

[OP 3.6]

Effect of Remobilization on Redox Potential, Metal Speciation and Toxicity of Contaminated Sediment Layers: The Case of Arsenic, Cadmium and Lead

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Dam sediments are periodically subject to resuspension processes which strongly modify their physical structure and the inherent chemical and biological equilibrium. The new microenvironmental conditions change the bioavailability of contaminants. Consequently, sediment toxicity may be modified. Little information exists about the dynamic of sediment restructuring after a resuspension event and about the speciation changes of potential toxic chemicals in freshwater sediments. The aim of this work was to study the impacts of a remobilization/settling sequence on anoxic dam sediments known for a high level contamination in As, Cd and Pb.

The resuspension was simulated at the laboratory by mixing sediment with oxyc water during 15 hours. Effects of perturbations were determined by comparing abiotic parameters evolution during five weeks in control systems (plexiglass cylinders in which sediments were carefully deposited without preliminary re-suspension: Undisturbed sediment (US)) and in the test system (cylinders which contained Re Deposited Sediments (RDS)). They were put in 2 microcosms filled with field water in anoxic conditions for the US and in oxyc conditions for RDS. Redox potential was measured with Pt-microelectrodes radially inserted in pre-drilled cylinders. The chemical extraction sequence was applied on 2 layers of sediment (0-5 cm and 9-14 cm depth) to differentiate between exchangeable, reducible, organic, sulfidic, and residual fractions of As, Cd and Pb. The toxicity of sediment layers was evaluated through a 96 h toxicity test performed with *Hydra attenuata* exposed to sediment pore water.

In the US, the redox potential showed no clearly vertical zonation. As a result of the resuspension event, the redox potential was raised from 63 ± 10 mV/SHE to 270 ± 5 mV/SHE. Five weeks after the resuspension, the redox evolution in the RDS allowed us to distinguish 2 sediment layers: The 0-5 cm layer where the redox potential was higher than in the US, and the deepest one where the redox was

similar for both sediments. Simultaneous to the redox increase, As, Cd, and Pb phase associations were modified. The As distribution changes were 1/an increase of As bound with Fe and Mn hydroxides (70% of total sediment As content in RDS, but only 29% and 19% in the 0-5 cm and 9-14 cm layers of the US, respectively), 2/ a decrease of As associated with the organic phase (6% in RDS against 51 and 37% in the US layers). The RDS sulfidic As content was between half the content of the 0-5 cm and 9-14 cm US layers (38% and 16%, respectively). Pb and Cd were less mobilized and remained predominantly associated with the sulfidic phase (between 50-70% for both metals in both sediments). After 5 weeks of restructuring, the only observed changes were a slight decrease in As and Cd bound with Fe and Mn hydroxides.

Another consequence of the resuspension event was an impoverishment of the RDS pore water in Cd (0.18 µg/L), As (217 µg/L), NH₄⁺ (6.9 mg/L), and dissolved organic carbon (26.3 mg/L), which were eliminated by mixing with water. This could explain the non-toxicity of RD pore water, whereas both US layers were toxic (*H. attenuata* 96 h LC 50%:16). During the 5-week experiment, these dissolved contaminants increased to similar or higher values than in the US except for the As and NH₄⁺ in the RDS 0-5 cm layer which remained lower. The 9-14cm depth layer of the RDS became toxic (LC 50%:35.4), whereas the 0-5 cm depth layer remained non toxic. In the conditions of our study, after the resuspension event, the contaminated sediment exhibited a loss of toxicity and modifications of the metal-binding phases, especially of As, in connection with mobilization. After 5 weeks of restructuring, the RDS pore water revealed toxicity again. This could be explained by a reduction of the freshly precipitated Fe and Mn oxyhydroxides which released adsorbed metals and metalloids in the pore water.

[OP 3.7]

German Federal Environmental Specimen Bank: Retrospective Monitoring of Organotin Compounds in Marine Samples and Evaluation of Results

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Within the framework of the Federal Environmental Specimen Bank-Program, the German Federal Environmental Agency (Umweltbundesamt) sponsored the development and optimization of an analytical method for the quantitative determination of organotin compounds in several biological matrices. Monobutyl tin (MBT), dibutyl tin (DBT), tributyl tin (TBT), diphenyl tin (DPhT) and triphenyl tin (TPhT) were analyzed following a protocol documented as a standard operation procedure. The method was validated by analyses of certified reference material (mussels) and by the performance of recovery experiments for all matrices and compounds.

From the marine ecological systems of the North Sea and Baltic Sea, brown algae, (bay) mussels, eel-pout muscle, and sea gull eggs were analyzed over several years between 1985 and 1996. The marine samples had been prepared following the German Federal

Environmental Specimen Bank guidelines and were stored at -150°C. The aim of these investigations was the retrospective monitoring of organotin compounds in order to identify if recent use restrictions had resulted in lower levels in biological samples.

For the interpretation of the results, data on production, use pattern, environmental fate, bioaccumulation, and ecotoxicological effects were compiled. TBT and TPhT were detected as major contaminants. The analyzed degradation products were found only at lower concentration levels. While the concentration of TPhT was decreasing in recent years, the concentration level of TBT remained relatively constant. There were no hints for a possible biomagnification of organotin compounds in the marine environment.

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