

# Role of strong ligands for the infiltration of trace metals into groundwater

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In order to evaluate the mobility of trace metals in aquifers, the interactions between metal ions, ligands and surfaces of solid particles have to be considered. In the simplest case, complexation of metal ions by ligands in solution may favor their transport with the water phase by competing with adsorption to solid surfaces. Other reactions have however also to be considered, such as the formation of ternary complexes on surfaces and dissolution reactions of the solid phases.

The speciation of metal ions in natural waters depends on the intricate network of natural ligands (inorganic ions, fulvic and humic acids etc.), of anthropogenic strong ligands (e. g. NTA, EDTA) and of major and trace cations. These interactions result in different extents of complexation in solution for various elements. Experimental results on the speciation of copper

and zinc in river and lake waters show e.g. that copper is very strongly complexed, whereas a large fraction of zinc occurs as free ions or weak complexes. The presence of strong ligands of natural or anthropogenic origin may contribute to the transport of metal ions in the dissolved phase.

The role of EDTA (ethylenediaminetetraacetate), as an example of a strong ligand of anthropogenic origin, for the infiltration of trace metals will be discussed in this context. Various metal ions may be transported together with EDTA in natural waters, depending on the equilibrium competition between metal ions and natural ligands and on the exchange kinetics of EDTA complexes. Exchange kinetics of Fe(III)EDTA with other metal ions in solution are extremely slow (Fig.1).

A model system of EDTA / metal ions / particle surfaces ( $\alpha$ -FeOOH, goethite) is used in order to simulate possible interactions within an aquifer. We examine surface complexation reactions,

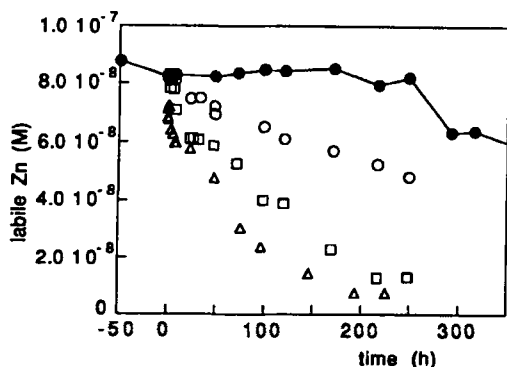


Fig. 1. Kinetics of the exchange reaction:  $\text{Zn}^{2+} + \text{Fe(III)EDTA} \rightarrow \text{ZnEDTA} + \text{Fe(III)}$ . Labile Zn (not bound to EDTA) was measured by voltammetry as a function of time after addition of Fe(III)EDTA to Glatt river water at  $\text{pH } 7.9 \pm 0.1$  in the dark. The concentration of labile Zn (initial concentration =  $8.23 \times 10^{-8}$  M) decreases subsequently to the formation of ZnEDTA, because this complex is not labile by the voltammetric method. (●): control, no addition of FeEDTA; (○):  $1 \times 10^{-7}$  M FeEDTA, (□)  $2 \times 10^{-7}$  M and (△)  $4 \times 10^{-7}$  M. (From: Xue, H. B., Sigg, L. and Kari, F. G., submitted to *Env. Sci. Technol.*)

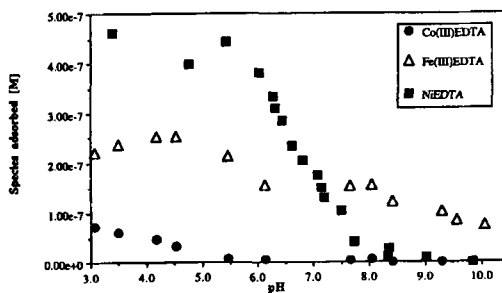


FIG. 2. Adsorption of various metal-EDTA complexes on  $\alpha$ -FeOOH as a function of pH ( $\alpha$ -FeOOH = 0.46 g/L; EDTA (total) =  $4.6 \times 10^{-7}$  M; I = 0.01 M  $\text{NaNO}_3$ ). The adsorption of NiEDTA increases with decreasing pH; other divalent metal-EDTA complexes behave in a similar manner. Fe(III)EDTA is adsorbed over a wide pH range and Co(III)EDTA is hardly bound to the surface. (From: B. Nowack, Ph. D. Thesis, ETH Zürich, in preparation).

formation of ternary complexes between surface groups, EDTA and metal ions, and dissolution reactions of  $\alpha$ -FeOOH. Adsorption of free EDTA and of EDTA complexes on the  $\alpha$ -FeOOH surface shows a strong pH dependence, which can be explained by specific surface complexation reactions. The complexes of trivalent metal ions (Fe(III), Co(III)) are less strongly adsorbed than those of divalent metal ions (Fig. 2). Under appropriate conditions (pH, concentration), exchange of metal ions complexed by EDTA with Fe(III) takes place. The results obtained in this simple system provide a basis for modeling the transport of metal ions into groundwater.