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Daily variations of Zn and Pb concentrations in the Deûle River in relation to the resuspension of heavily polluted sediments

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HIGHLIGHTS

- Transient phenomena could be detected by high-frequency on-line measurements.
- Boat traffic increases the electrolabile concentrations of Pb and Zn in the river.
- Increase of Pb and Zn levels was not due to benthic fluxes or pore water dilution.
- Release of Pb and Zn in the overlying water from AVS oxidation was discarded.
- Labile Pb and Zn concentrations in the river were controlled by sorption processes.

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ABSTRACT

Sediments in the Deûle River (northern France) are severely polluted by metals in the vicinity of several metallurgical plants. The aim of this paper is to identify the role played by the recurrent resuspension of these polluted sediments by boat traffic on the dissolved Pb and Zn concentrations in the river. For that purpose, several high-frequency on-line monitoring campaigns were performed. Our results clearly suggest that the resuspension of sedimentary particles into the overlying water significantly increased the dissolved electrolabile Pb and Zn contents. This increase does not persist for a long time because at night and during weekends and holidays, when the boat traffic strongly slows down, Pb and Zn concentrations drop again quickly. Our data also indicate that the biological processes (such as photosynthetic and respiration activities), diffusive and benthic fluxes, as well as dilution of pore water into the overlying water during sediment remobilization do not contribute significantly to the sharp increase of dissolved Pb and Zn concentrations in the river during the day. The good correlation between turbidity and electrolabile metal concentration allows us to discard slow AVS (Acid Volatile Sulfides) oxidation as well. Desorption of metals from sediment particles was clearly the most relevant process, responsible for the increase of dissolved Pb and Zn concentrations in the water column.

1. Introduction

Because of the high affinity between trace metals and particles, sediments behave as a sink for these contaminants, especially in river canals where flow is low. In sediments, the fate of trace metals is complex and depends on several physico-chemical and chemical parameters, such as the grain size of the particles, biodegradable organic matter input and content of sulphates (Durán et al., 2012; Eggleton and Thomas, 2004). In undisturbed sediments, reduction of iron and manganese (hydr)oxides and oxidation of organic matter by bacteria in the top one centimetre tend to dissolve trace metals into the pore waters. Therefore, early diagenetic processes may result in the partial mobilization of trace metals that may diffuse back to the water column (Emerson and Hedges, 2003; Metzger et al., 2007). Conversely, the production of sulphides by sulphate reducing bacteria results in the precipitation of metals as discrete phases and/or solid solutions (Morse and Luther, 1999).

The effects of contaminated sediments on the overlying water quality have been extensively studied using several approaches. The easiest is probably to perform laboratory experiments by checking a mixture of water and sediments (Oursel et al., 2013; Simpson et al., 2000) or to measure fluxes at the water–sediment interface with DGT probes (Metzger et al., 2007; Pradit et al., 2013), microelectrodes (Luther et al., 1999a,b; Stockdale et al., 2009), or incubation chambers (Kalnejais et al., 2010). A more sophisticated one is to mimic the aquatic system and to set up microcosms, such as flumes, some of them having

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big sizes to better model the reality (Couceiro et al., 2009; Thompson et al., 2011). In the two latter cases, researchers are more or less able to control some specific parameters to simplify the evolution of the system and the repeatability of the experiments. Models of the processes that occur in the river can be very useful but should still be taken with care (Banks et al., 2012). The third way is to work *in situ* with benthic chambers, DGT probes and microelectrodes (Viollier et al., 2003). This approach is interesting but the deployment is laborious and sometimes, particularly in our case, impossible to set up because of the intense fluvial traffic during day time and the shallowness of the water column (maximum 3–4 m depth). Additionally, benthic chambers do not take into account the hydrodynamics of the river, and *in situ* detection of trace metals with microelectrodes at the water–sediment interface is not yet fully operational. As for DGT probes, the measurements are too integrative against time to monitor short term events.

Finally, the last approach is to monitor directly the concentrations of trace metals in the river water in order to understand the role played by resuspended sediments on these concentrations. In this case, sampling frequency is a paramount parameter to evidence exchanges between sediment and water. High frequency monitoring (at least 1 measurement per hour) has already permitted to better understand the dynamics of the nutritive salts (Gammons et al., 2011), phytoplanktonic activity (Volkmar et al., 2011), trace metal behaviour (Kay et al., 2011; Louriño-Cabana et al., 2011) and to show that the short term evolutions (for instance daily cycles) can be larger than seasonal changes (Nimick et al., 2003).

Sediments in rivers, crossing industrial areas where metallurgical factories are located, are generally severely polluted by trace metals such as lead, cadmium or zinc (e.g. Vdović et al., 2006). In these areas, dredging is problematic because disposal of the contaminated sludge is not allowed and the cost to treat it is very high. The authorities then prefer to limit further benthic pollutant fluxes in the rivers hoping that the currently new deposited sediment layer will be less polluted and will bury the historic metallic contamination. However, the fluvial traffic in some river canals is very active and should increase in the next ten years to limit road transport (European Commission, 2011). Thus, the bottom sediment is resuspended by the ship's propellers several times per day, because of the shallowness of the water in the canals, and introducing polluted sediments into the overlying water.

The objective of this work is to gain new insights on the effect of recurrent remobilizations of sediments contaminated by trace metals, especially lead and zinc, on the water quality of the Deûle River. For that purpose, one of the best suited methods is the use of high frequency on line monitoring since phenomena are transient at the scale of the day and these perturbations are not easy to simulate in the laboratory. We report here the main processes (dilution, dissolution/precipitation, sorption process…) controlling metal exchanges between water and sediment, the affect of remobilization events on suspended particle matter and dissolved species and the impact of sediment remobilization on the quality of the water column?

2. Experimental

2.1. Study site

The study site is the Deûle River, in northern France, a tributary of the Scheldt River via the Leie River. It is a 60 km long river (with an average flow of 8 $m^3 s^{-1}$ at Wambrechies) whose riverbank has been channelled to facilitate fluvial traffic. Barges are allowed to navigate only during the periods that the locks are operated, leading to important remobilization of sediments during the day and to particles' settlement at night. The samplings were performed near the city of Auby, close to three zinc smelting plants (one closed down, Metaleurop and two others still in activity, Umicore and Nyrstar). This site is thus characterized by a heavy historical metallic contamination of the soils and sediments.

2.2. Sediment and SPM (Suspended Particulate Matter) sampling and analysis

Several sediment sampling campaigns have been performed in the previous years, especially the campaigns on May 25th 2011 and May 24th 2012 are important for this work. Sediment cores were collected with 35 cm long Perspex tubes in the middle of the Deûle River with a small boat. Immediately after sampling, the cores were sliced every centimetre under nitrogen atmosphere in a glove box and put partly in plastic bags and partly in centrifuge tubes to further extract pore waters. Back to the laboratory, the sediment bags were frozen at −18 °C prior to analyses.

A clean laboratory from the VUB was stationed at the former site of Metaleurop from April 15th to May 15th 2009. Eighty water samples were collected manually and treated immediately under clean conditions to recover the SPM by filtration.

2.2.1. Interstitial waters

Sediment slices were centrifuged for 30 min with a rotation speed of 2500 rpm. Supernatant anoxic pore waters were filtered under N_2 on 0.45 μm cellulose acetate filters (Alltech) and acidified with ultra-pure nitric acid. The Pb and Zn contents were then determined by ICP-MS (X Series Thermo Elemental). Calibration standards were made from 1000 mg L^{-1} standard solutions (Merck) carefully diluted in the range of concentrations present in the samples. An SLRS-4 certified water sample (NRC-CNRC) was included in each batch of samples for QA/QC. The recovery was better than 6% for Pb and Zn.

pH measurements in the interstitial water were performed directly in the sediment core with a combined glass electrode (Crison 52–21). The electrode was introduced in the sediment core through holes in the Perspex tube.

2.2.2. Sediment particles

In order to estimate the lability of Pb and Zn in sediments, sequential metal extractions have been carried out according to the method described by Rauret (1998) and completed for the residual fraction by Pueyo et al. (2008). Briefly, it consisted of 4 successive extraction steps performed on a wet sediment sub-sample with the following reagents: (i) acetic acid 0.11 M (*pro analysis*, Merck) under nitrogen to extract metals weakly adsorbed or present in carbonate minerals and labile sulphides; (ii) hydroxylammonium chloride 0.5 M (*pro analysis*, Merck) under nitrogen to solubilize metals associated with oxides and the remaining volatile sulphides; (iii) hydrogen peroxide 8.8 M (Merck) at 85 °C followed by ammonium acetate 1 M (*pro analysis*, Merck) to oxidize organic matter and pyritic compounds and (iv) fluorhydric acid 40% (*Suprapur*, Merck) and aqua regia to recover metals initially present in the refractory minerals (like clays, silicates, refractory oxides, etc.). The extraction procedure was validated using the certified sediment BCR601 (Institute for Reference Materials and Measurements). We found that the recovery for each step was better than 89% for Pb and 90% for Zn. A total extraction [step (iv)] was also made on a dried sediment sub-sample. The extracted metals were subsequently analysed by ICP-AES (Varian Vista, axial view). Calibration solutions were prepared for each of the extraction steps using the same reagents as for the samples (including also some major elements like Ca in the acetic acid solution) to take matrix effects into account.

2.3. Particles analysis

During the campaign of spring 2009, water samples were collected daily (at least 3 times a day including night periods) by a sampling system installed inside the clean container in 1 L acid cleaned polyethylene bottles. River samples were then filtrated in the clean container on 0.45 μm pre-weighted cellulose acetate filters (Millipore) with a peristaltic pump; the filters were put in Petri boxes and dried in a laminar flow hood. Afterwards, these filters were transferred to Teflon