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Seasonal variations of trace elements speciation and toxicity in dredged sediment deposit. Are redox conditions a key controlling parameter ?

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Initially reduced dredged sediments are highly reactive materials once deposited in oxic conditions. Several studies have shown their ability to generate toxic leachates when contaminated by trace element like Zn and Cd. This release occurs in the following months after their field deposition due to sulphide oxidation and probably organic matter mineralization. However, little is known regarding the long term behaviour of the contaminated neosoil they become. In this study, we aimed to identify and rank mechanisms responsible for in situ geochemical transformations with time of these materials deposited in oxic conditions. The soil parameters and the toxicity of soil leachates changes with time were investigated to conclude about natural attenuation.

Physico-chemical investigations and ecotoxicological determinations using standardized bioessays, were performed on wet samples from an experimental plot. This plot is constituted of a layer of 40 cm thick of contaminated sediment which has been laid on the top surface of a cultivated brunisol. Contaminants are mainly Zn and Cd (around 6000 and 200 mg kg-1 respectively). This plot allowed us to monitor a total of 7 years of geochemical changes. Determinations concerned soil parameters (granulometry, CEC, pH, organic matter content…), soil leachates composition and ecotoxicity, and elements speciation (including Zn, Cd, Fe and Mn) determined by sequential extractions. Principal Component Analysis (PCA) was finally performed to highlight explicative factors of toxicity and speciation changes.

The monitored soil parameters did not show significant variations with time but sequential extractions highlighted deep changes in speciation of every element. For Zn, results confirmed literature data, meaning that sulphide oxidation led to an increase in the acido-soluble fraction (from 30 to 80% of total Zn content) during the first months following the deposition. However, this mechanism appeared accessory in controlling speciation changes from the second year of characterisation. Actually, results showed that elements speciation changed periodically. These changes were particularly pronounced in the case of iron. The amount of iron extracted by hydrogen peroxide (pH 3) described harmonics with time. This fraction was high in winter and low in the end of spring. This result was also encountered for Zn and other elements. We hypothesized that in spring and summer times, iron precipitates in oxide minerals which are able to sorb most of trace elements. But in winter, iron oxide and associated elements dissolve due to water logging of small pores. The released cations may sorb on organic matter, which would explain the increase in the amount of elements extracted by the oxidant reactant.

In contrast, toxicity did not show such a seasonal trend, even though, as expected, it was higher in aged samples than in the initial sediment. PCA showed that toxicity was correlated to Zn and Cd concentrations in leachates as well as that of Ca. This result suggests a control of toxic elements in solution by an exchange mechanism on soil surfaces. Now, this mechanism does not directly depend on redox conditions in the soil, which is consistent with the lack of influence of seasonal cycles.

Finally, natural attenuation should not be expected in such a system. It appeared that scavenger phases are periodically destabilized due to redox variations. The released Zn and Cd are then available to refill the exchangeable fraction which should maintain the toxic aptitude of the dredged material for decades.