



## **Interferences on reductive dissolution and precipitation of iron (hydr)oxides in soils**

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Iron (hydr)oxides display a remarkable capacity for adsorbing a wide range of contaminants, including arsenic and other metals. In anoxic environments ( $E_h < 200\text{mV}$ ), iron (hydr)oxides are known to undergo a reductive dissolution which also means a mobilisation of associated contaminants. A re-oxidation of dissolved Fe(II) and a subsequent precipitation of mainly amorphous iron(hydroxides) occur when dissolved oxygen becomes present in the system. Hence, dissolved contaminants are immobilised again by co-precipitation and/or adsorption onto iron (hydr)oxides. In natural systems, behaviour of dissolution and precipitation of iron (hydr)oxides is often differing from that observed under laboratory conditions. This is due to the more complex composition of natural soil solutions and interferences by microbial activity. In this study, we adopt different approaches to improve consistency between actual data and model predictions for iron transport in a floodplain soil under water-saturated conditions.

The experimental setup should simulate flood events in soils which allowed to study the impact of annual flooding on soils which are situated near rivers. Soil column experiments were run in duplicate under saturated flow conditions. Soil material was taken from the top horizon ( $A_h$ ) of a floodplain soil near the Mulde river (Saxony-Anhalt, Germany). The redox potential and  $\text{CO}_2$  concentration in the column effluent were recorded on a permanent basis. The pH, electric conductivity, inorganic and organic carbon, and major and trace elements were also determined. Several stop flows of various periods of time were included in the experiments. All model calculations were done with the RICHY program, based on numerical modelling using the finite

elements method.

As a consequence of prolonged water saturation, remarkable drops of  $E_h$  to 200 mV led to a significant release of iron from the soil. Tracer experiments and flow interruptions revealed non-equilibrium conditions for iron mobilisation. With either parametric as well as nonparametric sorption isotherms, the model predictions of iron concentrations in the effluent did not fit the obtained data. The effects of the stop flows testified that a transport model based only on abiotic (reductive) dissolution did not include all processes affecting iron mobility. Thus, the model needed refinement, especially with regard to microbial activity. Several processes that took place in the soil columns were very likely to be induced by microorganisms. First, the behaviour of the mobilised iron indicated a strong complexation by organic ligands probably synthesized by microorganisms. The effluent samples still contained ca.  $25 \text{ mg L}^{-1}$  dissolved iron even after months of exposure to oxygen. Second, the results of inorganic and organic carbon analyses attested that a large amount of Fe-carbonate phases was present in the effluent following the stop flows. Because the soil material was carbonate-free, the formation of Fe-carbonate phases could also be ascribed to microbial activity. Elevated concentrations of  $\text{CO}_2$  in the effluent after flow interruptions (produced by microbial metabolism) resulted from an extended residence time in the soil column. Assuming that equilibrium conditions were present, this led to a higher concentration of carbonate in the liquid phase. This microbial induced carbonate may have formed the presumed Fe-carbonate phase. Additionally, elevated concentrations of manganese in the effluent forced the precipitation of iron-containing minerals. This also demonstrates the influence of soil solution composition on iron mobility.

Consequently, apparent reductive dissolution and re-precipitation of iron (hydr)oxides is clearly interfered by the composition of the soil solution and by biotic reactions induced by microorganisms. As a result the arsenic transport is also supposed to be predicted more precisely by a model adapted to these interferences on iron mobility.