

3.5: Metal Speciation

Learning Objectives

You should be able to:

- describe the reactions involved in the speciation of metals in the aquatic and soil environments.
- explain the equilibrium approach to modelling metal speciation.
- identify which water and soil properties impact the fate of metals
- describe how processes such as competition and sorption impact metal bioavailability
- explain why the environmental fate of metals is dynamic

Keywords: Metal complexation, redox reactions, equilibrium reactions, water chemistry, soil properties.

Introduction

Metals occur in different physical and chemical forms in the environment, for example as the element (very rare in the environment), as components of minerals, as free cations dissolved in water (e.g. Cd^{2+}), or bound to inorganic or organic molecules in either the solid or dissolved phases (e.g. HgCH_3^+ or AgCl^{2+}) (Allen 1993). The distribution of a metal over these different forms is referred to as metal speciation. Physical processes may also affect the mobility and bioavailability of metals, for example the electrostatic attraction of metal cations to negatively charged mineral surfaces. These processes are in general not referred to as metal speciation in the strict sense but they are discussed here.

Metal speciation reactions

The speciation of metals is controlled by both the properties of the metals (see the section [Metals and metalloids](#)) and the properties of the environment in which they are present, such as the pH, redox potential and the presence and concentrations and properties of molecules that could form complexes with the metals. These complex forming molecules are often called ligands and these can vary from relatively simple anions in solution, such as sulphate or anions of soluble organic acids, to more complex macromolecules such as proteins and other biomolecules. The adsorption of metals by covalent bond formation to oxide and hydroxide surfaces of minerals, and oxygen- or nitrogen-containing functional groups of solid organic matter, is also referred to as complexation. Since these metal-binding functional groups are often either acidic or basic, the pH is an important environmental parameter controlling complexation reactions.

In natural systems the speciation of metals is of great complexity and determines their mobility in the environment and their bioavailability (i.e. how easily they are taken up by organisms). Metal speciation therefore plays a key role in determining the potential bioaccumulation and toxicity of metals and should therefore be considered when assessing their ecological risks. Metal bioavailability and transport are in particular strongly related to the distribution over solid and liquid phases of the environmental matrix.

The four main chemical reactions determining metal speciation, so the binding of metal ions to ligands and their presence in solid and liquid phases, are (Bourg, 1995):

- adsorption and desorption processes
- ion exchange and dissolution reactions
- precipitation and co-precipitation
- complexation to inorganic and organic ligands

The complexity of these reactions is illustrated in Figure 1.

Figure in preparation

Figure 1. *Metals (M) speciation in the environment is determined by a number of reactions, including complexation, precipitation and sorption. These reactions affect the partitioning of metals across solid and liquid phases, hence their mobility as well as their bioavailability.*

Adsorption, desorption and ion exchange processes take place with the reactive components present in soils, sediments and to lower extent in water. These include:

- clay minerals
- hydroxides (e.g. $\text{Fe}(\text{OH})_3$) and/or carbonates (e.g. CaCO_3)
- organic matter

Metal ions react with these reactive components in different ways. In soils and sediments, cationic metals bind reversibly to clay minerals via cation-exchange processes (see section on [Soil](#)). Metal ions also form complexes with so-called functional groups (mainly carboxylic and phenolic groups) present in organic matter (see section on [Soil](#)). In aquatic systems similar binding processes occur, in which dissolved organic matter (or carbon) (DOM or DOC) plays a major role. The "dissolved" fraction of organic matter is operationally defined as the fraction passing a $0.45\ \mu\text{m}$ filter and is often referred to fulvic and humic acids.

As mentioned above and in the section on https://maken.wikiwijs.nl/147644/Environmental_Toxicology_an_open_online_textbook#!page-5415168, negatively charged surfaces of the reactive mineral and organic components present in soil, sediment or water attract positively-charged atoms or molecules (cations, e.g. Cd^{2+}), and allow these cations to exchange with other positively charged ions. The competition between cations for binding sites is driven by the binding affinity of each metal species, as well as the concentration of each metal species. Cation-exchange capacity (CEC) is a property of the sorbent, and defined as the density of available negatively charged sites per mass of environmental matrix (soil, sediment). In fact, it is a measure of how many cations can be retained on solid surfaces. CEC usually is expressed in $\text{cmol}_\text{c}/\text{kg}$ soil (see section on [Soil](#)). Increasing the pH (i.e. decreasing the concentration of H^+ ions) increases the variable charge of most sorbents (more types of protonated groups on sorbent surfaces release their H^+), especially for organic matter, and therefore also increases the cation exchange capacity. Protons (H^+) also compete with metal ions for the same binding sites. Conversely, at decreasing pH (increasing H^+ concentrations), most sorbents lower their CEC.

Modelling metal speciation

Metal speciation can be modelled if we have sufficient knowledge of the most important reactions involved and the environmental conditions that control these reactions. This knowledge is expressed in the form of equilibria expressing the most important complexation and/or redox reactions. For example, in the general case of a complexation reaction between metal M and ligand L described by the equilibrium:



The relationship between the concentrations (or more accurately the activities) of the species is given by:

$$K_f = \frac{[\text{M}_a \text{L}_b^{q+}]}{[\text{M}^{m+}]^a [\text{L}^{n-}]^b}$$

Figure 2. At pH 7.5, most Cu is bound to CO_3^{2-} , but at pH 6 the Cu is mainly present as the free Cu^{2+} ion and in complexes with chloride (as CuCl^+) and sulphate (as CuSO_4^0).

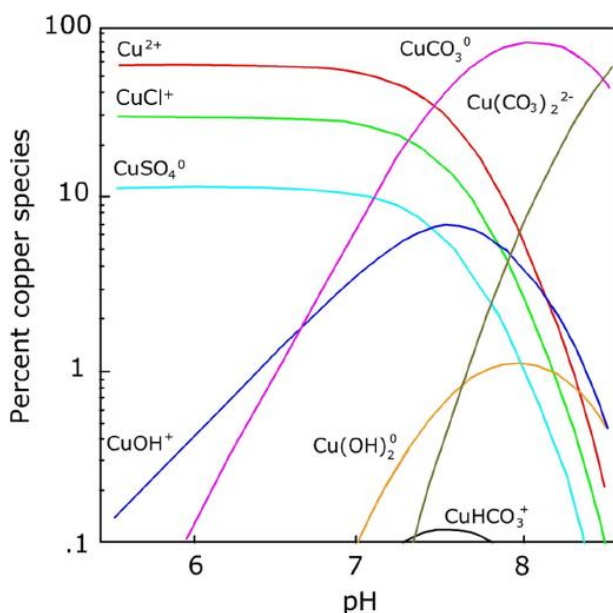


Figure 2. Copper speciation in salt water without DOC. Redrawn from Blust et al. (1991) by Wilma Ijzerman.

If redox reactions are involved in speciation, we can use the Nernst equation to describe the equilibrium between reduced and oxidised states of the metal:

$$E_h = E_h^0 - \frac{2.303RT}{nF} \log \frac{(Red)}{(Ox)}$$

Where E_h is the redox potential, E_h^0 the standard potential of the redox pair (relative to the hydrogen electrode), R the molar gas constant, T the temperature, n the number of transferred electrons, F the Faraday constant and $\{Red/Ox\}$ the activity (or concentration) ratio of the reduced and oxidized species. Since many redox reactions involve the transfer of H^+ , the value of $\{Red/Ox\}$ for these equilibria will depend on the pH. Note that the redox potential is often expressed as pe which is defined as the negative logarithm of the electron activity ($pe = -\log \{e^-\}$).

Using these comparatively simple equations for all the relevant reactions involved it is possible to construct models to describe metal speciation as a function of ligand concentrations, pH and redox potential. As an example, Table 1 presents the relevant equilibria for the speciation of iron in water.

Table 1. Equilibrium reactions relevant for Fe in water (adapted from Essington, 2003)

| Boundary | Equilibrium reaction | |
|----------|---|---|
| (1) | $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | $pE^\ominus = 13.05$ |
| (2) | $Fe(OH)_3(s) + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$ | $K_{sp} = 9.1 \times 10^3 \text{ L}^2 \text{ mol}^{-2}$ |
| (3) | $Fe(OH)_2(s) + 2H^+ \rightleftharpoons Fe^{2+} + 2H_2O$ | $K_{sp}^* = 8.0 \times 10^{12} \text{ L mol}^{-1}$ |
| (4) | $Fe(OH)_3(s) + H^+ + e^- \rightleftharpoons Fe(OH)_2(s) + H_2O$ | |
| (5) | $Fe(OH)_3(s) + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$ | |

Using these we can derive equations defining the conditions of pH and pe at which the activity or concentration ratio is one for each equilibrium. These are shown as the continuous boundary lines in Fig. 3. In this Pourbaix or pe -pH (or pE -pH) diagram, the fields separated by the boundary lines are labelled with the dominant species present under the conditions that define the fields. (NB. The dotted lines define the conditions of pe and pH under which water is stable.)

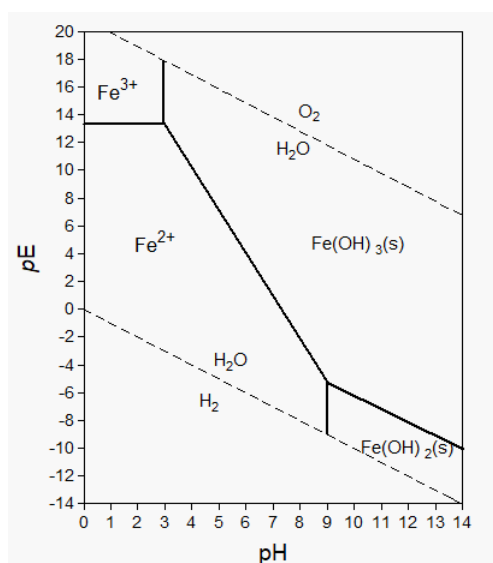


Figure 3. A pe -pH diagram for Fe in water showing the dominant species present under different conditions assuming a maximum soluble Fe(II) or (III) concentration of $10^{-5} \text{ mol L}^{-1}$ (adapted from Essington, 2003).

Environmental effects on speciation

In the environment there is, however, in general no equilibrium. This means that the speciation and hence also fate of metals is highly dynamic. Large scale alterations occur when land use changes, e.g. when agricultural land is abandoned and becomes nature. Whereas agricultural soil often is 'limed' (addition of $CaCO_3$) to maintain near-neutral pH and crop is removed by

harvesting, in natural ecosystems all produced organic matter remains in the system. Therefore natural soils show an increase in soil organic matter content, while due to microbial decomposition processes soil pH tends to decrease. As a result, DOC concentration in the soil porewater will increase, while metal mobility also is increased by the decreasing soil pH (Cu^{2+} is more mobile than CuCO_3). This may cause historical metal pollution to suddenly become available (the "chemical time bomb" effect). Large scale reconstruction of rivers or deep soil digging for land planning and development may also affect environmental conditions in such a way that metal speciation may change. An example of this is the change in arsenic speciation in groundwater due to the drilling of wells in countries like Bangladesh; the introduction of oxygen and organic matter into the deeper groundwater caused a change of arsenic speciation, enhancing its solubility in water and therefore increasing human exposure (see section on [Metals and metalloids](#)).

Dynamic conditions do not only occur on large spatial and temporal scales, nature is also dynamic on smaller scales. Abiotic factors such as rain and flooding events, weather conditions, and redox status may alter metal speciation. In addition, biotic factors may affect metal speciation. An example of the latter is the bioturbation by sediment-dwelling organisms that re-suspend particles into water, or earthworms that by their digging activities aerate the soil and excrete mucus that may stimulate microbial activity (see Figure 4A). These activities of soil and sediment organisms alter the environmental conditions and hence affect metal speciation (see Figure 4B). The production of acidic root exudates by plants may also have similar effects on metal speciation. Another process that alters metal speciation is the uptake of metals. Since the ionic metal form seems most prone to root uptake, or active intake over cell membranes, this process may affect metal partitioning over different species.

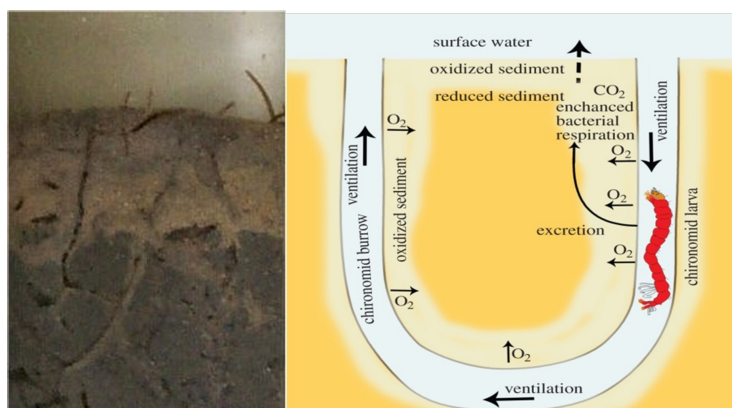


Figure 4. Illustration of small scale processes that alter metal speciation. (A) different bioturbation activities by various organisms, (B) the burrowing activities of a chironomid (midge) larvae can alter the environmental conditions and with that affect metal speciation in the sediment. Source: Martina Vijver.

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3.5. Question 1

What are the most important reactions involved in the speciation of metals in the aquatic and soil environments?

3.5. Question 2

What are the most important environmental parameters controlling these reactions?

3.5. Question 3

In the equilibrium approach to modelling metal speciation, dominance or pe - pH diagrams are used as a visual representation of speciation. What do the lines and fields in such diagrams represent?

Contributors

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