Manganese cycling in an acidic Adirondack lake

JEFFREY R. WHITE¹ and CHARLES T. DRISCOLL²

¹ School of Public and Environmental Affairs, Indiana University, Bloomington, IN 47405, USA
² Department of Civil Engineering, Syracuse University, Syracuse, NY 13210, USA

Key words: Acidification, Adirondacks, manganese, reduction, trace metal.

Abstract. There is considerable interest in the chemistry of Mn in acidic waters because of its role in the generation of acid neutralizing capacity during reduction processes, as an adsorbent in element cycling, and as a potential toxicant to aquatic organisms. Temporal and spatial variations in the concentration of Mn were evident in acidic Dart's Lake (1.0–2.3 µmol l⁻¹), located in the Adirondack Region of New York. Seasonal changes in pH and dissolved oxygen concentration had subtle effects on the chemistry and transport of Mn. Despite oversaturation with respect to the solubility of manganite during periods of stratification, vertical deposition of Mn was minimal. The conservative nature of Mn appears to be due to the acidic conditions in Dart's Lake.

Introduction

A major consequence of depressed pH observed in dilute surface waters is elevated concentrations of trace metals (Schofield, 1976a; Henriksen and Wright, 1978; Dickson, 1980; Johnson et al., 1981). In addition, low concentrations of complexing ligands result in low trace metal buffering capacity (complexation of aquo metal) in these waters. Since the aquo form of trace metals is often toxic to aquatic organisms (Schofield, 1976b; Sunda and Lewis, 1978; Baker, 1982; Spencer and Nichols, 1983), an evaluation of trace metal chemistry and cycling in dilute acidic lake systems is highly relevant.

Schofield (1976a) has reported elevated concentrations of Mn in Adirondack surface waters. The chemistry of Mn is complicated because of the potential for both proton and electron transfer reactions (equation 1).

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\text{MnOOH(s)} + 3\text{H}^+ + e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O};
\]

\[
\log K = 25.27
\]

Under both acidic and reducing conditions, solid phase Mn will tend to be solublized to Mn²⁺. This process is significant for several reasons:

1. The use of Mn as an alternate electron accepter generates acid neutralizing capacity and therefore can result in in-lake neutralization of acidity (Kelly et al., 1982).
2. The diffusion of Mn$^{2+}$ to oxygenated waters may result in oxidation followed by precipitation or adsorption to surfaces, and transport to sediments (Sholkovitz and Copland, 1982). The formation of particulate Mn oxyhydroxides is significant because of their adsorptive properties (Jenne, 1968). Particulate Mn may regulate the concentration of trace elements through adsorption reactions.

3. Elevated concentrations of Mn in the tissue of fish from acidic surface waters have been found to be correlated with high Mn concentrations in lake waters (Havey and Fraser, 1982). Structural deformities in fish vertebrae from these systems were attributed to elevated Mn in bone tissue. Therefore the chemistry and cycling of Mn in acidic surface waters is of particular interest.

   Acidic lake systems undergo temporal changes in the concentrations of Al which appear to be associated with pH fluctuations (Driscol et al., 1984). During the snowmelt period, waters that are high in H$^+$, Al and NO$_3^-$ are introduced to acidic Adirondack New York lakes (Driscol and Schafran, 1984). During summer stratification, biological processes of NO$_3^-$ retention (assimilatory, dissimilatory NO$_3^-$ reduction) result in the generation of acid neutralizing capacity and the neutralization of H$^+$ and Al acidity (Driscol and Schafran, 1984). Seasonal variations in pH and soluble Al concentration may in turn be significant to the cycling of trace metals. In acidic lakes slight increases in pH may result in a decrease in aluminum solubility and conversion of aqueous aluminum to a particulate form. It is well established that oxides of aluminum and other metals (Fe, Si, Mn) can regulate trace metal chemistry through surface adsorption processes (Hohl and Stumm, 1976; Davis and Leckie, 1978; Millward and Moore, 1982). Therefore in-lake formation of particulate aluminum may modify the cycling of trace metals through sorption (e.g., adsorption, coprecipitation) reactions (White and Driscoll, 1985).

   Manganese (II), however, is not a strongly hydrolyzing metal (Lindsay, 1979). Under acidic conditions (pH < 6.0), the kinetic rate of Mn$^{2+}$ oxidation is extremely slow (Stumm and Morgan, 1981) and the adsorption of Mn to metallic oxyhydroxides is minimal (Millward and Moore, 1982). However, in well-buffered waters (pH ~ 8) bacterial-mediated Mn oxidation has been demonstrated to occur rapidly (on the order of days) in freshwater lakes (Chipnick et al., 1982), and in more saline waters (Emerson et al., 1982). We anticipate Mn to be relatively conservative however, in acidic surface waters. Unfortunately, there is little information available on the chemistry and cycling of Mn in acidic lake systems.

   The intent of this study was to evaluate temporal and spatial fluctuations in Mn within an acidic lake and to assess the processes regulating aqueous concentrations and transport.