Cycling of iron and manganese in a Riparian wetland

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Introduction

Iron and manganese are common contaminants in waste streams from coal bed methane production and in acid mine drainage resulting from surface mining of coal and metallic ore deposits (Henrot and Wieder, 1990). Wetlands, both natural and artificial, have been proposed as natural filters to remove these and other contaminants from waste waters. There is currently inadequate knowledge of the specific mechanisms that control the mobility of iron and manganese in wetland systems, and of the long-term ability of wetlands to retain these metals.

Iron and manganese can exist in waste streams both as dissolved ions or as finely divided particles (colloids). In aerobic environments, dissolved iron and manganese are removed from water primarily through chemical oxidation, although some uptake of metals by wetland vegetation can also occur (deWet *et al.*, 1990). The mobility of iron and manganese can be enhanced in aerobic environments by complexation with bidentate organic ligands such as oxalate (Graustein, 1981). Inorganic oxidation of these metals is slow and the precipitation of iron and manganese oxides can be bacterially mediated.

Photoreductive dissolution of colloidal iron oxides in aerobic environments (McKnight *et al.*, 1988), reductive dissolution of iron and manganese by anaerobic bacteria (Portier and Palmer, 1989), and desorption of iron and manganese ions held on sediment cation exchange sites (Henrot and Wieder, 1990) have the potential to remobilize metals that have been removed from waste water by other processes. The possibility of iron and manganese remobilization must be considered when evaluating the long-term ability of wetlands to retain metals from waste streams.

The objective of this study is to determine the physical, chemical, and biological processes governing the cycling of iron and manganese in a natural freshwater wetland system. This information will guide efforts to design artificial wetlands for the treatment of waste solutions containing iron and manganese and allow more objective evaluation of the possible effects of the use of natural wetlands as a treatment technology for iron and manganese removal.

Methods

Study area. The wetland study site is located in the Talladega National Forest, northeastern Hale County, Alabama. The 15 ha. wetland was created through beaver damming of a stream channel, and consists of a complex series of ponds, riparian vegetation, and bottomland habitats. Study has focussed on the largest of the ponds, which is biologically zoned and has an areal extent of approximately 13,000 m^2. The pond is located immediately upstream of the most recent beaver dam and from the dam toward the upstream end consists of a small area of open water and larger zones dominated by *Nymphaea* water lily and *Juncus* sedge. The riparian vegetation zone begins immediately upstream of the *Juncus*. The wetland receives recharge from precipitation as surface runoff, from interflow within the soil zone, and from shallow ground water through the western hillslope.

Sampling and analysis. Rainwater, soil water, surface water and groundwater samples are collected monthly to provide information on solute sources and sinks, and to determine the spatial and seasonal variation in iron and manganese concentrations. Pond sediment pore waters were collected by diffusion-type sampler in July 1993. Temperature, pH, Eh and conductivity are determined in the field. The samples are titrated for alkalinity and analyzed for cations by ICP, for anions by ion chromatography, and for trace metals by GFAA in the laboratory. Solute speciation and mineral saturation indices were calculated using WATEQ4F (Ball *et al.*, 1987).

Results

Iron and Mn levels in rainwater are generally below the ICP limits of detection, except for

throughfall which can contain 0.04–0.36 mg/l Mn. Soil water contains significant concentrations of these metals during summer months (2–7 mg/l Fe and up to 2 mg/l Mn), and serves as a primary source of Fe and Mn to the wetland pond.

The wetland pond shows significant spatial variation in Fe and Mn concentration during summer months.

Highest levels are measured within the *Juncus* zone (8–20 mg/l Fe and 1.3–2.4 mg/l Mn) and lower concentrations are found within the open water or *Nymphaea* zones (0.3–0.7 mg/l Fe and 0.3–1.3 mg/l Mn). Winter samples have low Fe and Mn concentrations and show little spatial variation.

Similar concentration patterns for Fe and Mn are observed in the shallow (0–30 cm depth) pore waters of the pond sediment. Sediment pore water Fe concentrations average 100.9 mg/l within the *Juncus* zone, 18.6 mg/l within the *Nymphaea* zone, and 9 mg/l in open water zone sediments. Corresponding pore water Mn levels are 6.8 mg/l, 2.0 mg/l and 1.9 mg/l, respectively. Shallow sediment pore water Eh averages −130 mV in the *Juncus* zone, −0.01 mV in the *Nymphaea* zone and 15.3 mV in the open water zone. In general, Fe and Mn concentrations sharply increase with depth below the sediment/water interface, while Eh sharply decreases with depth beginning somewhat above the sediment/water interface.

Groundwater below the *Juncus* zone contains high levels of Fe (average for well 3 = 26.8 mg/l) and Mn (average for well 3 = 1.8 mg/l. Iron concentration generally increases with depth, while sulfate concentrations are essentially constant to 20 foot depth (average for well 3 = 0.16 mg/l). Measured Eh values change from reducing conditions during summer to oxidizing conditions during winter months.

Discussion

WATEQ4F calculations show that the pond water is saturated or supersaturated with respect to ferrihdrite and supersaturated with respect to all crystalline Fe oxides during summer months. The pond water remains supersaturated with respect to crystalline Fe oxides during winter months. Ferrihydrite can be observed precipitating on the pond bottom and on submerged vegetation, particularly within the *Juncus* zone. Iron and manganese oxyhydroxides are reductively dissolved through the action of bacteria living within the shallow pond sediments and stagnant surface water pools between *Juncus* root hummocks. The source of iron and manganese are from weathering and organic complexation in the A soil horizon, and by chemical diffusion from sediment pore waters.

Redox equilibria, rather than cation exchange reactions, control the distribution of Fe and Mn in the wetland sediment pore waters. The redox potential of the pore waters is controlled by the relative rates of oxygen diffusion from surface water and biodegradation of organic matter. Diffusion of oxygen takes place directly through the sediment and to greater depths around the root systems of aquatic vegetation. The low measured Eh values indicate that the rate of organic matter biodegradation is the primary redox control in the *Juncus* zone, but is slower in the *Nymphaea* and open water zones.

Mineral saturation index calculations indicate that the pore waters are undersaturated with respect to ferrihydrite, but are supersaturated with respect to pyrite below 10 cm depth within the *Juncus* zone. An upward diffusive gradient for Fe^{2+} was found within the upper 2 cm of wetland sediment in unvegetated areas where diffusion of oxygen away from plant roots is not important (Eric Roden, personal communication 1993). Reoxygenation of the ferrous iron at the sediment/water interface is mediated by both diffusion of oxygen through plant root systems and by iron oxidizing bacteria.

Iron and manganese accumulate in ground water through reductive dissolution of oxides present in the sediments, downward movement of ground water from the pond, and the lack of molecular oxygen in the sediments below the pond. A redox model has been developed to explain the vertical and spatial distribution of Fe, Mn, S, Eh and pH for the wetland sediment pore waters within the *Juncus* zone.

References

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