# Sediment pollution, chronic toxicity and metal bioaccumulation in freshwater macroinvertebrates from Pb/Zn mining districts

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**Conference theme number(s): 1**

**Introduction:** Mining activities for the extraction of metals have usually resulted in the disposal of soil tailings, which can leach metals to rivers and pose a significant risk for aquatic communities. Sediment and biota have been recognized as suitable monitoring matrices for long-term changes in water quality of European water bodies, but environmental quality standards, for both sediment and biota, have been developed only by some State Members. In present study, the assessment of two abandoned Pb/Zn mining districts was carried out through the integration of three lines of evidence (LOEs) to conduct a risk assessment using a weight of evidence (WOE) framework through a reference condition approach. The LOEs were sediment pollution, sediment chronic toxicity and metal bioaccumulation in field macroinvertebrate biomonitors.

**Methods:** The river catchments studied are located in in the Cantabrian region (northern Spain), and seven sites in two metal districts were studied: Arditurri Pb/Zn mining district in Gipuzkoa (Basque Country, 5 sites: END, OIA1, OIA2, ARD, OTS) and Reocín Pb/Zn mining district (Cantabria, 2 sites: SB013 and SB014). The LOE of sediment chronic toxicity was assessed through sediment *Tubifex tubifex* 28-day bioassay [1]. The LOE for risk of metal bioaccumulation was assessed using the INTISS score (Integrative Tissue concentration, [2]) calculated by means of several *in situ* biomonitors. For the sediment pollution LOE, and in the absence of sediment quality guidelines for the region, ecological backgrounds and thresholds for Cd, Pb and Zn were estimated from a database of 31-55 sites as representative of the reference (unpolluted) condition for Cd, Pb and Zn, in sediments from northern Spain, following the methodology proposed by [3]. The decision matrix developed for the WOE was made by ranking the three LOEs used.

**Results:** Comparing the Cd, Pb and Zn sediment concentrations with the ecological background values, they were more than 10 times higher at OIA2, ARD and OTS and more than 6 times higher at SB014 for Zn.

The three LOEs showed impairment due to sediment pollution and chronic toxicity in all test sites, and only in one test site the hazardous levels of bioaccumulation were not attained (SB013).

**Discussion:** Sediment ecological thresholds proposed for Cd, Pb and Zn are comparable to other thresholds proposed in other geographic areas, and have been proved to be an useful tool for the pollution assessment in areas affected by historical Pb/Zn mining activities in northern Spain. Sediment chronic toxicity and tissue residues in field macroinvertebrates have demonstrated that the sediment pollution poses a risk for the benthic communities, due to the toxicity and the bioaccumulation of hazardous metals in most sites, related to the Arditurri and Reocín historical mining activities. This assessment suggests applying management programs for reducing the source of metal pollution at these sites.

**References:** [1] ASTM E1706-05, 2005. [2] Rodriguez et al., 2021. *Aquat Toxicol* 238: 105918. [3] Méndez-Fernández et al. (2019) *Environ Pollut* 245: 1000-1013. [4] MacDonald et al. (2000) *Arch Environ Contam Toxicol* 39: 20-31.

# Ecotoxicological assessment of river sediments downstream of a firefighting training site

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**Conference theme number(s): 1**

**Introduction:** The use of firefighting foams, which are known to contain per- and polyfluoroalkylated substances (PFAS), can result in the dispersion of these contaminants into the environment during training exercises. As a result, training sites contribute to hotspots of PFAS contamination. This study reports on the PFAS contamination and ecotoxicity of sediment samples collected in two rivers downstream of a firefighter training site in Switzerland. It's a follow-up to previous studies conducted by the corresponding regulatory authorities which confirmed the spread of PFAS in the surrounding area, with elevated concentrations in both soil and water compartments.

**Methods:** Five sediment samples, one upstream and one downstream in each river, and one after their confluence, were collected for both chemical and ecotoxicological analyses. A total of 20 PFAS were analyzed on dry sediment sieved at 2 mm. Fresh sediments sieved at 2 mm were tested with the ostracod *Heterocypris incongruens* [1]. Growth inhibition and mortality rates after six days of exposure were compared to toxicity thresholds [2].

**Results:** For the bioassay, both mortality and growth inhibition were higher at the downstream sites (A2, B2) compared to the upstream sites (A1, B1) for both rivers (Fig. 1). The mortality rate was above the toxicity threshold of 20% at the two B sites and at the site downstream of the A/B confluence (A3).

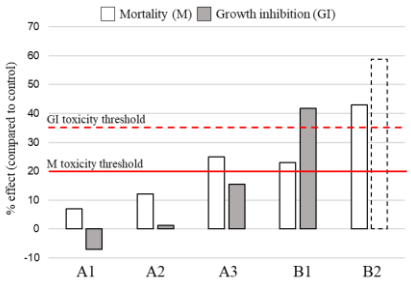


**Fig. 1:** *Effects measured in* H. incongruens *after 6 days of exposure to sediment samples from rivers A and B.*

For B2, the mortality reached the highest value of 43%, while the upstream site B1 showed significant sublethal effects with growth inhibition exceeding the toxicity threshold of 35% (Fig. 1).

Of the 20 PFAS analyzed, PFOS, PFDA and PFOA, were detected in all samples, except the control blanks. The risk assessment was carried out according to the PFOS sediment quality criteria (SQC) for the protection of benthic organisms from direct toxicity of 2.7 µg/kg dry weight (dw, 1% TOC), and according to the PFOS SQC to protect top predators from secondary poisoning of 1.85 µg/kg dw [3] (Tab. 1).

**Tab. 1:** Risk assessment for PFOS. Blue, RQ < 0.1; green 0.1 ≤ RQ < 1; yellow 1 ≤ RQ < 2; orange 2 ≤ RQ < 10, red, RQ > 10.

| Risk quotient (RQ) / Site | A1 | A2 | A3 | B1 | B2 |
|---|---|---|---|---|---|
| RQ - PFOS_benthic organisms | 0.01 | 0.33 | 0.52 | 0.07 | 5.91 |
| RQ - PFOS_secondary poisoning | 0.05 | 1.97 | 2.11 | 0.22 | 18.4 |

A maximum RQ of 5.91 (concentration of 34.1 µg/kg dw) was calculated for B2, classifying the sediment quality as unsatisfactory (orange). If we consider the SQC derived to protect top predators from secondary poisoning, the sediment quality is downgraded to poor (red, RQ 18.4). The two sites upstream of the study site (A1 and B1) are of very good (blue) or good (green) quality, depending on the protection objective.

**Discussion:** Both the risk assessment based on chemical analyses and the bioassay converge in showing an impact on sediment quality downstream of the firefighting training site. Ostracod mortality showed a clear upstream-downstream response in both rivers, with the highest mortality was observed in the sediment with the highest concentration of PFOS (and ∑PFAS). This suggests that ostracod mortality is sensitive for detecting effects related to the presence of PFAS in complex sediment samples. Further studies are needed to rule out other potential sources of PFAS in these rivers and to determine how far the contamination spreads.

**References:** [1] ISO (2012) ; [2] Casado-Martinez et al. (2016) *Chemosphere* **151**:220-4; [3] Casado-Martinez (2020) *Swiss Centre for applied ecotoxicology*.

# On the importance to test sediment toxicity in rare earth element enriched waters

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**Conference theme number(s): 1**

**Introduction:** Rare earth elements (REE) are essential metals for different components of our modern technology (e.g. smart phones, wind energy and electric cars). Enrichments of individual REE concentrations in rivers due to emissions from mining activities, fluid cracking catalyst production, fertilizer plants, wastewater treatment plants etc. have been found all over the world. Since the 1990s, the number of papers on rare earth toxicity has multiplied reflecting the growing concern, that increased concentrations could harm the environment. Due to their high tendency to form complexes with carbonates, hydroxides and phosphates, however, dissolved concentrations in the environment are mostly minor and the risk to aquatic organisms is often considered to be low. Insoluble complexes will precipitate and attach to organic material or sink to the sediments where they are considered not to be effective. But while some studies have demonstrated an elevated toxicity in REE contaminated environmental sediments (e.g. [1]), very few toxicity studies have been performed on REE-spiked sediments to support that assumption [2]. This presentation will base the argument for testing the toxicity of rare earth elements in sediment on a number of experimental results, mainly from the Panorama Project, and summarize what progress has been made in this regard up to the conference. A plea will be made not to dismiss REE as minor contaminant until this has been confirmed by sediment toxicity testing.

**Methods:**
Tests of toxicicty of REE (lanthanum, gadolinium) for

- nematodes in water phase acc. to ISO 10872 (mod.)
- daphnia in water phase acc. to ISO 6341 and modified; avoidance studies with sediment
- *Myriophyllum aquaticum*; sediment, ISO 16191

Synchrotron studies at Nanoscopium, Soleil, in Paris, France

**Results:**
Effects on nematodes: Comparing toxicity of La in media with and without precipitation revealed lower EC50 values, when precipitates were present.


Effects on daphnids: After 7 days of exposure, both metals had been accumulated in the intestinal tract and showed toxicity [3].
In a two-phase sediment-water system, Gd-enriched sediment led to an almost complete reduction in the residence time of daphnids on the sediment surface at concentrations of 1 µg/kg (van Drimmelen et al., in prep).

**Fig. 1:** Accumulation of La in the intestinal tract of D. magna after 72 hours of exposure.

Effects on the benthic plant Myriophyllum aquaticum: Gd spiked sediment strongly affected photosynthetic activity at 50 mg/kg, followed with higher concentrations by an impact on growth and development

**Discussion:**

- REE-Precipitates can be taken up and may become available in the gut of organisms
- Spiked sediments can impact the photosynthetic efficiency of benthic plants
- sublethal effects to REE-contaminated sediments may be ecologically relevant

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[2].Revel, M. et al. Critical Reviews in Environmental Science and Technology. 2024:1-42. 10.1080/10643389.2024.2406992.
[3].Revel, M. et al. Chemosphere. 2024;353:141509. 10.1016/j.chemosphere.2024.141509.

# Emerging contaminants (ECs) in inland water sediments of the anthropogenically affected areas in Poland. A One Health perspective.

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**Conference theme number(s): Theme 1 (Zero Pollution)**

**Introduction:** Recognizing the interconnections between human, animal, plant health, and the environment has led to the adoption of an integrated perspective on health, known as the One Health approach [1]. Additionally, One Health approach emphasizes the need for collaborative efforts to address emerging contaminants (ECs) issues. ECs refer to newly identified synthetic or naturally occurring chemicals in the environment whose hazardous effects on humans and natural ecosystems are not yet fully understood, or to chemicals recently recognized as posing risks to human and environment [2]. The continuous introduction of ECs into the environment undermines global environmental protection efforts, as substances once hailed for their beneficial properties have increasingly become recognized as pollutants of significant concern. Water sediments, functioning as a critical sink for pollutants, play a pivotal role in the long-term storage of contaminants [3]. Therefore, this study aimed to investigate the ECs contents in the various inland water sediments in Poland and to determine the related cumulative environmental risk.

**Methods:** Sediment samples were collected from various inland water reservoirs in Southern Poland, each influenced by various anthropogenic activities, as well as from a reference site – a drinking water reservoir serving the inhabitants of Krakow. Organic ECs were determined using an ultra high performance liquid chromatography (UHPLC) system (Vanqiush Flex Thermo Scientific), coupled with a triple quadrupole mass spectrometer (TSQ Altis Plus, Thermo Scientific). Inorganic ECs were measured using inductively coupled plasma – mass spectrometry (ICP-MS) system (Thermo Scientific) and inductively coupled plasma - optical emission spectrometry (ICP-OES) system (Optima 7300DV Perkin Elmer).
Environmental risk associated with the analyzed ECs concentrations was evaluated using the risk quotient (RQ) methodology, as developed by the US Environmental Protection Agency [4]. RQ values were determined by calculating the ratio of measured environmental concentrations (MECs) to predicted no-effect concentrations (PNECs) for each of the investigated ECs. The average concentrations of the investigated ECs were used as MECs for environmental risk calculations. Additionally, the worst-case scenario was evaluated by using the highest measured EC concentrations as MECs. PNEC values were obtained directly from the ECHA Chemical Database [5] or, when unavailable, from relevant scientific literature.

**Results:** The concentrations of investigated ECs, belonging to the following classes of substances: bisphenols (BPs), per- and poly-fluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), and heavy metals (HMs) will be presented. Additionally, the relationship between changes in EC concentrations and sediment properties across different locations will be discussed. Finally, the environmental risk, as represented by the Risk Quotient (RQ) values for both mean and worst-case scenarios, will be assessed.

**Discussion:** These preliminary results offer new insights into the presence of emerging contaminants (ECs) in aquatic sediments. They may also contribute to the development of future, comprehensive monitoring plans for sediment catchments, particularly in relation to the cumulative effects of emerging contaminants.

**Funding**: This work was supported by the EFSA EU-FORA Program (Cycle 2023/2024 and 2024/2025).

**References:** [1] Ortiz et al. (2022) *Xenobiot* **12**:56–63; [2] Wang et al. (2024) *The Innovation* **5**:100612; [3] Li et al. (2022) *Water Research* **224**:119065; [4] Khare et al. (2023) *Sci Tot Environ* **882**:163381; [5] https://chem.echa.europa.eu/.

# A regional systemic approach to assess spatial distribution, transfer, exposure and remediation of wide-spread PFAS pollution in Willebroek

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**Conference theme numbers: 1, 6**

**Outline:** Extreme persistence of PFAS and their environmental toxicity and bioaccumulation capacity, and adverse human health effects make PFAS a top priority pollutant group. Current 'one substance, one assessment' approaches to measure the risks and propose appropriate remediation for PFAS are difficult to apply through the different compartments given the extensive group of precursors and metabolites that can arise in the environment. Current knowledge is insufficient to understand the risks posed by diffuse pollution to both people and the environment ('one health' approach) and has not yet been translated and integrated into management nor remediation practices. The recently started LIFE PFASTER (PFAS systemic regional approach to Assess Spatial distribution, Transfer, Exposure and Remediation of wide-spread pollution in Willebroek, Flanders) project, aims to improve soil, sediment and water quality by developing a regional systemic remediation approach to reduce diffuse pollution with PFAS of soil, sediment, water and biota, including innovative, cost efficient methods to assess the spatial distribution and identification of exposure routes of the contaminants and the design and piloting of a replicable remediation approach beneficial for biodiversity and human health.

**Project site**: The project site considers the area that has been impacted by a former paper mill factory located in Willebroek, Flanders (Belgium), an exemplary case for a heavily PFAS contaminated area, characterized by a very diverse pattern of land use types.

Considering the long period of industrial activity and the shutdown of the plant more than 20 years ago has changed the context to a rather diffusely present contamination in terms of assessment and approach to tackle the contamination.

In this case it is not feasible to aim for a complete destruction of the contamination. We pursue an overall containment approach that optimizes long-term strategies for managing and remediating risks, with the attention for safe sinks and proposing the best available technique per location.

**Methods**: We aim to develop this holistic and systemic approach to be replicable in other situations with complex contamination and multiple stakeholders involved. A GIS-data platform, where different relevant data can be clustered, is a crucial element of the approach. In the PFASTER project it is used to share the measurement data amongst the partners. For the remediation approach it will be an essential tool where information is shared with the stakeholders.

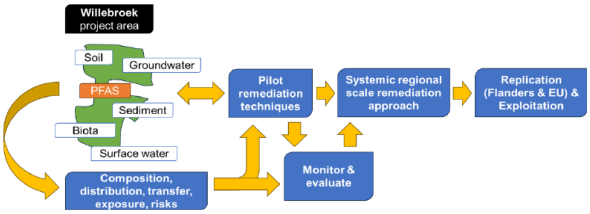


**Fig. 1:** *Different steps in the LIFE PFASTER project.*

**Role of sediments**: Sediment is an elementary link in the entire system. Wastewater has been discharged in one of the main streams and has spread over the entire hydrological network. Sediment removal and disposal on the banks of the different streams has spread the contamination on land. Also, certain peat pits in the nature reserve Broek de Naeyer have been used for a long period of time as settling basins for the paper mill. The characterization of contamination in sediment, the relevant posed risks and the different pathways from and to sediment are part of the project objectives. Moreover, this integrated approach will be guidance to the piloting of certain remediation techniques for PFAS in sediment.

Visit www.life-pfaster.eu for more information.

# Study of PFAS contamination in the Garonne and its watershed

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**Conference theme number(s): 1**

**Introduction:**

Per- and polyfluoroalkyl substances (PFAS) comprise more than 5,000 distinct compounds currently in use. These compounds are extensively employed worldwide from decades and spread in the environment. The toxicological, persistent and bioaccumulative properties of PFAS have been demonstrated in numerous studies. However, the behaviour of most PFAS is not fully understood, and there is a paucity of scientific data on their occurrence and fate in the environment, especially for emerging polyfluorinated ones.

The Garonne River is the fourth longest river in France. This 530-kilometre-long river has its source in the Pyrenees mountain range at the French-Spanish border and is subject to a variety of anthropogenic influences. Its watershed is home to a number of urban centers, including Toulouse and Bordeaux, as well as a diverse range of industrial facilities, from airports to nuclear power plants. The purpose of this study is (i) to document the spatial distribution and patterns of PFAS in the Garonne Basin sediments and water using both targeted (47 PFAS including long and short-chain carboxylates and sulfonates as well as selected perfluoroalkyl acid precursors, pre-PFAAs); and (ii) to assess the PFAS transfer towards the first link in the food chain, i.e., the biofilm.

**Discussion:**

A representative overview of the Garonne River watershed and the activities conducted along its course from source to estuary was obtained by collecting sediments, biofilms and water samples from the river and its tributaries. Twenty-three sites were sampled during two campaigns under low- and high-flow conditions.

Microwave assisted extraction was employed to facilitate the extraction of PFAS from the sediments and biofilm, with methanol and 50 mM of ammonium acetate as extraction solvent. Subsequently, samples were filtered through glass wool prior to purification on a graphite cartridge (Envi-Carb, 250 mg)[1]. Water samples were treated following USEPA1633 recommendations. Targeted analysis was conducted using high-performance liquid chromatography coupled with electrospray ionisation and tandem mass spectrometry (HPLC-MS/MS). The total oxidisable precursor assay (TOP assay)[2] was also conducted on sediment, biofilms and water samples. This step convert pre-PFAA (targeted and non-targeted ones) into PFAAs that can be measured via targeted analysis. This allows us to estimate the potential reservoir of non-targeted pre-PFAAs present in the water, sediments and biofilm. Results are currently be exploited and will presented.

In conclusion, this study will fill the gaps in the assessments and understanding of PFAS contamination in an anthropogenized watershed such as the one of the Garonne River. Our contribution is expected to demonstrate the impact of the different facilities and cities present in this basin on the occurrence of PFAS in sediments, further document the differences in PFAS pattern between sediment and biofilm, and further highlight the usefulness of the TOP assay to provide more extensive characterization of the PFAS contamination.

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# Quantitative analysis of PFAS distribution in aqueous environmental samples of the Hungarian section of the Danube River

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**Conference theme number(s): Theme 1 - Zero pollution**

**Introduction:** The abundance of Per- and polyfluorinated alkyl substances (PFAS) has become a global concern due to their persistence, bioaccumulation, and toxicity. They are characterized by their strong thermal and chemical stability, high polarity, and non-biodegradability, which makes them useful as coatings for textiles, papers, consumer products and lithium-ion accumulator batteries (LIB) [1].

**Methods:** This study focuses on investigating the occurrence of PFAS and the quantitative analysis of the Inorganic Fluoride (IF) and Adsorbable Organofluorine (AOF) compounds in water and sediment samples collected along the Danube River including the locations at the LIB factory in Komarom and Vadja paper factory in Dunafoldvar. Samples were analysed alongside grain size analysis of the sediments for 6 months to ascertain their spatial distribution, evaluation of their temporal trends and comparison of concentration obtained in both phases.

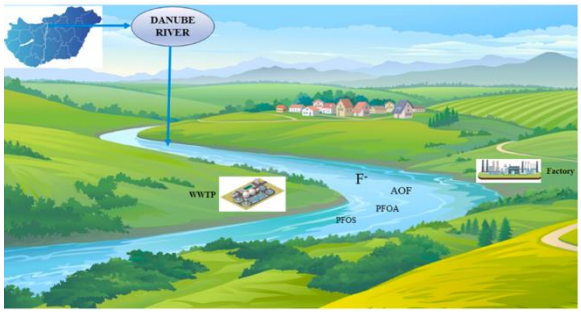


**Fig. 1:** PFAS distribution in the Hungarian section of the Danube River.

**Results:** A comprehensive study conducted on the Danube in 2015 revealed perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in the range of 5-40 and 5-30 ng/L, respectively, with measurements in the Hungarian section ranging from 5-20 and 5-15 ng/L [2]. In this study, the concentrations along the Hungarian stretch were 0.7-2.3 ng/L and 0.7-1.7 ng/L respectively. The concentration was 28 to 76 µg/L (average 45.1 ± 7.7 µg/L, median 45.3 µg/L), and 0.22 to 12.15 µg/L (with an average of 3.19 ± 2.62 µg/L and a median of 2.43 µg/L) for IF and AOF respectively.

**Discussion:** Due to the high average water yield (2350 m3/s) of the Danube River in its Hungarian stretch (417 km), the concentrations of fluoride anions, total adsorbable organofluorines, PFOA, and PFOS exhibit minimal fluctuation in the water phase. Sediment concentration is expected to exceed these limits. A correlation between AOF levels and sediment properties was also noted, indicating that fine-grained, organic-rich sediments are key sinks for PFAS.

**Acknowledgement:** The research presented in the article was carried out within the framework of the Sz´echenyi Plan Plus Program with the support of the RRF 2.3.1 21 2022 00008 project.

**References:** [1] Langberg et al. (2021). Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking.
[2] Loos et al. (2017) *Analysis of emerging organic contaminants in water, fish and suspended particulate matter (SPM) in the Joint Danube Survey using solid-phase extraction followed by UHPLC-MS-MS and GC–MS analysis.*

# The current situation with TBT in Sweden – contamination situation, sources, transport pathways and ongoing research

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**Conference theme number(s): 1**

Organotin compounds have had a broad use as e.g. biocides and stabilisers in plastics. Release of organotin compounds are associated with e.g. ports and marinas, sewage treatment plants, wood-, paper- and pulp industries, and textiles production. Notably tributyl-tin (TBT) is associated with wide-spread harm to aquatic environments. TBT was used in antifouling paints to prevent the fouling of a broad range of organisms. Due to contamination of the marine environment and impacts on marine life its use as an antifouling agent was banned globally in 2008.

The current contamination situation in coastal and freshwater environments was investigated in a nation-wide survey comprising 70 sites impacted by ongoing environmentally hazardous activities as well as contaminated sites. Concentrations of TBT in surface sediment (0-5 cm) was found to be generally higher at sites where maritime industries, *i.e.* harbours or marinas, are present compared to sites with no maritime industries present. Concentrations of TBT in deeper sediment (15-20 cm) were generally higher compared to surface sediment at sites with maritime industries, whereas no such difference between surface and deeper sediment was apparent at sites without maritime industries (average and median concentrations in surface vs. deeper sediments were 42.8 and 3.7 (n=76) vs. 207 and 11.6 (n=49) at sites with maritime industries, and 9.4 and 1.8 (n=51) vs. 9.3 and 2.5 (n=42) at sites without maritime industries). This demonstrates that concentrations of TBT in sedimenting materials have decreased at sites with maritime industries following the ban of TBT in antifouling paints. Results from monitoring of offshore sediment also show decreasing concentrations of TBT in surface sediment, and thus the situation appear to be improving on both larger scales (i.e. sea basins) and smaller scales (local).
In contrast concentrations of TBT and other organotin compounds were similar in surface- compared to deeper sediment at sites without maritime industries, indicating that emissions of TBT from other sources continue.

Despite the improving situation, maritime industries are highlighed as significant pressures that prevent achieving good chemical status with respect to TBT in many coastal water bodies under the water framework directive. In the nation-wide survey concentrations of TBT exceed the effect-based quality standard for sediment at 13 of the 14 surveyed sites with maritime industries. In the 80 samples from these sites, concentrations of TBT exceed by an average of 34 (median 3.6, maximum 1177) the sediment quality standard of 1,6 microg/kg DW (at 5 % TOC). Results from the national marine monitoring programme on biological effects shows that impacts from exposure to TBT on marine molluscs are common. It is therefore necessary to continue preventing further inputs to aquatic environments.

Land and sediments in the vicinity of boatyards, ports and marinas are sources to secondary pollution of aquatic environments. In Sweden most leisure boats are stored on land over the winter season, and there are several thousand such sites spread across the country. The soil at these sites often contains very high concentrations of TBT and other pollutants that have accumulated there over time from maintenance work such as abraisive blasting and painting of hulls. The storage sites are typically situated close to aquatic recipients, and contaminants may be transported through different pathways. Particle-bound emissions can occur from wind erosion and dust that is deposited in surface waters, or transport via storm water. Or, if the surface is not hardened, leaching and transport via groundwater. Local conditions influence which pathways are more important, and thus which measures may be the most cost-effective. Higly contaminated sediments close to marinas may also serve as a source to wider TBT contamination of the recipient, either by leaching of soluble fractions to the water-phase, or resuspension and transport of sediment particles by currents or propeller movements. Ongoing research on measures to prevent emissions from marinas with boat storage sites on land will be presented and discussed.

# Long-Term Monitoring of Chemical Sediment Composition in the German Bight: Insights into Past and Future Trends and Changes

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**Conference theme number(s): 1. Zero Pollution**

**Introduction:** Sediments are an important sink for organic and inorganic pollutants. They can reflect the current "health status" of the surrounding environment and act as a record of chemical composition and pollution levels in the past. Using sediment as an archive alongside regular monitoring activities is therefore an important tool in tracking the evolution of the environmental status as required for the Marine Strategy Framework Directive (MSFD).

**Methods:** The German Federal Maritime and Hydrographic Agency (BSH) has conducted continuous annual monitoring activities in the North See (German Bight) for several decades. The aim of this ongoing monitoring is to systematically collect data on the chemical and physical state of the North Sea, enabling long-term assessments on environmental changes. This presentation outlines the monitoring activities and provides insights from the chemical data collected over the past decades, along with additional data from current research projects.

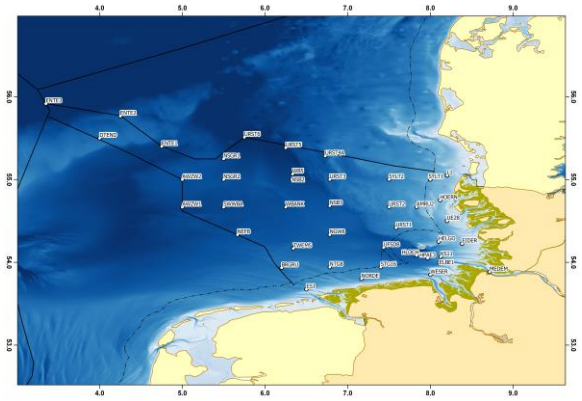

**Fig. 1:** BSH monitoring stations

**Results:**
The long-term monitoring data reveal changes in pollution levels in the German North Sea for various substances, including both organic and inorganic pollutants. For some substances, a decreasing trend in concentrations in surface sediments is observed (e.g. Hg, Pb), while others show no clear trend or even an increasing trend [1, 2, 3]. Furthermore, the data provides insights into the environmental impacts of substance bans and regulations illustrating how these regulatory measures are reflected in the monitoring data. Current data also help to assess potential new sources of emissions to the marine environment, such as those from offshore energy production (e.g. from corrosion protection) [4].

**Discussion:**
Continuous sediment monitoring offers valuable time-series data that reveal trends and changes in pollution levels. These data are instrumental in identifying emerging pollutants, which enables the implementation of timely mitigation measures. To achieve this, monitoring efforts must not only be sustained over time but also regularly updated to address evolving concerns. The list of substances monitored should reflect the current environmental priorities (e.g. PFAS), and new sources of emission, such as offshore energy production, should be integrated into monitoring strategies. Developing adaptive monitoring strategies will help to ensure pollution control and to develop actions to maintain healthy sediment conditions.

**References:**
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# The Rhône Sediment Observatory (OSR) monitoring network for suspended sediment and contaminants long-term assessment

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**Conference theme number(s): 1**

**Introduction:** The Rhône Sediment Observatory (OSR), created in 2009, aims to provide scientific knowledge for promoting a sustainable management of channel forms and sediment processes of this river [1], the largest by mean discharge in France and one of the largest tributaries of the Mediterranean Sea. We propose here a summary of the major developments and findings obtained on the monitoring of suspended sediment and associated priority substances in the Rhône River basin. We also focus on the evolution of the techniques and tools developed and applied for research and diffusion to stakeholders.

**Methods:** Monitoring of concentrations and fluxes of suspended particulate matter (SPM) and contaminants is based on continuous measurements of water discharge and turbidity/SPM, coupled with integrative sediment traps collected monthly for contaminants analyses. The OSR network includes 12 permanent stations in the Rhône River and major tributaries (Fig. 1, [2]). Different geochemical methods and models have also been developed and tested at various temporal and spatial scales to estimate the sources of SPM and associated contaminants.

**Results:** This comprehensive network has permitted to establish event-related, annual and interannual SPM and contaminants mass budgets across the entire Rhône River basin [3]. Sedimentary export to the Mediterranean was on average 5.21 Mt per year for the period 2009-2023, with very high annual variability (between 1.8 and 12.8 Mt). Nonetheless, on average, the Rhône system has a balanced sediment budget (inputs from tributaries versus outflow to the sea). In contrast, for contaminants (e.g., polychlorobyphenyls - PCBs, aromatic polycyclic hydrocarbons – PAHs, trace metal elements – TMEs, radionuclides), the annual outputs are often lower than the tributary inputs, suggesting that other sources must be taken into account. The various tributaries show very contrasting levels of contamination according to the contaminants studied, which can be explained by past or present activities on their watersheds. Overall, in the Rhône River, the concentrations of particulate contaminants have generally decreased or remained stable over the past 10 years and over the longer term. Nonetheless, contaminants concentrations remain higher in the Rhône River at the outlet than upstream.

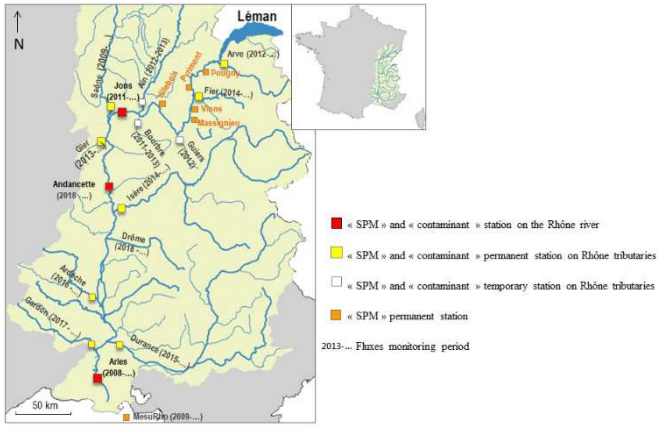


**Fig. 1:** The OSR monitoring network of SPM and associated contaminants along the Rhône River [2].

**Discussion:** Some sources of contaminants have yet to be characterized for budget that are not balanced. These sources include smaller mountain tributaries that could be highly contaminated by TMEs or direct discharges to the Rhône from urban areas (major sources of PAHs). Maintaining such a comprehensive monitoring network over a long period is essential to confirm or inform the trends observed, and to evaluate the policies implemented for the management of these contaminants.

**Acknowledgments:** This study was conducted within the OSR multi-partner research program funded through the Plan Rhône by the European Regional Development Fund (ERDF), AERMC, CNR, EDF & 3 regional councils (ARA, PACA & Occitanie).

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# Trends of per- and polyfluoroalkyl substances recorded in sedimentary archives upstream and downstream of the Lyon metropolis

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**Conference theme number(s): 1**

**Introduction:** Concerns about per- and polyfluoroalkyl substances (PFAS), known for their highly stable carbon-fluorine bonds, have sparked a global socio-environmental crisis. South of the city of Lyon (France), significant levels of contamination have been detected in various environmental matrices around the Pierre-Bénite industrial platform, which has synthesized, used, and released PFAS for several decades. Initial studies emphasize the role of this source, whose very specific molecular profile is marked by the predominance of long-chain carboxylates [1]. Sediment analyses conducted in the early 2000s revealed the evolution of discharges, with historical contributions up to 20 times higher than current levels [2]. In this context, the aim of our study is to better assess the level of sediment contamination at key sites along the Saône-Rhône river corridor. We also aim to determine the spatial and temporal extent of this pollution and identify the different phases of contamination throughout history.

**Methods:** The data used in this study originate from surface sediments and the analysis of six sediment cores encompassing the Lyon metropolitan area and documenting over four decades of river pollution. The sampling strategy was refined from 2012 to 2022, adapting to evolving scientific questions, public policy needs, and growing citizen concerns. In total, 3,874 PFAS concentrations distributed across 200 samples were compiled into a database suitable for geo- and chrono-statistical analysis.

**Results and Discussion:** In the Rhône River upstream of Lyon, PFAS concentrations in sediments are relatively low compared to other sediment cores. A trend of decreasing contamination levels is observed over the period covered by the archive (early 1980s–2022). The concentration levels do not exceed 2 ng/g for the sum of all measured PFAS. The compositional signature of PFAS is relatively similar to that reported at the national level [1], and sediment characteristics (organic matter content and grain size) may be key factors explaining the subtle variations within the sediment column.

Downstream of Lyon, at least three contamination phases can be identified over the period covered by the sedimentary archives (1980s–2022):

- The earliest phase is associated with PFOS and its precursors in the mid-1980s. This phase peaked in the early 1990s before decreasing sharply.
- The second phase is dominated by PFDA and PFDoDA, two long-chain PFCAs. Concentrations were already high in the 1980s, but the peak occurred in the late 1990s, followed by a rapid decline. The PFAS compounds present in the highest concentrations were PFDA, PFDoDA, and PFTeDA, with maximum levels reaching 23.3, 15.4, and 6.06 ng/g, respectively [2].
- The most recent phase is primarily characterized by PFUnDA and PFTrDA, also long-chain PFCAs. This phase began in the early 2000s, peaked in the early 2010s, and then declined rapidly, ending around 2017. These findings establish a link with PFAS compounds used in workshops at the industrial platform, which utilized Surflon® between 2013 and 2016 [3]. Notably, these same compounds have also been detected in soils and dust near or within this industrial site [4].

**Conclusion:** The contamination of sediments by PFAS, particularly long-chain PFCAs, poses a long-term challenge for managing contaminated sediment stocks. This issue also represent a strategic challenge for drinking water production and the ecological restoration of the river. Indeed, the biological compartment is severely contaminated locally, with bioaccumulation phenomena observed in fish and benthic invertebrates [5].

Finally, these results highlight a disconnection between the socio-political "crisis" surrounding PFAS and the measured contamination levels in the environment, despite the data being public and readily accessible.

**References:** [1] Munoz G et al. (2015) *Sci Tot Environ*, 517: 48-56; [2] Mourier et al. (2019) *Environmental Pollution*, 253, 1117-1125; [3] Ramboll (2023) *Arkema - Historical and Documentary Study*, excerpt; [4] ANCES (2023) *Technical note* 27 pp.; [5] Babut et al (2016) Research report, Irstea, 75 pp. hal-02603445

# Coastal microplastic monitoring: Harmonized protocols for sampling and analysis

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**Conference theme number(s): THEME 4**

**Introduction:** The explosion of research on microplastics (MPs) pollution in recent years has led to a better understanding of the extent of the spread of these contaminants. Many studies have shown that both humans and wildlife are potentially exposed, suggesting a need to better characterize the occurrence, distribution, sources and risk of exposure to MPs. Knowledge of the extent of MPs exposure, spatial and temporal trends, and the potential risks of MPs to human health is an essential prerequisite for the definition of protection and mitigation measures against MPs.

**Method:** There is no harmonized approach to MPs data collection, analysis and interpretation among the International Atomic Energy Agency (IAEA) member states (MSs). The IAEA project RER7016 aims to provide MSs of the European Technical Cooperation Region (TCEU) with the competencies to produce inter-comparable, reliable data that will enable MSs to improve their coastal management by effectively addressing the effects of climate change and pollution, including MPs. The first survey on MSs capacity to monitor MPs pollution showed that MSs were not sufficiently aware of the advantage of nuclear technology applications in monitoring MPs pollution.

**Results:** The focus of presented study is on the investigation of MPs in surface seawater and beach sediment on a European scale. It is well known that beaches are hotspots for MPs due to sea washing and the impact of tourist activities. The first step was to conduct a survey on the capabilities of the MSs involved in the RER7016 project to monitor MPs ranging in size from 0.3 mm to 5 mm in beach sand and surface water. According to their capabilities to monitor MPs, laboratories were classified from basic to advanced level by the criteria defined within the IAEA initiative "NUclear TEChnology for Controlling Plastic Pollution" (NUTEC). The second step was to develop harmonized sampling and analysis protocols through the exchange of expertise and best practices.

**Discussion:** The results of the survey have shown that although the MPs research is very important for studying marine pollution, it is still one of the most immature areas of monitoring. MSs that already have experience in MPs analysis, mostly do not conduct regular MPs monitoring. The need for harmonized methods and protocols has been clearly identified. The study presented here addresses this gap and presents the protocols for sampling and analysis of MPs in surface water and beach sand. The harmonization of protocols for sea sediment and biota are in preparation. This will enable the building of a European regional database for sharing and comparison of marine MPs pollution data. This database will allow researchers to analyze, consolidate and integrate their data at the regional level, which is important for evaluating the results of remedial actions taken at the global level. Ultimately, policymakers, researchers, and the public will benefit from not only the collected dataset but also from comparable data. This data have the potential to contribute to the achievement of SDG 14, the UN Ocean Decade Goal.

**Acknowledgment:** This work has been done within the framework of the IAEA RER7016 "Enhancing Coastal Management in Fresh and Saltwater Bodies by Using Nuclear Analytical Techniques, Including Monitoring of Microplastics". The IAEA Marine Environmental Laboratories are grateful to the Government of the Principality of Monaco for the support provided to the Environment Laboratories.

# Emissions - The long-term memory of sediments

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**Conference theme number(s): Theme 1 – Zero Pollution**

**Introduction**: Sediments are the long-term memory of anthropogenic (human caused) spills of chemicals. In many cases this has buffered the water quality, sediments remove contaminants from the water by sorption and settling. Alas, the reverse is also true, when the water quality improves sediments can become a source of contaminant emissions. We address the timescale of this impact and the relation with the Water Framework Directive (WFD) water quality standards.

**Methods:** This study consists of two parts. In *part one* we extrapolate the timescale to reach a good chemical status for chemicals with a historical background, TBT and PFAS, based on monitoring data and model extrapolation. In *part two* we calculate the potential impact of clean soil and sediment on the water quality when backfilling a deep lake connected to the river.

**Results:** *Part 1:* The use of the anti-fouling chemical TBT has been completely banned in the EU since 2008. Since the ban the TBT concentration in the water improves. However, the new Environmental Quality Standard $(EQS)_{sediment}$ is not yet reached. Extrapolation shows it takes at least till 2040 before the sediment is considered clean (Figure 1).

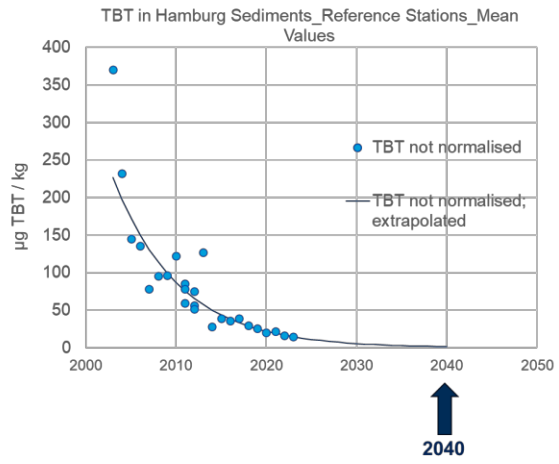


*Figure 1 Extrapolation of the observed TBT concentrations in Hamburg sediments to the moment the $EQS_{sediment}$ (proposal for directive on EQS, 2022) is reached (in 2040).*

*Part 2:* Based on the contaminant levels in soil and sediments suitable for beneficial use, the impact of backfilling a deep lake with soil and sediment on the WFD water quality can be estimated. To test if the impact on the water quality is acceptable the Netherlands uses an immission screening tool based on discharges (https://www.immissietoets.nl) Table 1 gives an impression on the impact of soil/sediment backfilling on the water quality impact for metals and PFAS.

*Tabel 1 Impression on the impact of backfilling on the water quality in the lake and bordering river.*

| | Does the emission from the soil/sediment meets the immission target (= have an acceptable WFD water quality impact)? | | | |
|---|---|---|---|---|
| | In the Lake | | In the river | |
| | during backfilling | after backfilling | during backfilling | after backfilling |
| **Metals** | | | | |
| antomony | ja | ja | ja | ja |
| arsenic | nee | ja | ja | ja |
| barium | ja | ja | ja | ja |
| cadmium | ja | ja | ja | ja |
| chroom | ja | ja | ja | ja |
| cobalt | nee | nee | ja | ja |
| copper | ja | ja | ja | ja |
| mercury | nee | nee | nee | ja |
| lead | ja | ja | ja | ja |
| molybdenum | ja | ja | ja | ja |
| nickel | ja | ja | ja | ja |
| tin | ja | ja | ja | ja |
| vanadium | ja | ja | ja | ja |
| zinc | ja | ja | ja | ja |
| **PFAS** | | | | |
| PFOS | nee | nee | ja | ja |
| PFOA | ja | ja | ja | ja |
| Mefosaa | ja | ja | ja | ja |
| Etfosaa | ja | ja | ja | ja |

**Discussion:** The lessons learned is that it can take decades after the use of chemicals has been stopped before the water quality improves sufficiently to meet the WFD water quality standard. The application of relative clean soils and sediment can have a negative impact on the water quality, especially during the backfilling. For many chemicals, even when their spill into the water is stopped today, it will take decades to reach background levels in the water quality due to the long-term memory of sediments.

**Acknowledgements:** We want to thank the Hamburg Port Authority for providing the data and the Ministry of Infrastructure and Water Management and RWS in the Netherlands for funding the research.

# Sediment risk assessment in Europe: comparison of environmental regulations

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**Conference theme number(s): 1 Zero pollution**

**Introduction:** Environmental regulation of chemicals in the EU was implemented to protect the environment against potential adverse effects caused by their use. Sediments are recognized as an integral part of aquatic ecosystems and, as such, sediment risk assessment is foreseen as part of the prospective risk assessment (before a substance is authorized for use and released into the environment) and retrospective risk assessment (once released) performed for the aquatic environment. As the chemical structure of a substance, and hence its mode of action, may allow its use for different commercial purposes, different regulations may apply for the same chemical.

The environmental assessment schemes that evolved during the last decades under the different regulations differ from each other. For many years, these differing assessments have been of no consequence, because there were mostly no points of contact between the different regulations that could have flagged inconsistencies. During the last decade though, surface water monitoring campaigns have been performed that have indicated risks for substances that are deemed safe for use.

This discrepancy has led the European Commission to set one of the objectives of the 'Chemicals Strategy for Sustainability' to move towards the introduction of the 'one substance, one assessment' approach. The aim is to improve efficiency, effectiveness, coherence and transparency of safety assessments across all relevant legislations. To support this EU strategy and the EU Green Deal, the EU funds a 7-year partnership under the Horizon Europe program (PARC, 2021-2028). In the context of PARC, we compared the environmental risk assessments for the aquatic ecosystem under prospective regulations and under the retrospective Water Framework Directive (WFD). Here, we would like to present the results of the comparison for the sediment compartment and reflect on whether current practice is aligned with the zero pollution ambition of a toxic-free environment by 2050.

**Methods:** We analysed the procedure, the protection goal and the conceptual approach for the following regulations: (EC) No 1107/2009 for the authorisation of plant protection products, (EU) No 528/2012 for biocides, (EU) 2019/6 for veterinary medicines, and (EC) No 1907/2006 for industrial chemicals (REACH), as well as for retrospective assessments, e.g. for surface water bodies under Directive 2000/60/EC (WFD).

**Results and discussion:** For the regulations with a mandatory aquatic risk assessment, usually the requirements for sediment risk assessment are less strict than for other environmental compartments (surface waters, soil) and the risk assessment is only required if certain conditions are met. The common approach across all regulations to trigger sediment risk assessment is the potential accumulation of the chemical in sediments. While partitioning (i.e. Log Koc/ow>3) seems determining for sediment consideration, there is ample room for flexibility in the consideration of additional criteria that should cover substances that may not be appropriately targeted through the Log Koc/ow trigger such as the indication of accumulation in sediments from environmental fate studies or high ecotoxicological potential. The hazard assessment for the sediment compartment, while similar under most regulations, follows a tiered approach but most often only lower tier approaches based on partitioning modelling are completed. Furthermore, aggregate exposure resulting from uses in different regulations is not effectively implemented. Surface water monitoring has expanded, can be very useful but is hardly ever done for sediments.

**Acknowledgements:** This project was financed by the EC under the Horizon Europe program (PARC, 2021-2028) and the Swiss Federal Office of the Environment (FOEN).

# Changes in trends of the seawater column parameters and concentration of elements in sediments from 2005 to 2024 in marinas located in the eastern Adriatic Sea

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**Conference topic: Theme 1 - Zero pollution**

**Introduction:** Marinas play an important role in Mediterranean tourism, extending the tourist season. However, there are many environmental challenges that need to be addressed in order to ensure that marinas remain sustainable and continue to provide recreational boating while minimizing the impact on the marine ecosystem. The greatest environmental challenges posed by marinas are associated with the application of antifouling paints to boat hulls that often contain toxic chemicals (such as copper and zinc). The antifouling paints are designed to constantly release biocides into the seawater at low doses, but over time these biocides accumulate in the sediment, harming marine ecosystem. There are strict regulations on boat maintenance, wastewater disposal and antifouling paint content that must be implemented in marinas as environmental protection measures. It is crucial to constantly monitor the quality of seawater and sediment in marinas to assess the effectiveness of these protective measures.

This study examines temporal trends in physico-chemical and microbiological parameters of seawater and element concentrations in surface sediments from 2005 to 2024 across 15 marinas in the Adriatic Sea. Seasonal analyses were carried out to assess improvements and/or deteriorations in marine environmental quality.

**Methods:** The trends in temperature, dissolved oxygen, pH and salinity in the bottom and surface layer of the seawater column are shown for two Adriatic marinas over a period of 15 years (2009-2024). In addition to the in-situ measurements, laboratory samples of 0.5 L were taken from the bottom and surface layer for microbiological analyses (total coliforms, faecal coliforms and faecal streptococci) and 1 L was taken from the surface layer for the analysis of hydrocarbons.

The sediments from the 15 Adriatic marinas were analyzed to evaluate trends in Fe, Cu, Zn, As and Pb concentrations before and about 10-15 years after the installation of the plant for the removal of metals from marinas' wastewater. Of these 15 marinas, two were studied in detail over a period of 19 years (2005-2024). Approximately 1 kg of surface sediment was sampled using the sediment grabber. The analysis was carried out using energy dispersive X-ray fluorescence (EDXRF).

**Results:** The trends of quality indicators for seawater and surface sediments (pH, dissolved oxygen, conductivity, microbiology, mineral oils and concentrations of selected elements) were evaluated for 15 Adriatic marinas over the last 2 decades. The results show a decrease in pH values and oxygen levels in seawater which is primarily attributed to climate change and increased sea primary production. On the contrary, environmental quality has improved in terms of microbiology and mineral oil concentrations. The treatment of wastewater from the service areas in most cases led to a decrease in Fe, Cu, Zn, As and Pb concentrations in the sediments as shown by the analysis of sediments 10-15 years after the installation of wastewater treatment plants. The diagram in Figure 1 shows a comparison of the results for sediments taken in marina Punat pier and service area before and after installation of the wastewater treatment plant.

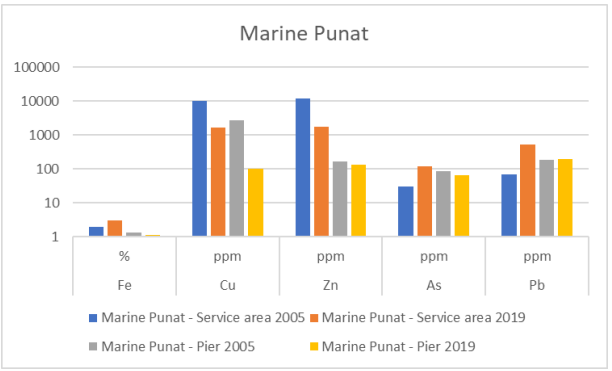


**Fig.** *Comparison of Fe, Cu, Zn, As and Pb contractions in sediments collected in Marina Punat at marina pier and marina service area in 2005 and 2019 (6 years after installation of the wastewater treatment plant).*

**Discussion:** The evaluation of the marine environment quality in the Adriatic marinas can be summarized as follows. The quality of sediments has improved in most marinas compared to the situation in 2005. In addition, a significant improvement has been observed with regard to the reduced input of mineral oils (petroleum hydrocarbons). As the main environmental risk is currently Cu input from antifouling paints, the solution could be to replace Cu-based antifouling paints with Si-based ones, which are substantially less toxic to marine organisms [1].

**Conclusion:** It has been shown that it is possible to improve and maintain a reasonably good seawater quality, and to slow down the accumulation of biocidal metals in sediments by careful implementation of environmental protection measures.

**Acknowledgments**: This study was carried out as part of the TC Project RER7016/IAEA "Enhancing Coastal Management in Fresh and Saltwater Bodies by Using Nuclear Analytical Techniques, Including Monitoring of Microplastics".

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[1] Science for Environment Policy (2023) European Commission DG Environment News Alert Service, edited by the Science Communication Unit, The University of the West of England, Bristol.

# Scaling complexity: novel hydraulic flume experiments on the interaction of sediments with nutrients and pollutants

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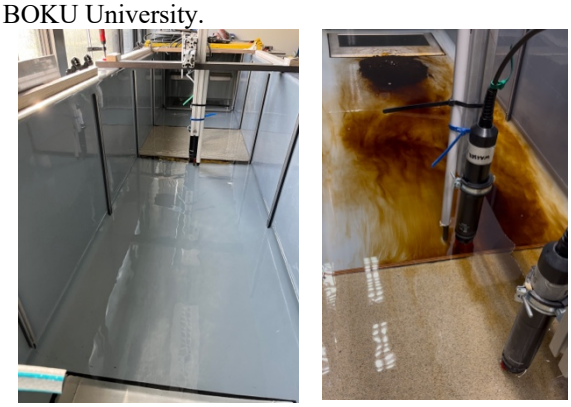
**Conference theme number(s): 1, 4**

**Introduction:** Aquatic ecosystems have been severely altered and disturbed by human influences. The result is a sharp decline in biodiversity in rivers. Despite existing research results, there is a knowledge gap regarding the local effects of nutrient and pollutant inputs in modified river systems and how these affect transport, deposition, and remobilisation [1]. Closing this gap is important for improving aquatic ecology and water management in general. A novel method for analysing nutrient and pollutant transport in hydraulic flumes is presented. The aim is to improve our process understanding of the interaction between sediments, nutrients, and pollutants.

**Methods:** The novelty and originality of the flume experiments compared to conventional approaches are: (i) adjustable hydraulic conditions; (ii) regulation of the water temperature; (iii) specification of physico-chemical parameters; (iv) controlled addition of nutrients in liquid form (e.g. fertiliser, manure) and particle-bound (e.g. arable soil); (v) reproduction of natural morphological aspects of a river (e.g. surface and subsurface layer of a river bed). ISE probes in the water and sediment were used to record the distribution of ammonium over time. Water and sediment samples were analysed for nutrient distribution in a certified chemical laboratory at BOKU University.



(a) (b)

**Fig. 1:** Hydraulic flume for investigating the interaction between sediments and chemical substances: (a) before the experiment: one sediment core and filled with tap water; (b) start of an experiment with animal manure.

**Results:** The initial results show clear differences in the temporal and spatial distribution depending on whether the nutrients are added in a particle-bound or liquid form. It was shown that the addition of animal manure produces an initial peak and then releases nutrients more evenly. When adding soil, variations in the concentrations and the time course were recorded. There were also differences regarding the structure of the sediment body (layers with different grain sizes) and the release of nutrients from these sediment bodies. The time course of the ammonium concentration is clearly different when finer substrate ($d < 0.8$ mm) is placed on coarser suspended sediment ($d < 8.0$ mm) than when the two layers are installed in the channel in reverse order.

**Discussion:** The novel approach of using adapted hydraulic flumes aims to investigate the hypothesis that particle-bound nutrient input and pollutant transport is also strongly influenced by the morphological characteristics of the river and the substrate composition. Consideration on a local scale is particularly important for the benthic environment [2]. In addition, this study investigated the hypothesis that temporal factors, such as sequential nutrient supply, may lead to an under- or overestimation of particle-bound nutrient dynamics in rivers, depending on when and where samples were taken in nature. This method offers the possibility to verify the previous findings (under optimum laboratory conditions) on pollutant binding (e.g. distribution coefficient Kd) in adjustable physico-chemical and hydraulic complexity. This allows the transport and fate of pollutants in rivers to be investigated and a deeper understanding of these processes to be gained.

**Acknowledgements:** The project is funded by the Disruptive Innovation – Early Career Seed Money funding programme of the Austrian Academy of Sciences (ÖAW) and the Austrian Science Fund (FWF).

**References:** [1] Flödl et al. (2023) *Limnologica* **98**: 125991; [2] Casas-Mulet et al. (2021) *River Res Applic.* **37:**988–1002.

# Electrokinetic decontamination of Tributyltin (TBT) in dredged sediment

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**Conference theme number: 1 (Zero Pollution)**

**Introduction:** Tributyltin (TBT), an organotin compound used in antifouling paints, has caused significant environmental contamination. TBT strongly binds to sediment, limiting its degradation. The European Commission (DG-ENV) plans to set strict Environmental Quality Standards (EQS) for TBT in sediments, often close to or below the detection limits of current analytical methods. This necessitates the development of effective remediation techniques. This work investigates the electrokinetic decontamination of a marine dredged sediment using different setups and enhancing solutions.

**Methods:** Two types of reactors were used: a single-compartment flow reactor and a concentric two-compartment reactor. We tested different energy sources to facilitate desorption, along with various electrode configurations and enhancing solutions. In total, we conducted 24 different treatments. Before and after each experiment, we analyzed TBT and its degradation products (dibutyltin - DBT, and monobutyltin - MBT) using the method described in [1].
Freeze-drying of the samples for 24 hours was used to remove water. Approximately 0.2 grams of each sample were weighed and placed it in a focused microwave extraction tube. A known amount of $^{119}$Sn-labeled MBT, DBT, and TBT (a certified tracer mixture from ISC-Science) was added. 4 ml of an acetic acid/methanol mixture (3:1) was also added. The samples were then extracted for 4 minutes at 80°C in a focused microwave oven.
For the analysis 1.5 ml of the extract were transferred to a glass vial. Then, 4 ml of an acetic acid/acetate buffer (pH 5.4), 0.2 ml of a 1% (w/w) sodium tetraethylborate solution and 1 ml of hexane were added. The vial was capped and shaken for 5 minutes. The hexane layer was separated from the aqueous layer. Most of the hexane extract was transferred to a gas chromatography vial using a Pasteur pipette. The hexane was then evaporated under a gentle stream of nitrogen. For GC-MS Analysis 1 µ of the final extract was injected into a gas chromatograph coupled to a triple quadrupole mass spectrometer equipped with an electron ionization source (Agilent model 7000).

**Results and Discussion.** The highest extraction efficiency was achieved using the flow reactor. Optimal conditions included an applied electrical current of 0.15 A for 2 hours, the application of ultrasound, and the use of 0.25 M citric acid as the electrolyte (see Figure 1).
After treatment, TBT concentrations were below the detection limit of the analytical method. DBT concentrations decreased by 65%, and MBT concentrations decreased by 23%.
To assess the overall reduction of the entire organotin family (TBT, DBT, and MBT), we conservatively assumed that the TBT concentration was equal to the detection limit (0.3 ng/g). Based on this assumption, the overall decontamination efficiency was 47.6%.
These results demonstrate the potential of electrokinetics as a promising technique for decontaminating TBT-contaminated sediments under specific treatment conditions.

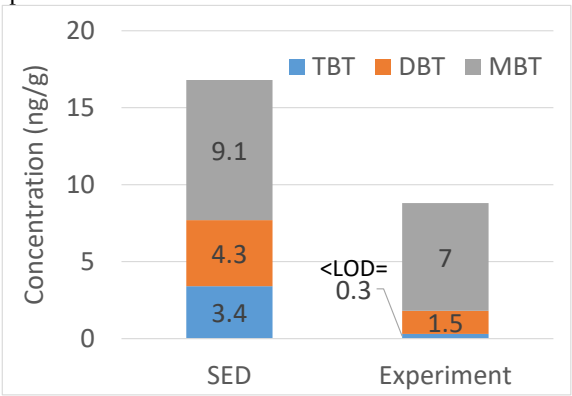


**Fig. 1:** *Concentration of TBT, DBT and MBT in the raw sediment (SED) and after the experiment which showed the maximum removal efficiency.*

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**References:** [1] Potes-Rodríguez, H., Marchante-Gayón, J. M., Rodríguez-González, P., Filgueiras, A. V., Viñas, L., Pérez-Fernández, B., ... & Alonso, J. I. G. (2024). *Microchemical Journal*, *207*, 111753. [2] Llorente, I., Ruiz-Fernandez, J., Nevshupa, R., & Castellote, M. (2024). *Journal of Soils and Sediments*, *24*(12), 3863-3876.

# Assessing the impact of dredge disposal on different ecosystem components in the Belgian part of the North Sea

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**Conference theme number(s): 1**

**Introduction:** Harbours and navigation channels are dredged throughout the year to prevent siltation. In the Belgian part of the North Sea (BPNS), dredged material is disposed at five designated areas, located in three different benthic habitats (fine muddy sand *Abra alba*, muddy *Macoma balthica* and sandy *Nephtys cirrosa* habitat). Possible effects of dredge disposal are burial of benthic organisms and habitat changes due to sediment changes [1]. The Marine Strategy Framework Directive requires monitoring to check how this type of pressure influences the good ecological status of the marine benthic ecosystem.

**Methods:** The study covered 15 years (2005-2019) of monitoring in the BPNS, including three different ecosystem components (macrobenthos, epibenthos and demersal fish). The Benthic Ecosystem Quality Indicator (BEQI, www.beqi.eu) scores were calculated for the three benthic habitats, in which diversity, species composition, density and biomass were compared between the five impact areas and the control sites. These Ecosystem Quality Ratio scores (EQR) range between 0 and 1, where values below 0.6 imply that the benthic system in the impact area deviates significantly from the respective reference sites. Linear mixed-effects models (LMM) were performed to investigate the relationship between the amount of dredge disposal (pressure) and the EQR scores (impact) in the three habitats for the three ecosystem components.

**Results:** The highest impact was observed for the macrobenthic community in the *Abra alba* habitat, a site that received high and continuous dumping (on average 5.3 million tonnes dry matter per year). The LMM for the *Abra alba* habitat shows a significant decrease in the EQR scores for macrobenthos with increasing pressure (Fig. 1). The LMM shows a similar trend for macrobenthos within the *Macoma balthica* habitat, although the higher EQR scores suggest a smaller impact, even when receiving a relatively high amount of disposed material (Fig. 1). Most probably, the composition of the disposed material was not that different from the muddy sediment in the receiving habitat. For the *Nephtys cirrosa* habitat, the impact on the macrobenthic community was low, as overall high EQR scores were calculated, independent of pressure (Fig. 1). However, only limited amounts of dredged material were disposed at the sites in this habitat, which might influence the impact-pressure correlation. Also, the epibenthic and fish communities in the *Abra alba* habitat were affected, probably related to changes in the macrobenthic community at the impact site. For the other habitats, the impact on the epibenthic and fish communities was much lower, probably related to the higher mobility of these species groups. This is reflected in the LMMs for both ecosystem components (not shown). Although it was statistically not possible to detect a different impact, this did not imply an equal impact in the three habitats.

**Discussion:** The impact of dredge disposal varied with pressure (i.e. amount of dredged material), ecosystem component and habitat type. The EQR scores decreased with increasing pressure in all three habitats, though the impact was most clear in the *Abra alba* habitat for all three ecosystem components. The present study shows that benthic indicators of different ecosystem components are very useful to assess human pressure.

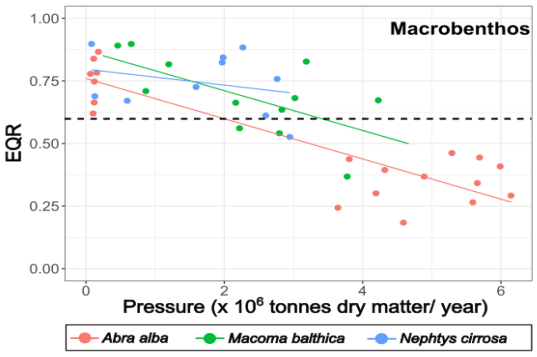


**Fig. 1:** Average EQR scores in function of pressure for macrobenthos in the three benthic habitats. The dashed line represents the threshold EQR score 0.6.

**References:** [1] Bolam and Rees (2003) *Environmental management* **32**: 171-188.

# Tribochemical decomposition of aromatic pollutants in dredged sediment

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**Conference theme number: 1 (Zero Pollution)**

**Introduction:** Over the past years, enormous efforts have been made in order to find new paths of chemical reactions, that could lead to the highly desirable thermodynamic and kinetic targets in various applied chemical processes. The nonconventional approaches involve non-thermal ways of activation of chemical reactions, many of which can have unusual reaction trajectories and products. Recently, the concept of a new technology for processing polychlorinated biphenyls waste through mechanically activated chemical treatment was proved (triboREMEDY project).
Our studies were focused on deep understanding of fundamental mechanisms underlying tribochemical activation for different classes of materials including metals, ceramics, polymers, surface coatings and liquids using a combination of advanced and original techniques including Mechanically Induced Gas Emission Mass Spectrometry. In this work, we explore the potential of tribochemical approach to solving challenging problems in decontamination of dredged sediments.

**Methods:** A model system consisting of a quartz sand as the main mineral component of sediments and various polycyclic aromatic hydrocarbons (anthracene and phenanthrene) and aniline, which simulated the contaminants. Sand and contaminants were loaded with various proportions into steel mechanochemical vial containing steel balls. The mixture was subjected to high-energy milling for 1 to 5 hours. After the test, milled sand was added to DMSO-d6 and solid fraction separated from the liquid phase. The obtained liquid was analysied using Nuclear Magnetic Resonance spectrometry ($^{1}H$ and $^{13}C$).

**Results and Discussion:**
NMR spectra showed that chemical transformations in all model contaminants initiated during the first hour of treatment and intensified after 5 hours (Fig. 1). In aniline, mechanochemical degradation started at amine group and continued at bencene ring. Similar degradation of aromatic structures were found for polyaromatic compounds. The resonance peaks became less intense and widened indicating possible distortions and tensions.

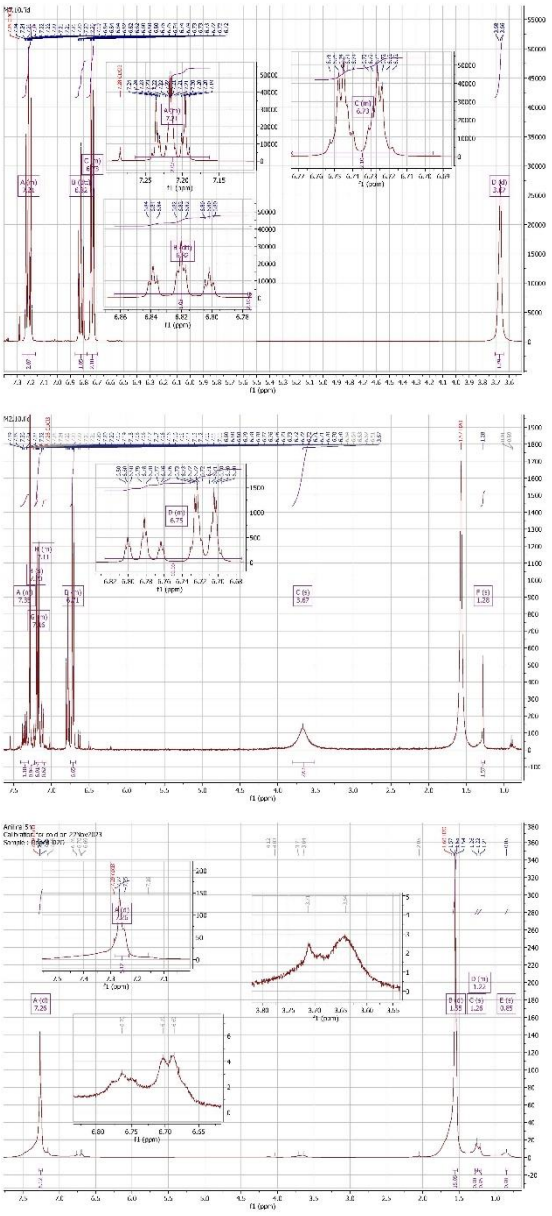

**Fig. 1. Top – pure aniline, middle – after 1 h treatment, bottom – after 5 h treatment.**

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