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Characterization of mineralogical metal carriers in dredged sediments deposit

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Sediments originating from periodic waterways dredging were traditionally deposited on soil without specific precaution or planned treatments. It may be of environmental concern especially when they came from historically heavy metals-contaminated areas (zinc, lead) like north French coal basin. The chemical risk is the breakdown of heavy metals-carrier phases (electronic structure: oxidation state and nature of chemical bonds; crystal chemistry) liberating toxic elements which can migrate to the underlying soil and groundwater. In this framework, dredged sediments are currently studied to determine heavy metal contents, their distribution among phases, and the stability of these phases.

The main purpose of this work is to better understand and constrain mobility and bioavailability of heavy metals along an annual cycle. More particularly, the study presented here aims to identify and characterize the Pb- and Zn-carrier minerals in a ten-years-old dredged sediment deposit by combining chemical and spectroscopic techniques.

Traditional chemical sequential extractions methods were applied on untreated sediments sampled at different depths of the deposit. Results indicate that Pb and Zn are rather concentrated in the "acido-soluble" fraction (assumed carbonates) and the "reducible" one (Fe and Mn oxides) than in other ones.

Chemical analyses of major elements by X-ray fluorescence and diffraction showed that the sediment essentially consists of a silty and clay fractions and carbonates.

Optical and scanning electron microscopy observations confirmed the major mineralogy of the sediment, but also revealed micro-phases and heterogeneous fine-grained matrix not detected by laboratory X-ray diffraction due to a low sensitivity. Among these phases, we identify iron oxihydroxides, phosphates (apatite, undetermined iron bearing phosphates), sulphides (inherited sphalerite, framboidal pyrite) and sulphates (gypsum, barite).

Electron microprobe analyses provide evidence of significant Zn content in phosphates, low Zn content in carbonates, pyrite or sulfates and traces of zinc in the fine-grained silicate matrix. But, the estimated Zn content associated with the carbonate fraction is inconsistent with the Zn content determined by sequential chemical extraction. This demonstrates the lack of selectivity of the latter to distinguish heavy metals associated with carbonates and other unknown phases.

Complementary microanalyses using synchrotron radiation techniques were performed at the Diamond Light Source (UK). They provide evidence of heterogeneous low zinc contents in carbonates, reactional textures involving iron-oxides around carbonate grains, diffuse lead (and zinc) in the fine grained silicate matrix and well-correlated iron-zinc associations.

In this presentation, we will present a summary of the results obtained so far, the questions to be answered and our further works.