The influence of organic ligands on trace metal speciation

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Trace metals dissolved in ground and surface waters in general do not occur as metal ions but as metal-ligand complexes. The complexing ligands can be inorganic anions like hydroxide, chloride or carbonate. However, depending on the situation, the speciation of trace metals can be totally dominated by organic complexes. Geochemical models ignoring these organic ligands may produce grossly erroneous results concerning trace metal speciation in ground and surface waters. As the aqueous speciation of metal ions is directly related to solubility and sorption of trace metals, in consequence these phenomena may also be misjudged by orders of magnitude. Hence, any assessment of the behaviour of contaminant trace metals, e.g. escaping from an underground repository, critically depends on a sound treatment of the influence of organic ligands on trace metal speciation.

The 'backdoor approach'

In the past, it was tried to get a handle on this problem by including complexation data of all kinds of organic ligands into geochemical speciation models. However, this effort proved to be futile as the number of potentially complexing organic ligands is large, and information about the concentration of these organic ligands in ground and surface waters is sparse and varies over orders of magnitude. In addition, conventional geochemical models cannot be used to calculate the effects of natural organic ligands (humic and fulvic substances). We started to solve these problems by a new modelling approach, the so called 'backdoor approach', beginning with the question, 'What properties must an organic ligand have in order to significantly influence the speciation, and hence the solubility and sorption, of a given trace metal ?' (Hummel, 1992). First, simple organic ligands were treated by this approach (Hummel, 1993), later the backdoor approach was extended to cope with humic and fulvic acids (Hummel, 1997, and Glaus *et al.*, 1997).

U(VI) speciation as a specific example

In order to demonstrate the usefulness of the backdoor approach in assessing the influence of organic ligands on trace metal speciation, a specific example will be shown here. The contaminant trace metal is chosen to be U(VI), and the organic ligands considered are oxalate, EDTA (ethylenediaminetetraacetate) and humic substance. Oxalate is a simple natural dicarboxylic acid forming the strongest metal complexes within this class of ligands. EDTA is widely used for decontamination processes and represents strong synthetic complexing ligands. Humic substances are ubiquitous constituents of natural waters. They are known to form rather strong metal complexes.

The specific variant of the backdoor approach shown here reveals the concentration (in g/L) of organic ligand needed in order to complex 90% of the dissolved trace metal. Fig. 1 shows the results for U(VI) complexation with oxalate, EDTA and humic substances as a function of pH and log pCO_2. The latter quantity is the logarithm of the CO_2 partial pressure the water being in equilibrium with. Surface water in equilibrium with atmospheric CO_2 corresponds to a value of log $pCO_2 = -3.5$. As can be seen in Fig. 1, the general features are the same for all organic ligands. At low pH the protonation of the organic acid causes an increase of the total amount of ligand needed to maintain the 90% complexation level. Likewise, at high pH the increasing competition due to the formation of U(VI)-hydroxide complexes causes an increase in the ligand concentration needed for 90% U(VI) complexation. The strongest effect is seen at high pH and high CO_2 partial pressure because of the increasing competition of U(VI)−carbonate complexes. The plateau of the EDTA surface around neutral pH is caused by the competition of Ca−EDTA complexes. The level of this plateau is directly related to the calcium concentration assumed in the calculations. In Fig. 1 the Ca concentration was fixed to 0.0001 M. In most natural waters the Ca concentration is higher than that value and thus, the EDTA surface shown in Fig. 1 represents the worst case with respect to the influence of EDTA on U(VI) speciation. For a detailed discussion of competition effects and parameter uncertainties in the case of oxalate see Grenthe *et al.* (1997).

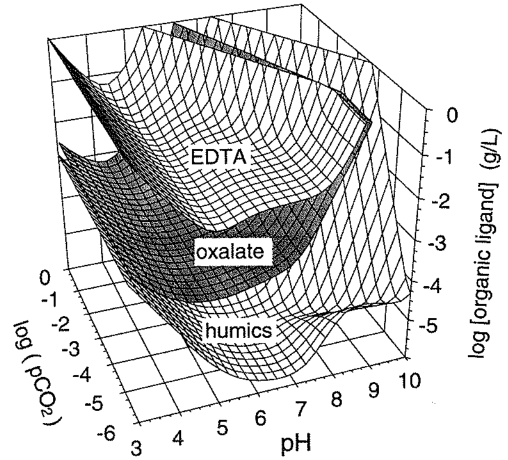

FIG. 1. 'Floating towel' representation of the conditions at which 90% of total dissolved U(VI) is bound to EDTA, oxalate or humics.

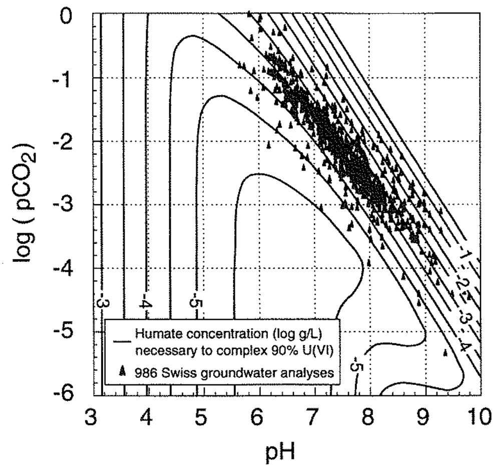

FIG. 2. Two-dimensional representation of the 'floating towel' showing contour lines of humic substance concentration at which 90% of total dissolved U(VI) is bound to humics.

As can be seen in Fig. 1, 0.01 mg/L humic substance is sufficient in neutral and slightly acidic surface waters to dominate the U(VI) speciation, but we need at least 1 mg/L organic acid to achieve the same level of complexation with oxalate. In the case of EDTA, concentrations of another two orders of magnitude higher values (0.1 g/L) are needed to have 90% of U(VI) complexed by EDTA. In the case of ground waters, located at the steep slope in the background of Fig. 1, generally higher ligand concentrations are needed to reach 90% U(VI) complexation. As an example, the surface for humic substance complexation is shown in Fig. 2 as a contour plot. In addition, pH and log pCO_2 values of almost one thousand Swiss ground water analyses are plotted in Fig. 2. It can be seen from that figure that almost all ground water data cluster in a narrow band of 0.1 to 1 mg/L humic substance needed for 90% U(VI) complexation. The situation is similar for oxalate and EDTA, but on progressively higher levels of ligand concentration. The sequence remains the same as in the case of surface waters.

This sequence is unexpected at the first glance. For most trace metals (e.g. transition metal and rare earth metals) the sequence is EDTA < humic substance < oxalate, i.e. EDTA has the strongest influence on trace metal concentration. In the case of U(VI), the opposite behaviour is found with EDTA causing the weakest influence on U(VI) speciation. Or, the other way round, we need very high EDTA concentrations for dominating the U(VI) speciation. What is the explanation of this erratic behaviour of EDTA? The reason is found in the molecular structure of the U(VI)-EDTA complex. In general, EDTA binds a metal ion with six functional groups (four acetate groups and two amine groups). Dissolved U(VI) has the structure of a linear O=U=O oxo-cation, and EDTA can bind this molecule with a maximum of only four functional groups instead of the usual six bonds. The result is a rather weak complex compared with other trace metals. In addition, the strong competition of Ca-EDTA complexes (where EDTA can bind Ca with all six functional groups) further decreases the influence of EDTA on U(VI) speciation.

Conclusions

In summary, the backdoor approach, in combination with computer graphic to visualise the results, is a valuable tool to explore the influence of organic ligands on trace metal speciation. It provides qualitative and quantitative information and allows general answers concerning the importance of organic ligands in ground and surface waters. Parameter variations reveal not only the most important parameters but also the sensitivity of the results due to uncertain data. Moreover, unexpected results, as shown in the case of U(VI) speciation, may even lead to new insights in the field of aqueous complex chemistry.