ContaSed2015

Contaminated Sediments: Environmental Chemistry, Ecotoxicology and Engineering

8-13 March, 2015
Congressi Stefano Franscini, Monte Verità, Ascona, Switzerland

Program and Abstract Book

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Welcome and Preface

Recent sediments are major sinks for chemical contaminants in aquatic ecosystems and are largely involved in the fate of pollutants in the environment. The ecological relevance of sediment quality is widely acknowledged, but approached differently in various scientific fields. Sediments govern the biogeochemical cycle of pollutants and nutrients and play a key role for the bioavailability of hazardous pollutants and the resulting toxic effects. In addition, biodegradation of organic pollutants in aquatic sediments is of major relevance in chemical risk assessment. At contaminated sediment sites, processes like remobilization, bioturbation and the triggering of sediment slumps are also important factors in risk assessment. As archives of contaminants, dated sediments enable to reconstruct historic records of environmental pollution.

The conference Contaminated Sediments (ContaSed) aims at providing a platform to top experts as well as junior researchers from different scientific disciplines presenting their recent results and novel approaches on the analysis, assessment and remediation of contaminated sediment. Addressed topics include: sedimentary archives and historical trends; reconstruction of changing pollutant loads into aquatic ecosystems and identifying their drivers; transformation processes and degradation products of sediment contaminants; pore water partitioning of chemicals and bioavailability of hazardous substances and pathogens; role of sediment-water interface processes on biogeochemical pollutant dynamics; as well as *in-situ* and *ex-situ* remediation techniques of contaminated sediments. The conference is covering studies about legacy and emerging organic pollutants, heavy metals, microbes, as well as engineered nanomaterials. Recent advances in environmental chemistry, ecotoxicology and engineering are presented and discussed among participants from fundamental and applied scientific research, experts in risk assessment and regulators from public authorities.

Approximately 80 scientists from 22 countries are attending ContaSed 2015 from 8 to 13 March 2015. The conference program encompasses 14 sessions with 44 lectures. In addition, about 30 posters are presented. A panel discussion session deals with future perspectives of studies on contaminated sediments.

On Tuesday evening the host Congressi Stefano Franscini organizes a public panel discussion in Italian: “Tavola Rotonda: Contaminazione del Lago Maggiore da parte di inquinanti persistenti organici” or in English “Round table: Contamination of Lago Maggiore by persistent organic pollutants”.

On Wednesday afternoon the participants are invited to an excursion to Sottoceneri including visits to Lugano, Monte Brè, Gandria and Lake Lugano.

We wish you successful and enjoyable days on Monte Verità with lots of intensive information exchange and networking.

The ContaSed 2015 Organizers

Walter Giger Bernhard Wehrli Christian Bogdal Thilo Hofmann Paolo Demaria

Conference Organizers and Speakers

Organizing Committee

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Eddie Zeng, Chinese Academy of Sciences, China

Invited Speakers

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Derek Muir, Environment Canada, Canada
Martin Reinhard, National University, Singapore
Peter Santschi, Texas A&M University, USA
Anna Sobek, Stockholm University, Sweden
Jeroen Sonke, Geosciences Environment Toulouse, France

General Information

The conference takes place at the Congressi Stefano Franscini (CSF), the conference center of ETH Zurich, located at Monte Verità, Ascona, Switzerland. The conference facilities, the restaurant and the bar are located in the main building called Bauhaus Building.
For further information on Monte Verità and on connections to Ascona, please refer to the white CSF folder included in your conference bag.

Conference rooms

All lectures will take place in the Auditorium on the ground floor of the Bauhaus Building. All posters will be displayed from Monday to Thursday in the Balint Room, on the first floor of the Bauhaus Building. We kindly ask you to take your poster with you when you leave. Posters left in the room after Thursday evening will be discarded.

Oral Presentations

Lectures are presented as power point files on either a Windows or a Mac computer. The beamer has an additional third channel, so the use of own computers is possible, but compatibility with the video system should be tested ahead of time. Members of the organizing committee will be available to assist you in uploading and testing your presentation. All speakers are kindly requested to stay within their time slot indicated in the program. Chairpersons will control that speakers keep their time.

Poster Presentations

Please refer to the numbered posters list in this book to locate the correct board where you can place your poster. Posters can be displayed in the Balint room from Monday to Thursday. We have planned two Poster Sessions: on Monday from 16.45 to 18.45 and on Tuesday from 13.45 to 15.45. During both sessions poster authors should attend their posters for discussion. Further spontaneous discussions in the poster room are welcome and encouraged at any other time (breaks, after meals, in the evening).

CSF Award

The *CSF Award* has been established in 2009 by the director and the scientific board of the Congressi Stefano Franscini. The Award will be conferred by a jury formed by the Organizing Committee to the best presentation (oral or poster) given by a young scientist during the conference.

Wireless and computer room

There is a free wireless network in the Bauhaus Building and in the Semiramis Building. Please refer to the CSF folder you have received at registration for further information on the use of the wireless (password, settings, etc.).
A computer room with a printer is available for you 24 hours a day. The room is located at the ground floor of the main building, few steps after the Monte Verità hotel front desk.

Meals and refreshments

Lunches and dinners will be served at the Monte Verità Restaurant, on the first floor of the Bauhaus building.

On Thursday evening the Conference Dinner will take place at the Monte Verità restaurant as well.
All coffee breaks will be served at the Bar Roccia, on the first floor of the Bauhaus Building. The Bar Roccia will also be open for you every evening from 21.00 to midnight.

Social events

On Wednesday there will be an excursion in the Lugano area, including lunch at Monte Brè, a walk along the lake and a short boat cruise on Lake Lugano. We will depart from Monte Verità around 10.30 and return in time for dinner.
The Conference Dinner will take place at Monte Verità on Thursday.

Disclaimer

The conference organizers do not accept any liability for personal injuries sustained, or for loss or damage to property belonging to congress participants (or their accompanying persons), either during, or as a result of, the conference.
Registration fees do not include insurance.

Program

Sunday, 8 March 2015

From 14.00	Arrival, registration, hotel check in
18.00	*Welcome drink*
19.00	*Dinner*

Monday, 9 March 2015

8.15- 8.30	**Chiara Cometta** and **Lorenzo Sonognini** Welcome address

Polycyclic Aromatic Hydrocarbons

Walter Giger

8.30 – 9.00	**Derek Muir (Keynote Lecture)** Profiles of polycyclic aromatic compounds in dated lake sediment cores
9.00 – 9.20	**Eddy Zeng** Polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) in continental shelf sediment of China: Implications for anthropogenic influences
9.20 – 9.40	**Marc Schwientek** Integrated assessment of sediment quality in catchments: Impact of urbanization on particle bound pollutant fluxes
9.40 – 10.00	**Gesine Witt** Solid phase micro extraction as a tool to study ecological effects of PAHs in Baltic Sea sediments
10.00 – 10.30	*Break*

Metals

Halka Bilinski

10.30 – 11.00	**Jeroen Sonke (Keynote Lecture)** Reconciling peat bog and lake sediment records of atmospheric Hg deposition
11.00 – 11.20	**Philippe Behra** Comparison of sorption of different contaminants on natural aquifer sand
11.20 – 11.40	**Lars Duester** Spatial high resolution analyses of pore waters at the sediment water interface

12.00 – 13.30	*Lunch*

Radionuclides and Metals — **Jean-Luc Loizeau**

13.50 – 14.20	**Peter Santschi (Keynote Lecture)** Bio- and geopolymeric ligand molecules as binding agents for natural and fallout radionuclides in terrestrial and marine environments
14.20 – 14.40	Discussion
14.40 – 15.10	*Break*

Semipolars — **Marijan Ahel**

15.10 – 15.40	**Juliane Hollender (Keynote Lecture)** Target, suspect and non-target screening approaches to identify organic contaminant records in lake sediments
15.40 – 16.00	**Remy Hennet** Pharmaceutical fingerprinting as a dating tool for recent sediments
16.00 – 16.20	**Emmanuelle Vuillet** Determination of 20 targeted micropollutants in sediments as a national survey
16.20 – 16.40	Discussion
16.45 – 18.45	**Posters**
19.00	*Dinner*

Tuesday, 10 March 2015

Surfactants and Semipolar Compounds — **Uri Zoller**

9.00 – 9.30	**Marjian Ahel (Keynote Lecture)** Historical changes of input and diagenetic fate of aromatic surfactants and their degradation intermediates in the aquatic sediments
9.30 – 9.50	**Pablo Lara-Martin** Historical records of sewage-derived organic contaminants in Jamaica Bay (NY): surfactants vs pharmaceuticals

9.50 – 10.10	**Vesna Micic** Bacterial wax esters in recent fluvial sediments as possible indicators of environmental stress
10.10 – 10.30	**Vladimir Beskoski** Biotransformation of perfluorooctanoic acid by the action of microbial consortia isolated from sediment polluted with perfluorinated compounds
10.30 – 11.00	*Break*

Persistent Organic Pollutants

Christian Bogdal

11.00 – 11.30	**Anna Sobek (Keynote Lecture)** POPs in Baltic Sea sediment: archive of the past and source for the future?
11.30 – 11.50	**Espen Eek** Recent developments in methodologies for determining transport and chemical activity at the sediment-water interface
11.50 – 12.10	**Licia Guzzella** Novel brominated flame retardant, PBDE and HBCD contamination in sediments and biota from Lake Maggiore (Northern Italy)
12.15 – 13.45	*Lunch*
13.45 – 15.45	**Posters**
15.50 – 16.10	**Saer Samanipour** Pollutant distributions between sediments and the benthic water column in a deep lake: Application of passive sampling and GCxGC to less-studied and legacy halogenated contaminants in Lake Geneva
16.10 – 16.50	**Christian Bogdal** Legacy and (re)emerging persistent organic pollutants in Swiss lake sediments
16.50 – 17.20	*Break*

Nanoparticles

Bernhard Wehrli

17.20 – 17.50	**Bart Koelmans (Keynote Lecture)** Implications of nanoparticles and nanoplastics in aquatic ecosystems
17.50 – 18.20	**Lee Ferguson** Today's status and future directions in the analysis of manufactured nanomaterials in the environment

18.20 – 18.35	**Andreas Gondikas** Sediment enrichment with TiO_2 engineered nanomaterials from the use of sunscreens
18.35 – 18.50	**Laura Sigg** Agglomeration and dissolution of Ag and TiO_2 nanoparticles – Nanoparticle accumulation in sediments?
19.00	*Dinner*
20.30–22.00	Tavola Rotonda (Public event in Italian) Contaminazione del Lago Maggiore da parte di inquinanti persistenti organici

Wednesday, 11 March 2015

DDT and Mercury in Lago Maggiore

Richard Luthy

8.30 – 8.50	**Licia Guzzella** DDT and Hg contamination of Lake Maggiore (Italy): historical trends and studies for evaluating the on-site bioavailability (use of passive samplers and benthic invertebrates)
8.50 – 9.10	**Elisa Bizzotto** Characterization of DDT and Mercury contaminated sediment in Toce River and Lake Maggiore (Pallanza Bay)
9.10 – 9.30	**Diana Lin** Field assessment of natural attenuation from DDT in Pallanza Bay, Lake Maggiore
9.30 – 09.50	*Break*
10.00–18.30	**Excursion to Monte Brè, Gandria and Lake Lugano**
19.30	*Dinner at Monte Verità*
	Walter Giger (Afterdinner Talk) *The Old Man and the Sediment* – some highlights of four decades sediment research

Thursday, 12 March 2015

Effects and Risk Assessment

Benoit Ferrari

8.30 – 9.00	**Marc Babut (Keynote Lecture)** Environmental risk assessment of bottom sediments: unfounded claim or actual perspective?
9.00 – 9.20	**Nicolas Creusot** Bio-analytical strategy based on in vitro and in vivo bioassays for effect-based monitoring of bioactive organic chemicals in river sediments
9.20 – 9.40	**Audrey Bolard** Sediment contamination and its negative influence on the macro-invertebrate community of a chalk river in Western Europe
9.40 – 10.00	**Carmen Casado** Biodynamic modelling for contaminated sediments- a readily transferable tool to regulation?
10.00 – 10.30	*Break*

Remediation

Thomas Bucheli

10.30 – 11.00	**Martin Reinhard (Keynote Lecture)** Trace organic contaminants in the urban water cycle of Singapore
11.00 – 11.20	**Nathalie Cottin** Restoration of a PCB contaminated river: effect on Lake Bourget
11.20 – 11.40	**Jonas Gunnarsson** Ecological effects of thin-layer capping with activated carbon on benthic macrofaunal communities - The other side of the coin
11.40 – 12.00	Discussion
12.00 – 13.30	*Lunch*

Effects and Risk Assesment

Hans-Peter Kohler

13.30 – 14.00	**Helmut Bürgmann (Keynote Lecture)** A genetic contamination? Wastewater as a point source of antibiotic resistance genes in sediments of Lake Geneva
14.00 – 14.20	**Nadia Casatta** Endocrine disrupting chemicals in coastal lagoons of the Po River delta: sediment contamination, bioaccumulation and effects on Manila clams
14.20 – 14.40	**Jean-Christoph Auguet** Impact of local and global metal contaminations on microbial communities of Pyrenean lakes

14.40 – 15.00	**Aurea Chiaia-Hernandez** Temporal records of organic contaminants in lake sediments and their impact on *Daphnia* populations
15.00 – 15.30	Discussion
15.30 – 16.00	*Break*

Remediation

Thomas Bucheli

16.00 – 16.30	**Gerard Cornelissen (Keynote Lecture)** Sediment remediation with activated carbon and biochar – immobilization mechanisms and large-scale field tests in Norway

DDT and Metabolites

16.30 – 16.50	**Martin Reinhard** Transformation and mineralization of DDE in Palos Verdes Shelf sediments
16.50 – 17.20	Discussion

Future Perspectives

Lee Ferguson

17.20 – 18.40	**Panel Discussion** **Marc Babut, Bernhard Wehrli**

19.00 ***Conference Dinner*** ***CSF Award*** ***Special Awards***

Friday, 13 March 2015

Sedimentology and Petroleum Hydrocarbons

Steve Rowland

9.00 – 9.30	**Flavio Anselmetti (Keynote Lecture)** The role of physical sedimentology in the context of chemical contaminations	
9.30 – 10.00	**David Hollander** Sub-surface oil plumes, sedimentary oil deposition and other unexpected consequences and impacts in the aftermath of the Deepwater Horizon oil-well blowout	
		Hans-Peter Kohler
10.00 – 10.30	**Martin Jones (Keynote Lecture)** Aerobic and anaerobic biodegradation of petroleum hydrocarbons	
10.30 – 10.50	**Steve Rowland** Identification of aromatic acid metabolites produced by two year laboratory biotransformation of crude oil under sulfate-reducing and methanogenic conditions, by GCxGC-MS.	
10.50 – 11.20	*Break*	
		Walter Giger
11.20 – 12.00	**Summary, Outlook, Closing**	
12.00	*Lunch and departure*	

Posters List

Posters are sorted alphabetically by presenting author. Please refer to this list to locate the board where your poster can be displayed. Pins are available in the poster room.

1. Elimination of sulphur interference during the determination of tributyltin in sediment
Awad Aqeel Al-rashdi

2. Geochronology and contaminated sediments: evaluation of the historical contamination in Lake Maggiore
Elisa Bizzotto, S. Ceccon, F. Colombo and L. Conti

3. Comparison of the impact of two WWTPs discharge on PAHs in suspended particular matter (SPM) and sediment contamination in chalk streams
Axelle Chiffre, A. Bolard, E. Chanez, F. Degiorgi and P.M. Badot

4. Legacies from early industrial activities in Swiss lakes sediments
Nathalie Dubois, M. Lavrieux, R. Liechti , A. Gilli, I. Brunner, L. Freydier and A. Lück

5. Current pollution load of sediments and suspended matter in Lake Rummelsburg (Berlin) and whose mobilization potential and ecotoxicological impact on the aquatic ecology
Michaela Dumm, K. Terytze, A. Schulte, J. Bölscher, R. Suthfeldt and B. Vogt

6. Establishing of monitoring of river sediments in Croatia
Stanislav Frančišković-Bilinski, H. Bilinski and K. Maldini

7. Distribution and persistence of butyltin compounds (BuT) in coastal sediments from the eastern Adriatic (Croatia)
Martina Furdek, J. Dautović, M. Ivanić and N. Mikac

8. Multi-residue analysis of pharmaceuticals and pesticides in river sediments and corresponding surface and ground water in Serbia
Svetlana Grujić, I. Matić, T. Radović and M. Laušević

9. Remediation of dioxin-contaminated marine sediments using thin-layer capping with activated carbon and other sorbents: evaluation of bioavailability assessment techniques
Jonas Gunnarsson*,* A. Gustafsson, S. Josefsson, G. Cornelissen, I. Allan and M. Schaanning

10. Remediation of contaminated sediments in the Baltic Sea: evaluation of toxicity risk reductions to humans and fish following activated carbon amendment
A. Gustafsson and **Jonas Gunnarsson**

11. Integrated ecological risk assessment of pesticide run-off using the TRIAD weight-of evidence approach: a case study in the Rio Madre de Dios River, Costa Rica

Jonas Gunnarsson, M.J. Arias, F. M. Torres, S. Echeverría ,C. Ruepert, P. van den Brink, R. Rämö, M. Tedengren and L.E. Castillo

12. Integrated Ecological Risk Assessment (ERA) of aquaculture and anthropogenic pollution in the Phu Long commune, Cat Ba Island, Vietnam

P. Bruce, **Jonas Gunnarsson**, N.T.T. Lan, N.T. Thu and T.T. Hien

13. Bioassays in sediment assessment for investigative monitoring in the context of the WFD: Results of the sampling campaign from 2010 to 2012

Matthieu Hémart, Y. Marneffe, R. Pirotte, V. Wrona, P. Naport, V. Rollin, C. Corin and A. Classens

14. Microbial diversity response to chronic petroleum contamination in coastal sediments

Mathilde Jeanbille, J. Gury, R. Duran, J. Tronczynski, J.-F. Ghiglione, H. Agogué, O.B. Saïd, N. Taïb, D. Debroas and J.-C. Auguet

15. The influence of carbonaceous materials on freely dissolved PAHs content and toxicity of soil, sediment and sewage sludge

Izabela Jośko, M. Kołtowski and P. Oleszczuk

16. The analytics of polyaromatic hydrocarbons (PAHs) in new certified reference materials of soil samples

A. Kiełbasa, **Iwona Krzemień – Konieczka**, R. Gadzała-Kopciuch and B. Buszewski

17. Determination of pharmaceutical residues in surface water using ultra high performance liquid chromatography with UV-Vis detector

A. Piwońska, A. Kiełbasa, **Iwona Krzemień-Konieczka,** R. Gadzała-Kopciuch and B. Buszewski

18. New certified reference materials (CRMs) of soil for the analysis of polychlorinated biphenyls

Iwona Krzemień-Konieczka, M. Sprysnkyy, R. Gadzała-Kopciuch and B. Buszewski

19. Assessing impact of the remobilisation of metal-contaminated sediments in the Rhine River during the dredging of a dam by coupling chemical and biological approaches

J.D. Lebrun, M. Dufour, E. Uher, J. Faburé, R. Charlatchka, L.C. Fechner and **Benoit J.D. Ferrari**

20. Evaluation and selection of test methods for assessment of contaminated sediments in the Baltic Sea – The CONTEST project

Kari K. Lehtonen, A. Ahvo, N. Berezina, M. Breitholtz, B. Eklund, K. Jørgensen, M. Linde, E. Schultz, J. Strand , K. Ström and B. Sundelin

21. Soil and sediment testing of very hydrophobic, low solubility organic substances

Miriam Leon Paumen, G. E. Bragin, L. K. Low, A. D. Redman, J. D. Butler, D. J. Letinski, C. A. Sutherland, B. A. Kelley and T. F. Parkerton

22. Hormones and sterols in sediments of the Danube River and its tributaries in Serbia

Ivana Matić, S. Grujić, Z. Jauković and M. Laušević

23. Assessment of anthropogenic pressures on the pristine karst lakes in two Croatian National Parks using multi-parametric sedimentary records

Iva Mikac, N. Bacic, V. Hodak Kobasic, Z. Fiket, S. Terzic, N. Mikac and M. Ahel

24. Determining the release of hydrophobic organic contaminants from sediment by *in-situ* benthic flow-through chambers

Lukas Mustajärvi, E. Eek, G. Cornelissen, A.-K. Wiklund-Eriksson, and A. Sobek

25. Dynamics of heavy metals level in bottom sediments of the River Prut (Republic of Moldova)

Larisa Postolachi, V. Rusu, T. Lupascu and T. Mitina

26. Biomass from organic waste materials for sustainable remediation

Gabriel Sigmund, M. Kah, H. Sun and T. Hofman

27. Removal of polycyclic aromatic hydrocarbons and their alkyl homologues during *ex situ* stimulated bioremediation of contaminated soil

Tatjana Šolević Knudsen, V. Beškoski, G. Gojgić-Cvijović, B. Jovančićević and M. M. Vrvić

28. Evaluation of the effect of PCB-containing architectural coatings on sediment quality

Philip Spadaro, S. Bowerman, J. Dittman, C. Moody, D. Profusek and K. Maitland

29. Adsorption of chlorophenols on pristine and functionally modified multiwalled carbon nanotubes

Jelena Tričković, M. Kragulj, S. Maletić, S. Rončević, Á. Kukovecz, Z. Kónya and B. Dalmacija

Abstracts

Lectures abstracts are sorted chronologically according to the program. Presenting authors are listed in bold.

Poster abstracts are sorted alphabetically by presenting author, whose name is listed in bold.

Abstracts have been edited for consistency of style but not in their contents, which remain responsibility of the authors.

Profiles of polycyclic aromatic compounds in dated lake sediment cores

Derek Muir[a], J. Kirk[a], C. Manzano[a], X. Wang[a], M. Evans[b],
J. Keating[b],J. Kurek[c], J. Summers[d], and J. Smol[d]

[a] *Environment Canada, Aquatic Contaminants Research Div., Burlington, Canada*
[b]*Environment Canada, Aquatic Contaminants Research Div., Saskatoon, Canada*
[c]*Department of Geography and Environment, Mount Allison University, Sackville, Canada*
[d]*Department of Biology, Queen's University, Kingston, Canada*

Lake sediment cores have been used for decades[1] to reconstruct loadings and historical inputs of Polycyclic Aromatic Compounds (PACs) from urban storm water runoff, municipal/industrial effluents and atmospheric deposition. In North America interest in PACs has increased recently due to identification of pollution from coal-tar pavement sealants, emissions from shale gas and oil sands development, and assessment of crude oil spills into freshwaters. This presentation will first review recent literature with the goal of highlighting novel approaches for assessing sources such as use of larger suites of PACs (alkylated PACs (aPACs), dibenzothiophenes (DBTs)), GCxGC separations, $^{13}C/^{12}C$ isotope ratios, and application of paleolimnological techniques such as microfossil assemblages and black/spherical carbon. The second part of the presentation will be on the application of some of these techniques to interpret the history and impacts of atmospheric loadings of PACs to the Athabasca oil sands development area (Alberta, Canada). Dated sediment cores from 19 lakes were analysed: 11 were within about 50 km (near field) of the bitumen upgrading facilities in the development area north of Ft McMurray and 8 at 75-185 km distance (far field). Sixteen lakes were remote, undisturbed and received only atmospheric inputs, while 3 larger far-field lakes had small communities within their catchments. Total (Σ)PAC (46 analytes) concentrations increased in all near-field lakes, beginning at the early 1970s, particularly C1-C4-aPACs and C1-C4- DBTs. Maximum post-2000 ΣPAC fluxes were 1.8 to 24-times greater than pre-1960 background levels. Increasing ΣPAC was also evident in far-field lakes, although post-2000/pre-1960 enrichment factors were generally much lower (1.0-3.9-fold). C1-C4 aPACs and DBTs predominated in all samples, representing 55 to 89% and 1.8 to 17% of the ΣPACs, respectively. C3-DBT/C3-phenanthrene and C2-DBT/C2-chrysene ratios, along with other indicators of combustion sources, suggest a shift to petrogenic and unweathered aPAC sources in post-1970s sediments of near-field cores. Ratios of retene to total unsubstituted PACs were higher in pre-1960 sediments than in the modern sediments in all near-field lakes indicating a greater proportion of wood combustion and terrestrial plant inputs compared with recent times. Trends in lake primary production were estimated from sedimentary chlorophyll concentrations using visible reflectance spectroscopy (VRS-chla) while crustacean zooplankton (Cladocera) microfossil assemblages were analysed to assess effects of environmental stressors. VRS-chla increased substantially, especially in the post late-1970s sediments, and an overall increase in relative abundances of *Daphnia* was observed beginning in the 1960s to 1970s. The results illustrate that a combination of detailed chemical and paleo-ecological analyses can provide insights into the past and current impacts and dynamics of PACs and other pollutants in lake ecosystems.

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[1] Wakeham, S.G., Schaffner, C., Giger, W., 1980. Polycyclic aromatic-hydrocarbons in recent lake-sediments. 1. Compounds having anthropogenic origins. Geochim. Cosmochim Acta 44,403-413.

Polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) in continental shelf sediment of China: Implications for anthropogenic influences

Eddy Y. Zeng[a, b]**,** L.-Y. Liu[a], J.-Z. Wang[a] and Y.-F. Guan[a]

[a] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China*
[b] *School of Environment, Jinan University, China*

Anthropogenic impacts on China's coastal marine environment were investigated by assessing the spatial and temporal variations of polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, and total organic carbon (TOC) in both surface and core sediments collected from the continental shelf of China, embracing Yellow Sea, inner shelf of the East China Sea (ECS), and the South China Sea (SCS). Sedimentary PAHs were mainly from mixed residues of biomass, coal, and petroleum combustion. Long-chain n-alkanes (n>C21) were mainly derived from terrestrial higher plants. The concentrations of anthropogenic PAHs (27–224 ng/g dry weight) and *n*-alkanes (120–1680 ng/g dry weight) in surface sediments were at the low to moderate end of the global range, suggesting moderate influences of anthropogenic activities on the coastal marine environment of China. The spatial distributions of both PAHs and *n*-alkanes concentrations suggested a greater load of terrestrial organic materials in the Yellow Sea than in the SCS, reflecting the difference in anthropogenic activities (e.g., energy consumption) between northern and southern China. Temporally, concentrations of PAHs, *n*-alkanes, and TOC increased with time and peaked at either the surface or subsurface layers. These increases were probably reflective of elevated inputs of organic pollutants and/or organic materials to marginal seas off China in recent years, and attributed partly to the impacts of intensified anthropogenic activities in mainland China. The historical socioeconomic development in China was well reconstructed by the historical profiles of Σ_{15}PAH concentrations in the sediment cores. In general, Σ_{15}PAH concentrations started to increase from the background pollution level posed by agricultural economy at the turn of 20th century, decreased during the Chinese Civil War (1946−1949) and Great Cultural Revolution (1966−1976), and increased rapidly as a result of increasing coal combustion associated with the rapid urbanization and industrialization since the implementation of the Reform and Open Policy (since 1978). The decline of Σ_{15}PAH concentrations from subsurface maximum until sampling time was inconsistent with current-day economic development in China, and may possibly suggest emission reductions due to decreasing proportional use of domestic coal and increasing consumption of cleaner energies (natural gas and liquefied petroleum gas).

Integrated assessment of sediment quality in catchments: Impact of urbanization on particle bound pollutant fluxes

Marc Schwientek[a], H. Rügner[a], M. Rode[b] and P. Grathwohl[c]

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Transport of many urban pollutants in rivers is coupled to transport of suspended particles, potentially dominated by storm water overflows and mobilization of legacy contamination of sediments. Concentration of these pollutants depends on the mixture of “polluted” urban and “clean” background particles. In the current study, the total concentration of polycyclic aromatic hydrocarbons (PAHs), the amount of total suspended solids (TSS) and turbidity were measured on a monthly basis in water samples from 5 catchments with contrasting land use in Southwest Germany and 3 catchments in the Bode Basin in Eastern Germany over up to 1.5 years. In addition, single flood events with large changes in turbidity were sampled at high temporal resolution. Linear correlations of turbidity and TSS where obtained over all catchments investigated and over an extended turbidity range (up to 2000 NTU for the flood samples). Linear correlations were also obtained for the total amount of PAH and suspended sediment concentrations even for very high turbidity or TSS values (> 2000 NTU or mg l^{-1}, respectively). From the linear regressions concentrations of PAHs on suspended particles were obtained – and which varied by catchment. The values comprise a robust measure of the average sediment quality in a river network and may be correlated to the degree of urbanization represented by the number of inhabitants per total flux of suspended particles. The findings are promising for other particle-bound contaminant fluxes (PCBs, phosphorus, and several heavy metals, etc.). Using on-line monitoring of turbidity (e.g. by optical backscattering sensors) mass flow rates of PAH over time could be calculated. Results showed that by far the largest proportion of annual PAH loads occurs during the short periods with relative high turbidities > 100 NTU. Recent investigation focus on the type and provenance of the different particles. Total organic carbon and carbonate content as well as grain size distributions were measured for suspended particles representing different time periods of pronounced events. These results will also be presented.

Solid phase micro extraction as a tool to study ecological effects of PAHs in Baltic Sea sediments

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The Baltic Sea is one of the greatest brackish semi-enclosed oceans in the world and due to its geographical position heavier polluted than other marine areas. Little is known about the large-scale distribution of polycyclic aromatic hydrocarbons (PAHs) in Baltic Sea sediments when the question of the pollutants' bioavailability, i.e. their ecotoxicologicl potential is addressed (1). Passive sampling offers novel adequate possibilities to study the fate, partitioning and risk of hydrophobic organic chemicals in the Baltic Sea (2, 3) such as polycyclic aromatic hydrocarbons. Solid Phase Microextraction (SPME) was applied to provide the first large scale dataset of freely dissolved concentrations and chemical activities for 9 polycyclic aromatic hydrocarbons (PAHs) in Baltic Sea sediment cores. Polydimethylsiloxane (PDMS) coated glass fibers were used for ex-situ equilibrium sampling in sediment cores. The PAH amount on the fiber was measured by automated thermal desorption and GC-MS analysis. From the PAH concentrations in the fiber coating (C_{PDMS}) we examined (i) spatially resolved freely dissolved PAH concentrations (C_{free}); (ii) baseline toxicity potential on the basis of chemical activities (a); (iii) site specific mixture compositions; (iv) diffusion gradients at the sediment water interface and within the sediment cores and (v) site specific distribution ratios (K_D). Contamination levels were low in the northern Baltic Sea, moderate to elevated in the Baltic Proper and highest in the Gulf of Finland. Benzo[a]pyrene showed low background levels in the Bothnian Sea and one order of magnitude higher levels in the Gulf of Finland. The sum chemical activity depended on both concentrations and mixture composition, and it was 1 - 4 orders of magnitude below the reported level for acute baseline toxicity. The SPME method is a very sensitive tool that opens new possibilities for studying the in-situ distribution and thermodynamics of hydrophobic organic chemicals like PAHs at trace levels in marine environments.

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Reconciling peat bog and lake sediment records of atmospheric Hg deposition

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Lake sediments, the most widely studied natural archive, show a three-fold (3±1) increase in Hg accumulation rates from the pre-industrial (c.a. 1850) to the 20th century at remote locations on different continents and across different climate zones. Peat archives have been suggested to show larger, 40-fold increases in Hg accumulation rates from pre-industrial to modern times. The discrepancy has fueled debate over which archive we should trust. Uncertain, but substantial, pre-1850 and late 19th century Hg emissions from large-scale gold, silver, and mercury mining in a recent historical emission inventory have led to a second debate on the impact of early anthropogenic Hg emissions. Several studies suggest negligible pre-1850 and much lower late 19th century Hg emissions. A revised historical inventory of anthropogenic Hg emissions as well as continued model development that includes coastal marine sediments as a large global Hg sink provide a new basis to re-examine historical Hg emissions. I show that by using identical reference periods to assess Hg enrichment in peat and sediment archives the apparent mismatch vanishes. Modeling suggests that the remaining difference relates to the longer timescales associated with Hg cycling in the terrestrial catchments of sediment archives.

Comparison of sorption of different contaminants on natural aquifer sand

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In order to better understand sorption mechanisms of contaminants on natural aquifer sand and compare their behaviour, both batch and column experiments were performed by studying the role of physical-chemical and/or hydrodynamic parameters such as pH, ionic strength, electrolyte composition, ligand and flow rate. The natural aquifer sand, sample of detritic sediments from the Vosges (France), was mainly composed of quartz (99 %), feldspars (1 %) and clays (0.1 %) plus some traces of pyrite and of (hydr)oxides of Fe and Mn. Its specific surface area is 0.16 m^2/g and its point of zero charge around 6, what shows the effect of Fe (hydr)oxide coating at the surface of main minerals. The compounds studied were: Ag(I), As(III) and As(V), Cd, Cu(II), Hg(II), Pb, phosphate, organotin (TBT, tributyltin), and humic acid (HA). Concentration range was from nM to mM depending on the chemical studied. For some of them, competition experiments were performed. Dissolution from sand minerals was checked by ICP-MS, ICP-OES or IC analyses. Analytic speciation was performed for some compounds such as As, Ag and organotin.

Sorption of Cd, Cu, Pb and TBT did not depend on time contrary to the other compounds. Sorption kinetics of Ag was rather low, equilibrium being reached after 4 days. Hg and As sorption depends strongly on time, flow rate changing their fate. Redox state of Cd, Cu, Hg, Pb, phosphate and TBT was stable, while Ag(I) and As(V) can be reduced depending on experimental conditions.

Sorption depends on the affinity of compounds to specific minerals. The strongest sites are: (hydr)oxides and clays for Ag, Cu, Hg and Pb; (hydr)oxides for As and Cd; mainly silica for TBT. Due to mineral dissolution, Fe, Al and sulphate are present at rather high concentrations. Fe content is much higher than the concentration which would be expected in the case of equilibrium with Fe(III) (hydr)oxides at a given pH. Traces of pyrite are the main source of Fe and sulphate and control the redox, explaining Ag(I) or As(V) reduction. Moreover pyrite and Fe(III) (hydr)oxides can affect speciation of some of these compounds during experiments.

Comparing global affinity of compounds, it comes the following sequence for comparable experimental conditions: Ag > Hg > Pb > Cu > TBT > Cd > As(V) ≈ phosphate. Strong HA retardation occurred for pH < pzc, while HA behaved as a tracer at pH > pzc. On the other hand it was shown that clays can play the role of colloidal scavenger of trace elements during their peptisation.

The main conclusion of such an overview is that all the minerals, even those present at low surface concentration, can control the transport of trace compounds meaning that it is necessary to get the best knowledge of their speciation and sorption mechanisms at atomic scale for reactive transport modelling at larger scale.

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Spatial high resolution analyses of pore waters at the sediment water interface

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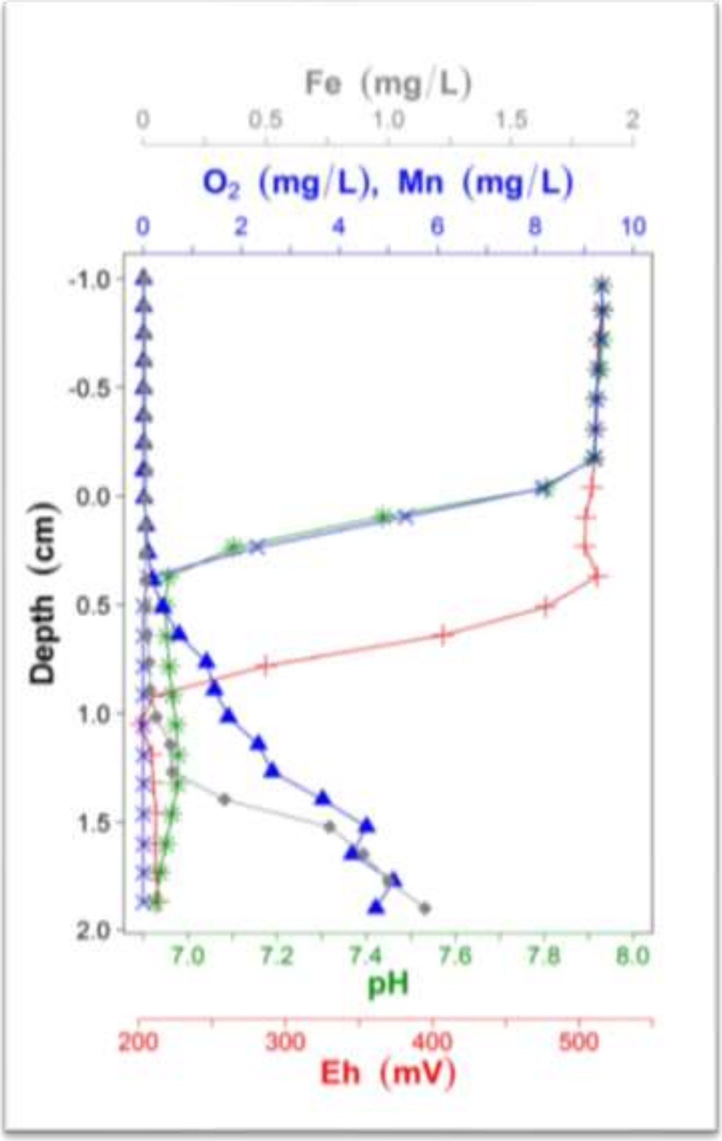
To gain a better understanding on biogeochemical processes that govern the fate of nutritive substances and pollutants at the sediment water interface, methods with a high spatial resolution are required. The availability of numerous micro-sensors and -electrodes (e.g., O_2, redox potential, pH value, H_2S, N_2O) improved considerably the possibilities to study these heterogeneous and often dynamic aquatic environments at sub-millimetre scale. Via the combination of a micro profiling system with a new micro filtration probe head connected to a pump and a fraction collector, a **mi**cro profiling and micro **s**ampling **sy**stem ("missy") was developed that enables for the first time a direct, dynamic and automate sampling of small volumes (<500 µL) at a spatial high resolution of a few millimetre to sub-millimetre scale. With missy it is, as an example, possible to combine the benefits of the micro sensor profiling with the multi element capability of ICP-MS. In the future speciation and fractionation questions in organic and inorganic environmental chemistry on processes occurring at the sediment water interface will be addressed via this suction based direct sampling technique. The figure displays an exemplary sediment pore water depth micro profile of Mn (▲) and Fe (◆) in correlation to O_2 (×), redox potential (+) and pH value (✳) profiles (Fabricius et al. 2014). In the presentation (i) the missy setup, (ii) running applications, as well as (iii) potential future applications will be detailed.



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Recent developments in methodologies for determining transport and chemical activity at the sediment-water interface

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The sediment-water interface can be a source of abiotic transfer of contaminants to the overlying water as well as a zone for contaminant exposure of benthic fauna and subsequently a source of contaminants to the aquatic food chain. This has led to an increased focus and research to determine both the contaminant activity gradient and the contaminant mass transfer across the sediment-water interface. Determination of sediment to water flux of persistent organic pollutants (POPs) are usually accomplished according to one of two methods: 1) direct flux assessment where a small part of the sediment surface is isolated (in situ or in the lab) and the amount of POPs diffusing out of the sediment surface is collected in an infinite sink material; and 2) determination of pore water and overlaying water concentrations (in situ or ex situ) followed by calculation of flux from the concentration difference and transfer rate.

Recent innovations to address challenges related to this include the design of two new field measurement tools. 1) A novel flow through flux chamber enabling measurement of flux while renewing the water inside the chamber in order to supply oxygen to the benthic fauna. A separate abstract is submitted describing this tool (Mustajärvi et al.). While our presentation will focus on: 2) A novel tripod pore water probe deploying passive samplers at different depth intervals both in the pore water and in the overlying water. The passive samplers are attached to a single rod penetrating the sediment bed to a predefined depth. The compact design of the probe ensures that the influence from the presence of the probe will have minimal effect on the overlaying water movements and therefore also minimal influence on the in situ sediment to water mass transfer coefficient and on the bioturbation activity of the benthic fauna. The novel tripod pore water probe is designed to be deployed at deep waters (used down to 120 m depth). The probe is also fitted with a releasable camera to monitor the deployment and document the penetration depth of the probe in the sediment. This makes it possible to determine which passive samplers have been exposed to the pore water and which to the overlying waters.

These new tools will allow for more detailed studies of POP flux and concentration gradients in the benthic boundary layer including the influence of hydrodynamics, bioturbation, particle re-suspension, and the particle water re-distribution of POPs.

Bio- and geopolymeric ligand molecules as binding agents for natural and fallout radionuclides in terrestrial and marine environments

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Master variables for controlling mobility of metal ions (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+}) and radionuclides (e.g., ^{239,240}Pu, ^{129}I, ^{234}Th, 2^{31}Pa, ^{210}Pb, ^{210}Po, ^{7}Be) in aquatic systems include pH, pE, organic carbon and nitrogen concentrations. Trace elements can be bound by many organic macromolecules e.g., in enzymes and pigments. Metal ions also serve as binding agents for aggregating pedogenic humic acids (e.g., Ca^{2+}, Fe^{3+}), and by providing rigity and/or gel formation ability to aquagenic microbial exopolymers. Furthermore, there is increasing evidence that many natural and anthropogenic radionuclides are strongly bound to specific binding moieties in natural organic matter, NOM, which then serve as specific carrier molecules for selected radionuclides, but also allow these carrier molecules to control the radionuclide's relative mobility/immobility and transport in aquatic systems. The evidence comes from close examination by spectrophotometry, GCMS, HPLC, NMR and ES-ICR-MS, of chemically or physically separated NOM fractions after further purification by biochemical, chromatographic or isoelectric focusing procedures have been applied to radiolabeled samples from aquatic systems or laboratory cultures. Recent examples (from Refs. 1-6, and unpublished results) for master variable control of selected radioisotopes of I, Pu, Th, Pa, Be, Po, Pb will be discussed, with evidence that pH controlled incorporation into aromatic moieties (e.g., I) acid polysaccharides (e.g., Th), siderophore hydroxamates (e.g., Pu, Pa, Po), proteins (e.g., Po), and Fe-containing macromolecules (Pb) in soils, ground and surface waters is occurring.

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Target, suspect and non-target screening approaches to identify organic contaminant records in lake sediments

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Lake sediment cores provide a valuable record of historical persistent contamination since they can act as integrators of many inputs within a catchment. In this study a comprehensive screening of medium polar organic contaminants using high resolution mass spectrometry (HRMS) coupled to HPLC was carried out to provide records of historical contamination of previously unreported compounds. A combination of target, suspect and non-target screening using LC-ESI-HRMS/MS was performed on extracts from sediment cores from Lake Greifensee and Lake Lugano located in the north and south of Switzerland, respectively. In the target analysis on average 16 of 200 compounds were detected in both lakes with the most prominent substance classes corresponding to personal care products, pesticides, and biocides. A suspect list was compiled from consumption data of pesticides and pharmaceuticals and refined using the expected method coverage and a combination of automated and manual filters on the resulting measured data. Non-target identification efforts were focused on masses with Cl and Br isotope information available that exhibited mass defects outside the sample matrix, to reduce the effect of analytical interferences. In silico methods combining the software MOLGEN-MS/MS and MetFrag were used for direct elucidation, with additional consideration of retention time/partitioning information and the number of references for a given substance. The combination of all available information resulted in the successful identification of three suspects (the biocide chlorophene, the pharmaceutical flufenamic acid and the pesticide lufenuron) and two nontarget compounds (the bacteriostatic agent hexachlorphene and the mothproofing agent flucofuron), confirmed with reference standards, as well as the tentative identification of two chlorophene congeners (dichlorophene, bromochlorophene) that exhibited similar time trends through the sediment cores. The temporal pattern of the pollution between 1950 and 2010 was reconstructed for all suspect and non-target compounds, revealing different trends. The concentrations of many urban contaminants originating from wastewater correlated with the highest phosphorus input into lake Greifensee as a proxy for treatment efficiency, while concentrations of substances that only came into use more recently or for that the usage increased peaked later.

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Pharmaceutical fingerprinting as a dating tool for recent sediments

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Pharmaceutical compounds are introduced or removed for societial use at documented dates according to the regulatory approval process, and the timing of their release to the environment is therefore constrained. Certain pharmaceuticals are non-reactive and undergo little degradation under most in vivo, environmental, or routine wastewater treatment conditions. Groups of pharmaceuticals that include various antibiotics and contrast agents are prescribed and used in large quantities. The quantities used are documented by publically available sale data and regulatory information. Such compounds are reported at low concentrations in water and sediment samples using reliable analytical methods that have recently been improved for this compounds. Dating tools for the age of deposition and accumulation rates of recent sediment materials in freshwater and saltwater bodies typically consist of radioisotope measurements (beryllium-7; cesium-137; lead-210; and other radionuclides) and other techniques (i.e., carbonaceous particles; luminescence; chemical profiles and trends). These techniques have limitations and their interpretation is at times uncertain reflecting analytical capabilities and the complex dynamics of sediment transport and deposition. Using groups of pharmaceutical compounds to complement the established methodologies can provide valuable additional discretization and improve the dating and interpretation of sediment core and sediment pore water data. Contrast agents for magnetic resonance and X-ray imaging are by design non-reactive and stable, making them good candidates as environmental tracers targetting a relatively narrow period of time (i.e. last 70 years). The history of introduction of contrast agents is complex but well documented. For example, in the United States, iodine-based contrast agents were first introduced in 1950 and more than twenty additional such compounds were introduced at different times between 1954 and 2011; seven of these contrast agents were removed from use between 2001 and 2003. Contrast agent that contain the rare earth element gadolinium were first introduced in 1988 and eight additional gadolinium-based contrast agents were introduced between 1989 and 2011. Similarly for antiobiotics, fluoroquinolone group antibiotics were first intoduced in 1986 and more than twenty additional fluoroquinolones have since been introduced and six of the fluoroquinolones were removed from the market between 2002 and 2004. The detection of these anthropogenic compounds in sediment and sediment pore water samples can benefit and complement the arsenal of readily available dating tools for the modern era and assist in the investigation of the age and orign(s) of sediments in areas impacted by human activities.

Determination of 20 targeted micropollutants in sediments as a national survey

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A multi-residue method for analysing 20 organic micropollutants in sediments based on the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) approach was developed. The procedure involved salting-out liquid-liquid extraction using acetonitrile and clean-up with dispersive solid phase extraction (dSPE), followed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) or gas chromatography-mass spectrometry (GC-ToF-MS). The validated analytical procedure exhibited recoveries between 40% and 98% for every target compound and allowed the quantification at limits comprised between 0.5 and 23 ng/g depending on the compound.

The list of target substances contained 2 alkylphenols, 3 PAHs not commonly included in monitoring programs, 6 pesticides or metabolites, 5 pharmaceutical compounds, 2 hormones, 1 UV filter and bisphenol A. To collect a large dataset regarding the occurrence of these substances in sediment, 154 sampling points were analysed as a national survey. Of the 20 target compounds, 9 were determined at least once, and the sediments contained a maximum of 7 substances. The most frequently detected were PAHs (frequency, 77 %; max., 1,400 ng/g). The pharmaceutical compounds, hormones and pesticides were rarely detected in the samples; the most frequently detected was carbamazepine (frequency, 6%; max. 31 ng/g). In some cases, the levels of PAHs and bisphenol A exceeded the PNEC (predicted no-effect concentration) values.

This prospective study approach would help contributing to discussions on future monitoring programs. Indeed, the results presented will contribute to the further selection of substances to be integrated in the monitoring programmes of the French water agencies in the various river basins.

Historical changes of input and diagenetic fate of aromatic surfactants and their degradation intermediates in the aquatic sediments

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This paper aims to give an overview on the current knowledge about the input, distribution and fate of the major classes of anionic and nonionic aromatic surfactants in freshwater and marine sediments. Aromatic surfactants belong to the most prominent classes of high producton volume (HPV) chemicals with the total world consumption reaching several million tons per year. Moreover, due to their predominant usage in aqueous solutions, most of the applied quantities end up in wastewater effluents, while the percentage of surfactant-derived residues that eventually reaches aquatic environment strongly depends on their behaviour and fate during wastewater treatment. Significant differences were observed between the two major classess of aromatic surfactants, alkylbenzene sulfonates and alkylphenol polyethoxylates, regarding thier transformation pathways and partitioning behaviour in wastewater treatment plants (WWTPs), which are then strongly reflected in their distribution in the aquatic environment, including association with suspended particles and consolidated bottom sediments. Complex metabolic patterns of both classes of aromatic surfactants make thier mass balance in the aquatic environment a highly challenging task. Nevertheless, several studies demonstrated that vertical distribution profiles of aromatic surfactant-derived compounds in undisturbed sediments provided excelllent historical records of the prevailing usage patterns over the past several decades but also clearly reflected the effects of different risk reduction measures on the composition and exposure concentrations of surfactant residues. Moreover, differences between the diagenetic fate of alkylbenzene sulfonates and the alkylphenol polyethoxylates, will be dicussed taking into account both biotransformation processes and physico-chemical partitioning in order to provide a basis for their ecotoxicological assessment.

Historical records of sewage-derived organic contaminants in Jamaica Bay (NY): surfactants vs pharmaceuticals

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This study deals with the vertical distribution of a wide range of surfactants and pharmaceuticals (PhACs) in dated sediment cores, a powerful approach for monitoring the exposure of aquatic systems to wastewater during several decades. Sediment sampling was carried out in Jamaica Bay in 1996 and 2008. This bay is adjacent to New York City, being impacted by $1.1\text{x}10^9$ L/day of biologically treated sewage discharged by 6 wastewater treatment plants (WWTPs). Sediment cores were dated measuring ^{137}Cs and ^{210}Pb activities. Ten surfactant classes (including anionic, non-ionic and cationic compounds, as well as metabolites) and more than 50 PhACs were analyzed. The highest levels of target compounds in surface sediment samples -up to 80 ng/g of PhACs and 200 µg/g of surfactants- were measured in the inner part of Jamaica Bay, characterized by very high burial rates and hypoxic conditions prevailing in the near-bottom waters. Sediment cores were taken in that area and the vertical distribution of surfactants and PhACs along the sedimentary column was investigated in order to: a) confirm the dating of the sediment cores by radionuclides, b) study changes over time in the WWTP efficiencies and contaminant inputs, and c) determine whether target compounds are susceptible of undergoing anaerobic degradation and/or diffusion using the “matched cores” approach. Two different concentration maxima were observed for surfactants in sediment layers corresponding to the mid-late-1980s (700 µg/g), and the mid-1960s (500 µg/g). These changes over time are attributed to upgrades in WWTP treatment performances that occurred at those periods. Only 16 PhACs could be detected in sediment cores and their concentrations were much lower (< 100 ng/g) than those for surfactants. However, they showed a growing trend over the last decades, which is in agreement with the continuous increase in the production and use of these chemicals. Their sediment records were also consistent with first use dates. As an example, ibuprofen could be observed at an average concentration of 10 ng/g in sediment horizons from 2008 till 1974, when it was first sold. Concentration of propranolol (developed in the 1960s) increased up to 12 ng/g from 1977 to 1985, and then it decreased towards the surface of the core (3 ng/g). Metoprolol, developed in 1978 and showing less side-effects than propranolol, became a generic product in 2006, which improved its sales recently and can explain the exponential increase in its concentration from 5 to 35 ng/g over the last decade. This was also observed for some other pharmaceuticals, such as the antibiotic clarithromycin, developed in 1991 and gone generic in 2005 (its maximum concentration was detected in the core surface, being 16 ng/g). Psychiatric drugs, such as carbamazepine or fluoxetine, which are slowly biodegraded in the water column, could be also detected in sediments at concentrations between 2 and 10 ng/g in spite of their high solubility. No significant differences in surfactant and PhAC concentrations could be measured when comparing date-matched sediment horizons from cores sampled in 1996 and 2008, indicating their lack of biodegradation/diffusion over that period of time.

Bacterial wax esters in recent fluvial sediments as possible indicators of environmental stress

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Intensive anthropogenic activities may periodically induce a high nutrient and/or contaminant input to rivers. These fluctuations in environmental conditions affect aquatic organisms and might cause temporary algal blooms, but can also enforce some prokaryotes to accumulate storage compounds as a hedge against starvation. Such an environmental stress can be documented in the molecular record of river sediments.

We investigated the molecular record in Danube River surface and core sediments and identified wax esters (WE) with 28 to 34 carbon atoms, being most likely of bacterial origin.

The identified WE consist of various combinations of linear (*n*), *iso* (i), *anteiso* (*ai*) aliphatic acid and alcohol moieties, showing different isomeric distributions for compounds with odd and even carbon numbers (Figure 1).

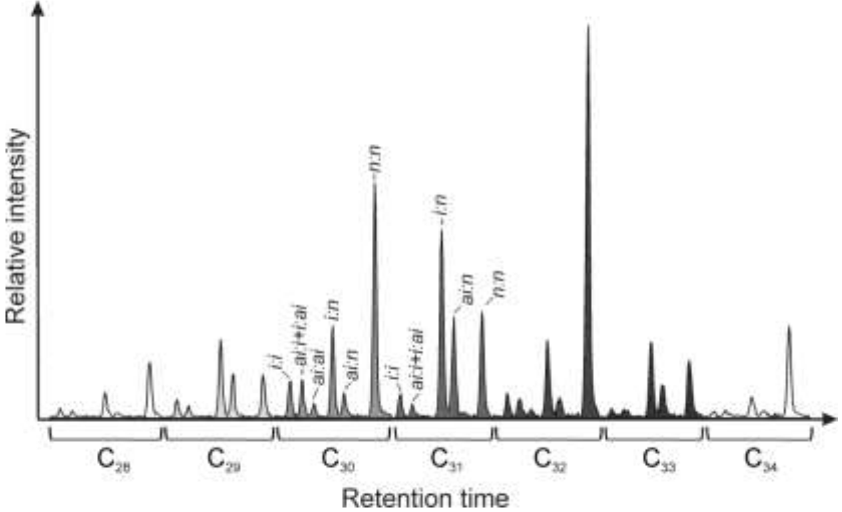

Figure 1. Partial chromatograms of molecular ions of C_{28}–C_{34} WE in a representative sample, showing the distributions of homologues.

WE concentrations in surface sediments vary from 0 to 741 µg kg^{-1} with a significant enrichment recorded at locations with high concentrations of organic nitrogen and total phosphorus and a relative high proportion of aquatic vs. terrestrial organic matter, all pointing to high primary productivity. In a 70 cm long core of rapidly deposited sediment WE concentrations decrease significantly with depth following first-order kinetics, suggesting a loss of WE within few years' time.

Cluster analysis of DGGE band patterns revealed different bacterial community compositions in up- and downstream surface sediments.

WE have seldom been investigated in rivers, but we speculate that they are markers for environmental stress. Which environmental conditions encountered in these sediments cause bacteria to generate wax esters remains, however, unclear.

Biotransformation of perfluorooctanoic acid by the action of microbial consortia isolated from sediment polluted with perfluorinated compounds

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Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are manmade chemicals that can be found in the environment because of their wide use in chemical production since 1950s. Their unique properties such as surface activity, water and oil repellency, thermal and acid resistance made them popular for usage in many industrial processes such as in protective coatings for textiles, carpets, leather, food containers and wiring insulations for telecommunications (Zareitalabad et al., 2013).

The focus of this study was to confirm biotransformation of Perfluorooctanoic Acid (PFOA) by the action of microbial community isolated from locations known for long term pollution with PFOA. Microorganisms that inhabiting polluted environment are already naturally adapted to higher concentrations of pollutant chemicals. For some of those microorganisms we can expect that they can metabolize some particular pollutant. For example, the microbial community from PFOA-polluted site is expected to biotransform/biodegrade PFOA.

For the isolation of microbial consortia, sediment samples from Osaka Ajifu Waterway known for long term PFOA pollution were used. PFASs content in the sediment sample were (ng kg^{-1} dw): PFBA 390, PFPeA 1100, PFHxA 2300, PFHpA 1100, PFOA 9500, PFNA 1900, PFDA 2600, PFUnDA 1500, PFDoDA 16000, PFTrDA 4600, PFTeDA 18000, PFBS <200, PFHxS <200, PFOS <200, PFDS <200, respectively.

For enrichment and isolation of microbial consortia three different media were used: for total chemoorganoheterotrophs Nutrient Broth; for hydrocarbon degrading microorganisms Bushnell Haas broth amended with *n*-heptane and for total yeast and molds Malt Extract broth were used. PFOA were added in all media, to stimulate growth of zymogenous microorganisms and to inhibit PFASs sensitive one.

Thermo Fisher Ultimate 3000 and Exactive LC/MS system was used in the untargeted analysis. Exactive was operated in negative-ion mode with a resolving power of 100,000. In all enrichments supplemented with PFOA, substances with negative mass defect were detected. It inferred that these ions had many fluorine atoms. Peak intensities of these compounds seemed to increase during the enrichment period suggesting relative increase in their concentration. Our study suggests that microbial community isolated from environment polluted with PFOA is a source of microorganisms who can conduct biotransformation of this emerging contaminant. However, further research is needed to confirm these data.

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Zareitalabad, P., et al., Chemosphere 91 (2013) 725-732.

POPs in Baltic Sea sediment: Archive of the past and source for the future?

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The Baltic Sea is polluted with POPs, and high levels in biota have been a matter of great concern during the last decades. Sedimentation is a major removal process for POPs from the water column, and large amounts are stored in sediment. Here we present data on POPs (e.g. PCBs and dioxins) in dated sediment covering the 20th century sampled at 12 areas in the Baltic Sea. POP concentrations have decreased drastically in Baltic Sea sediment since the peak years. The general trend in all sediment cores was an early increase in concentration starting in the 1940's-1960's in coastal samples, and 10-20 years later in offshore samples, followed by a peak concentration and thereafter a reduction (40-80%) until today. Temporal trends of PCB concentrations in coastal sediment followed the temporal trend of estimated global emissions of PCBs. PCB concentrations in coastal impacted sediment responded quickly to changes in global industrial use, whereas concentrations in offshore and reference sediment needed longer to respond. We also assessed the impact of sediment release of POPs on concentrations in perch at eight coastal stations in the northern Baltic Sea. This was done by using chemical activity ratios based on the freely dissolved concentration in pore water and bottom water. Activity ratios for dioxins were higher than 1 at all stations (27±22). The coastal sediments may therefore act as a source of dioxins to the water column. The concentrations of dioxins and PCBs in bottom water were significantly correlated with concentrations in sediment pore water and with concentrations in perch caught in the same areas. The results from this study demonstrate that continued efforts to reduce levels of POPs in coastal sediments will have positive effects on concentrations of these contaminants in lower trophic levels of Baltic Sea ecosystems.

Recent developments in methodologies for determining transport and chemical activity at the sediment-water interface

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The sediment-water interface can be a source of abiotic transfer of contaminants to the overlying water as well as a zone for contaminant exposure of benthic fauna and subsequently a source of contaminants to the aquatic food chain. This has led to an increased focus and research to determine both the contaminant activity gradient and the contaminant mass transfer across the sediment-water interface. Determination of sediment to water flux of persistent organic pollutants (POPs) are usually accomplished according to one of two methods: 1) direct flux assessment where a small part of the sediment surface is isolated (in situ or in the lab) and the amount of POPs diffusing out of the sediment surface is collected in an infinite sink material; and 2) determination of pore water and overlaying water concentrations (in situ or ex situ) followed by calculation of flux from the concentration difference and transfer rate.

Recent innovations to address challenges related to this include the design of two new field measurement tools. 1) A novel flow through flux chamber enabling measurement of flux while renewing the water inside the chamber in order to supply oxygen to the benthic fauna. A separate abstract is submitted describing this tool (Mustajärvi et al.). While our presentation will focus on: 2) A novel tripod pore water probe deploying passive samplers at different depth intervals both in the pore water and in the overlying water. The passive samplers are attached to a single rod penetrating the sediment bed to a predefined depth. The compact design of the probe ensures that the influence from the presence of the probe will have minimal effect on the overlaying water movements and therefore also minimal influence on the in situ sediment to water mass transfer coefficient and on the bioturbation activity of the benthic fauna. The novel tripod pore water probe is designed to be deployed at deep waters (used down to 120 m depth). The probe is also fitted with a releasable camera to monitor the deployment and document the penetration depth of the probe in the sediment. This makes it possible to determine which passive samplers have been exposed to the pore water and which to the overlying waters.

These new tools will allow for more detailed studies of POP flux and concentration gradients in the benthic boundary layer including the influence of hydrodynamics, bioturbation, particle re-suspension, and the particle water re-distribution of POPs.

Novel Brominated Flame Retardant, PBDE and HBCD contamination in sediments and biota from Lake Maggiore (Northern Italy)

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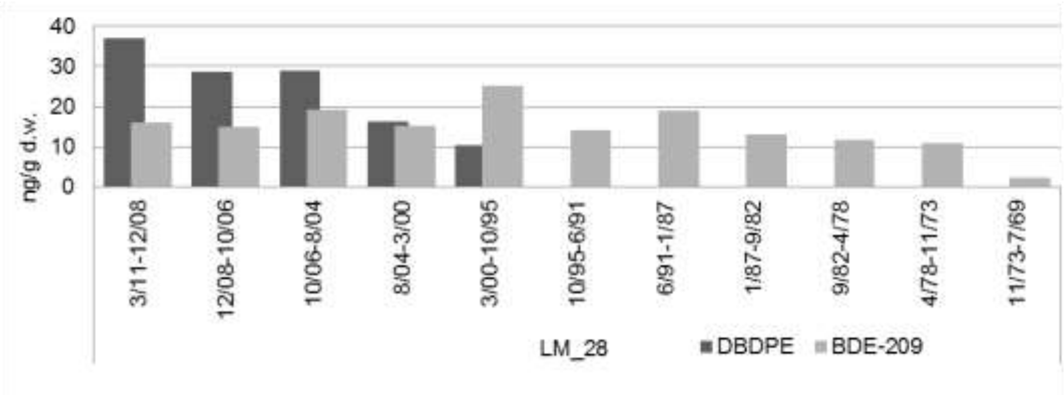
The reduction in the use of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) has opened the way for the introduction of “novel” BFRs (nBFRs) in place of the banned formulations. Important representatives of this group are decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), hexabromobenzene (HBB), and pentabromoethylbenzene (PBEB). Here, the contamination due to nBFRs, PBDEs, and HBCD has been investigated in the sediments from Lake Maggiore and its tributaries with the aim of characterizing in detail the possible presence of temporal trends and/or identifying potential sources of contamination. The positive correlation of DBDPE with BDE-209 confirmed the wide and important use of this compound in the Lake Maggiore basin and the hypothesis that this compound will soon become one of the most important nBFRs used in Northern Italy (figure below). Moreover, the spatial distribution and bioaccumulation potential of nBFRs, PBDEs, and HBCD in the Lake biota have been investigated in a littoral and a pelagic food web. With this purpose, the trophic level-adjusted BMFs (BMF_{TL}) and the Trophic Magnification Factors (TMFs) of BFRs were calculated and compared to each other. Results showed that, despite the high concentrations measured in the sediments of Lake Maggiore, DBDPE was below the detection limit in all the considered biological samples, probably because of its high log Kow value (Log K_{ow} = 11), which reduced the potential bioaccumulation in organisms. The calculated BMFs showed that tetra- and penta-BDE biomagnified, while octa-, nona-, and deca-BDE were still bioavailable and detectable in the fish muscles, but they do not biomagnified. Considering the other BFRs, only HBCD showed a moderate biomagnification potential. Finally, comparing the calculated values of BMF_{TL} and TMF, a significant positive correlation was observed between the two factors, suggesting that the use of BMF_{TL} to investigate the biomagnification potential of organic chemical compounds might be an appropriate approach when a simple food web is considered.



Pollutant distributions between sediments and the benthic water column in a deep lake: Application of passive sampling and GCxGC to less-studied and legacy halogenated contaminants in Lake Geneva

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The partitioning and concentration distributions of hydrophobic contaminants between the sediments and the benthic water column have not been investigated extensively for deep (>50 m) water bodies. These processes are difficult to study due to the analytical challenges of measuring trace level concentrations (i.e., pg/L) of the hydrophobic compounds in the water column, as well as the logistical hurdles of sampling at large depths. We analyzed both the benthic water column and the sediments of Lake Geneva in a location 1200 m from shore and 700 m from a wastewater treatment plant (WWTP) outfall. We employed the passive sampling methodology for the benthic water column (i.e., at 166.5 m water column depth, which was at 50 cm altitude from the sediment bed) for several less-studied and legacy halogenated contaminants. We also investigated contaminant loadings in sediments at three other locations in the lake, at depths ranging from 80 m to 310 m. Target analytes were quantified with GCxGC-μECD, and analyte detections were further confirmed using GCxGC-ENCI-TOFMS. We also employed the GCxGC retention times of target analytes to estimate several environmental partitioning properties, including organic matter-water partition coefficient, $K_{oc\text{-}w}$ (applicable to analytes having boiling point <400 °C). We were able to detect and quantify several less-studied hydrophobic halogenated contaminants such as pentachlorothiophenol, 4-bromobiphenyl, and tribromobenzene in both sediments and the water column, as well as several legacy compounds such as polybrominated diphenyl ethers (PBDEs) and organochlorinated pesticides (OCPs). We compared the observed sediment-water distribution with the estimated distribution based on equilibrium partitioning, computed using the estimated $K_{oc\text{-}w}$. Some of our target analytes such as PBDEs were found to be in partitioning equilibrium between the two compartments, whereas others (OCPs) were not. Potential origins of these discrepancies are discussed. The application of the passive sampling method and analysis by GCxGC enabled us to investigate several less-studied and legacy halogenated contaminants present at low concentration levels in the benthic layer and sediments of a deep aquatic system like Lake Geneva.

Legacy and (re)emerging persistent organic pollutants in Swiss lake sediments

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Global warming is recognized as a major global issue nowadays. In the present study the impact of global warming on the occurrence of persistent organic pollutants (POPs) in remote Alpine areas is investigated. We analyzed several legacy POPs, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and organochlorine pesticides (OCPs) in dated sediment cores from high-Alpine lakes in Switzerland.

Lake Oberaar, which is mainly fed by glacier meltwater from the Oberaar Glacier was the first lake to be analyzed and showed a surprising historical trend of POP concentrations. Concentrations of POPs peaked in the 1960s-1970s, which is in accordance with the global production, usage and emission history of these contaminants. However, after the late 1990s in Lake Oberaar a second distinctive peak of POPs was observed. To explain this trend, we suggested the glacier hypothesis, stating that the Oberaar Glacier is the source of POPs. Thus, POPs have been accumulated in the ice decades ago and are now being released at high rate due to the fast melting of the glacier.

To further confirm this hypothesis, we sampled and analyzed sediment cores from Lake Stein and Lake Engstlen, which are two close-by lakes located at a similar altitude, but differing in their water source. Whereas Lake Stein is fed by meltwater from the Stein Glacier, Lake Engstlen has no glacier in its catchment area. The comparison of POP time trends showed a noticeable increase of POPs in recent sediment layers from Lake Stein, while POP concentrations steadily decreased in sediments from Lake Engstlen. This contrast confirmed the glacier hypothesis.

Currently, in an interdisciplinary project, including the fields of glaciology, analytical chemistry, sedimentology, and environmental fate modeling, processes affecting these hazardous chemicals in temperate glaciers are investigated. We investigate POPs in the Silvretta Glacier. We quantify and model POPs in ice cores from the Silvretta glacier and sediment cores from the pro-glacial lake receiving ice meltwater.

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Implications of nanoparticles and nanoplastics in aquatic ecosystems

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Nanometer sized particles; either soot, black carbon, common organic colloids, manufactured nanomaterials, micro- and nanoplastics are known to be ubiquitous in the environment. It is well known that these particles bind hydrophobic organic contaminants (HOC) very effectively, with possible implications for environmental transport, environmental technologies and ecotoxicological effects. Much of this has been studied intensively the past decades, with increasing attention for sorption to fullerenes, carbon nanotubes and more recently micro- and nanometer sized plastic particles. The hypothesis that this association affects HOC transport or that such particles act as 'Trojan horse' is appealing, but how strong is the evidence that these carbon-based particles act as an important vector for transport of HOCs? Lately, the idea of microplastic acting as a vector for increased bioaccumulation in biota received a lot of interest form the scientific community as well as the general public. Plastic-associated chemicals may include HOCs absorbed from ambient water or chemicals that are native to the polymer like additives or monomer residues.

In this talk an overview of the recent insights with respect to sorption of HOC to carbon-based nanoparticles will be provided, as well as transport modelling of these particles. Because of the recent interests in the role of microplastic in the environment, the role of this material in transport and bioaccumulation will be discussed and emphasised.

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Today's status and future directions in the analysis of manufactured nanomaterials in the environment – Addressing challenges in the analysis of carbon nanoparticles in aquatic sediments and benthic organisms

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The emerging use of manufactured nanomaterials (MNMs) results in the increasing release of these materials into the environment. For persistent materials the major sinks will be soils and finally sediments. Our current inability to quantify and characterise these materials in sediments and sediment pore waters limits the reliability of environmental exposure and risk assessment of MNMs. In environmental media natural nanoparticles (NNPs), with similar size, shape and composition as their engineered analogues, are present in mass concentrations that are orders of magnitude higher than the PEC of all currently considered MNMs. It is mainly this background of naturally occurring nanoparticles that not only hampers the quantification of MNMs but also requires the identification and distinction of NMNs from their natural counterparts. The ubiquity of NNPs calls for the exploitation of properties of both, the NNPs and MNMs that would help to discriminate engineered and natural nanomaterials. Apart from the similarity to the existing background particles the complexity of environmental sample matrices and physiochemical processes altering the state of the MNM is complicating a fully quantitative assessment of MNMs concentration and state in natural waters and sediments. Although progress in developing capable analytical methods has been slow, it has also become clear that current analytical techniques can be implemented to overcome some of these obstacles. New methodological approaches, analytical concepts and improvements of existing methodology and analytical equipment allow for the distinction of engineered from natural particles in certain cases. While labelling with stable isotopes helps to investigate MNM behaviour at realistic environmental concentrations, the use of elemental ratios with FFF-ICPMS and single particle analysis (in ICP-MS or electron microscopy) enables the identification in natural media. These methods take advantage of the nature of MNMs to discern them from naturally occurring analogues. The presentation will review the current techniques utilised in the detection and characterisation of MNMs in water, soil and sediments. It will assess the current developments with respect to standardisation, the needs arising from the proposed definition of nanomaterials in the EU and the implications arising from implementations into regulation.

A wide variety of engineered carbon nanoparticles have been developed during the past several decades, for use in electronic, structural, and consumer applications. One of the most important classes of engineered carbon nanoparticles are single-walled carbon nanotubes (SWNTs). These nanoparticles are filamentous manifestations of a repeating aromatic carbon structure formed into an open cylinder. Because of their unique physicochemical properties and potential for large-scale commercialization, concerns have emerged over potential adverse effects of engineered carbon nanomaterials such as SWNTs in the aquatic environment. These concerns include direct toxicity to aquatic organisms as well as potential effects on distribution of hydrophobic organic contaminants (HOC) through adsorptive sequestration. This presentation will focus on a summary of work performed to date in my laboratory aimed at elucidating the analytical chemistry and environmental fate of these novel contaminants in aquatic sediments and benthic organisms. One of the most challenging problems we face in assessing fate of SWNT in the aquatic environment is the lack of reliable analytical methods for detecting these species in complex environmental samples. Near Infrared fluorescence (NIRF) spectroscopy has advanced as a highly selective and information-rich technique for sensitive detection and structural characterization of SWNT materials. We have combined asymmetric flow field flow fractionation (A4F) with NIRF spectroscopy as a promising tool for determination of SWNT in the environment. The combination of these two techniques allows trace (part-per-billion) detection and quantitation of SWNT in aquatic sediments and biota. In laboratory studies, we have observed that SWNTs can be stabilized in colloidal solutions by coating with natural organic matter, but that this stability is highly dependent on solution ionic strength. Increasing ionic strength leads to aggregation of SWNTs as well as deposition of these materials to suspended particulates. In addition, SWNTs adsorb HOCs strongly from aqueous solutions. Taken together, these results indicate that these carbon nanomaterials will associate strongly with sediments in aquatic systems, where they may become important in modulating fate of co-occurring molecular contaminants. Results of laboratory microcosm and field mesocosm studies are fully consistent with these findings. However, both laboratory experiments and mesocosm studies have shown that benthic organisms do not significantly bioaccumulate SWNT after exposure to contaminated sediments. The implications of our findings will be interpreted in context of potential hazards posed by contamination of aquatic systems with SWNTs.

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Sediment enrichment with TiO_2 engineered nanomaterials from the use of sunscreens

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Engineered nanoparticles (ENPs) are used in consumer products and are released in the environment in which they are likely to participate in biogeochemical reactions that may have adverse environmental effects. Predicting the fate and reactivity of the ENPs in an environmental system is a challenging task that incorporates a great deal of assumptions. In order to accurately determine the fate of ENPs released in natural systems, it is necessary to develop methods for measuring them in real-world systems.

In this work, we study the release of TiO_2 ENPs from sunscreens into surface waters during bathing activities. We use previous lab-scale studies to predict the fate of TiO_2 ENPs and then test several methods for detecting them in the environment. The Old Danube Lake in Vienna, Austria was used for our study, due to its intensive use for bathing activities by the Viennese people during the summer, combined with low water inflow and outflow rates. In order to quantify the release, we first used a mass-based approach: we studied temporal trends of Ti elemental ratios in bulk samples from the lake's suspended matter over a period of 18 months. In addition, we studied spatial and temporal trends of Ti elemental ratios in the sediments of the lake.

Our mass-based analysis indicated the release of TiO_2 ENPs during the summer season, most likely from the use of sunscreen and its wash-off during bathing activities. However, the increase of Ti elemental ratios was not linear during the summer, indicating simultaneous release and removal of the particles from the water column, likely caused by hetero-aggregation and sedimentation of the particles. Bulk elemental analysis of sediment samples collected throughout the lake's area revealed pockets with increased Ti elemental ratios. Analysis of sediment cores also revealed increasing Ti elemental ratios with time. Our results demonstrate that settling on the lake's sediment is the most likely fate of the TiO_2 ENPs and sediments are the ultimate sink for this type of ENP in the studied system. However, their presence there is overwhelmed by a plethora of naturally occurring Ti-bearing particles.

Agglomeration and dissolution of Ag and TiO_2 nanoparticles – Nanoparticle accumulation in sediments ?

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Engineered nanomaterials may reach natural waters during their production, transport and use. The fate of these engineered nanomaterials in natural waters depends in particular on agglomeration, leading to formation of larger agglomerates, and on dissolution processes, by which metal ions are released into solution. These processes will determine to which extent engineered nanoparticles introduced in natural waters may agglomerate and settle to the sediments.

Under conditions close to those of natural waters, silver nanoparticles (AgNP) agglomerate to different extent depending on their coating and on the concentrations of Ca^{2+} ions and of dissolved organic matter (Topuz et al. 2014). TiO_2 nanoparticles strongly agglomerate under the same conditions and rapidly reach larger particle sizes over 1 µm.

AgNP can dissolve by oxidation to Ag(I), as a function of pH, presence of ligands such as chloride, thiols, dissolved organic matter, and of oxidants. Dissolved Ag(I) includes Ag^+ ions and complexes with the available ligands. Dissolution experiments of AgNP under conditions of a range of natural waters with different composition illustrate the influence of these various factors (Odzak et al. 2014). In contrast, the solubility of TiO_2 is extremely low and is not expected to be relevant under natural water conditions.

On the basis of these experimental data, the fate of nanoparticles with respect to accumulation in sediments and to chemical transformations under the prevailing conditions in sedimentary environments will be discussed. In the case of TiO_2 NP, agglomeration is expected to lead to rapid settling to the sediments without further chemical reactions. In contrast, AgNP may undergo various transformation processes by dissolution and surface reactions and may finally reach the sediments as precipitates of various composition. The conditions in the sediments (oxygen content, pH, organic matter) will influence the fate of engineered NPs and lead to aging processes of the nanoparticles, which will affect their reactivity.

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DDT and Hg contamination of Lake Maggiore (Italy): historical trends and studies for evaluating the on-site bioavailability (use of passive samplers and benthic invertebrates)

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The DDT and mercury contamination of Lake Maggiore, the second-largest Italian lake, was caused by a factory producing technical DDT and using a mercury-cell chlor-alkali plant. The factory discharged its waste water in the River Toce from 1948 to 1986. In this study a 10-year monitoring campaign (2001–2011) studying sediment core profiles was undertaken to track the actual DDT and Hg contamination of the lake and to reconstruct the historical trend from 1950 up to now.

Background Hg levels in the region can be referred to geochemical origin (0.05–0.01 mg kg^{-1} d.w.) and to gold mining activities.The huge DDT contamination of Pallanza Basin sediments collected in 2001 was considered strictly in agreement with the exceptional flood event of the Toce River registered in October 2000. During the alluvial events of the Toce River (1993 and 2000), *p,p'*-DDT concentrations in sediments prevailed on those of metabolite ones, reaching 50-80% of the ΣDDT levels. The mean concentrations measured in 2001 for ΣDDT in sediments exceeded the North American sediment quality guidelines, showing a high possibility of toxicity for benthic community, while an increased sediment quality was estimated in recent sediments (2007/2011). Mercury levels in the Pallanza basin show a range of 0.2–4 mg kg^{-1} d.w., with a peak up to 4.13 mg kg^{-1} d.w. in 2005-2007 due to a high hydrological event, showing that the Toce can still drive contaminated sediments (up to 1 mg kg^{-1} d.w.) to the lake.

In recent year (2008-2013) new environmental studies were undertaken both using passive samplers (PE and SPMD) for DDT and two representative taxa of lacustrine macrobenthos (oligochaetes and chironomids) for evaluating the on-site bioavailability of contaminants for aquatic organisms.

Particularly SPMD filled with triolein and PE (Polyethylene membrane) loaded with PRC (Performance Reference Compounds, i.e. labelled-DDx compounds) were used for calculating DDT concentrations in water (surficial or upper sediments) and in pore water of sediments in different stations in the Lake Maggiore. The time-integrated response of passive samplers (10-28 days) overcomes the variability often associated to water monitoring campaign and clearly evidences the mean water concentrations.

At the end the use of biological indicators as native benthic invertebrates showed to be a powerful approach to evaluate on-site bioavailability. Different taxa may be used according to their ecological traits and trophic role in the aquatic foodweb. Oligochaetes and chironomids are very abundant in Lake Maggiore and are indicators to specific environmental condition of sediments, showing a different capacity to bioaccumulate according to organic carbon content, Redox conditions, chemical speciation or biodegradation of contaminants, ect..

Characterization of DDT and Mercury contaminated sediment in Toce River and Lake Maggiore (Pallanza Bay)

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A DDT manufacturing facilities settled in the first half of 1900 along the River Toce, about 20 km from Pallanza Bay (Lake Maggiore). DDT production started in the 1940s and ceased in 1996, when Italian authorities required investigation to evaluate distribution of DDx and mercury in sediments.

In order to evaluate potential environmental risks and to assess the need for sediment remediation, ENVIRON, on behalf of Syndial, proposed an extensive characterization plan. The characterization plan was approved by the Italian Environmental Ministry, that charged ARPA Piemonte (Regional Agency for Environmental Protection of Piemonte) to validate the environmental investigation and analytical results. In 2009-2013 several field following activities were organized and performed by ENVIRON, under supervision of ARPA Piemonte and in collaboration with researchers from the Italian National Center for Research (CNR-IRSA, CNR-ISE):

- chemical concentrations were investigated at various depths in 130 sediment cores. To collect high quality sediment chemistry data, a lightweight sediment-water interface gravity corer was used on silty sediment in the lake Maggiore. Near the mouth of the River Toce, with presence of sand and coarse sediment, an innovative method was used: for the first time Piston Cores were performed in a lake with the “Angel Descent” method;
- sediment toxicity to invertebrates was studied testing field collected sediment on several species: tests were performed using commercial lab (Springborn Smithers) and lab facilities of ARPA/CNR-IRSA, to validate test results;
- an ecological survey was performed investigating seasonally site-specific invertebrate community. The taxonomical evaluation was performed by the University of Milan, and reviewed by researchers from CNR-ISE;
- bioaccumulation was investigated evaluating tissue concentrations in several fish species and field collected benthic organisms. As further investigation, bioaccumulation tests were performed by ARPA/CNR-IRSA, that exposed oligochetes (*L. variegatus*) to field collected sediments;
- bathymetric and morphologic surveys were performed and hydrodynamic parameters were measured to implement a sediment transport model, to understand system variability under different hydrological scenarios;
- radiodating analyses were undertaken to better understand sediment accumulation rates and to examine historical trends in chemical loading;
- a Sediment Profile Imaging (SPI) camera survey was performed throughout Pallanza Bay and mouth of Toce River to investigate gradients in sediment grain size, transport patterns, geochemical processes, and benthic community dynamics.
- This presentation provides a summary of the approach adopted to characterize sediments, with focus on data collection methods used and perspectives on results evaluation (still ongoing).

Field assessment of natural attenuation from DDT in Pallanza Bay, Lake Maggiore

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Natural attenuation processes from DDT-contaminated sediment in Pallanza Bay, Lake Maggiore, Italy, has been quantitatively assessed with in situ measurements. Field studies have been carried out using a toolset comprising sediment traps, benthic chambers, and innovative passive sampling devices. Sediment transport in the Bay is mainly driven by large flood events, which convey and deposit sediments from the Toce River into the Bay. Sediment deposition within the Bay appears to be relatively clean of DDT and concentrations are two orders of magnitude less than average sediment concentrations in the top 10 cm of the bioactive layer in the Bay. Therefore, deposition of new sediment should facilitate natural attenuation by burying the older and more contaminated sediment.

The results provide evidence that natural attenuation processes are occurring within the Bay and is characterized by different sediment depositional behavior due to currents and morphology. These observations are based on DDT concentration profiles and concentration gradients in the sediment and water near the sediment surface. Aqueous concentrations in the overlying water were measured to be below 1 ng/L and below EU Water Framework Ecological Water Quality Standards of 25 ng/L [1].

Field measurements will continue to measure these processes and refine our understanding of recovery processes for Pallanza Bay.

[1] Directive of the European Parliament and of the Council 16 December 2008. Environmental Quality Standards.

Environmental risk assessment of bottom sediments: unfounded claim or actual perspective?

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What is an “environmental risk”? Does the widely accepted definition of risk, i.e. a combination of *hazard* and *probability of exposure*, fit with sediment risk assessment practices? Based on a literature review as well as on the author’s personal experience, this presentation will critically review some sediment assessment tools, such as sediment quality guidelines, and their uses, or sediment assessment frameworks. In several respects, it seems rather clear that the self-declared sediment risk assessments described in many papers or guidance documents are mostly focusing on hazard assessments. Very few manuscripts explicitly addressed the issue of exposure, and those which did, e.g. (Johnston et al., 2002) or (Babut et al., 2006), developed a qualitative or semi-quantitative approach, and did not provide a probabilistic assessment of exposure.

That said, what is needed in a management perspective? In other words, is the theoretical definition of risk critical for making a management decision targeting (contaminated) sediments? Approaches allowing to clearly and consistently relate assessment endpoints and management options appear more important, along with a thorough assessment of the sources of uncertainty.

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Bio-analytical strategy based on *in vitro* and *in vivo* bioassays for effect-based monitoring of bioactive organic chemicals in river sediments

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It is now widely accepted that chemical analysis of selected priority pollutants, provides an incomplete view of environmental chemical contamination as regard to thousands of compounds occurring in aquatic systems. Bio-analytical approaches combining effect-based and chemical tools allow a more integrative characterization of contamination and identification of key pollutants that contribute to adverse effects (e.g. endocrine disruption, developmental effects) on exposed organisms.

In the frame of a large French screening study on surface waters in 2012, we used *in vitro* (reporter/natural gene response in cultured cell lines) and *in vivo* (gene response in zebrafish embryos) mechanism-based bioassays to establish toxicological profiles. Such effect-based diagnosis was then compared to chemical analysis of selected pollutants.

We apply this strategy for the monitoring of dioxin-like (DL) chemicals in sediments by establishing bioassay-derived TCDD equivalents (Bio-TEQ). First, *in vitro* screening showed ubiquitous contamination of French rivers by DL chemicals with activity levels similar to those reported in several European rivers (1-100 ng TCDD-EQ/g d.w). Then, targeted chemical analyses demonstrated only partial contribution of the priority PAHs to the DL activity (< 30%). Finally, *in vitro* DL activity was confirmed at the whole organism level using living zebrafish embryos with similar site ranking on the basis of in vitro and in vivo bio-TEQs. In addition, abnormal developments were also reported in embryos after exposure to the most active extracts. Altogether these results support the integrated use of *in vitro* and *in vivo* mechanism/effect based tools. Such findings argue for the further establishment of hazard threshold values for DL activity in sediments.

In addition, the toxicological assessment was extended to the detection of endocrine disruptors acting on either estrogen (ER), androgen (AR), glucocorticoid (GR) and pregnane (PXR) receptors using *in vitro* assays. Such profiling allowed to classify and identify hotspot polluted sites where *in vivo* effects were investigated; the identity of responsible compounds is under investigation using effect-directed analysis approach.

Overall, this study demonstrates the usefulness of effect-based profiling as a complementary approach to current regulatory chemicals analyses for the monitoring of chemical quality status in the frame of the water framework directive.

Sediment contamination and its negative influence on the macro-invertebrate community of a chalk river in Western Europe

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Since 2009, the Loue river, a famous trout and grayling chalk stream of northeast France, has been affected by repeated increased fish mortality and loss of macro-invertebrate diversity and density. Water quality assessment carried out so far did not provide evidence for an increase in pollution levels. Hence, the water quality is likely not the reason for the observed recent fish mortality. In this study, we tested whether insoluble chemicals trapped in river sediments could be involved in the decrease of macro-invertebrate diversity and density.

For this aim, ten sites situated along the first 60 kilometers of the river were studied. For each site, three sediment samples were collected and screened for different molecules separately. In parallel, quantitative macro-invertebrates samples were collected from the same sites and the abundance and diversity of the community were assessed. Taxonomic identification was performed at family and if possible at genus level. The Plecoptera, Ephemeroptera and Trichoptera were all determined at genus level and used to calculate a biodiversity score.

The sediment screening showed that eight out of the ten sites were contaminated by pesticides. Main contaminants were chlorpyrifos, permethrin, deltamethrin and cypermethrin. In some cases, sediment concentrations of cypermethrin and deltametrin reached values that can affect macro-invertebrate communities. For example, the concentrations that cause acute toxicity to the amphipod *Hyalella azteca* were significantly exceeded at several sites.

Importantly the correlation between the macro-invertebrate biodiversity score index and the level of toxic contamination of the sediment was negative and significant. Hence the level of sediment pollution is strongly correlated with the diversity and the abundance of macro-invertebrates, suggesting that pollution has a strong impact on the aquatic fauna of the Loue river.

Biodynamic modelling for contaminated sediments- a readily transferable tool to regulation?

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Sediments have several characteristics that make them a demanding environmental compartment to study. The large heterogeneity in its nature and composition encompasses a large variability in bioavailability and toxicity, challenging the development of environmental quality standards and effect concentrations for effective risk assessment. For a single organism a large range of effect concentrations may be measured for sediments having the same total concentrations depending on sediment properties [1]. A proposed alternative is to use as dose metrics a measure of internal exposure such as bioaccumulation because, for a contaminant to cause toxicity, it is assumed that it must be first taken up and accumulated by the organism.

For most organisms living in close contact with the sediment overlying water, pore water, sediment contact and diet all may contribute to some extent to the total load of a chemical substance in the body of the organism. Thus effective risk assessment for this environmental compartment should ideally use models that are capable of aggregating exposure through all relevant routes, taking into consideration species-specific biological features and natural history, and site-specific physico-chemical characteristics [2,3].

All these processes are captured when applying biodynamic approaches. Biodynamic processes have been translated into conceptual and quantitative models that are capable to explaining differences in bioaccumulation patterns among species and environments for several metals [4]. Indeed, it is possible to derive net bioaccumulation predictions at a location as well as estimations of the relative prevalence of exposure routes by combining the quantified constants describing physiological processes with site-specific concentrations and geochemical conditions [4]. While biodynamics has become the new paradigm for describing bioaccumulation among scientists, it is recognised among the regulatory community as a promising powerful tool for improving ecological risk assessment [3].

In the particular case of the sediment compartment, the use of biodynamic models is especially complex due to the differences in feeding and digestion strategies among benthic organisms and also due to the difficulty to determine ingestion rates and feeding preferences [5]. The advances achieved over the last years will be reviewed to discuss on whether this level of development is enough for the implementation of this concept as a praxis-oriented tool for the sediment compartment and its potential ecotoxicological and regulatory implications.

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Restoration of a PCB contaminated river: effect on Lake Bourget?

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Lake Bourget is the largest natural lake in France. Like most peri-alpine lakes, the growing urbanization of its watershed from the beginning of the XXth century was associated to the dramatic degradation of its ecological health in the 1950'. The control of anthropogenic nutrients and organic matter inputs from the watershed, and the protection of the lake from direct wastewater treatment plant discharges were achieved in the 1980'. However, there was still a major problem with PCB contamination in the 2000', and local consumption advisories and bans of some fish species (artic char, bream, roach and eel) are still enforced. The PCB pollution of the lake is due to the historical contamination of the river Tillet by an electric transformers factory located in the watershed. The industrial site and the upstream-bed were first restored in 2008. The upper river-bed was partially decontaminated by sediment scrapping, but PCB flux was still high enough to modify the lake water quality. Recently, the downstream-bed has been entirely decontaminated with the creation of a new bed river and in-situ granular activated carbon amendment.

In this context, before and after the river depollution, we measured the PCB fluxes to the lake to study the effects on sediment biofilm composition, aquatic invertebrates and fish's contamination. Before restoration, the Tillet sediment was contaminated up to 1500 µg/kg DM of PCB. The suspended solids in the river contained 1300-2000 µg/kg DM during dry weather and 3000-5000 µg/kg DM of PCB during stormy period. The remobilization of sediment and the erosion of banks during floods dramatically increased the PCB flux to the lake. Body residue analysis in indigenous invertebrates or in caged species (*Chironomus riparius*, *Gammarus fossarum* and *Daphnia magna*) exposed at different seasons revealed that ambient PCB concentrations in the river were highly bioavailable and thus represented a real risk for trophic transfer toward fishes. The river restoration took place from January 2013 to November 2013. Present PCB concentrations in the bulk river water, sediments and fishes demonstrated the achievement of the remediation works. The macroinvertebrate community of the river appeared less impaired, with an increase in the relative density of TEP (*Trichoptera*, *Ephemeroptera*, *Plecoptera*) from less than 1% before restoration to more than 10 % in June 2014. PCB concentration in *Coregonus lavaretus,* an endemic lake Bourget fish, significantly decreased from February to October 2014.

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Ecological effects of thin-layer capping with activated carbon on benthic macrofaunal communities - The other side of the coin

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Remediation of contaminated sediments *in situ* using thin-layer capping with carbonaceous materials (CM) such as activated carbon (AC) is a recent technique that has proven successful in reducing the bioavailability and sediment-to-water transfer of hydrophobic organic compounds e.g. PCBs, PAHs and dioxins by several orders of magnitude. Thin-layer capping with CM could offer an efficient remediation technique, especially in larger contaminated areas, where conventional capping or dredging is not an option. A prerequisite to any sediment remedial action, however, is that its benefits in reducing contaminant bioavailability are not concomitantly leading to negative ecological effects on the benthic community. Most capping studies with CM have reported no- or mild effects on benthic organisms. These studies have generally been done in laboratory conditions or in highly contaminated field sediments with already severely disturbed benthic communities. In our studies we have tested the effects of various CM and mineral materials on marine coastal benthic communities using: 1) single species 10-day toxicity tests; 2) long-term mesocosm experiments with intact sediments including native micro- meio- and macrofaunal organisms; 3) large-scale studies in the field. Our results from the 10-day toxicity tests showed no toxic effects on benthic fauna, only avoidance reactions in some organisms like increased swimming were observed. In the mesocosms and the field experiments, however, severe effects on the benthic community were observed following capping with AC. Capping with mineral materials only (e.g. clay, sand, limestone) usually had mild and transitory effects, whereas capping with AC led to a ca 50 % reduction in both species abundance and diversity. The severity of the effect of AC increased with time and was still evident 4 years after capping. In this paper we summarize our major results on the effects of thin-layer capping on benthic communities. We also try to relate the negative effects of capping with AC to the various ecological traits of the benthic species (eg feeding and bioturbation modes) in order to get a better understanding of the mechanisms behind the observed toxicity.

A genetic contamination? Wastewater as a point source of antibiotic resistance genes in the sediment of Lake Geneva

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Antibiotic-resistant bacteria and the genes conferring antibiotic resistance (ARGs) are currently discussed as emerging environmental contaminants. Wastewater can be an important source of ARGs for the receiving aquatic environments. We investigated the resistance load in the wastewater of Lausanne and other Swiss wastewater treatment plants and found that treated wastewater contributes significant amounts of resistance to the receiving environments. Based on these results we analysed the spatial distribution of different ARGs (*sul*1, *sul*2, *tet*(B), *tet*(M), *tet*(W) and *qnrA*) in Lake Geneva sediments in the vicinity of a point source of treated wastewater. We found that the total and relative abundance of ARGs in close proximity to the sewage discharge point were up to 200-fold increased compared to levels measured at a remote reference site (center of the lake) and decreased exponentially with distance. Similar trends were observed in the spatial distribution of different ARGs. We also compared the ARG contamination with Mercury levels, another wastewater-derived contaminant. While both types of contamination show clear spatial relationship to the wastewater discharge point, the distributions of ARGs and THg were only moderately correlated, indicating differences in the transport and fate of these pollutants or additional sources of ARG contamination. The spatial pattern of ARG contamination and supporting data suggest that deposition of particle-associated wastewater bacteria rather than co-selection by, for example, heavy metals was the main cause of sediment ARG contamination. The observation of accumulation of antibiotic resistance genes in sediment raises questions how risks associated with this kind of contamination should be evaluated, and how the dissemination of antibiotic resistance factors with wastewater can be reduced.

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Czekalski, N. et al. Wastewater as a point source of antibiotic resistance genes in the sediment of a freshwater lake. ISME J (2014.

Endocrine disrupting chemicals in coastal lagoons of the Po River delta: sediment contamination, bioaccumulation and effects on Manila clams

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Characterized by limited biotransformation activities and tolerating high accumulation levels of xenobiotics, bivalves are widely used as “bioindicator species”. Among them, the clam *Ruditapes philippinarum*, imported in the Venice lagoon in 1983, quickly spread along Adriatic coasts, leading Italy to become the first European producer of this organism. The lagoons located in the area of the Po River delta host some of the most important aquaculture systems for *R. philippinarum* in Italy, with a mean farming density of 500 individuals/m^2. These coastal lagoons receive freshwaters but also contaminants from the Po River, which drains the most densely populated and productive regions of Italy (Casatta et al., 2015). Despite being exposed to such chemical transport, there is a substantial lack of information on the presence of emerging and priority chemicals, and on the risk they may cause to human health and the environment. Accordingly, the present work investigated contamination and effects of legacy and emerging contaminants in clams exposed for three months to the sediments of six coastal lagoons (Caleri, Marinetta, Barbamarco, Canarin, Scardovari and Goro) of the Po River delta. To this aim, a sample drawn from a common stock of *R. philippinarum* was exposed *in situ* in each lagoon during gonad development and maturation. Patterns of sediment contamination and clam bioaccumulation of metals (Cd, Cr, Ni, Hg, Cu, Zn, Pb, As), PBDEs, DDTs, PAHs, PCBs and alkylphenols were inferred, suggesting a spatial trend of contamination potentially related to river transport. Stress response in clams was investigated in terms of biometric indicators, histology and gene expression on ecotoxicological target *loci*; trends were related to exposure level. Moreover, the interaction of local environmental conditions within each lagoon with contaminants bioavailability in shaping stress response was unravelled. Potential implications for clams farming management were also discussed.

Casatta N, Mascolo G, Roscioli C, Viganò L. (2015) Tracing endocrine disrupting chemicals in a coastal lagoon (Sacca di Goro, Italy): sediment contamination and bioaccumulation in Manila clams. Science of the Total Environment, In Press.

Impact of local and global metal contaminations on microbial communities of Pyrenean lakes

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Mountain lakes are both a natural heritage of the Pyrenean massif and natural receptors allowing the detection of global changes or anthropogenic contaminations. Recent studies showed that the integrity of this heritage is threatened either by metal deposition from the atmosphere, either by metal contamination from past mining activities. Unfortunately, to date no study has been undertaken to determine the consequences of such contaminations on the biodiversity and functioning of these ecosystems. Because of their critical ecological role in lake ecosystems (i.e. biogeochemical recycling of major nutrients), metal's impacts on microbial communities (ie Bacteria, Archaea and microeukaryotes) may potentially have system-wide implications. Hence, the primary goal of the work described here was to compare microbial community structures in water column and sediment samples collected from mountain lakes with differing levels of metal contamination. Our results showed that some heavy metals and metalloids concentrations such as As, Cd, Cu and Pb were way above ecological risk indices in most locally and atmospherically impacted lakes. In agreement, we observed an erosion of the biodiversity in atmospherically contaminated lakes. We also found that metals, and particularly Pb, Zn, Sb and Tl, had a greater effect on microbial community composition than physico-chemical or geo-morphometric parameters. This was particularly true for eukaryotic assemblages, which seemed less resilient than prokaryotic assemblages. Overall, we identified for each domain of life potential biomarkers of metal contaminations. These results suggest that anthropogenic metal contaminations reaching mountains lakes have modified the biodiversity of these remote habitats and potentially altered the ecological services they sustain.

Temporal records of organic contaminants in lake sediments and their impact on *Daphnia* populations

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Currently, there is little knowledge about the influence and/or adaptation of aquatic organisms on the increase or decrease of organic pollutants. Analysis of the genetic architecture of *Daphnia* resting eggs (ephippia) from Lake Greifensee revealed that lake eutrophication was associated with a shift in species composition and population structure. However, whether the shift in species composition was directly caused by phosphate or if phosphate concentrations are only a proxy for other parameters like chemical contamination is not known. Measurements of emerging contaminants such as pharmaceutical and personal care products started in the 1990s, thus the exposure before this time is not well studied. Therefore a comprehensive screening analysis using liquid chromatography- high resolution mass spectrometry (LC-HRMS/MS) was performed on dated sediment extracts between 1950 and 2010 obtained from Lake Greifensee located in the north of Switzerland with the aim to reconstruct the environmental contamination of the lake and provide records of anthropogenic impact. In addition, the effect of selected compounds found in the lake was assessed in experimental studies using resting eggs produced by the *Daphnia longispina* species complex, key species in large lake ecosystems. Experimental determined bioconcentration factors (BCF) show that personal care products, pesticides, pharmaceuticals, and biocides can be taken up by ephippia from the water column or the pore water in the sediment. Based on the sediment concentrations and BCF values, estimated internal concentration (C_{lip}) were calculated with triclocarban having the highest internal concentrations, followed by tonalide and triclosan. Maximum C_{lip} are observed in the 1970s with a correlation between the highest C_{lip} of organic contaminants and highest phosphorus concentrations. Additional laboratory experiments showed an increase in mortality and developmental abnormalities for hatchlings in the exposure treatments and a significant increase in hatching success in the exposed resting eggs compared with controls. Such an effect has not yet been reported from ecotoxicological assays with resting eggs. The significance of this study lies in the ability to provide present and historic records on the occurrence and fate of a wide range of organic contaminants with different physicochemical characteristics and to provide insights to understand the potential impact of organic contaminants on aquatic organisms relying on resting stages during their life cycle.

A Mixture of Environmental Organic Contaminants in Lake Sediments affect Hatching of *Daphnia* Resting Eggs Markus Moest, Aurea C. Chiaia-Hernandez, Martin P. Frey, Juliane Hollender and Piet Spaak. Environ Toxicol Chem., 2014 2014; 9999:1–8
Bioaccumulation of Organic Contaminants from Sediments in *Daphnia* Resting Eggs
Aurea C. Chiaia-Hernandez, Roman Ashauer, Markus Moest, Tobias Hollingshaus, Piet Spaak and Juliane Hollender. Environ. Sci. Technol., 2013, 47 (18), pp 10667–10675

Sediment remediation with activated carbon and biochar – immobilization mechanisms and large-scale field tests in Norway

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Activated carbon (AC) and biochar can bind many organic pollutants so strongly that their bioavailability and risk are strongly reduced. This binding is 100 to 1000 times stronger than binding to humic, amorphous organic matter, and occurs for a wide array of organic compounds.

Three important aspects of AC sorption are the following. First, sorption to "clean" AC is 10-100 times stronger than sorption to "environmental" AC in water, soil or sediment, because natural organic matter fouls the AC surface. Second, the sorption to AC is strongly nonlinear; because of a limited number of sorption sites, it is much stronger at low concentrations than at high ones. Third, mass transfer from contaminated sediment particles to the AC may be so slow that full effectiveness is only reached after years to decades.

Two large-scale field tests will be presented. In Trondheim, Norway, we tested powdered AC alone or in combination with sand or clay as a thin-layer capping material for PAH-contaminated sediment. Several novel elements were included, such as measuring PAH fluxes, no active mixing of AC into the sediment, and the testing of new manners of placing a thin AC cap on sediment, such as AC+clay and AC+sand combinations. *In situ* sediment-to-water PAH fluxes were measured using recently developed benthic flux chambers. Compared to the reference field, AC capping reduced fluxes by a factor of two to ten. Pore water PAH concentration profiles yielded a reduction factor of two to three compared to the reference field. Effects of the AC on the benthic macrofauna composition and biodiversity were more modest for AC+clay than AC-only or AC+sand.

In the Grenlandfjords, Southern Norway, the authorities are trying to find solutions for an extensive dioxin contamination (53 km2). A large-scale remediation trial was set up where activated carbon was added as a thin-layer cap. Thin layer capping with activated carbon showed an increasing effectiveness in time, with up to 85% reduction in dioxin fluxes after 5 years and up to 90% reductions in chemical availability (in situ passive samplers) and biological availability (bioaccumulation).

The role of physical sedimentology in the context of chemical contaminations

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Depositional processes and lithologic composition of a sediment define the predisposition of a sedimentary system to become contaminated if a pollution were to occur in the watershed. Knowledge of the sedimentary processes and of the major sediment constituents are essential in evaluating and understanding a contamination. Especially important are postdepositional processes that may redistribute the toxic substances and eventually re-contaminating the water body. The spatial extent of a contaminated layer can only be addressed by a thorough investigation of the depositional basin or sedimentary system, ideally by using geophysical methods. This knowledge will provide ideal sampling locations, as single sites or unsuitable sampling sites will result in a wrong or misleading pollution assessment.

Various contaminants have variable affinity to be attached to the different classes of lithologic components, i.e. with organic vs. inorganic particles. Changes in lithologic composition thus may alter the potential of a sediment to serve as a host for a contamination, requiring thorough lithologic knowledge when assessing pollution on a source-to-sink scale. The pathway of a contaminant through the spheres (atmosphere, hydrosphere, cryosphere) into the lithosphere moreover often includes the biosphere.

Sediment dating and the interplay between continuous and episodic sedimentation needs to be taken into account, when attempting the reconstruction of timing and sources of contamination. In such studies, sediments provide the unique opportunity to establish time series of pollution, even back to prehistoric times, when first human-environment interaction took place. A series of sediment archives and their pollution histories will be presented, which document the potential and challenges of sediment-based reconstructions of contamination processes.

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Sub-surface oil plumes, sedimentary oil deposition and other unexpected consequences and impacts in the aftermath of the Deepwater Horizon oil-well blowout

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The *Deepwater Horizon* (*DWH*) oil-well blowout was unprecedented in nearly seven decades of global marine oil exploration and production. The DWH event in the northern Gulf of Mexico released ~5 million barrels of liquid hydrocarbons over a duration of 87 days. Although there have been many large marine oil spills in the past, including tanker accidents and the shallow marine IXTOC-1 blowout off Mexico none has occurred at such extreme depths (1,500 meters), pressures (150 bars) and low temperatures (4˚C). These unique deep-water physiochemical conditions resulted in the chemical partitioning of rising hydrocarbons leading to the formation of a large subsurface hydrocarbon plume comprised of dissolved and microdroplets of oil between 900-1300 meters depth and the development of a large slick of surfacing oil extending from the offshore to coastal regions. Because of these novel aspects, mitigation efforts were designed primarily using expert opinion instead of a firm basis in peer-reviewed science. Examples of response decisions suffering from this lack of basic science include the use of large quantities of dispersants at the well head and on the surface, burning of surfacing oil offshore, and the freshwater releases from the Mississippi River and its diversionary channels to push back or dilute oil coming ashore in sensitive marsh areas. Utilizing a high-resolution approach to the analyses of pre- and post-DWH blowout sediments, this study delineates: a) the sedimentological and organic geochemical inputs, and redox-metal chemical and benthic faunal and habitat impacts of a deep-water petroleum blowout, b) the mechanisms of sedimentary oil deposition, c) the role of oil spill response strategies in augmenting sedimentary oil deposition and its „footprint“.

In the aftermath of the DWH we document an order of magnitude increase in sediment mass accumulation rates and a region-wide decrease in sediment grain size. In this interval, accumulation rates of Polyaromatic Hydrocarbons (PAHs) increase by 300-fold including petrogenic and pyrogenic sources. Within the blowout region, coherent spatial and temporal patterns of changing sediment accumulation rates, sediment texture, hydrocarbon sources, sediment redox conditions and benthic faunal abundance and diversity emerge to document the mechanism(s) responsible for and the geographic and depth-related constraints on sedimentary oil deposition. The primary hypotheses that can account for sedimentary oil deposition include, 1) direct contact between the sediments and the subsurface oil plumes (“*toxic bath-tub ring”*) and 2) intense oil-mineral-algal biopolymer flocculation and widespread sinking of these oil-associated surface particles (*the “dirty blizzard”*) including the enhanced inputs of pyrogenic petroleum components and terrestrial-derived components (lithic and organics) associated with the opening of river flood gates. Benthic foraminiferal abundance, diversity and community structure indicate that benthic habitats were significantly impacted and, in some locations, a complete die-offs of fauna occurred in association with the changes in sedimentary regime and the inputs of PAHs at lethal and sublethal levels. Spatial analysis of sediments in the region surroundng the DWH blowout site indicate that a substantial portion (4-12%) of the DWH oil reached the seabed. To conclude we will discuss the role of oil spill response stategies in controlling/increasing the „footprint sedimentary oil deposition.

Aerobic and anaerobic biodegradation of petroleum hydrocarbons

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The role of microorganisms in the removal of petroleum hydrocarbons from the environment has now been known for over a century (Söhngen, 1913) and it has been recognised that microbial degradation is the most important process involved in the weathering and eventual disappearance of petroleum from the marine environment. The ability of microorganisms to actually remove hydrocarbons, rather than just disperse them, has been harnessed and developed as an important and environmentally benign tool for the clean-up of oil spills. This bioremediation is often carried out by the addition of fertilisers containing inorganic nitrogen and phosphorous, to stimulate the growth of hydrocarbon degrading microorganisms. The ability to degrade hydrocarbons is widespread throughout many genera of microorganisms, though it is only in the last fifteen years or so that it has become widely recognised that microbial hydrocarbon degradation can occur in the absence of oxygen. Numerous methods of monitoring the progress and extent of petroleum biodegradation are used, though some of the commonly employed methods include measuring the concentrations, or relative concentrations (i.e. changes in the distributions), of hydrocarbons in complex petroleum mixtures by gas chromatography and gas chromatography-mass spectrometry. Such studies have shown that different hydrocarbon components in oils biodegrade at different rates. The preferential degradation of n-alkanes before branched and cyclic alkanes has given rise to biodegradation parameters such as the n-C_{17} to pristane and total petroleum hydrocarbons (TPH) to 17α(H),21β(H)-hopane ratios, which are useful in assessing bioremediation effectiveness in environments where the heterogeneity of oil contamination has meant that absolute concentration measurements are equivocal. Some of these hydrocarbon molecular parameters are also used in oil spill fingerprinting and thus a good knowledge of the effects of biodegradation on them is necessary. However, while the relative susceptibilities to degradation of different hydrocarbon classes in oils was thought be well known, recent studies have shown that different degradation conditions, such as depleted oxygen conditions, can not only affect the rates of degradation but also the relative rates of different compound classes. Furthermore, biodegradation rarely completely oxidises crude oils to CO_2, since they are extremely complex mixtures of hydrocarbons and non-hydrocarbons and it is now known that biodegradation is associated with an increase in functionalised metabolites such as naphthenic acids in the biodegraded residues. Although these functionalised metabolites are themselves extremely complex mixtures, they are providing novel insights into the fundamental biochemical mechanisms of the biodegradation process, with, for example, relatively high abundances of succinate metabolites being found in anaerobic oil degradation experiments under sulfate reducing conditions, but not under methanogenic conditions.

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Identification of aromatic acid metabolites produced by two year laboratory biotransformation of crude oil under sulfate-reducing and methanogenic conditions, by GCxGC-MS

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Anaerobic biotransformation of the hydrocarbons of crude oils is an important alteration mechanism, both subsurface in geological reservoirs and in aquifers and in anoxic deep sea environments (e.g. the site of the Gulf of Mexico Macondo well spill). Characterisation of the products of such processes is therefore important.

Here we report improved identification of an extended range of aromatic acid metabolites of anaerobic biodegradation of crude oil hydrocarbons over two years in laboratory microcosms, by comprehensive multidimensional gas chromatography-mass spectrometry (GCxGC-MS), using synthesised reference compounds. The products of both sulfate-reducing and methanogenic conditions were identified. This approach reveals the extent and indicates the pathways of transformation of up to three ring aromatic hydrocarbons with at least C3 alkylation, in complex mixtures. The methods should now be applied to samples from environmental scenarios such as the Macondo well spill site.

Posters

Elimination of sulphur interference during the determination of tributyltin in sediment

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During the determination of organotin compounds in sediment samples, high levels of sulphur-containing compounds, which are abundant in sediment, can impair detection and quantitation of tributyltin by eluting with a retention time very close to that of TBT or by forming alkyl sulphide compounds during the derivatization step. Elemental sulphur and alkylsulphides interfere with the TBT and DBT compounds making quantification difficult.The explanation of sulphur interferences that occur during organotin determinations using flame photometric detection is based on the emission spectra of sulphur and tin in the flame. In the flame, organotin compounds give rise to excited organotin species SnC and SnH , which emit in the blue region of the spectrum at 390 nm and in the red at 610 nm. The emission band at 390 nm is up to 100–1000 times more intense than the emission band at 610 nm. However, at 390 nm, the main-interfering sulphur species (S_2*) also emits. This interference of sulphur species with organotin compounds has been previously documented[1,2,] . In order to decrease the matrix effects and increase the selectivity of the butyltin extraction, clean-up procedures were incorporated. This based on the use of doubly functionalized mesoporous silica which collect sulphied compounds from the sediment extract before the detection of TBT. The idea of this method is based on the partitioning of the analyte between a sub-micron solid and a liquid phase as a colloidal sol. By tailoring the size of the particles to approximately 250 nm diameter, they can be easily dispersed in aqueous solution, without the need for any mechanical or hand shaking and the solid can then be readily recovered, together with the matrix, by simple filtration or centrifugation. The use of modified silica particles allows complete elimination of the elemental sulphur and alkysuphide from the sediment extract, improving the quantification of the butyltin compounds. The main developed method was validated using the sediment certified reference material PACS-2. The advantages of the developed clean-up procedure over alternatives are the effective removal of elemental sulphur and alkylsulphides interferences without butyltin losses during the clean-up step. The improved method was applied successfully to sediment samples collected from a small boatyard in Saudi Arabia that were highly contaminated with sulphur.

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Geochronology and contaminated sediments: evaluation of the historical contamination in Lake Maggiore

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As part of a series of investigations carried out by ENVIRON in the Lake Maggiore, 210Pb and 137Cs analysis was undertaken to better understand the sediment accumulation rate and to evaluate historical trends of contaminant loading in sediments. Activities were performed investigating several sites, chosen to span a range of likely sediment accumulation rates. Coring activities were performed on silty sediment using a light weight gravity corer, with the aim of obtaining undisturbed samples.

Results show that concentrations of contaminant concentrations have overall declined significantly in the last 40 years: the most significantly elevated concentrations occur in the period of the mid-1960s.

The poster presents adopted methods, results and considerations about the chemical loading in sediment and temporal trend.

Comparison of the impact of two WWTPs discharge on PAHs in suspended particular matter (SPM) and sediment contamination in chalk streams

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Chemical contaminations were assessed in suspended particulate matter (SPM) and sediment sampled in 2 chalk streams of the Franche-Comté region (France) with a karst watershed. Concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in samples upstream and downstream the discharge of two wastewater treatment plants (WWTP). SPM were collected with six trap systems in each station during a flood event. PAHs diagnostic ratio was assessed to estimate the pollution emission source of SPM and sediment. PAHs concentrations were higher in samples collected downstream of both discharges and were above toxicity thresholds. SPM and sediments sampled in the area with the highest anthropogenic activities were more contaminated than sampled from the rural site. The isomer ratio suggests a pyrolytic source for PAHs.

Legacies from early industrial activities in Swiss lakes sediments

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Switzerland was one of the first industrialized countries. The industrialization in the 19th century began with the production of textiles and later expanded to the construction of machines, food products, chemicals and pharmaceuticals. The industrial revolution then started at the end of the 19th century, while the 1950's marked the transition from an industrial economy to a service economy.

This presentation will focus on 2 regions with early and famous industrial developments: The Glarnerland (Eastern Swiss Alps) and its textile industries and the Joux Valley (Jura Mountains) with its watch-making industries. Sediment cores were recovered from lakes situated downstream of the industrial parks: Lake Walen and Lake Joux, respectively.

The main objective of this study is to determine how the evolution of specific industrial activities is reflected in the sedimentary record. Temporal variations in trace metal deposition are reconstructed using continuous and high-resolution XRF core scanning and discrete ICP-MS measurements following sediment digestion. Finally a comparison of the heavy metal industrial fluxes in these two contrasting sites is presented.

Current pollution load of sediments and suspended matter in Lake Rummelsburg (Berlin) and whose mobilization potential and ecotoxicological impact on the aquatic ecology

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The Lake Rummelsburg in Berlin is an oxbow lake of the river Spree in a densely populated area of Berlin. For almost a century, the riverside was a location of various industries, the consequence being that untreated industrial and municipal wastewater dumped in the water body during that period. Currently the area develops to residential and local recreation use. Previous studies detected a high contamination in sediments by various pollutants as well as a low biodiversity [1], [2], [3]. Remediation measures initiated by the *Department of Urban Development and the Environment* of Berlin [4] did not improve the ecological situation as expected [1].

One of the aims of the research project RuBuS (*Accounting and physicochemical characterization of the current sediment dynamics in Lake Rummelsburg*, Research Project at Freie Universität Berlin) is to ascertain the level of pollution of the youngest and uppermost deposited sedimentary layers. Sediment sampling have carried out on 15 locations all over the lake with drill cores. The upper 15 cm of the drill core samples have divided into each 3 cm thin layers for separate examination. In addition, 18 sediment traps collected suspended matter over a period of 6 months (May-November 2014).

The scope of investigation includes the determination of inorganic (Hg, Cd, Cr, Pb, Ni, Cu, Zn) and organic compounds (PAH, hydrocarbon in the range C_{10}-C_{40} and C_{10}-C_{22}, selected nitro-compounds, selected organotin compounds, PCB, AOX and EOX) as well as the physico-chemical conditions of the sediment and the suspended matter. The examination of soluble and mobilizable sediment-bounded pollutants takes place based on a 24h batch test (DIN EN 12457-4:2003-01). Furthermore, certain toxic effects of the lake sediments have been detecting by ecotoxicological tests. It deals specifically with the luminescent bacteria test with *Vibrio fischeri* (DIN EN ISO 11348-2:2009-05), the Duckweed growth inhibition test with *Lemna minor* (DIN EN ISO 20079:2006-12) and the sediment contact test with *Arthrobacter globiformis* (DIN 38412-48:2002-09) as relevant test methods.

First analytical results of the drill core samples still show a high contamination with all of the mentioned pollutants of every single layer, except nitro-compounds and EOX.

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Assessing impact of the remobilisation of metal-contaminated sediments in the Rhine River during the dredging of a dam by coupling chemical and biological approaches

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The hydroelectric dam of Marckolsheim (Northeast of France) is one of numerous structures located along the 1200 km of the Rhine River, where sediments have been accumulated for several decades. For the maintenance and the safety of the dam, dredging by pumping/dilution with direct discharge in the Rhine was organized in 2013 by the French firm EDF (owner of the dam) in accordance with local regulations. Dredging can generate the remobilisation of sediments that are contaminated by non-degradable compounds such as metals, and subsequently lead to alterations of the aquatic ecosystem.

In order to assess the environmental impact of the dredging project, a long-term monitoring study using both chemical and biological tools was performed at two sampling sites located upstream and downstream from the discharge area. Environmental monitoring began three years before the project to acquire data on the natural evolution of metal contamination of the Rhine during full annual hydrological cycles (seasons, floods, etc.). Thus, DGT (or Diffusive Gradient in Thin films)-labile, dissolved and total concentrations of Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn were measured monthly in river water as well as metal concentrations in suspended matter samples from October 2010 to July 2013 at both sites. In parallel, size-calibrated zebra mussels (*Dreissena polymorpha*), which are filter-feeders that have the advantage of accumulating metals from both dissolved and particulate fractions, were caged and transplanted at both sites to assess metal bioavailability.

During the long-term monitoring, low temporal variations in metal contamination were observed in the Rhine and transplanted mussels. DGT–labile concentrations showed that speciation of some metals in the water column was modified during the dredging project in 2013 (4 weeks). In particular, Co and Mn were remobilised under more labile chemical forms that are potentially more available for biota. Besides, dredging led to significant accumulations of Pb, Cr and Mn in caged mussels exposed to the discharge. Nevertheless, the mussels recovered their initial state with respect to their basal levels of contamination two weeks after the end of the dredging, due to their ability to excrete metals. This suggests a transient impact of the discharge on these organisms. Furthermore, chemical analyses indicated high Cu and Zn concentrations in suspended sediments when compared to ones measured in the Rhine during the long-term monitoring. Nevertheless, no significant increase of Cu and Zn levels was measured in transplanted mussels probably because these essential metals are well regulated by aquatic organisms. These results highlight the interest of coupling chemical and biological approaches for a better assessment of environmental risk.

Establishing of monitoring of river sediments in Croatia

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Sediment is an essential, integral and dynamic part of our river basins and a healthy river needs sediment as a source of life. Unfortunately, the sediment also acts as a potential reservoir of long series of dangerous chemicals. Certain level of pollution leads to a negative impact on the level of biological diversity in rivers, what is now considered unacceptable by society and therefore it led to the development of the European Water Framework Directive (WFD). This Directive aims to achieve good status for all European waters by 2015, and it is clear that there is a direct relationship between sediment quality and achieving this objective of the WFD. Another important reason for the establishment of regular monitoring of sediments is that unlike water, which represents the current state of a particular watercourse, sediment represents a sort of record of the state of pollution in the long run. Therefore it is necessary, in addition to regular water monitoring, to establish also regular monitoring of sediments, in order to gain a real insight into the status of pollution of particular watercourses and to determine trends over a longer period of time.

In the Republic of Croatia routine river sediment monitoring does not exist yet. First scientific investigations of river sediment geochemistry in Croatia started 1989 (Prohić and Juračić, 1989) in the Krka River estuary, while first systematic research of a river basin in Croatia was performed by Frančišković-Bilinski (2005) in Kupa River drainage basin. Up to now, several detailed studies of both toxic metals and organic pollutants have been conducted in this drainage basin and some other rivers, also Croatian scientists participated in river sediment research in other countries.

In 2008 Croatian water authorities (Hrvatske Vode) started preliminary sediment monitoring program, what was successfully conducted. In the first year of preliminary program only 14 stations existed, while in 2014 number of stations increased to 21. Number of monitored watercourses and of analysed parameters also increased.

Finally, Croatian water authorities (Hrvatske Vode) recently decided to establish permanent monitoring network of river sediments throughout the state. The goal is to set up about 80 stations, which will cover all most important and most contaminated watercourses in all parts of the country. A study, which will examine in detail the suitability of each of proposed locations as well as selection of parameters which will be monitored in sediments, is in progress. The network of sediment monitoring stations will besides new stations include also locations covered earlier by the preliminary program, to enable continuation of existing data series on those locations. Current plan for establishing of monitoring of river sediments in Croatia is presented and discussed in details.

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Distribution and persistence of butyltin compounds (BuT) in coastal sediments from the eastern Adriatic (Croatia)

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Butyltins (BuTs) have been introduced into the marine environment by the use of tributyltin (TBT) as biocide in antifouling paints since 1960s. However, after it was established that TBT has various toxic effects on the non target organisms, like the appearance of imposex in gastropods at very low levels (1-2 ngL^{-1}), the use of TBT-based antifouling paints has been banned in many countries worldwide, including the whole Europe, while in Croatia they are banned since January 2008. The first measurements of BuT concentrations in seawater and mussels from the Croatian Adriatic coast sampled during 2009-2010 showed a widespread pollution with TBT, suggesting an ongoing use of those paints, despite restrictions (Furdek et al., 2012). Here we present the first data on BuT concentrations in sediments from the Croatian Adriatic coast collected in the period 2009-2013. In order to elucidate factors influencing the level of BuT pollution, locations with different intensity of maritime activities (marinas, ports and reference sites) were selected for sampling of surface sediments and sediment cores. BuT concentrations in the surface sediments ranged from 5 to 1362 ng(Sn) g^{-1}(d.w.), while contamination levels in marinas and ports were similar and significantly higher than those at reference sites. Extremely high concentrations were found in sediments taken below the service hoists in marinas, where BuT concentration reached the enormous value of 66344 ng(Sn) g^{-1}(d.w.). Obviously, the ban cannot solve the problem of TBT contamination of the marine environment immediately, since contaminated sediments represent its long term source. TBT degradation in sediments occurs in much slower rates than in seawater, thus making TBT very persistent in sediments, from where it may be released back to the water column.

Influence of sediment characteristics (grain size and total organic carbon (TOC)) on the TBT degradation efficiency in various contaminated sediments was further studied. TBT degradation efficiency was assessed in 9 sediment cores by determination of TBT and its degradation products with depth (dibutyltin (DBT) and monobutyltin (MBT)), and evaluated using Butyltin Degradation Index, BDI=(MBT+DBT)/TBT. Two types of depth profiles were observed: first, in which efficient degradation was indicated by the decrease of TBT and BuT concentrations with depth with BDI values higher than 1, and second, where weak degradation was indicated by small depth variations of TBT and BuT concentrations and BDI values less than 1. In general, TBT and TOC distributions followed the same depth pattern, while statistically significant correlation was found between TBT and TOC, as well as between BDI and TOC. Grain size distributions did not show significant correlation with other parameters. Therefore, results of this study strongly suggest that organic matter, by controlling TBT adsorption/desorption processes, influences the TBT degradation efficiency and consequently defines its persistence in contaminated sediments, which thus increases in sediments rich in organic matter.

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Multi-residue analysis of pharmaceuticals and pesticides in river sediments and corresponding surface and ground water in Serbia

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Pharmaceuticals and pesticides are recognized as major pollutants of the environment and water resources [1, 2, 3]. Therefore, the aim of this study was development of the analytical methods for the simultaneous determination of twenty five selected pharmaceuticals and pesticides, belonging to the various chemical classes, in river sediments and their corresponding surface and ground water with the purpose of monitoring the contamination levels. The methods were based on the solid-phase extraction as the sample preparation method for water samples, and the solvent extraction for the sediment samples, followed by the liquid chromatography–tandem mass spectrometry. The optimized solid-phase extraction was performed using Oasis HLB cartridge, 100 ml of the water sample with the pH value adjusted to 6 and methanol-dichloromethane (1:1) mixture as extraction solvent. The optimized solvent extraction was carried out by shaking the sediment sample at 200 rpm for 90 min. with methanol-dichloromethane (1:1) mixture, followed by ultrasonication for 45 min. and centrifugation for 10 min. High recoveries were obtained for extractions from both water and sediment samples for the majority of analytes. Low limits of detection were achieved for all investigated compounds in the water sample (1–5 ng L^{-1}) as well as in the sediment (1–3 ng g^{-1}). Applicability of the developed methods was demonstrated by determination of pharmaceutical and pesticide residues in 30 surface water, 44 groundwater and 5 sediment samples from five sampling locations at the Danube River Basin in Serbia. Sixty percent of target compounds were detected in environmental samples. Pharmaceuticals diazepam and erythromycin, and pesticides dimethoate and malathion were detected just in the river sediments. Only in surface and/or groundwater samples drugs trimethoprim, metamizole metabolites 4-FAA and 4-AAA, sulfamethoxazole, lorazepam, azithromycin and pesticide carbendazim were found. Pharmaceutical carbamazepine and pesticides carbofuran, atrazine and propazine were found in both sediment and surface or groundwater samples. However, at each sampling location, the target compounds found in groundwater were not detected in the corresponding sediment. The most frequently detected analytes in river sediments were pesticides dimethoate and atrazine, found in 60% of analyzed samples, while pharmaceuticals were less frequently detected. In all analyzed water samples, carbamazepine and metamizole metabolites 4-AAA and 4-FAA were the most frequently found analytes. Carbamazepine was found in 50% and 23% of analyzed surface and ground water samples, respectively. The most frequently found pesticide in water samples was carbendazim, detected in 20% of surface water samples and 16% of groundwater samples.

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Remediation of dioxin-contaminated marine sediments using thin-layer capping with activated carbon and other sorbents: evaluation of bioavailability assessment techniques

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Remediation of contaminated sediments *in situ* using thin-layer capping with various materials and particularly carbonaceous materials such as activated carbon (AC) has proven successful in reducing the bioavailability and sediment-to-water release of hydrophobic organic contaminants, e.g. PCBs, PAHs and dioxins, by several orders of magnitude. In two projects called CARBOCAP and OPTICAP, Swedish and Norwegian researchers have evaluated various capping materials for thin-layer capping *in situ*, using both mesocosms and large-scale field experiment. In this study we collected sediment from a dioxin-contaminated area in the Grenlandfjord, Norway. The sediments, held in boxcores, were treated with a thin cap of either clay or crushed limestone only, or amended with activated carbon (AC) or Kraft Lignin (KL). Two test organisms, a surface gastropod (*Nassarius nitidus*) and a deep burrowing polychaete (*Nereis* spp.) were added to the boxcores for bioaccumulation assays. Passive samplers (SPMDs) were placed in the water column and the boxcores were kept in a flow-through mode for 99 days. At the end of the experiment passive samplers, animals and sediment surface samples (0-3 cm) were collected for chemical analyses of dibenzo-*p*-dioxins and dibenzofurans, hexachlorobenzene, and octachlorostyrene. Bioavailability analyses of these compounds were conducted on a sub-set of sediment surface samples using synthetic digestive fluid extraction (DFE) or using Low-density Polyethylene pore water extraction (LDPE). This study presents the results from the bioavailability measurement method using digestive fluid extraction (DFE) compared with the results from the bioaccumulation values, i.e. concentrations accumulated in the test organisms (BAF). Amendment with active sorbents (AC or KL) led to a significant reduction in bioaccumulation by the two test species. AC was more efficient than KL as sorbent. A 90% reduction in bioaccumulation was obtained with 3 cm caps with 3.3% AC. DFE measurements corresponded well with the bioaccumulation results. The addition of a 3 cm cap amended with AC measured by DFE resulted in a 93% reduced dioxin/furan-bioavailability, compared to a 91% reduction in the gastropod and a 75% in the polychaete. Our results are promising in terms of developing faster screening tools for assessing toxicity risks to biota from contaminated sediments, and to evaluate the efficiency of various capping materials, as these bioavailability methods are more rapid (days instead of months) and more cost-efficient compared to traditional bioaccumulation assays using live organisms.

Remediation of contaminated sediments in the Baltic Sea: evaluation of toxicity risk reductions to humans and fish following activated carbon amendment

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Several remedial actions of contaminated sediments have been used over the last decade, including dredging and after-treatment of the contaminants *ex situ*. Treatment *in situ* (i.e. on site) by covering the contaminated sediment with a thin cap amended with a strong sorbent such as activated carbon (AC) has recently been proposed as a less disruptive and more economic remediation option compared to dredging. Field trials in the USA and in Norway have demonstrated that the sediment-to-water desorption and bioavailability of sediment-associated contaminants can be decreased by 75-90 % after capping with AC. In this study a steady-state human and ecological risk assessment model was used in order to evaluate the ecological and human risk reduction following remediation by thin-layer capping with AC. *Norrsundet,* a bay on the Swedish East Coast, north of Gävle, severely contaminated from historic pulp-mill emissions (PCDD/Fs, PAHs, PCBs) was chosen as a case study. Laboratory toxicity tests on field-collected sediment from Norrsundet were run in order to test for eventual acute toxicity to benthic fauna due to the contaminants or due to the AC used for remediation. By this approach, it was possible to balance the positive effects i.e. the risk reductions, against negative effects, such as eventual ecological effects on benthic communities of the capping itself. The results showed that: i) the predicted risk to humans was reduced to acceptable levels in a remediation scenario with 1-2% AC concentration; ii) AC amendment did not cause any acute lethal effects on the selected test species, however, sediment avoidance reactions were observed in the highly sensitive benthic amphipod species *Monoporeia affinis*, showing that the amphipods tried to swim away from the AC-amended sediment compared to non amended controls. This remediation technique thus leads to a considerable risk reduction and seems to be a promising future remediation technique. However, more field pilot tests are needed to evaluate possible negative effects of AC on benthic communities, before this technique can be recommended in the Baltic Sea, especially if large areas with apparently healthy benthic communities are to be remediated.

Integrated ecological risk assessment of pesticide run-off using the TRIAD weight-of evidence approach: a case study in the Rio Madre de Dios River, Costa Rica

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The “TRIAD” an ecological risk assessment (ERA) tool based on the combined weight of evidence (WoE) from several lines of evidence (LoE) was used in order to assess the ecological risks from pesticide contamination in the *Rio Madre de Dios* (RMD), a watershed that drains water from banana and pineapple plantations in the Caribbean lowlands of Costa Rica. The TRIAD is a tiered ERA method, where contamination risks are assessed based on the integration of data from three independent LoE from: 1) chemistry, 2) toxicology, 3) ecology. Within a research project called “TROPICA” (Tiered Risk Assessment of Pesticide Use in Costa Rican Agriculture) chemical, toxicological, and ecological measurements were carried out ca 2-3 times a year in the Rio Madre de Dios, a river system that receives drainage water from banana and pineapple plantations. In two companion studies of the TROPICA project, TIER 1 and TIER 2 ERA analyses were done using toxicity testing in the laboratory and *in situ* respectively, in order to assess the risks from pesticide contamination in the RMD watershed. In this study we gathered all chemical, toxicological and ecological data from these two studies over a sampling period of 3-4 years, scaled all the data into risk values from 0-1 values, where 0 corresponds to the minimum and 1 to the maximum risk values, using various scaling techniques. Then the scaled data from the three independent LoE were integrated using geometric means and contamination risk values and their standard deviations were calculated for each sampling season and for the total project duration. Our results show that the RMD river is at high chemical risks from both pesticides (0.7) and nutrients (PO_4) (0.6 - 0.7), that the toxicity risk to aquatic organisms is low to intermediate (based on biomarker, toxicity tests and mixture toxicity calculations using MS-PAF or the PERPEST model), and that the ecological risks to benthic invertebrates is relatively high (0.5 – 0.7), but not due to pesticide concentrations but rather due to low oxygen levels and eutrophication. Overall the integrated contamination risk to native aquatic organisms in the RMD was moderate (0.4) to high (0.6) indicating that mitigation measures are imperative and urgently needed in order to protect the native wildlife from pesticide and nutrient contamination.

Integrated Ecological Risk Assessment (ERA) of aquaculture and anthropogenic pollution in the Phu Long commune, Cat Ba Island, Vietnam

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With increased industrialization, economical development, a growing population along with increasing threats due to climate change, Vietnam urgently needs new methods in ecological risk assessment (ERA). In this study we applied an adapted version of the TRIAD, an ERA tool, based on the combined weight of evidence from several lines of evidence (LoE), in order to assess the risks from anthropogenic pollution on the marine environment of Cat Ba Island, in northern Vietnam. In a TRIAD data from different LoE are collected and then scaled from 0-1. Integrated risk values can then be determined to provide evidence-based management options. In this study the TRIAD was modified in order to also include socio-economical data, gathered from interview studies. Physico-chemical measurements (nutrients, contaminants, O_2, suspended solids) and ecological/biological measurements (community structure of phyto-, zooplankton and benthic fauna) were gathered from three different coastal sites. Socio-economical data (yield from aquaculture and fishery) was gathered through interviews in the local community. Results from the three LoE show medium to high risk for several physico-chemical variables, such as oil, mercury, nitrogen and coliforms. The ecological LoE shows low to medium risks for zoobenthic- and plankton communities and a high risk for economic activities dependent on ecosystem services, such as aquaculture and fishery. When the three LoE are integrated, the overall environmental risk is high or intermediate with significant spatial and seasonal variations, as well as varying levels of uncertainty. The TRIAD approach was here applied for the first time in Vietnam and received a positive response from Vietnamese academia and policy-makers. However, the quality of the assessment relies on good references sites, earlier studies for background levels and relevant environmental quality criteria. We found that it was difficult to find appropriate reference sites and data from earlier published studies. To enable a higher reliability and efficiency of risk assessments and management of coastal marine resources in Vietnam more environmental monitoring programs and available databases need to be set up.

Bioassays in sediment assessment for investigative monitoring in the context of the WFD: Results of the sampling campaign from 2010 to 2012

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Sediments are the ultimate reservoir of many chemical pollutants from point (industrial and urban effluents, disused industrial sites) or diffuse sources (agricultural pesticides). They are thus "memory" of contamination. Conversely, they can also be a source of contamination (Lamy MH., 2000) and release these substances years or even decades after pollution has ended.

If traditionally sediments were evaluated in a waterways dredging context, they are also clearly considered as part of the aquatic ecosystem quality. Contaminated sediments pose a potential risk to the ecosystem and human health: either they have a direct adverse effect on biological life habitat, or via the benthic organisms that form the base of the food chain, they indirectly affect higher trophic levels, such as fish, birds or humans.

In order to assess the current status of sediment pollution, bioassays can be used as suitable monitoring tools to answer the Water Framework Directive (WFD) requests and ascertain the causes of a water body failing to achieve the environmental objectives. They integrate all contaminants effects including additive and synergistic effects of unknown substances and breakdown products.

A sediment quality recurrent monitoring throughout Wallonia (Belgium) has been set up, taking into consideration physico-chemical parameters (including Prioritary Substances List from the WFD) and ecotoxicological effects of collected environmental samples in a triad-type approach. Different species (*Chironomus riparius*, *Heterocypris incongruens* for whole sediment, *Vibrio fischeri*, *Pseudokirchneriella subcapitata* and *Brachionus calyciflorus* for pore waters) are used in this approach. Indeed, they provide different information due to the way of exposure (ingestion, tegumentary contact) and they represent different trophic levels (decomposer, producer or consumer).

Between 2010 and 2012, 31 stations were selected to perform ecotoxicological characterization from a list of 54 stations of the surface water quality monitoring network (surveillance monitoring of WFD) in order to better assess the bioavailability of pollutants and toxicity associated to the simultaneous presence of several pollutants.

If the sediments were generally weakly to moderately toxic (26 stations out of 31 sampled), sediments from 5 stations were problematic because they were very toxic to extremely toxic. These stations consist primarily of large rivers but also a stream of smaller size.

All these measures also provided the opportunity to try to correlate the physico-chemical and ecotoxicological parameters in order to better understand interactions between the sediment contaminations from past and present and the biological compartment of the river.

Microbial diversity response to chronic petroleum contamination in coastal sediments

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Half of the human population in the world is concentrated on coasts. Consequently, coastal ecosystems ecologically support human activities and are highly impacted by anthropogenic pressure, and especially petroleum input. Hydrocarbons are likely accumulating in sediments, which harbor a great eukaryotal and prokaryotic diversity involved in major ecological services, among them : nutrient cycling and pollutants removal. Despite their ecological importance, suprisingly little emphasis has been placed on the response of microbial benthic communities to hydrocarbon contaminations and their consequences on ecological services sustainability within coastal sediments.

Using high-throughput sequencing targeting 16S and 18S ARNr genes, we investigate the eukaryotic and procaryotic diversity in both impacted and pristine sediments samples from different geographical areas around Mediterranean sea, Gulf of Biscay and English Channel. While they were significantly different between geographical areas, both prokaryotic and eukaryotic richness and phylogenetic diversity were not different between highly and low contaminated samples. At the community level, still no effect of contamination was detected among prokaryotes. This pattern was corrobored when focusing on the predicted functional diversity, determined with the PICRUSt program. In contrast, the contamination degree was significantly affecting eukaryotic communities (Permanova p-value=0.025), indicating a lower resilience capacity of eukaryotes, as compared to prokaryotes. Using IndVal calculation following multivariate regression tree construction, we detected several groups of Bacillariophyceae (Diatoms) as contamination indicators. Our results are a step forward in unravelling structuring processes of eukaryotic and procaryotic life in response to hydrocarbons inputs.

The influence of carbonaceous materials on freely dissolved PAHs content and toxicity of soil, sediment and sewage sludge

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The contamination of various matrices, including sediments, soils and sewage sludges may result in threat to living organisms. The application of selected materials with high affinity to contaminants, that can reduce their bioavailability and indirectly also their toxicity, may be a promising solution of the problem. The aim of this study was the determination of the freely dissolved PAHs content (C_{free}) and the toxicity of sediment, soil, sewage sludge with and without the addition of selected adsorbents. Three different carbonaceous materials (CM) potentially useful in remediation were applied: activated carbon (AC), biochar (BC), and multi-walled carbon nanotubes (MWCNTs). The influence of dose (1, 5 and 10%) and contact time (aging was performed over 3 years) on the effectiveness of the toxicity and C_{free} reduction was estimated. The concentration of C_{free} PAHs content was measured by passive method with polyoxymethylene (POM). The assessment of toxicity was made based on the solid phase – OSTRACODTOKIT F test with *Heterocypris incogruens* as a test organism. Two parameters were evaluated: mortality of *H. incongruens* and growth inhibition. CM decreased the amount of C_{free} PAHs content as well as the toxicity of tested matrices. The range of C_{free} PAHs content reduction differs depending on matrices, kind of CM and CM dose. Results of the study may be useful for the estimation of potential application of carbonaceous materials for the detoxification of different environments, including sediments.

Keywords: sediment, sewage sludges, soil, toxicity, carbonaceous materials

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The analytics of polyaromatic hydrocarbons (PAHs) in new certified reference materials of soil samples

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Polyaromatic hydrocarbons (PAHs) are interesting compounds for environmental chemists, analysts and toxicologists as well. The most important thing is that, PAH extracted from environmental matrices must be determined with adequate precision and accuracy. Certified reference materials (CRMs) are an indispensable part of systems which control and evaluate the quality of analytical results. CRMs have to meet the following general requirements: stability, homogeneity, analyte content determined with the relevant precision and accuracy (using validated methods) and cohesive documentation – certificate as well. All of the above parameters are very important, because they affect the quality of the resulting material. Finally the production of reference material is a complex, multi-stage process [1,2].

In our study over new reference materials of PAHs in soil we have applied six compounds: pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene. These compounds were extracted from soil on the accelerated solvent extraction (ASE) way. As solvent the dichloromethane:acetone (1:1) was used. The method is characterised with the best recovery (87-106 %) and the repeatability (SD = 2,9 - 4,1). To the final analysis we applied high performance liquid chromatography with fluorescent detector (HPLC/FLD) and gas chromatography with mass spectrometry (GC/MS). Both methods are characterised by the similar precision. Hence, the HPLC/FLD and GC/MS are equivalent themselves. The application of such CRMs is large and requirements in the face producers are still grow.

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Determination of pharmaceutical residues in surface water using ultra high performance liquid chromatography with UV-Vis detector

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A fully validated UHPLC-UV/Vis method for the identification and quantification of pharmaceutical residues in surface water samples, containing non-steroidal anti-inflammatory drugs (paracetamol, diclofenac, naproxen, ibuprofen, salicylic acid) was developed. Reversed-phase ultrahigh performance liquid chromatography with an ultraviolet detector, different columns, different mobile phases, and gradient elution were used to obtain the best separations within the shortest possible time. The developed method was based on several methods of similar drugs [1-3]. The proposed method uses Waters® XSelect™ CSH Phenyl-Hexyl column (150 mm x 3.0 mm, 3.5 µm) with a gradient elution using 0.1% TFA and 0.1% TFA in acetonitryl. Solid-phase extraction was examined as a preconcentration step. In developing process different commercial sorbents and elution methods were tested. The Waters Oasis® HLB column, with the highest recoveries (over 80% for most of the drugs), was chosen for the analysis of surface waters. Calibration curves for all drugs were prepared with R^2 value above 0,9997 for all drugs. Limits of quantification ranged from 1.44 to 2.72 µg/ml for all drugs after optimization of all analytical steps. Limits of detection ranged from 0.44 to 0.91 µg/ml respectively.

Waste water samples were obtained from Central Wastewater Treatment Plant in Toruń. Three types of samples were analyzed: unpurified sewage, biologically purified sewage and purified sewage. In all types of samples paracetamol was detected (concentration ranged from 0.718 µg//l to 4.559 µg/l). Naproxen was also detected in every sample, but under *LOQ* level. Diclofenac was detected in biologically purified sewage. Salicylic acid was detected in unpurified sewage sample in concentration 10.624µg/ml.

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New certified reference materials (CRMs) of soil for the analysis of polychlorinated biphenyls

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Certified reference materials (CRMs) play an important role in the research for environmental samples. They are used for developing, validation and checking of research techniques and to calibrate analytical equipment as well. CRMs are characterized by such properties as homogeneity, stability and well-documented chemical and physical properties [1, 2]. Increasing interest from laboratories according to a variety of matrices and analytes contained is still growing. During the research study we have tried to developed the new reference materials of soil for the analysis polychlorinated biphenyls (PCBs), belonging to the group of persistent organic pollutants (POPs). POPs are characterized by their stability in the environment, ability to be transported via air over large distances, and bioaccumulation in the food chain, which constitutes a threat to human environment and life. Their chemical durability and wide sphere of applications resulted in their widespread contamination in the environment. PCBs get into soil and water mainly through the fall of solid colloids, from sewage and by being washed out of buried garbage and industrial waste [3].
PCBs were isolated from soil using an accelerated solvent extraction (ASE). We compared the recovery of compounds for several temperatures. Additionally, different solvents, in order to select the best conditions for the method (recovery 82 - 107%), were applied as well. Quantitive analysis of six congeners of PCBs was performed by addition of an internal standard, in the form of congener 209. The analytical chromatographia technique was gas chromatography (GC) hyphenated with mass spectrometry (MS).

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Evaluation and selection of test methods for assessment of contaminated sediments in the Baltic Sea – The CONTEST project

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The purpose of the CONTEST project (2014-15) is to test, develop, evaluate and select suitable biological methods to be applied in the quantitative and qualitative assessment of toxicity of anthropogenically contaminated sediments in the Baltic Sea marine region. The project output supports development of new legislation concerning the management of contaminated sediments. There is a growing need to establish reliable, scientifically-based assessment methods to assess and classify the degree of contamination in sediments to enable making decisions on regulatory actions concerning the reducing of pollution from different sources, removal and re-location of contaminated materials, and on-site remediation measures and the follow-up of these. In CONTEST, carefully selected ecotoxicological methods currently in use in toxicity assessments will be tested under laboratory conditions using contaminated Baltic Sea sediments. Various biological endpoints (survival, reproduction, behaviour, malformations, growth) measured in different species relevant for the Baltic Sea will be examined and evaluated for their sensitivity, methodological feasibility and cost-effectiveness. The practical outcomes of the project include a shortlist of recommended methods and quantitative assessment criteria of sediment toxicity for the methods selected, and general guidelines for ecotoxicological testing of contaminated sediments in the Baltic Sea.

During 2014, a set of pilot experiments were performed by the participating laboratories. Chemical analysis of the contaminated harbour sediment chosen as the test matrix confirmed the presence of high concentrations of polycyclic aromatic hydrocarbons, organotins and trace metals, and the sediment was diluted according to the results obtained from the preliminary amphipod toxicity test. The following tests using whole sediments or sediment elutriates were performed: amphipod survival (*Corophium volutator*, *Gmelinoides fasciatus*), copepod survival (*Nitocra spinipes*), *Daphnia magna* survival (acute toxicity), sediment avoidance (*C. volutator*), bacterial luminescence (*Vibrio fischeri*), algae growth inhibition (*Pseudokirchneriella subcapitata*, *Ceramium tenuicorne*), SOS/umu genotoxicity (*Salmonella*) and imposex in female gastropods (*Nassarius reticulata*). The results of this first round of experiments showed large variability in the sensitivity of the different biotests. Most of the tests applied showed concentration-dependent effects on the test organisms. New experiments will be carried out in 2015.

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Soil and sediment testing of very hydrophobic, low solubility organic substances

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Due to the hydrophobic nature of most petroleum and petrochemical products, these substances will tend to distribute and adsorb to soil and sediment once released to the environment. Recent regulations in Europe and China are requiring soil and sediment toxicity tests for product hazard characterization. One major challenge is the use of total substance concentration in soil and sediment which do not reflect the fraction that is bioavailable and hence relevant for risk evaluation. Further, standard test guidelines do not clearly address equilibration of the substance with the soil/sediment media; and standard dosing methods do not incorporate time for equilibration, or address the appropriate test concentrations for very hydrophobic substances needed to demonstrate an acceptable no effect level.

Long term soil and sediment toxicity testing with plants, earthworms, and blackworms has been performed on non-ionic non polar hydrophobic organic substances. Based on chemical structure, high log Kow (>10) and very low water solubility (<0.02 mg/L), these substances would not be bioavailable, and hence, would not be expected to cause adverse effects to soil/sediment organisms owing to low solubility in pore water. However, testing these materials at standard elevated concentrations and without equilibration leads to a greater chance of causing physical effects on these organisms, which only confound interpretation of findings. No long-term effects were observed when testing followed an aging period after spiking, and a lower spiked soil / sediment exposure concentration of 100 mg/kg. The contrasting results demonstrate a need to allow for partitioning, and use more relevant concentrations to ensure generation of data that facilitate sound environmental assessment of hydrophobic chemical substances.

Hormones and sterols in sediments of the Danube River and its tributaries in Serbia

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Hormones and sterols have emerged as a subject of environmental concern since they significantly contribute to the deterioration of the water and the sediment quality, and potentially cause adverse health effects [1, 2]. Considering the fact that hormones and sterols belong to the common group of steroid compounds and that they have common sources and routes of entering environment, there is a demand for analytical methods for their simultaneous determination. There are just a few methods reported for simultaneous analysis of human/animal and plant sterols and hormones, and all of them are based on GC-MS [3, 4]. Therefore, the aim of this study was development and optimization of new LC-MS method for determination of twenty selected steroids in river sediments. Parameters that affect extraction (extraction solvent, weight of the sediment and time of ultrasonic extraction) and clean up efficiency (elution solvent and the packing type of the clean up cartridge) were optimized. It was found that optimal parameters were: ultrasonic extraction of 2 g of the sediment sample using methanol as extraction solvent during 10 min. in three repeated extraction cycles, followed by the clean up using silica gel/anhydrous sodium sulphate cartridge and methanol as elution solvent. Extracts were analyzed by liquid chromatography-linear ion trap-tandem mass spectrometry, with atmospheric pressure chemical ionization. Chromatographic separation of analytes with identical quantification reactions (estrone and estriol; 17α- and 17β-estradiol; epicoprostanol, coprostanol, α- and β-cholestanol) was achieved. The developed and optimized method provided high recoveries (73–118%), low limits of detection (0.8–18 ng g^{-1}) and quantification (2.5–60 ng g^{-1}) with the RSDs generally lower than 20%. Applicability of the method was demonstrated by the analysis of six sediments from the river Danube and its tributaries the Tisa, the Sava and the Morava. Out of twenty monitored steroids, twelve were detected in river sediments. Human/animal and plant sterols were detected in all investigated samples. Cholesterol and β-sitosterol were found at the highest concentrations up to 1507 ng g^{-1} and 1359 ng g^{-1}, respectively. High levels of epicoprostanol detected in all river sediments (up to 1230 ng g^{-1}) indicated strong sewage contamination. Mestranol was the only hormone detected in just one sediment sample.

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Assessment of anthropogenic pressures on the pristine karst lakes in two Croatian National Parks using multi-parametric sedimentary records

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Lakes are highly vulnerable aquatic ecosystems, which are exposed to increasing anthropogenic pressures, including anthropogenically-enhanced eutrophication and discharges of various toxic contaminants. This problem is expecially pronounced in conservation areas such as National Parks. Accurate and timely assessment of antropogenic pressures in such systems is the key prerequisite for their environmental sustainability and management. Lake sediments represent a major sink for many anthropogenic constituents and consequently, undisturbed sediments represent natural archives for the identification of different sources of individual contaminants as well as for the reconstruction of the historical patterns of anthropogenic pressures on the given aquatic system. In this work, we performed a comprehensive investigation of the anthropogenic impacts on two karst lake systems in Croatia, situated in the Plitvice Lakes National Park and Krka National Park. The investigation employed a multiparametric approach, based on multielemental analysis of major inorganic constituents (Al, K, Fe) and trace metals (Li, Ag, Cd, Sn, Pb, Bi, Cr, Co, Ni, Cu, Zn and Sb) and a number of classic and emerging organic contaminants (aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, surfactants and their metabolites and benzophenone). Dated cores of recent sediments were analysed for the selected contaminants using highly specific methods, involving inductively coupled plasma mass spectrometry (ICP/MS), gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). One of the key aspects regarding metal contamination was to decouple anthropogenic impacts from the inputs originating from the natural geological background of the area. It was shown that, for most of the anthropogenic metals, a significant increase in concentration coincides with the period characterised by increasing traffic and tourist activities around the lakes and can be linked to some characteristic milestones of the National Park management. Selected organic contaminants proved to be excellent molecular markers of specific anthropogenic sources in the studied systems. A similarity between the distribution patterns of Pb and PAHs suggested traffic as an important common source of these contaminants in the period in the 1980-2000s. On the other hand, enhanced concentration of LAS (up to 4.7 mg kg-1), indicated a significant input of untreated wastewaters into the Plitvice lakes. This issue warrants further attention, in particular because this input might be responsible for an accelerated eutrophication, observed in the lakes. Assessment of the anthropogenic pressures using multiple chemical indicators provided a useful tool for the decoupling anthropogenic and natural sources and created a basis for a better understanding of their relative importance for lake conservation.

Determining the release of hydrophobic organic contaminants from sediment by *in-situ* benthic flow-through chambers

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This study presents a novel *in-situ* benthic flow-through chamber for determination of release of hydrophobic organic contaminants (HOCs) from sediment to water. Sediment can act as a source of HOCs to water. For instance, Sobek et al. (2014) observed high chemical activity ratios between pore water and bottom water for dioxins in coastal areas of the Baltic Sea, demonstrating a potential release of dioxins from sediment to the water column. Lab and modelling studies (Thibodeaux et al. 2003 and Granberg et al. 2008) have shown that bioturbation is an important parameter increasing the release of HOCs from sediment to water. *In-situ* measurements of the release of HOCs from sediment to water related to bioturbation have not been done previously. The design of our novel benthic flow-through chamber was developed based on a closed benthic chamber, which has proven useful in assessing diffusive flux of HOCs from sediment to water (Eek et al. 2010). However, since the previous version of the chamber was closed to ambient water, oxygen deficiency inside the chamber could stress the benthic fauna and lead to cessation of bioturbation activity. This means that the closed chamber does not measure the HOC flux as it occurs under natural conditions. The novel design of the flow-through benthic chamber enabled measurement of sediment to water flux while the water inside the chamber was kept at ambient oxygen concentration by constantly pumping ambient water through the chamber. In order to measure the flux from the sediment enclosed by the chamber, incoming water was stripped of its content of HOCs by pumping the water through a sorbent. HOCs released from the sediment was captured on a second sorbent in the water flow from the chamber. The relative importance of bioturbation can be studied by comparing the sediment to water flux measured with a flow-through chamber and the flux measured by a closed chamber. The advantages of the *in-situ* determination of flux over micro- or mesocosm studies in the laboratory and determination by modeling are: 1) it yields a direct measurements of the sediment-water flux with the least sample alteration; 2) it does not require assumptions that are necessary in modeling. The flow-through chamber could potentially be used to distinguish the effect of benthic fauna species composition on the release of HOCs by coupling chamber measurements to species composition and abundance data. For instance, to evaluate the effect on HOC release due to the invasive and deep burrowing polychaete *Marenzelleria* spp, which has colonized the Baltic Sea in the last decades.

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Dynamics of heavy metals level in bottom sediments of the River Prut (Republic of Moldova)

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Bottom sediments of the river are repositories for various elements, acting both as sinks and sources of supplying of elements to overlying water horizon. Metals discharged into aquatic systems are mostly adsorbed on suspended particles and fine grained sediments. Taking into account the toxic properties, metals and their compounds are included in the list of Directive 2006/11/EC with the main hazardous pollutants for the environment. Mobilization-immobilization processes on the particle surface of sediments occur through/participation interstitial water. During the desorption process from sediments, heavy metals are accumulated in interstitial water, and then can be mobilized in the water horizon overlying the bottom sediments. Reverse process, the immobilization from water in sediments, also occurs through interstitial water. Concentrations of heavy metals in the water horizon overlying the bottom sediments and in the interstitial water of bottom sediments can vary greatly, and the direction of mobilization-immobilization processes determines pollution - self-purification processes of water bodies.

The objectives of our research were (i) to evaluate the peculiarities of spatial and multi-annual dynamics of heavy metals (Cu, Ni, Cr, Zn, Pb, Cd) level in bottom sediments along the Prut River, (ii) to perform the comparative analysis of heavy metals content in interstitial water and bottom sediments and (iii) to establish the desorbed amounts of heavy metals during the re-suspension of bottom sediments performed in field conditions. In order to determinate total content of heavy metals in bottom sediments the procedure recommended by the Geological Agency of USA was used. Content of heavy metals in interstitial water was determined after centrifugation of fresh (wet) sediments. Re-suspension of the bottom sediments was performed in field conditions by „aquarium” method. Heavy metal analyses were conducted using atomic absorption spectrometry.

The obtained results revealed the accumulation of most metals in bottom sediments on the lower course of the Prut River. Maximal content of Zn was recorded on the middle course of the river. The ability of bottom sediments for heavy metals binding decreases in the following order: Fe>Mn>Zn>Ni>Cr≥Cu>Pb>Cd.

The results indicate that the re-suspension of sediments, carried out in the field conditions, causes the increase, in the water layer, of Cu content about 1.5 times and Zn of 1.8-6 times, in comparison with data recorded until the re-suspension. In such conditions, the quantities of mobilized metals in the water layer are for Cu about 19-52% and for Zn 23-100% of their content in the interstitial water of bottom sediments. Thus, during the re-suspension, bottom sediments can become a relevant source of heavy metals which are mobilized in the water horizon overlying sediments.

Biomass from organic waste materials for sustainable remediation

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Green sustainable remediation strategies such as the use of compost and biochar are receiving growing attention. Co-composting of contaminated soils and sediments can enhance biodegradation of organic contaminants, while biochar can provide immobilisation. Although a lot of research efforts were dedicated to the sorption of hydrophobic contaminants and metals to biochar, the understanding of the sorption of ionisable organic contaminants remains limited.

To gain a better understanding of the sorption behaviour of ionisable contaminants to biochar, sorption batch experiments with a series of biochars with different ash contents and a series of structurally similar organic acids were performed. Combining comprehensive characterization of the sorbents and sorption dataset allowed the identification of sorption mechanisms and driving factors of sorption. Results showed that in addition to factors known to play a role for the sorption of hydrophobic contaminants, additional factors should be taken into account for ionisable contaminants. The pH dependent lipophilicity ratio D, ash content and ionic strength were identified as key factors for the sorption of ionisable organic contaminants to biochars.

Further experiments will focus on the combined use of compost and biochar. The influence of compost on the sorption behaviour of biochar, as well as the influence of biochar on the degradation of organic contaminants will be investigated. The resulting knowledge will support fundamental understanding of factors driving sorption and degradation, when applying biochar and compost to remediate contaminated soils and sediments, and help further develop sustainable remediation strategies.

Removal of polycyclic aromatic hydrocarbons and their alkyl homologues during *ex situ* stimulated bioremediation of contaminated soil

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Polycyclic aromatic hydrocarbons (PAH) keep attracting great concern due to their environmental persistence but also due to their toxicity and carcinogenicity. Their alkyl homologues are more abundant and persist longer than parent compounds, and some of them are considered more toxic. Nevertheless, many environmental studies are dealing with parent PAH molecules only, while the reports on their alkyl homologues are still scarce and usually limited on selected isomers.

The aim of this research was to investigate the changes in the distribution of two-, three-, and four- ring PAH and their alkyl homologues during ex situ stimulated bioremediation of a soil contaminated with heavy residual fuel oil. The results of this experiment were compared with the results of natural biodegradation of the same soil that was not subjected to the processes of stimulation.

In the soil investigated in this research, the following analytes were detected and monitored: C1-C3 alkyl homologues of naphthalene; C0-C3 phenanthrenes; C0-C1 fluoranthene/pyrenes; C0-C1 benz(a)anthracene/chrysenes and triaromatic steroids.

During the period of six months, benz(a)anthracene/chrysenes were ony slightly affected while no changes were noticed in the distribution and abundance of triaromatic steroids. However, the biodegradation process resulted in a gradual removal of all other monitored PAH and their alkyl homologues.

In the set of naturally biodegraded samples, parent PAH molecules were more degraded than their alkyl homologues, while the lower alkyl homologues were more affected than the higher ones. According to the current knowledge, these changes during the natural biodegradation might be characterized as expected, although, to the best of our knowledge, such a detailed analysis of all of these compounds, treated and analyzed under the same conditions, has not been reported yet.

In the set of samples exposed to the stimulated bioremediation, the opposite trend was observed. Within the homologue series of naphthalenes, phenanthrenes and fluoranthene/pyrenes, higher alkylated homologues were more degradable than the lower ones, while the lower alkylated homologues were more degradable than their parent molecules.

Based on these results, a general conclusion can be drawn that the conditions applied during this stimulated bioremediation process of contaminated soil result in more pronounced reduction in the concentrations of alkyl PAH homologues comparing to their parent molecules. Moreover, under the conditions applied, higher alkyl PAH homologues were more degradable than the lower ones. However, the extent and the applicability of this process, as well as the further fate of these persistent pollutants, still remain to be investigated.

Evaluation of the effect of PCB-containing architectural coatings on sediment quality

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In recent years, architectural coatings and other common materials have been identified as a possible source of contamination to urban stormwater runoff and ultimately to sediments in urban waterways. Recent investigations have identified polychlorinated biphenyls (PCBs) in commonly used building materials, including caulk and paints. However, existing studies have not focused on bridge coatings. Constituents present in bridge coatings could potentially migrate from the coating to urban waterways directly through coating chips, dust, leaching into rainwater, or indirectly through stormwater runoff. To understand if constituents in the bridge coatings could affect sediment quality in the Willamette River in Portland Oregon, we conducted an investigation to collect samples of weathered coatings, sediments, and stormwater to predict the potential impact of the coatings on the sediment quality near two bridges.

We developed a conceptual model describing the potential pathways along which weathered coatings could affect the sediment quality and five different matrices were sampled over a two week field effort. A sampling method specific to coatings was developed by modifying existing methodologies for indoor coatings. Following the collection of data, sediment modeling techniques were used to evaluate the potential contribution of the coating to the sediment.

Laboratory analysis of samples from this investigation detected concentrations of PCBs and metals in the coatings, dust, and leachate. We evaluated these detections by calculating the mass of constituents present in coatings, estimating stormwater loading using the Simple Method, and predictively modeling sediment chemistry using SEDCAM, a one dimensional mixing model. Additionally, a principal components analysis (PCA) was conducted on PCB congeners and a statistical comparison of PCB concentrations in sediment upstream and downstream of each bridge was performed.

The results of these evaluations, through multiple lines of evidence, suggest that sediment quality adjacent to these particular bridges has not been impacted by their coatings. However, the study results suggest that certain coatings, particularly older ones with higher concentrations of PCB, could have an impact on sediment quality under some conditions. The results of this analysis could be helpful for other entities evaluating bridge coatings or other architectural coatings as a source of PCBs.

Adsorption of chlorophenols on pristine and functionally modified multiwalled carbon nanotubes

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Recent studies have demonstrated that carbon-based nanomaterials (CNMs) have very strong adsorption affinity toward many organic pollutants. In addition to the promising application as special adsorbents in environmental analysis, water treatment technologies and environmental remediation, the CNMs, once released to the environment, might play an important role in the fate and behaviour of common organic pollutants due to strong adsorption affinity that alter the partitioning of organic compounds between environmental compartments. The understanding of adsorption mechanism is essential for assessing the environmental risks of both organic compounds and CNMs, as well as their technological relevance in many environmental applications.

This work studies the adsorption of four chlorinated phenols (2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol and pentachlorophenol) in aqueous solutions on multiwalled carbon nanotubes (MWCNT). To investigate the influence of oxygen containing functional groups, adsorption parameters for the phenols were determined for original MWCNT (OMWCNT) and functionally modified MWCNT (FMWCNT) by acid treatment for 3 h and 6 h.

The correlation between adsorption affinity and SSA indicated that OMWCNT have higher adsorption affinities for larger molecules such as tetrachlorophenol and pentachlorophenol, which suggests that mesopore filling is not the dominant mechanism controlling the adsorption. In addition, a positive correlation between molecular hydrophobicity and adsorption affinity was obtained for OMWCNT, indicating the importance of hydrophobic interactions in the adsorption process. To investigate the role of π–π interactions, K_d values at two equilibrium concentrations (0.01 and 0.5 S_W) were normalized by hydrophobicity. Obtained K_d/K_{OW} values for all MWCNT decreased from 2,4-dichlorophenol to pentachlorophenol and were negatively correlated with the electron-acceptor property of the molecules.

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