SL 297

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# Reactivity and Mobility of Metals in Wetlands[1]

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## Introduction

Much attention has been directed at nutrient cycling in Florida's wetland ecosystems, particularly nitrogen and phosphorus. However, the role of metals in wetlands has received scant attention. Metals, such as iron, copper, zinc, cadmium, mercury, and lead, are present in many upland or terrestrial soils and wetlands. Sources of metals in wetlands include natural deposition and influx from man-made sources, including atmospheric deposition, runoff from agricultural fields, and wastewater discharge from municipalities, landfills, and other sources. Some metals are required for plant growth, while others, such as lead, cadmium, and nickel, have no known botanical function. Some metals, such as copper, selenium and zinc, are essential to plants and animals but can be toxic at high concentrations. Others, such as cadmium, mercury, and lead are toxic even at relatively low concentrations. Furthermore, certain metals such as mercury have a tendency to bioaccumulate at high levels of the food chain. This biomagnification effect can lead to serious health hazards for animals and humans.

The objective of this document is to educate the public concerning the role of metals in wetlands, their function, changes they undergo, and the potential hazards associated with their presence and accumulation in wetlands.

## Comparison of wetlands and terrestrial ecosystems

Wetlands are characterized by soil conditions that include water saturation at or near the soil surface for a substantial part of the year. This water saturation limits gaseous oxygen diffusion deep into the soil which occurs naturally in drained, upland soils. As a result, dissolved oxygen is consumed by microbial respiration and the microbial population then shifts to the utilization of nitrate, iron, manganese, sulfate, and other oxidized materials. Consequently, different chemical and microbial processes occur in wetlands.

Soil chemical and microbial processes affecting metal transformations, mobility, and bioavailability are very different in wetland soils as compared with upland soils. When changes occur in the oxidation status of soils through drainage, metal transformations between chemical forms occur which affects their mobility and availability to plants and animals. For example, iron is more soluble and thus

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mobile in flooded anaerobic soils compared to drained aerobic soils. Soil oxidation conditions also influence the pH, a major factor influencing metal chemistry. As oxidized soils are flooded and become anaerobic, the pH tends to converge toward neutrality, regardless of whether the soil was initially acid or alkaline. Thus, the range of pH in typical wetland soils is much smaller than for upland soils. The different types of organic matter between wetlands and uplands also influence metal cycling, as humic materials associated with wetland sediments more tightly bind metals than humic materials of drained wetlands or terrestrial ecosystems.

## Forms and transformations of metals in soil and water

All soils and sediments contain some concentration (usually low) of metals from natural sources. These background levels can vary widely depending on parent material, sedimentation processes, wetland age, etc. Usually, human activities cause concentrations of metals to increase in wetlands to the point of posing health or ecological risks. However, elevated concentrations of metals do not necessarily result in problem releases to water or excessive plant uptake. In addition, the chemical forms present, and processes affecting transformations between these forms, are important to assessing risk. There are a number of chemical forms in soils that differ in their mobility and availability. These include water-soluble metals, metals soluble as free ions, metals soluble as inorganic or organic complexes, exchangeable metals, metals precipitated as inorganic compounds, metals complexed with large molecular-weight humic materials, metals adsorbed or occluded to hydrous oxides, metals precipitated as insoluble sulfide, and metals bound within the crystalline lattice structure of primary minerals. All of these forms are affected by hydrologic conditions, which in turn affect pH, organic matter, and ultimately metal availability and mobility.

Water-soluble metals are the most mobile and plant-available form. Exchangeable metals are those bound to soil surfaces by cation-exchange processes and considered weakly bound. These may be displaced relatively easily to the water-soluble form. Together, metals in the soluble and exchangeable forms are considered readily mobile and available and as such pose the most risk to biological organisms. On the other extreme are metals bound within the crystalline lattice structure of clay minerals, which are essentially unavailable and only become available after mineral weathering over long periods of time. Other metals are precipitated as inorganic compounds and include metal oxides, hydroxides, and carbonates. The stability of these inorganic metal compounds is primarily controlled by pH. At near-neutral to somewhat alkaline pH, metals tend to be immobilized. If pH becomes moderately to strongly alkaline or acidic, metals may be converted to mobile forms.

## Reactions of metals in wetlands

Removal or loss of metals from wetlands may occur through many processes, including plant uptake, adsorption (binding to soil particles), and precipitation (formation of solid compounds). Uptake rates and tolerance of metals vary among plant species. Some terrestrial plants are capable of storing high concentrations of metals in roots and other tissue as demonstrated by the hyperaccumulation of arsenic by some fern species in Florida (Al-Agely et al., 2005).

Surface runoff of metals is a process by which metals can be mobilized from upland soils or during drainage of wetlands. In wetlands where the soil remains flooded for most of the year, metals are immobilized and largely prevented from leaching and surface runoff losses. However, after drainage and oxidation has occurred, soluble metal concentrations increase, especially in wetlands that become acidic upon oxidation, as is typical of many coastal wetlands. Metal sulfides are often formed in coastal marine sediments through reaction of sulfide (produced during organic matter decomposition coupled with the utilization of sulfate by microorganisms) with metals. These metal sulfides are fairly stable in flooded soils. However, drainage of these soils results in dissolution of metal sulfides and oxidation of the sulfides to sulfate, which leads to lower pH, which in turn tends to dissolve other metal forms. Thus, hydrologic conditions and water movement can have major impacts on movement within wetlands and between terrestrial and wetland ecosystems.

Metal cycling in wetlands is very dependent on pH. Drainage of wetland soils often decreases pH, which alters metal solubility. Likewise, metals bound to organic matter are released upon decomposition leading to enhanced bioavailability during water drawdowns and drought. The processes contributing to metal immobilization in wetland soils also contribute to retention of metals released into wetlands from point and nonpoint sources, assuming favorable hydrology and reasonable loading rates. A strong association of metals with humic materials (which is responsible for the dark color typical of many of Florida's surface waters) is largely responsible for binding metals and rendering them unavailable. The process of soil accretion typically occurring in wetlands results in the gradual burying of metals, placing them in an environment where immobilization becomes more effective.

Many metals help to sequester nutrients in soils, in particular phosphorus. In low pH soils, many iron and aluminum compounds react with available phosphorus and form new compounds that can be stable in soils. For soils with high pH, calcium and magnesium carbonates can react with phosphorus leading to formation of other stable compounds. In fact, many times these metals are added to soils or wetlands for the direct purpose of sequestering phosphorus. Water-treatment residuals, which contain high amounts of aluminum, are added to soil to react with phosphorus and decrease its availability and mobility in the landscape. Calcium carbonate is also added to wetlands to react with phosphorus, leading to formation of calcium phosphates and decreases in available phosphorus in the water column.

## Summary

Wetlands are potentially effective traps, or sinks, for metals due to their relative immobility in flooded soils. However, changes in hydrologic conditions, such as drainage or drought, alter the pH, which then has major effects on metal forms and concentrations. Also, drainage increases microbial activity and organic matter decomposition, which releases metals bound to organic materials thereby increasing their availability. To minimize potential risks of metals to biological organisms, wetlands should remain flooded to decrease metal availability and export.

## Literature Cited

Al-Agely, A., D.M. Sylvia, and L.Q. Ma. 2005. Mycorrhizae increase arsenic uptake by the hyperaccumulator Chinese brake fern (Pteris vittata L.). Journal of Environmental Quality 34: 2181-2186.