Delayed immobilization of heavy metals in soils and sediments under reducing and anaerobic conditions; Consequences for flooding and storage

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Introduction: Along the main Dutch rivers, numerous restoration and redevelopment projects are carried out to improve safety in cases of high discharges and flooding. Often, large amounts of contaminated sediments are stored under water in depots or sandpits. This practice is based on the assumption that anaerobic conditions will develop over a short time period, and cause heavy metals to immobilize through sulfide precipitation. In this paper [1] we show that the generality of this assumption may be seriously questioned.

Methods: Anaerobic pore water compositions of six existing depots, containing sediments from either aquatic or terrestrial origin, were measured to obtain reliable field references. Reduction experiments were performed with SOFIE cells [2], in which time-dynamic measurements of reducing pore waters were carried out at the reigning redox conditions. A parallel experiment tested the possibility if sulfide-deficiencies could be compensated by the reduction of added gypsum, thus increasing the available pool of reactive S. Model calculations [3] were performed to distinguish between the thermodynamic and kinetic processes.

Results: Reduction of flood plain soils showed that dissolved organic matter (DOM) concentrations increased up to 7-fold over time, as a result of nutrient-mediated metabolic boost of oxygen utilizing bacteria. The association of metals to DOM increased significantly due to the loss of reactive Mnoxide and Fe-oxyhydroxide sorption phases during reduction. DOM released metals only slowly, therefore kinetically hindering the phase shifting to stable metal sulfide precipitates. The observed effects lasted at least ten months. In aquatic sediments, reduction rates of sulfates were six times faster, and the release of DOM occurred in lower amounts than in soils from terrestrial origin. It is shown that the addition of gypsum stimulates the formation of sulfides, thereby decreasing dissolved concentrations of most metals. To achieve this successfully, also an effective electron donor, e.g., degradable organic matter, must be added.

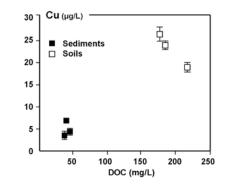


Fig. 1: Cu vs DOC in pore water in six depots. Depots on the right (Moorlag, Asselt, Meers) contain soils from terrestrial environments, depots on the left (Slufter, Amerika haven, IJsseloog), contain sediments of aquatic origin.

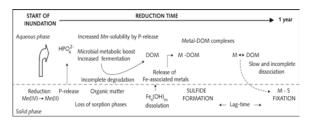


Fig. 2: Reduction in time. Reductive production of nutrients (P, Mn) increases the metabolic organic matter fermentation and the production of DOM, and prolongs the retention of metals in solution (M=metal; S=sulfide)

Discussion: For depots containing flood plain soils, the same kinetic mechanisms were observed as in the reduction experiments (elevated production of DOM and associated metals). It was concluded that reduction of flood plain soils may not necessarily result in efficient metal trapping, and groundwater is potentially at risk. When storage is considered, a distinction should be made between sediments of terrestrial and aquatic origin.

References:

[1] Vink JPM et al. (2010) J Soils Sediments (in press).
[2] Vink JPM (2002) Environ. Sci. Technol. 36:5130-5138.
[3] Vink JPM, Meeussen JCL (2007) Environ. Poll.
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