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Evolution of Metallic Trace Elements in Contaminated River Sediments: Geochemical Variation Along River Linear and Vertical Profile

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Metal pollution in riverine systems poses a serious threat that jeopardizes water and sediment quality, and hence river dwelling biota. Since those metallic pollutants can be transported for long distances via river flow, river management has become a great necessity, especially in times where industrial activities and global climate change are causing metal release and spreading (by flooding events). These changes are able to modify river hydrodynamics, and as a consequence natural physico-chemical status of different aquatic system compartments, which in turn alter metal mobility, availability and speciation.
Vertical profiles of sediments hold the archive of what has been deposited for several tenths of years, thus they are used as a tool to study what had been deposited in rivers beds.
The studied area lies in the Orne river, northeastern France. This river had been strongly modified physically and affected by steelmaking industrial activities that had boosted in the middle of the last century. This study focuses on several sites along the linear of the Orne river, as well as vertical profiles of sediments.
Sediment cores were collected at sites where sedimentation is favoured, and in particular upstream two dams, built in the second half of the XXth century for industrial purposes. Sediment cores were sliced into 2-5cm layers, according to suitability, and analysed for physical and physico-chemical properties, elemental content and mineralogy. Data of the vertical profile in a sediment core is important to show the evolution of sediments as a function of depth, and hence age, in terms of nature, size and constituents. The physical properties include particle size distribution (PSD) and water content. In addition, the physico-chemical properties, such as pH and oxido-reduction potential (ORP) of interstitial water from undisturbed cores were also detected. Total elemental content of sediment and available ones of extracted interstitial waters was detected using ICP-MS and ICP-OES for trace and major elements respectively. Well crystallized minerals were detected by X-Ray Diffraction (XRD), while amorphous and poorly crystallized phases were identified with scanning and transmission electron microscope (SEM and TEM respectively), combined with Energy Dispersive X-Ray Spectroscopy (EDXS). Such microscopic techniques also provided information about metal carriers. To have an insight about the metal speciation at molecular level, X-Ray Absorption spectroscopy (XAS) was performed at Zn K-edge.

The first analyses of Orne sediment cores evidenced different particle size distribution and sediment consolidation levels. Yet the cores showed that below a layer of apparently recent sediments (about 10-20 cm), lie highly contaminated ones. Zn and Pb content in deep sediment layers reach several thousands ppm, where they appeared mainly as Zn and Pb sulphides. Also, the high content of iron in deep sediments resulted in the presence of different iron phases: hematite, wuestite, magnetite, goethite, sulphides (pyrite), as well as undefined iron-silicate. In addition, interstitial waters contained high values of available metals (Zn: 500-35000 ppm, Pb: 150-5700 ppm, Cd: 1-10ppm), which might cause a greater concern than solid-bound metals, especially when river bed sediments are disturbed.