ECG Environmental Briefs **ECGEB No 17**

Modelling Metal Speciation in Natural Waters

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The behaviour and toxic effects of metals in natural waters are strongly impacted by speciation – the distribution of a metal among its different possible chemical forms. Computer models compute speciation at chemical equilibrium and are powerful tools if used with an understanding of their limitations.

The aquatic speciation of a metal refers to its distribution among its possible forms within a surface water. These forms include the free hydrated ion, complexes with small ligands such as carbonate, and with larger, chemically complex ligands such as humic substances, adsorbed on the surfaces of natural particles, and in mineral precipitates. There may be a number of chemical entities present in surface water which influence the speciation of a metal:

i. Small inorganic ligands such as chloride (Cl^-), sulphate (SO_4^{2-}) and carbonate (CO_3^{2-}) ions. Metals can bind to these ligands to form solution complexes;
ii. Protons (H^+), which will compete with metals for binding to ligands;
iii. Other dissolved metal ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+}/Fe^{3+}) and aluminium (Al^{3+}), which will also compete with metals for binding to ligands;
iv. Chemically complex dissolved ligands, particularly humic substances, which bind metals and protons as small ligands do, but which require complex modelling approaches;
v. Chemically active components of suspended matter. including mineral oxides such as those of iron(III), manganese (IV), and clays;
vi. In human–influenced waters, such as those receiving effluents from sewage treatment works, man-made ligands such as EDTA may be present in sufficient quantities to influence metal speciation (1).

The reaction of a metal with a ligand can be written quite simply, e.g. for the equilibrium between a copper ion and carbonate ion:

$$Cu^{2+} + CO_3^{2-} \Leftrightarrow CuCO_3^0$$

Here Cu^{2+} and CO_3^{2-} are the free (unbound) forms of copper and carbonate in water. The double arrow indicates that this reaction is reversible. At equilibrium, the relative concentrations of Cu^{2+}, CO_3^{2-} and $CuCO_3^0$ will be constant:

$$K_{CuCO_3} = [CuCO_3^0]/[Cu^{2+}][CO_3^{2-}]$$

The term K, the equilibrium constant, can be found for a particular reaction by experiment. A chemical speciation model uses a database of equilibrium constants, for the reactions of metals, protons (H^+) and ligands, to predict the speciation of the metals from the total concentrations of metals and ligands present. For example, the calcium (Ca^{2+}) ions in water can compete with copper for binding to the carbonate ion:

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3^0;\ \ K_{CaCO_3} = [CaCO_3^0]/[Ca^{2+}][CO_3^{2-}]$$

Given values of K_{CuCO_3} and K_{CaCO_3}, a chemical speciation model can automatically account for the competition between copper and calcium for binding to carbonate.

Metal speciation is important in understanding the transport of metal ions through surface waters and their potential effects on aquatic organisms. The extent to which a metal binds to ligands on the surfaces of suspended sediments, relative to its tendency to bind to dissolved ligands, will affect its tendency to be lost when sediment settles out of the water – in lakes, for example. The uptake of potentially toxic metals by organisms is partly controlled by their speciation but also by competition with ions such as magnesium and calcium.

Speciation in natural waters

A particular feature of natural waters is the presence of chemically complex ligands, both in dissolved form and on the surfaces of natural particles (sediments). These include humic substances, which are the dominant component of dissolved organic matter in natural waters, and minerals including oxides of iron(III) and manganese(IV), and clays.

Humic substances are formed from the breakdown of plant and animal matter. Their functional groups include carboxylic and phenolic acids and amines that are

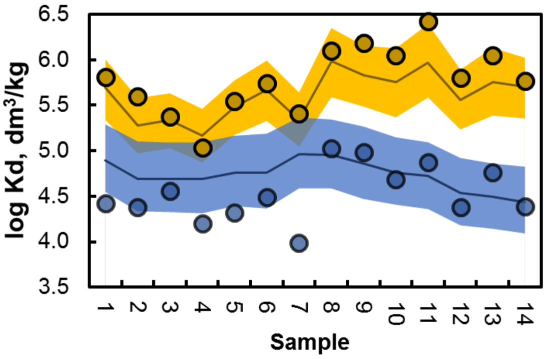

Figure 1*. Observed and predicted partition coefficients, Kds, for lead (yellow) and copper (blue) in a tributary of the River Ribble, north west England. The shaded areas show the uncertainty (±2 standard deviations) in the predicted partition coefficients. Data are from (5).*

capable of binding protons and metals. Their chemical complexity arises from their heterogeneity: each molecule has a number of functional groups, each with its own chemical environment, so that they exhibit a range of metal binding strengths. Many of the functional groups can combine to form multidentate binding sites which have particularly strong metal binding affinities. Despite this complexity, sophisticated models for humic substances have been developed and are used in researching metal speciation in natural waters (e.g. 2,3). Minerals also have functional groups that bind protons and metals. The most important of these are oxides of metals such as iron(III) and manganese(IV), and aluminosilicate minerals, i.e. clays. Models have been developed for these substances (e.g. 4). They are commonly found in sediments, although they may also occur as colloidal particles. These may be small enough to pass through the filters typically used to separate 'dissolved' and 'particulate' materials in waters. Particles in surface waters may also contain other materials such as algal and bacterial cells which can bind metals (6).

Testing models against data from the natural environment tells us how well speciation measurements agree with the theory defined by modelling. **Figure 1** shows an example of observed and predicted distributions of metals between solution and natural particles in a river. Such results can help us to assess aspects of the modelling, for example:

- Is the model as it stands useful in making predictions of metal chemistry in the field?
- Can we identify reasons why the model may perform poorly for some samples? Could it be due to uncertainties in the measured data, or could it be due to more fundamental issues that may require further model development?

A speciation model also makes more detailed predictions, for example about which ligand(s) metals are bound to. **Figure 2** shows the predicted average speciation of lead. We can see that lead associates strongly with ligands, particularly iron(III) and manganese (IV) oxides. This includes iron(III) oxide, which is measured as 'dissolved', but is actually present as colloidal particles. This type of observation gives us insight into which measurements and model parameters are likely to be most important and allows us to target research efforts to improve models for the future.

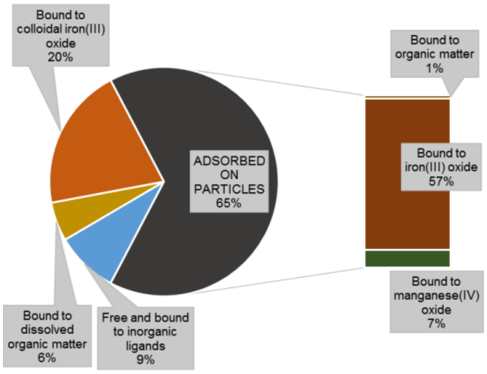

Figure 2. *The predicted average distribution of lead among its dissolved and particulate forms.*

General resources

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