

## Modelling trace metal dynamics in wetland sediments: The effect of the rhizosphere on the sediment redox profile

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Wetlands are a complex system in which to evaluate the behaviour of trace metals. Most wetland sediments are characterized by steep redox gradients, resulting from the sequential utilization of different electron acceptors during the degradation of organic matter. Concentration differences of redox species of over an order of magnitude per centimeter have been observed in wetland sediments (Brendel and Luther, 1995). Metals in wetland sediments may be immobilized due to precipitation or sorption to different organic and inorganic soil constituents. Adsorption onto iron and manganese oxides are important processes where the soil's oxidation potential is high, such as in the rhizosphere of wetlands plants (Otte *et al.*, 1995), where iron oxyhydroxide plaques may form on the surface of roots. As the soil becomes more reduced, iron and manganese oxides are depleted, and trace metals are usually immobilized as sulphides. The ubiquitous presence of organic ligands that can form both soluble and insoluble metal complexes, as well as plant uptake of metals, contribute to the complex trace-metal dynamics in wetland sediments.

In addition to the microbiologically mediated processes, redox profiles in wetland sediments are also affected by biological processes associated with the presence of higher plants. Many wetland plants have evolved mechanisms to supply oxygen to the roots, and to transfer oxygen from the roots into the surrounding sediment (Mendelssohn 1993). These processes maintain an oxidizing potential in the rhizosphere, which is important for root survival. This narrow oxidized zone protects roots from phytotoxins such as  $\text{HS}^-$ , which are common in swamps at low redox potentials, and prevents transport into the root of highly soluble Fe(II) ions by precipitating them at the root surface following oxidation to Fe(III) (Grosse, 1997). The degree of iron plaque accumulation on roots is highly variable, and depends on the concentration of ferrous iron in solution as well as its complexation with organic ligands and the availability of other exchange sites on

different soil mineral and organic fractions (Mendelssohn, 1993). The rates of oxygen transfer into the sediments can be substantial and highly variable. They are dependent on the type of vegetation and root size, as well as the chemical composition and oxygen demand of the sediments (Brix *et al.*, 1996).

In addition to oxygen transfer, there are other effects that plants may have on the redox profiles that develop in wetland soils: (1) Evapotranspiration, which under saturated conditions increases the downward flow and therefore transport from the surface to the rhizosphere. (2) Root exudation of sugars, amino acids, and other readily metabolizable compounds, as well as root death, all of which provide a source of carbon to the microbial community responsible for the various redox reactions occurring in the sediments. (3) Competition with the microbial community for nitrate, which reduces the amount of denitrification that takes place and may lower the sediment redox potential.

Clearly, the interactions between sediment biogeochemistry processes and higher plants play a major role on trace metal mobility in wetlands. One of the most important factors related to these interactions is believed to be the oxygen transfer from roots to sediments, which is difficult to measure and manifests itself indirectly (i.e. decreased ferrous iron concentrations, presence of root plaques, and increased redox potential in the porewater of the rhizosphere).

The objective of this research was to develop a mathematical model that can simulate the complex dynamics that occur in wetland sediments. Such a model can be used as a tool to interpret results from field measurements, and assess how trace metals in wetlands respond to external forcing functions such as changes in nutrient loading or plant distribution.

To model the profile of the redox conditions in saturated wetland soils, we described the degradation of organic matter and the sequential reduction of

electron acceptors, taking into account transport processes such as diffusion, bioturbation, irrigation, and advection due to evapotranspiration and groundwater recharge/discharge. Depending on which electron acceptor is being utilized by the microorganisms degrading the organic substrate, the soil is divided into six different zones: aerobic respiration, denitrification, manganese reduction, iron reduction, sulphate reduction, and methanogenesis. The microbial utilization of the electron acceptors in each of these zones is described by the appropriate stoichiometric equations. Effects of plants are included by adding proper source/sink terms to account for organic carbon release (i.e. litter, exudates, root turnover), oxygen release, nutrient uptake (e.g. nitrogen), and evapotranspiration induced advection. The model describes the vertical profiles of twelve coupled constituents in sediments including solid (particulate organic matter, manganese oxides, and iron oxides) and dissolved substances (dissolved organic carbon, oxygen, nitrate, sulphate, ammonia, dissolved manganese, dissolved iron, sulphide, and methane).

The microbial degradation of the organic matter is described by a Monod-type formulation. Oxygen consumption by reduced compounds (e.g.  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{HS}^-$ ), and precipitation of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ , with  $\text{HS}^-$  and other minerals such as phosphorus and carbonate, are formulated as first order reactions, described by a set of coupled differential advection/diffusion equations (Smith and Jaffé, 1997). Diffusion of different chemical species across redox boundaries allows for many biotic and abiotic redox reactions (e.g. abiotic reduction of  $\text{MnO}_2$  by  $\text{HS}^-$ ). The model formulation allows for an easy incorporation of additional reactions that are identified as being important. Although wetland soils are not close to reaching chemical equilibrium conditions, the pE at a specific sediment depth is approximated to that of the dominant redox couple. The dominant redox couple in each sediment layer is assumed to be that given by the half reaction of the respective electron acceptor.

With the computed concentration profiles of the oxidized and reduced electron acceptors, species such as organic carbon and ammonia, estimated pE, and measured values for the pH and alkalinity, we then use MINTEQA2 (an EPA supported chemical speciation model) to determine the chemical speciation under equilibrium conditions for specified trace metals at each location in these sediments. The difference between the concentrations from the transport calculations and these equilibrium concentrations of the trace metals determines how far from

equilibrium a reaction is. The rate at which equilibrium conditions are approached is assumed to be the product of a rate constant and the gradient given by this concentration difference. This allows for a dynamic formulation of the trace metals in the sediments, considering changes in oxidation state, complexation with different ligands, and precipitation. Sorption of trace metal and other ionic species onto solid organic carbon and onto manganese and iron oxides is described by the double layer surface complexation model, accounting for interactions among these species.

The model was transcribed into a set of differential equations, one for each chemical component, where, for each iteration, the transport code interacts with the chemical speciation code to determine the new equilibrium conditions that affect the reaction kinetics. Simulations for steady state conditions of the vertical profiles of the principal redox species as well as Ni and Zn, compared well with field data collected from a small lake in central New Jersey. Simulations with and without typical oxygen transfer rates from the root system to the sediments have shown the effect of this process on the wetland soil redox profile and the availability of oxides for sorption of trace metals and metalloids.

A series of simulations will be presented to illustrate the effect of different root-oxygen-release rates and root density distributions on the redox profiles in wetland sediments, and on the resulting immobilization of trace metals (cadmium, and copper) and metalloids (arsenic, as arsenate and arsenite) in these sediments.

## References

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