensive.

As a relevant alternative, passive sampling constitutes an innovative tool [1,2]. Over the last decade, different types of passive samplers have been developed for several micropolluants and tested through an EU project for use in support of the implementation of the WFD (Screening methods for Water data InFormaTion in support of the implementation of the WFD, SWIFT-WFD).

The Chemcatcher® passive sampling device was developed by Portsmouth University in the frame of an EU project (Standardised Aquatic Monitoring of Priority Pollutants by Passive Sampling, STAMPS) [3,4]. It is commonly applied in the integrative accumulation phase in order to calculate time weighted average concentrations (TWACs) of pollutants. It has the particularity of being adapted to polar or hydrophobic organic, organo- metallic and inorganic contaminants depending on the receiving phase and the diffusion limiting membrane.

Under the WFD, a number of priority substances must be determined in water. The short chain chlorinated n-alkanes (SCCPs) are listed among them, as dangerous priority substances [5]. These compounds are classified as persistent organic polluants (POP) and are strongly bioaccumulative. Analytical difficulties encountered for the determination of SCCPs together with their presence at ultra-trace levels in the aquatic environment make them a major challenge as for their sampling and their quantification in waters at a concentration level close to their Environmental Quality Standard (EQS) of 0.4 µg.L-1.

The objective of this work is to study the applicability of Chemcatcher® type passive samplers for SCCPs determination in water.

First, a feasibility study was carried out. Noteworthy, this enabled to demonstrate a linear accumulation of SCCPs in the sampler together with a chromatographic pattern similar to the one's of the spiking mixture. Secondly, kinetic laboratory tests allowed to optimize the configuration of the sampler, testing three types of receiving phase and two types of diffusive membrane. The optimized configuration was then calibrated by using a home-made continuous water flow-through exposure system [6]. The sampling rate measured was of 0.53 L.day-1, which is close to rates published for other organochlorinated priority substances.

Taking into account a detection limit for SCCPs of 0.3 µg.L-1, a sampling rate and time of respectively 0.5 L.day-1 and 15 days, the Chemcatcher® aquatic passive sampler would enable to measure a concentration of SCCPs as low as 0.04 µg.L-1 in the water body, which is ten times lower than the EQS. Forthcoming studies will evaluate the influence of environmental conditions by performing *in-situ* calibration [7]. This work constitutes one of the very first application of passive samplers for the monitoring of SCCPs in waters.

Acknowledgements

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Assessing the behaviour of pharmaceuticals and transformation products in a stratified lake using a multimedia fugacity model

POSTER P61
(**#Modelling**)

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A growing variety of chemicals are produced by modern industry and used all over the world. New anthropogenic chemicals are also constantly being encountered in the environment. Since wastewater treatment plants often have limited trace chemical removal efficiency, municipal sewage waters are a major entry route to the environment for many contaminants. Among emerging pollutants with a recognized environmental impact are traces of pharmaceutical substances [1], and their metabolites and transformation products [2]. Since the concentrations of pharmaceuticals are typically micrograms per litre, at highest, measuring them is demanding. However, modelling the environmental fate of the pollutants can be used to gain sufficient estimates of the environmental concentrations, with relatively little effort.

Fugacity models have been traditionally used for modelling the environmental fate of persistent organic pollutants. Constant emissions cause pharmaceuticals to reach a pseudo-persistent state, but a somewhat different model composition is beneficial for the assessment of pharmaceuticals. Thus a new version of a previous multimedia fugacity model [3] was developed. The new model, FATEMOD-Q, allows for environments that consist of any number of compartments and arbitrarily definable intra-system flows. In addition, transformation reactions between chemicals are supported.

The new model was successfully used to assess the behaviour of ibuprofen, diclofenac, and carbamazepine, and their transformation products in lake Päijänne, central Finland [4]. A model environment, built to correspond to previous environmental samplings, was used to identify the most important processes affecting the environmental concentrations, and e.g. the ability to account for depth dependency of photolysis [5] was found to be of great importance when modelling environmental fate in stratified humic lakes. The model was then used as a platform to rationalize the effects of various environmental conditions on previous sampling results, and e.g. the roles of various properties of lake dynamics and photodegradation were identified.

Although pharmaceutical concentrations, and especially environmentally formed transformation product concentrations, are typically clearly lower than any direct toxicity threshold measured for them, gathering information on a large number of contaminants with low concentrations is necessary when estimating the effects of mixture toxicities and chronic stresses on ecosystems. In addition to assessing the fate of a number of contaminants with relatively little effort, the developed model is well-suited as a platform for exploring the roles of various processes and phenomena on the environmental behaviour of anthropogenic contaminants. A work to utilize the model to understand the effects of seasons [6] and dynamically changing environmental conditions on pharmaceutical levels is also in progress.

Acknowledgements

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Optimization of the plant sample preparation procedure for metal analysis using Wavelength Dispersive X-Ray Spectroscopy (WDXRF)

POSTER P62
(**#Modelling**)

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Plants are known as good biomonitors in contaminated areas due to their tendency to accumulate toxic metals. Methods based on direct solid sample analysis are more favourable because they avoid utilization of aggressive and toxic agents, which is in line with green chemistry principles [1]. Besides non-destructiveness, X-ray fluorescence spectroscopy (XRF) is suitable for plant analysis because it offers wide linearity range (from ppm level to 100 %) and possibility of analysis of almost whole PSE (from Be to Am) [2].

Plant sample preparation procedure for WDXRF analysis includes grinding and drying at 60° C. After obtaining a homogeneous mixture, the plant sample is mixed with a certain amount of binder (Hoechst wax C micropowder) and pressed in a hydraulic press (Retsch PP 25) in order to obtain stable pellet (32 mm diameter).

The plants are mostly made of light elements (O, N and C) which are transparent for X-rays. During analysis of elements with a higher atomic number, X-rays penetrate quite deep into the sample. It is important to establish the minimum thickness of the pellet that will provide reliable results during determination of the heavier elements in the plant matrix. Samples are measured under conditions of high vacuum and slightly elevated temperature, and for that reason herbal matrix is prone to physical changes after analysis. It is important to determine ideal ratio between mass of the sample and the binder that will provide a stable pellet without affecting determination of elements which are present in low concentrations.

During this study, two types of plant samples were analysed: fir and pine needles. Samples were collected in 2017 during autumn. The influence of pellet mass (thickness) on elements concentration was examined by measuring pellets prepared from 1, 2, 3, 4 or 5 g of plans material. By preparing pellets with: 0, 5, 10, 15, 20 and 25 % of wax, the influence of binder ratio was examined. Analysis was performed on ARL™ PERFORM’X Sequential Wavelength Dispersive X-Ray Fluorescence Spectrometer (Thermo Fisher Scientific, Switzerland) combined with ARL software program UniQuant [3].

In both types of plant samples the following elements were determined: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Zn, Sr and Zr. Both fir and pine needles show similar trends. As quantity of binder increases, the concentration of Ca and K increases, because wax as binder can contain small quantities of those elements. Repeatability of elements that were found in higher concentrations (Mg, Al, Si, P, S, Cl, K and Ca) is high, while repeatability for low concentration elements (Ti, Fe, Ni, Zn, Sr) decreases as percent of binder increases. Reason for that phenomenon is that dilution with wax is affecting elements in low concentration more than high concentration elements. For light elements results show small impact of pellet mass on the measurements because observed X-rays have low penetration depth. Elements with higher Z number are usually present in smaller concentrations in plants and such measurements are less precise, especially when the smaller pellet mass is analyzed. We can say that UniQuant, as standardless method of analysis, which uses the advanced Fundamental parameters Algorithms for data processing, is well adjusted and able to deal with analysis of different sample masses.

When physical properties of pellets are investigated, addition of 20% of wax provides the most stabile pellets with flattest surface. For adequate pellet stability, recommend mass of pellets should be 4 g, but it has been shown that 3 g is acceptable in the case of a small sample quantity. In case when we have less than 3 g, it is recommended to carefully place sample as thin layer on the top of 3 g of boric acid inert carrier.

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Extraction methodologies for UV-filters and synthetic musk compounds from soils and tomatoes

POSTER P63
(**#Modelling**)

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In the last decades there's been an increase in the utilization of personal care products, either cosmetics, shampoos, shower gels or sunscreens, because of the importance that people give to their appearance. These products contain, among others, two classes of compounds that have been raising some concern: the synthetic musk compounds (SMCs) and the UV-filters (UVFs). This concern is mainly due to their persistence in the environment, ability to biomagnify in biota trophic networks and their estrogenic potential. One of the major destinations of these compounds after their use is the wastewater treatment plants (WWTPs), where it is already known that they are not degraded, but they are mostly transferred to the sludge (1,2). To take advantage of the treated sludge, it can be used is as agricultural fertilizer. However, the potential of transfer of SMCs and UVFs from sludge to soils needs to be considered. Moreover, after the soils' fertilization, the possibility of the crops uptake these compounds also need to be taken in consideration, since they are mostly intended for human consumption (3).

Therefore, the main focus of this work was to develop a green and fast methodology to extract SMCs and UVFs either from soils and tomato in order to further assess the potential uptake of these compounds in amended soil – tomato system. The selected methodology was a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) methodology followed by a gas chromatography – tandem mass spectrometry (GC-MS/MS) to analyse six SMCs (6 polycyclic, 2 macrocyclic and 5 nitro musks) and six UVFs (BZ, EMC, EDP, 4MBC, OC and DTS).

The method was then validated, assessing the linearity ranges, coefficients of determination, limits of detection (LODs) and quantification (LOQs), accuracy and precision (intra and inter-day). Samples of different soils and different supermarket tomatoes were also analysed.

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Microcalorimetry: a powerful tool to investigate stoichiometric constraints on small ectotherms

POSTER P64
(#**Modelling**)

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Environmental conditions constraint populations and ecosystem dynamics through their direct effect on individual metabolism. However, besides temperature, individual metabolic responses to environmental factors remain unclear. As an example, if dietary stoichiometric constraints are well known to reduce individual growth rate, their direct consequences on metabolic rate still require clarications. It is commonly assumed that dietary stoichiometric constraint increases metabolic rate of small ectotherms but experimental support remains scarce. Here, using a microcalorimetric approach, we determine the standard metabolic rate
(SMR) of Daphnia magna, fed with a stoichiometric balanced diet (C/P: 160) versus im-balanced diet (C/P: 1440). Regardless of dietary treatment, daphnids presented the same somatic C/P ratio demonstrating their strict homeostatic regulation. However, daphnids fed imbalanced signicantly increased their SMR while reducing their growth rate. This result suggest that homeostatic regulation costs increases with increasing mismatch between consumers and resources. To meet this higher energetic demands, individuals reallocate energy from growth to maintenance resulting in the reduced growth rate observed. Beyond this theoretical framework we showed that microcalorimetry is a powerful tool for monitoring small-sized organisms' metabolic rate. This method opens promising perspectives to understand the consequences of various environmental factors on organismal metabolism.

Off-line flash pyrolysis as an extraction technique in analysis of polycyclic aromatic hydrocarbons in solid environmental samples - optimisation of the temperature program

POSTER P65
(**#Modelling**)

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Polycyclic aromatic hydrocarbons (PAH) are widespread environmental pollutants. Due to their carcinogenic, mutagenic and teratogenic properties they keep attracting a lot of attention in the environmental pollution studies.

Numerous extraction and analytical methods can be used for analysis of PAHs in solid environmental samples [1]. Solvent extraction techniques usually give highest recoveries and the highest precision in analyses of these analytes. However, most of them require large volumes of solvents and they are also labour demanding and time consuming. Because of that, solventless extraction techniques, such as thermal desorption and pyrolysis, coupled with online GC or GC-MS analysis, are becoming more and more popular [2]. The main disadvantage of these techniques is use of small sample size, which can result in significant analytical errors. Analytical off-line pyrolysis, as an extraction technique for subsequent instrumental analysis, offers greater freedom in selection of the sample size. However, the temperature program requires a careful optimisation in order to avoid transformation of the analytes and formation of undesirable byproducts.

The aim of our present study was optimisation of the temperature program for the analytical off-line flash pyrolysis as an extraction technique in analysis of polycyclic aromatic hydrocarbons in a solid environmental sample. Flash open system pyrolysis was chosen because fast heating rate, short holding time and constant nitrogen flow can minimize secondary reactions and production of undesirable byproducts. The sample used was a street dust sample previously proven to be rich in different PAHs [3]. For the pyrolytic extraction experiment, a particle size fraction from 250 to 63 µm was chosen.

Pyrolysis of solid environmental samples was performed in open system (Pyrolyser, Model MTF 10/15/130 Carbolite, UK) at four temperatures: 600, 500, 400 and 300 ^{o}C in nitrogen atmosphere with holding time of 1 minute, and heating rate of 100 ^{o}C/min. Sample size used in pyrolysis experiments was from 2.0771 to 2.2648 g. Mass of liquid pyrolytic products was increasing with increase in the pyrolysis temperature (1.0 mg at 300 °C, 7.0 mg at 400 °C, 13.9 mg at 500 °C and 16.3 mg at 600 °C).

The pyrolysates were separated into fractions of saturated, aromatic and polar compounds by column chromatography. Mass of aromatic fraction was between 1.2 and 0.3 mg, decreasing with decrease in the pyrolysis temperature. PAHs in the aromatic fractions were analysed by GC-MS. For the comparison purposes, the original dust fraction from 250 to 63 µm in size was extracted using Soxhlet apparatus, and the aromatic hydrocarbons were isolated using column chromatography and analysed by GC-MS.

The results indicated that the pyrolysates obtained at the temperatures higher than 300 °C contained a lot of undesirable byproducts such as fragments of natural and artificial polymers. These results correlate with increased yield of pyrolysates and aromatic fraction. Furthermore, higher temperatures promoted condensation of aromatic hydrocarbons and production of large polycondensed aromatic molecules and formation of methylated polycyclic aromatic compounds (such as methyl- dimethyl - trimethyl – and tetramethyl- naphthalene and phenanthrene), especially at temperature of 500 and 600 °C.

According to these results it can be concluded that the optimum temperature for analytical off-line flash pyrolysis as an extraction technique in analysis of polycyclic aromatic hydrocarbons in solid environmental samples is 300 °C.

Acknowledgements

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POSTER P66
(**#Modelling**)

Imidazolium ionic liquids as components of microemulsion in microemulsion electrokinetic chromatography of steroid hormones and polyphenols

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Microemulsion electrokinetic chromatography (MEEKC) is a promising method for separating ionic and neutral analytes in complex matrix, where a microemulsion is used as the background electrolyte (BGE). Separation is achieved due to differences in the electrophoretic mobility of the analytes and the distribution coefficients between the microemulsion (ME) and the aqueous phase, which contributes both to an increase in efficiency and selectivity of the separation. In recent years, there has been an active interest in the use of ionic liquids (ILs) in methods of separation and concentration [1]. Due to their unique physicochemical properties, such as high solubility, devisable synthesis, capacity to interact with analytes, and a change to EOF caused by adsorption onto the capillary wall, the application of ILs in CE has received considerable attraction.

Recently we have shown the great potential of ILs based on imidazole as modifies micelles for on-line concentration of ionogenic and neutral analytes (steroids, biogenic amines) in MEKC [2,3]. The variety of combinations of cations and anions in the composition of ILs provides the possibility of their application both as a microemulsion-forming agent and as an "oil" in "oil-in-water" ME.

In this paper, we have studied the following possibilities of ILs in MEEKC for separation of hydrophobic analytes (steroids and polyphenols):

- the hydrophilic ILs on the basis of imidazolium (C12MImCl, C16MImCl) as modifiers of the electrophoretic system and as surfactants to stabilize microemulsions;
- ILs with short alkyl chain as modifies of ME and hydrophobic ILs (C6MInNTf2, C6MImBF4, C8MImBF4) as an "oil" in the microemulsion composition.

The influence of the concentration of ILs, the pH of the BGE, the nature of oil and the ratio of the components of the microemulsion on the efficiency and selectivity of analytes separation were determined. Sufficient increase in resolution has been achieved by addition of (2-Hydroxypropyl)-β-cyclodextrin into the BGE. Estimated characteristics of the distribution of analytes between the microemulsion and the aqueous phase by Micellar Enhanced Ultrafiltration (MEUF) method were obtained. The results are compared with the use of a traditional cationic surfactant, cetyltrimethylammonium bromide.

The sensitivity in capillary electrophoresis is often insufficient for the low concentrations of analytes in real samples. Different variants of on-line sample concentration, such as field amplification (FASS) and enhancement (FESI), several modes of sweeping have been examined using ILs to improve the detection sensitivity of analytes by MEEKC. Great potential on quantitative analysis of trace amounts analytes in complex matrix (biological liquids) was shown.

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Cadmium exposure from food products – a local study

POSTER P68
(**#Modelling**)

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Cadmium poses extremely high danger for consumers since it has been recognised as being primarily toxic to the kidney. It was confirmed by many studies that cadmium can cause renal failure, bone demineralisation or increase risk of cancer such as in the lung, endometrium, bladder, and breast. Thus, this highly toxic heavy metal was classified as a human carcinogen (Group 1) on the basis of numerous occupational studies. It is thought that foodstuffs are the main source of cadmium exposure for the non-smoking general population. The food groups that contribute most of the dietary cadmium exposure are cereals and cereal products, vegetables, nuts, starchy roots or potatoes and their high consumption e.g. as a result of local dietary habits may significantly increase the potential Cd exposure. The main reason for the high levels of cadmium in human foodstuffs is a high transfer factor properties of plants. Consequently, the bioconcentration of Cd from soil to the foodstuffs produces the human diet as a primary source of Cd exposure among non-smoking, non-occupationally exposed populations.

In 1988, as a result of the arrangements of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) the safe level of Cd intake as provisional tolerable weekly intake (PTWI) of 7 μg/kg bw was accepted. Due to the long half-life of Cd in human kidneys this value was recently updated and the Panel on Contaminants in the Food Chain of European Food Safety Authority (EFSA) has established a reduced tolerable weekly intake (TWI) for cadmium of 2.5 micrograms per kilogram of body weight (μg/kg bw), based on an analysis of new data [1-4].

This work provides an update on Cd exposure form major contributors of dietary Cd by highlighting the assessment of Cd levels in foods in central region of Poland.

Samples from the Lodz region namely bread, flour, potatoes of different varieties and food products containing potatoes were mineralized in the UltraWAVE oven system (Milestone) with concentrated nitic acid. Analysis of cadmium content was carried out using the atomic absorption spectrometry technique with flame atomization (FAAS), SOLAAR M6 (Unicam). The correctness of the proposed method was verified by analyse of the reference materials with the certified Cd content (carrot CS CR-1 and hay IEAE-V-10) and a satisfactory agreement was achieved between certified values and gathered results.

The obtained Cd levels in chosen food products were directly compared with the cadmium admissible amounts in potatoes, rye and wheat and regulated by law. The results have shown that for most of the studied flour and bread samples the permissible content of cadmium was not exceeded. Moreover, it can be also concluded that the presence of additives in the form of poppy seed, sunflower seeds, sesame seeds etc., can essentially affect the content of cadmium in bread. Similarly, for the majority of the potato samples the measured Cd concentrations were within permissible limits. It was proven as well that potato variety generally has no effect on the cadmium content.

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Analysis of biosurfactants in crude supernatants of microorganisms

POSTER P69
(**#Modelling**)

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It is known that a large variety of microorganisms are able to synthesize strong biosurfactants and release them into the environment. These compounds can reduce the surface tension of water from 72 mN / m to less than 30 mN / m. Biosurfactants attract attention as promising natural surfactants, as they have several advantages over chemical surfactants, such as low toxicity, inherently good biodegradability and environmental acceptability. Therefore, the use of these compounds instead of chemical surface active compounds is interesting in terms of environmental protection.

For this reason, the development of methods to detect their presence and to study their structure is actual task. In this study, 34 strains of various microorganisms were grown. For each sample, the surface tension was measured by the method of pendant drop. Then Liquid Chromatography - Tandem Mass Spectrometry analysis was performed on crude sample supernatants (Electrospray Ionization (ESI) with a Q-Exactive Orbitrap™ mass spectrometer (Thermo Scientific) providing a mass accuracy lower than 3 ppm and an ultra-high resolution). In 14 of 34 cases, the surface tension of the solution of the supernatant appears less than 35 mN / m. If in each of the samples exhibiting a low value of surface tension, the presence of a biosurfactant has been confirmed by LC-MS analysis, we also found these substances – in lower concentrations – in some samples with a high value of surface tension, demonstrating the interest of combining analytical techniques.

From these 34 samples, were identified 21 different substances, which mass correspond to biosurfactants. Some of them are isomer, and these isomeric compounds have the same m / z but different retention times. In order to clarify the structures and distinguish between isomeric compounds, a LC-MS/MS analysis was carried out, which in some cases made possible to accurately determine the whole structure of the biosurfactants. Most of them are lipopeptides, some of them contain a cyclic peptide part, and differ in the position of amino acids in the peptide fragment.

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