

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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Introduction. Dam sediments are periodically subject to resuspension processes which strongly modify their physical structure and the inherent chemical and biological equilibrium. Gradients (oxygen, redox potential, nutrients) which control the sediment structure are then markedly disrupted with special respect to the oxygen status : the mixing of anoxic sediments with oxic water cause a change from reducing to oxidizing conditions and the consequences of such events are an increase of redox potential and shifts in microbial and chemical processes. A new 'steady-state' is sometimes long to reach. These new microenvironmental conditions modify the chemical behaviour of molecules, and the bioavailability of contaminants. Consequently, toxicity of sediment may be modified.

Data addressing this issue on sediments from freshwater systems are lacking : 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. This was the aim of this work which studied the impacts of a remobilization / settling sequence on anoxic sediments of an hydroelectric reservoir located downstream old-time mining sites and highly contaminated in arsenic, cadmium and lead.

Materials and methods. The resuspension was simulated at the laboratory by mixing a sediment sample with oxic water during 3 x 5 hours; the sediment was then let to settle down during 2 days. Effects of perturbations were determined during five weeks by comparing abiotic parameters evolution in control systems (plexiglass cylinders (h: 23 cm, d: 7 cm, sediment height: 20 cm) in which sediments were carefully deposited without preliminary re-suspension) and the test system (similar cylinders which contained remobilized sediments). Cylinders were put in two microcosms filled with field water in anoxic conditions for the controls and in oxic conditions for the remobilized sediments.

Redox potential was measured with 4 Pt-microelectrodes (length: 50 mm, diameter: 4 mm) radially inserted in pre drilled cylinders at different depths.

Changes in As, Pb, Cd speciation were studied on 2 layers of sediment (0-5cm and 9-14cm depth). Chemical extraction sequence was applied to differentiate between exchangeable, reducible, organic, sulfidic, and residual fractions of As, Cd and Pb. Classical chemical sediment characterization was also simultaneously performed on these two sediment layers.

Toxicity of sediment layers was evaluated through 96h toxicity test performed with *Hydra attenuata* exposed to sediment pore water.

Speciation analysis, toxicity tests were performed following the resuspension event and 5 weeks after. Redox potential measurements were made just after the resuspension event, and 3 and 5 weeks after.

Results. In the undisturbed sediment (US), the redox potential showed no clearly vertical zonation. As a result of the resuspension event, the redox potential raised from 63±10 mV/ Standard Hydrogen Electrode (US) to 270 ±5 mV/SHE (Re Deposited sediment RDS). After 3 weeks of restructuring in microcosm, the total height of RDS was only about 15 cm in cylinders because of slow compaction, and the redox potential decreased with depth whereas US characteristics remained unchanged. Five weeks after the resuspension, the redox potential evolution allowed to distinguish 2 sediments layers: the 0-5cm layer where the redox potential was higher than in the US, and a deepest one where the redox was similar for both sediments.

Simultaneously to the redox potential increase, metals and metalloids phases associations were modified. The impact of the resuspension on the As distribution were 1/an increase of As bound with Fe and Mn oxyhydroxides (70 % of total sediment As content in RDS but only 29 % and 19 % respectively in the 0-5cm and 9-14cm layers of the US, 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 (19%) was between halfway the content of the 0-5cm and 9-14cm 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 in the RDS.

Another consequence of the resuspension event was an impoverishment of the RDS pore water in Cd (0.18 µg/L), As (217 µg/L), ammonium (6.9 mg/L), Dissolved Organic Carbon (26.3mg/L), which were eliminated with the dilution water used for the mixing. The 0-5 and 9-14cm depth layers of US contained respectively 0.25, 0.13 µg/L of Cd, 2140, 1060 µg/L of As, 19, 58 mg/L ammonium, 38.6, 32 mg/L of DOC. This could explain the non toxicity of RDS pore water whereas both layers of US were

toxic (*Hydra attenuata* 96h-Lethal Concentration of 50 % individuals: 16%). During the 5 weeks experiment, dissolved metals, metalloid and ammonium concentrations in RDS layers increased to similar or higher values than in the US except for As and ammonium in the 0-5cm layer which remained lower. The 9-14cm depth layer of the RDS became toxic (*Hydra attenuata* 96h LC 50%: 35.4) whereas the 0-5 cm depth layer remained non toxic.

Conclusion. In the conditions of our study, after resuspension event, the contaminated sediment exhibited a loss of toxicity and modifications of the metal-binding phases especially of arsenic, in connection with mobilization. After 5 weeks of restructuring, the RDS pore water showed again toxicity. This could be explained by reduction of freshly precipitated Fe and Mn oxyhydroxides which released adsorbed metals and metalloids in the pore water.