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Manganese cycling in an acidic Adirondack lake

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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).

$$\mathrm{MnOOH(s)} + 3\mathrm{H}^+ + e^- = \mathrm{Mn}^{2+} + 2\mathrm{H_2O};$$
$$\log K = 25.27 \qquad (1)$$

Under both acidic and reducing conditions, solid phase Mn will tend to be solublized to Mn^{2+}. 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 (Driscoll *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 (Driscoll 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 (Driscoll 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 ($pH \sim 8$) 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.

Methods

Site and Sampling Description

Water column and sediment trap monitoring programs were used to investigate important mechanisms regulating the chemistry and cycling of Mn in an acidic lake. The study site, Dart's Lake, is located in the North Branch of the Moose River (43°47′N, 74°51′W), immediately downstream from Big Moose Lake. A detailed description of the site, field program and analytical methods are available elsewhere (Driscoll *et al.*, 1987; Schafran and Driscoll, 1987). Sediment traps (set in triplicate at 6- and 14-m depths) were used to assess the flux of particulate material settling through the water column in the pelagic region of the lake. The sediment trap design was consistent with the criteria established by Bloesch and Burns (1980), including an aspect ratio (height/diameter) of 9 for each collector. Water chemistry and sediment trap samples were collected every 2 to 3 weeks.

Analytical methods

Stream height was measured on sampling dates using flow-calibrated staff gauges at the inlet and outlet to monitor discharge. To provide an estimate of water flux through Dart's Lake, correlations were made between on-site measurements of instantaneous discharge and continuous discharge recorded at the nearby Independence River site (Donnatsberg, New York) and a site on the Hudson River (Newcomb, New York). Correlations of flow per watershed area for Dart's Lake were similar to either one or both continuous discharge sites throughout the study period. Thus the estimated continuous flow for Dart's Lake is believed to be representative of actual flow conditions. Our discharge data suggest that 95% of the outlet flow enters the lake at the major inlet (Driscoll and Schafran, 1984).

To determine "dissolved Mn and Fe", centrifugation (5,720 G for 30 min.) was used to separate particulates from solution (Salim and Cooksey, 1981) and the supernatant was acidified (0.5% v/v Ultrex HNO_3). Sediment trap samples were also analyzed for metals (Al, Fe, Mn), particulate carbon (Menzel and Vaccaro, 1964), as well as total and fixed solids (Standard Methods, 1976). To determine the metal content, two 40-ml aliquots were decanted from homogenized sediment trap samples. One aliquot was centrifuged, (5,720 G for 30 minutes), the supernatant acidified (0.5% v/v ultrex HNO_3) and analyzed as "dissolved metal". The second aliquot was first acidified to pH 1.0, digested for 1 hr at 25 °C, and centrifuged to remove undissolved particulates; the supernatant was analyzed as "total metal". The difference between "total metal" and "dissolved metal" content yielded the acid-labile metal associated with deposited materials, including amorphous oxides (Hsu, 1977). The flux of this acid-labile fraction was of interest in this study since deposition of "freshly formed" metals may occur in this form. Analysis of metals in sediment trap and water column samples was conducted by atomic absorption spectrophotometry with graphite furnace. The total error (sampling and analytical error from triplicate analyses presented as $\bar{X}$, S.D., 95% C.I.) associated with soluble Mn, Fe, and total monomeric Al analyses was $1.38 \pm 0.02\,\mu mols\,l^{-1}$ (95% C.I. = 1.32–$1.43\,\mu mols\,l^{-1}$), $1.18 \pm 0.04\,\mu mols\,l^{-1}$ (95% C.I. = 1.08–$1.28\,\mu mols\,l^{-1}$), and $19.5 \pm 0.2\,.\mu mols\,l^{-1}$ (95% C.I. = 19.2–$19.8\,\mu mols\,l^{-1}$), respectively. The fractional uncertainties for sediment trap collection and analysis are available elsewhere (White and Driscoll, 1985).

In addition to the water column program, laboratory batch adsorption experiments were conducted. Aliquots of fresh wet surficial sediment from the pelagic sampling station of Dart's Lake (dry weight = 0.1 g) were suspended in polyethylene bottles containing 1 liter solutions of $2.0\,\mu mol\,l^{-1}$ Mn. The suspensions were adjusted with HNO_3 and NaOH to yield a range of pH levels from 3.0 to 6.0. Following equilibration for 24 hr, suspensions were separated by centrifugation (5,720 G for 30 min) and analyzed for pH and "dissolved Mn". Schindler *et al.*, (1980) present data for lake enclosure experiments which suggest that 24 hr is sufficient time for the adsorption of Mn to natural lake particles to reach equilibrium. Separate aliquots of sediment were also analyzed for dry weight for determination of the mass of adsorbed Mn per unit mass of sediment.

Deposition rate and K_D calculations

Gross deposition rates (D_g for Al, Mn, Fe and organic carbon) were calculated as the mass of particulate constituent deposited in sediment traps over a collection period.

$$D_g = CV/(A_t t) \tag{2}$$

where D_g is equal to gross deposition rate ($\mu mol\ m^{-2}\ d^{-1}$), C is the sediment trap concentration ($\mu mol\,l^{-1}$) of particulate associated constituent, V is the sediment trap volume (l), A_t is the area of the sediment trap orifice (m^2), and t is the collection period (d).

In addition to gross deposition, specific deposition rates were determined by normalizing the D_g value for the mass of metal present above the sediment traps during the collection period.

$$D_s = D_g/M \tag{3}$$

where D_s is the specific deposition rate in mols of particulate associated metal per mol soluble metal per day (d^{-1}), D_g is gross deposition rate (equation 1), and M is the average mass of metal per m^2 of water column above the trap ($\mu mol\ m^{-2}$). High specific deposition rates indicate efficient scavenging or extensive removal processes occurring, while low levels of D_s suggest conservative behavior.

The metal distribution coefficient (K_D) is a parameter which is indicative of the intrinsic affinity of a metal for particulate matter in an aqueous system. Using sediment trap data for particulate flux rates (P_g; mg m^{-2} d^{-1} of total solids, dry weight) and D_s values, in-situ K_D values were determined as follows:

$$K_D = D_s Z/P_g \tag{4}$$

where K_D (cm^3 g^{-1}) is a function of the gross particulate flux (based on total solids content of trap samples; (Standard Methods; 1976)), and the depth to the sediment trap (Z, m). Distribution coefficients (K_D) were also determined from batch adsorption studies,

$$K_D = C/c \tag{5}$$

where C is the total mass of metal sorbed to a mass of adsorbent (μmol per g of dry weight sediment), and c is the soluble metal concentration following equilibration (μmol cm^{-3}).

We also calculated the solubility of Dart's Lake solutions relative to a readily forming solid phase. Manganese data collected from a synoptic survey of 212 Adirondack lakes (Schofield, 1976a) suggest that manganite (MnOOH (s); equation 1) may be regulating Mn solubility in Adirondack lake systems (Whie, 1984), although such data are not conclusive evidence. The manganite solid phase has also been demonstrated to be a readily-forming solid phase in supersaturated inorganic solutions (Hem and Lind, 1983; Murray *et al.*, 1985). As a general indicator of the potential for in-lake formation of Mn particulates, we determined the saturation index (SI; equation 6) of Dart's Lake waters relative to the solubility of MnOOH (s) using water chemistry data and the chemical equilibrium model MINEQL (Westall *et al.*, 1976). MINEQL corrects calculations for variations in temperature and ionic strength.

$$SI = \log IAP/K \tag{6}$$

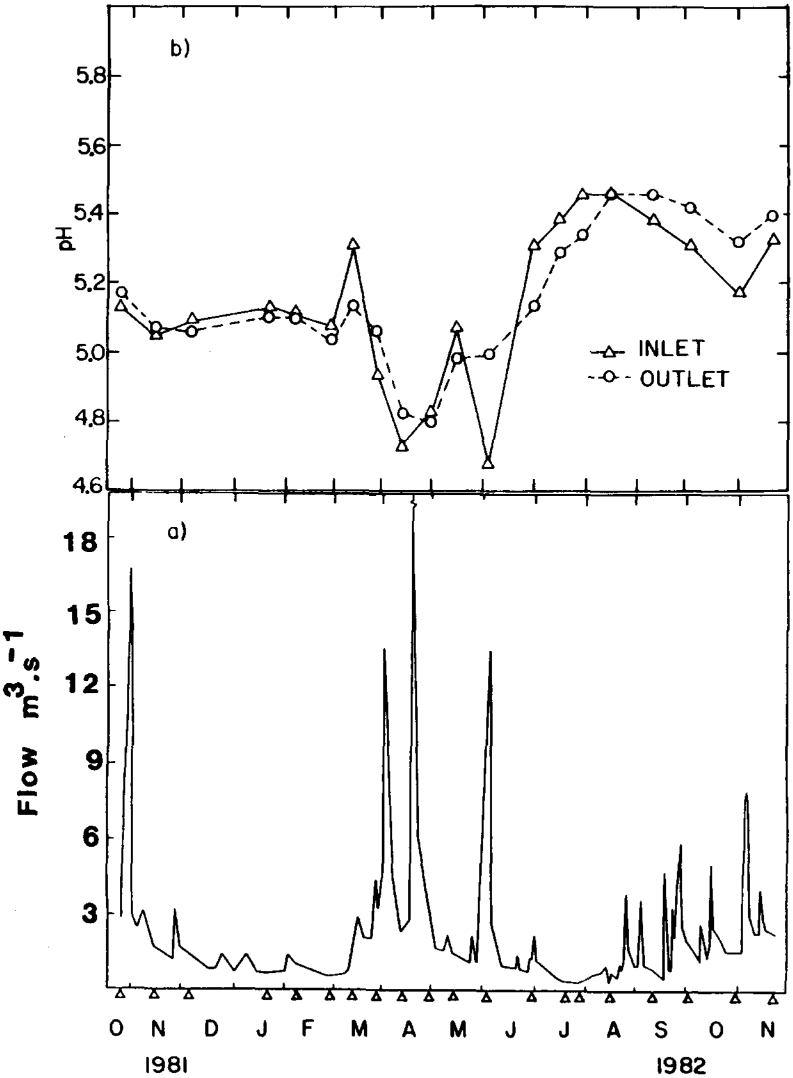
where IAP indicates the ion activity product of Dart's Lake solutions and K (equation 1; Lindsay, 1979) is the thermodynamic solubility product. Negative values of SI indicate undersaturation with respect to the solubility of manganite, while positive values suggest oversaturation. During conditions of oversaturation there is the potential for in-lake formation of particulate Mn.

A detailed description of the water chemistry of Dart's Lake is beyond the scope of this paper. However information on the water chemistry is available elsewhere (Driscoll *et al.*, 1987; Schafran and Driscoll, 1987).

Results

Inflow-outflfow chemistry

The flux of Mn into and out of Dart's Lake was primarily related to stream hydrology, as well as pH, and Mn concentration (Figure 1). Streamflow during the study year was highly variable, with elevated discharge occurring in autumn and during the spring snowmelt period; low flow was observed in summer and winter (Figure 1a). Water residence time varied



seasonally from a median of approximately 22 days in spring to 90 days during summer. Stream pH was also variable (Figure 1b). Winter pH values were consistently 5.1 until spring snowmelt, when pH declined to an April/May minimum of 4.8. Increases in pH occurred throughout the summer, reaching a maximum in August (pH = 5.4). A major rain storm in June, however, briefly interrupted the increase in inlet pH (Figure 1b).

Dissolved Mn concentrations in the inlet and outlet streams varied little

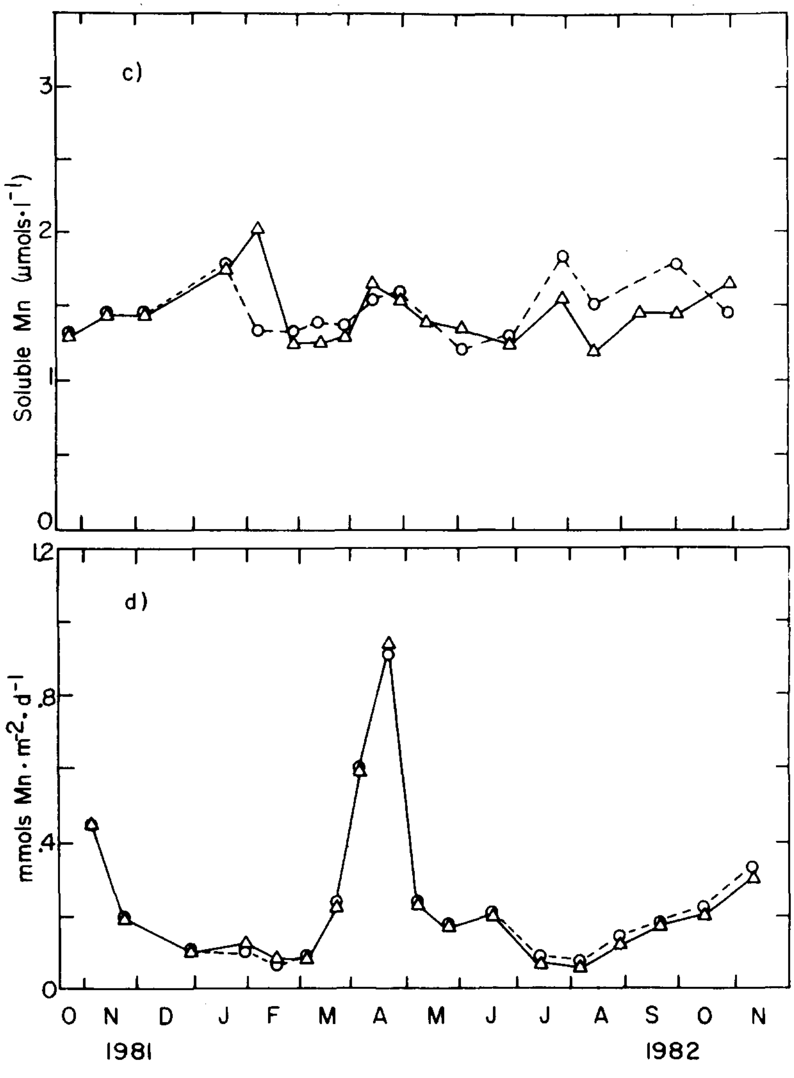


Figure 1. Temporal variations in (a) discharge, (b) inlet and outlet pH, (c) inlet and outlet concentrations of soluble manganese, and (d) manganese flux rates to and from Dart's Lake.

during the study period. Concentrations were slightly reduced (C.V. = 1.7% for precision of Mn sampling and analysis) during low discharge in winter and summer. The increases in Mn during late summer and fall in the inlet and outlet (Figure 1c), corresponded with the erosion of the thermocline in Dart's Lake and undoubtedly in Big Moose Lake. This increase was apparently associated with the release of Mn from the hypolimnion to the upper waters. In general, however, Mn concentrations in the inlet and outlet were consistently between 1.0 and 2.0 μmols l^{-1}. Mn flux to and from Dart's Lake was greatest during spring and fall periods of elevated Mn concentrations (1.8 μmol l^{-1}) and high discharge. In contrast, low flow rates during winter and summer resulted in significantly lower influx and efflux of Mn (Figure 1d). Overall, influx and efflux of Mn were nearly equivalent throughout the study year. Note that particulate Mn comprised typically less than 6% of the total concentration of Mn in these waters, and concentrations of total suspended solids in the inlet waters were less than 1 mg l^{-1}.

Water column chemistry

Certain physical and biochemical transformations in the water column and sediments appeared to influence Mn cycling. Dart's Lake is dimictic; complete turnover (isothermal conditions) occurred in November and April during the study year, resulting in an orthograde distribution of soluble Mn (Figure 2). During winter stratification, elevated concentrations of Mn (> 1.7 μmols l^{-1}) were observed in the hypolimnion (Figure 2) which corresponded with low concentrations of dissolved oxygen

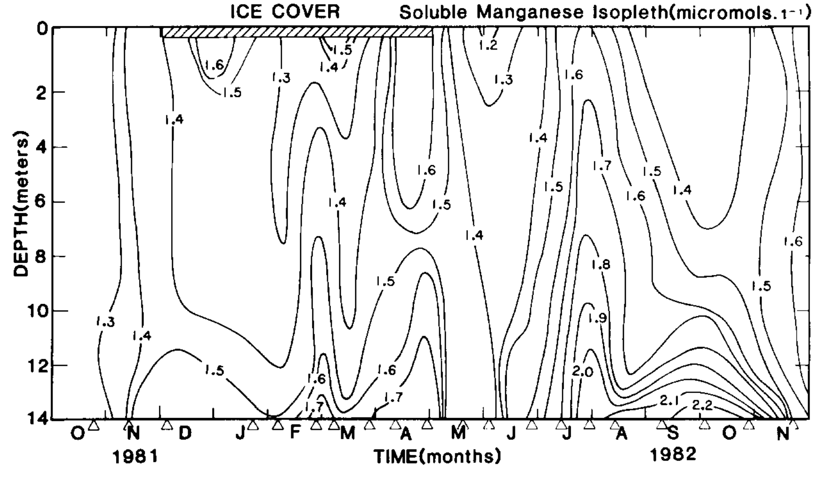


Figure 2. Temporal and spatial variations in soluble manganese within the water column of Dart's Lake.

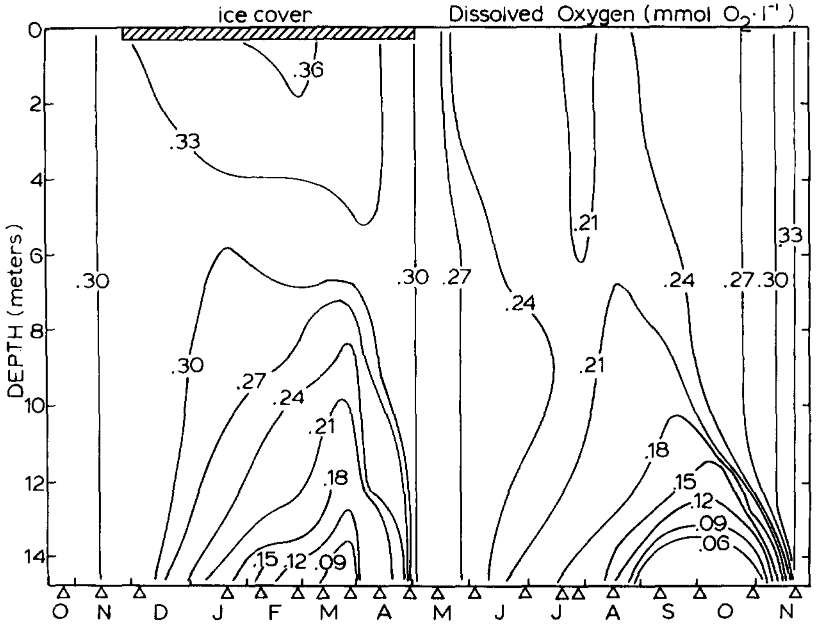


Figure 3. Temporal and spatial variations in dissolved oxygen within the water column of Dart's Lake.

(D.O. = 0.09 mmol O_2 l^{-1}; Figure 3), elevated Fe concentrations ($> 14 \mu mols\, l^{-1}$) and pH (pH = 5.6) near lake bottom. Low pH waters were evident during winter and spring immediately beneath the ice and coincided with elevated concentrations of Mn. This trend may be attributed to inputs of acidic meltwater which were less dense than the bulk of the lake water (temp. = 0 °C). As a result of the thermal structure of the lake, this acidic water was transported along the lake-ice interface.

Following spring turnover, hypolimnetic enrichment of Mn was observed during summer stratification (maximum Mn = $2.2 \mu mols\, l^{-1}$; Figure 2). During this period reduction in D.O. (Figure 3), and elevated concentrations of Fe and dissolved organic carbon (DOC), (see Schafran and Driscoll, 1986) were also evident in the vernal hypolimnion. Reduction processes in the sediments under low oxygen concentrations were undoubtedly responsible for increases in pH and the enrichment of DOC, Fe, and Mn in the hypolimnetic waters. Concentrations of epilimnetic Mn were initially low during summer stratification. In late June and July considerable Mn was apparently introduced to the epilimnion from the hypolimnion by wind-induced mixing. Thermal profiles of the lake support mixing during this period. The peak in Mn concentration was followed by a decrease in epilimnetic Mn until fall turnover.

Despite extensive temporal and spatial variations in D.O and pH, Mn concentrations remained between 1.2 and 2.2 μmol l^{-1} during the study period. In fact iron exhibited a much larger concentration range (1–28 μmol l^{-1}) than Mn. Although both metals undergo reduction reactions, the kinetics of Fe oxidation is considerably faster than Mn under moderately acidic conditions (Stumm and Morgan, 1981), and in the surficial sediments of Dart's Lake pools of Fe were significantly greater than Mn (800 μmol Fe g^{-1}, 2 μmol Mn g^{-1}; White 1984).

Water column deposition patterns

Gross deposition of particulate Mn, determined through sediment trap collection, exhibited pronounced temporal variation during the study (Figure 4). The mean values of D_g–Mn in the 6 and 14-m traps were 3.6 and 6.2 μmols Mn m^{-2} d^{-1}, respectively. Note that gross deposition of Mn was strongly correlated with both Fe and Al deposition (Table 1), particularly for Fe deposition to 14-m traps ($r = 0.80$, $p > 0.001$). The specific deposition of Mn (D_s–Mn) for the upper waters (6-m trap) and entire water column (14-m trap) also varied seasonally (Figure 5). Since D_s is a function of the water column pool of soluble Mn and the gross deposition rate (D_g), the errors associated with the data were similar to D_g values.

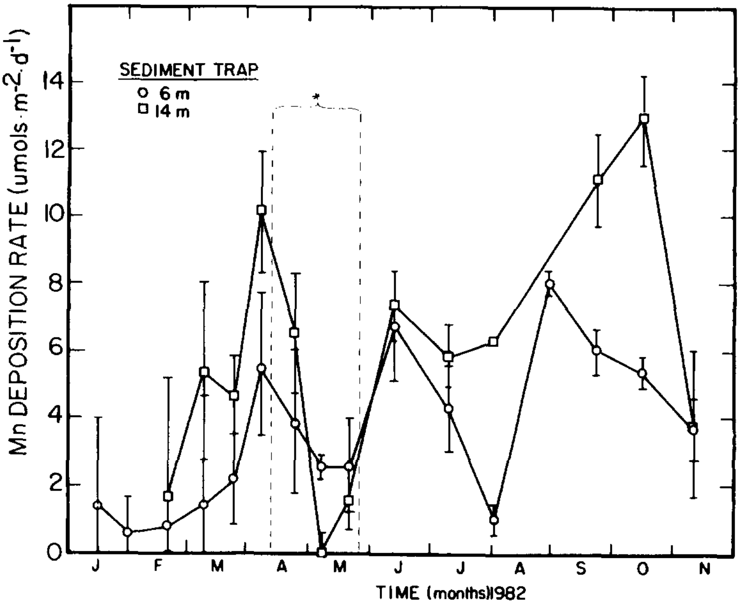


Figure 4. Temporal variations in the gross deposition rate (D_g) of manganese within the Dart's Lake water column. Note that during the snowmelt and spring turnover period* resuspension of particulate matter and over collection of sedimenting materials may have occurred.

Table 1. Linear Regression of Mn Deposition in Dart's Lake Sediment Traps as a Function of Particulate Constituents

Constituent	6 meter trap		14 meter trap	
	r	p<	r	p<
Fe	0.63	0.009	0.80	0.001
Al	0.70	0.003	0.62	0.018
Organic C	0.47	0.068	0.44	0.135

The patterns of Mn deposition would appear to be qualitatively consistent with SI values with respect to MnOOH solubility (Figure 6). During the initial stages of winter stratification, solutions were highly undersaturated with respect to the solubility of MnOOH and Mn deposition to sediment traps was minimal. As winter stratification proceeded SI values increased, particularly in the lower waters corresponding with an increase in Mn deposition. During snowmelt and spring turnover, solutions were highly undersaturated. While the interpretation of sediment trap data during this period should be made with caution, due to the elevated influx of particulates and the potential for resuspension from turbulence, vertical deposition of Mn was extremely low.

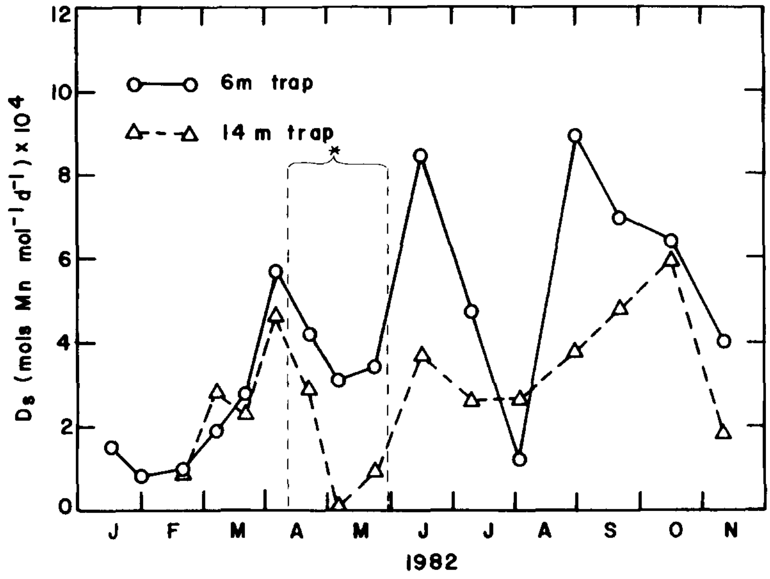


Figure 5. Temporal variations in the specific deposition rate (D_s) of Manganese within the Dart's Lake water column. Note that during the snowmelt and spring turnover period*, resuspension of particulate matter and over collection of sedimenting materials may have occurred.

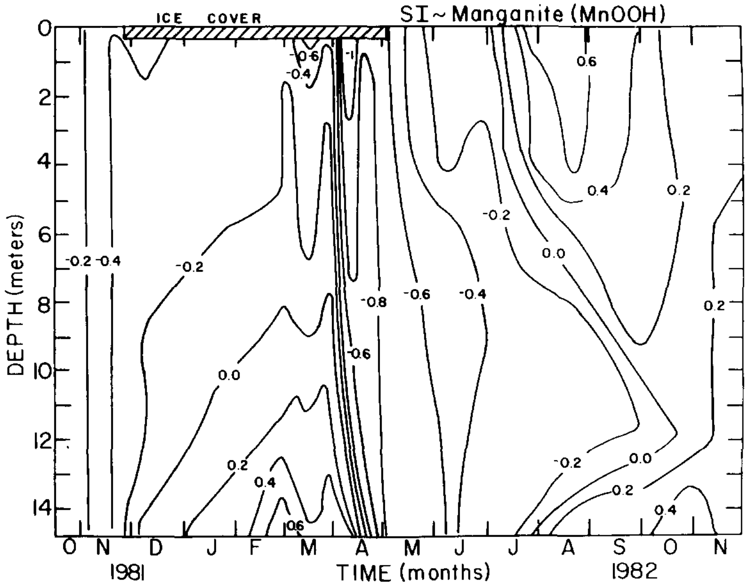


Figure 6. Temporal and spatial variations in the solubility index for manganite within the Dart's Lake water column (log K_{SO} = 25.27; Lindsay, 1979).

In the hypolimnitic waters SI values and Mn deposition to the 14 m sediment traps increased during summer stratification, peaking prior to fall turnover. Manganese deposition to 6 m was elevated at the start of summer stratification. Sedimentation rates were reduced in the upper waters from late June to early August. This period of reduced vertical deposition coincided with the introduction of Mn from the hypolimnetic to epilimnetic waters (Figure 2). The introduction of Mn to the upper waters coupled with an increase in pH resulted in peak SI values with respect to the solubility of MnOOH. High positive SI values corresponded with a resumption of elevated Mn deposition to the 6 m sediment trap in late August. For the remainder of summer stratification, SI values and Mn deposition decreased in the epilimnetic waters.

Discussion

Seasonal variations in the concentration and transport of Mn in aquatic systems may be attributed to changes in hydraulic regime (Troutman and Peters, 1982; Davis and Galloway, 1982) and in-lake processes (Scholkovitz and Copland, 1982; Chapnick *et al.*, 1982; Emerson *et al.*, 1982). The variations in discharge in the Dart's Lake system certainly influenced the flux of Mn to and from the system, however, changes in solution chemistry had little impact on in-lake retention of Mn.

Our results suggest that Mn was a relatively conservative solute in Dart's Lake. Mass balance calculations indicate that annual Mn influx (0.50 mmol m^{-2} d^{-1}) was similar to Mn efflux (0.57 mmol m^{-2} d^{-1}). This trend which was also evident on a seasonal basis, indicates no net deposition of Mn occurred in Dart's Lake. In fact Dart's Lake may have served as a net source of Mn (rates of Mn influx and efflux may not be significantly different). This pattern is in contrast to Al which was significantly retained in Dart's Lake, particularly during summer base flow conditions (Driscoll, 1984). Except for mobilization of Mn to hypolimnetic waters during stratification periods, no significant changes in Mn concentrations were observed in the water column. In addition, depositional losses were extremely low compared to the available Mn pool in the water column ($D_s = 2.8 \times 10^{-4} \pm 1.7 \times 10^{-4}$ mol Mn mol Mn^{-1} d^{-1}). Observed rates of Mn specific deposition were in contrast to the behavior of Pb and Al, which exhibited 50 to 75 times higher specific deposition rates (D_s: $1.32 \times 10^{-2} \pm 0.93 \times 10^{-2}$ mol Pb mol Pb^{-1} d^{-1}; $2.06 \times 10^{-2} \pm 0.93 \times 10^{-2}$ mol Al mol Al^{-1} d^{-2} on average over the study period (White, 1984)).

Another method of assessing the conservative nature of Mn is through the distribution coefficient, K_D. In-situ values of K_D-Mn determined from sediment trap and water column data (equation 4), are presented in combination with K_D-Mn values determined by batch sediment adsorption studies (equation 5) (Figure 7). Note that K_D values, as determined by adsorption studies, increased with increasing pH. It appears that the pH of Dart's Lake was sufficiently low such that the affinity of Mn for particulate matter was considerably reduced.

Our observations of Mn chemistry for acidic Dart's Lake are consistent with those of Schindler *et al.*, (1980) for the Experimental Lakes Area of Canada. Their work involved experimentally acidified lake enclosures in a dilute lake, to which were added radioisotopes of several metals. In neutral-pH control enclosures Mn was extensively (84%) sorbed to particulate matter. Acidification of these waters to pH 5.1 resulted in a reduction in Mn partitioning to particles in suspension; only 1% of added Mn was removed from solution through sorption to particles. Although K_D values were not presented in the enclosure study (Schindler *et al.*, 1980), our sediment titration results demonstrated a dramatic increase in log K_D-Mn at pH values above 5.0 (Figure 7). Therefore, differences in the partitioning of Mn between particles and solution may simply reflect differences in lake pH.

Distribution coefficients for Mn (log K_D–Mn = 3.74 ± 0.34) were also considerably lower than values observed for Pb (log $K_D - Pb = 5.45 \pm 0.20$) and Al (log $K_D - Al = 4.93 \pm 0.18$). These observations are consisent with the fact that Pb and Al undergo hydrolysis at lower pH values than Mn(II).

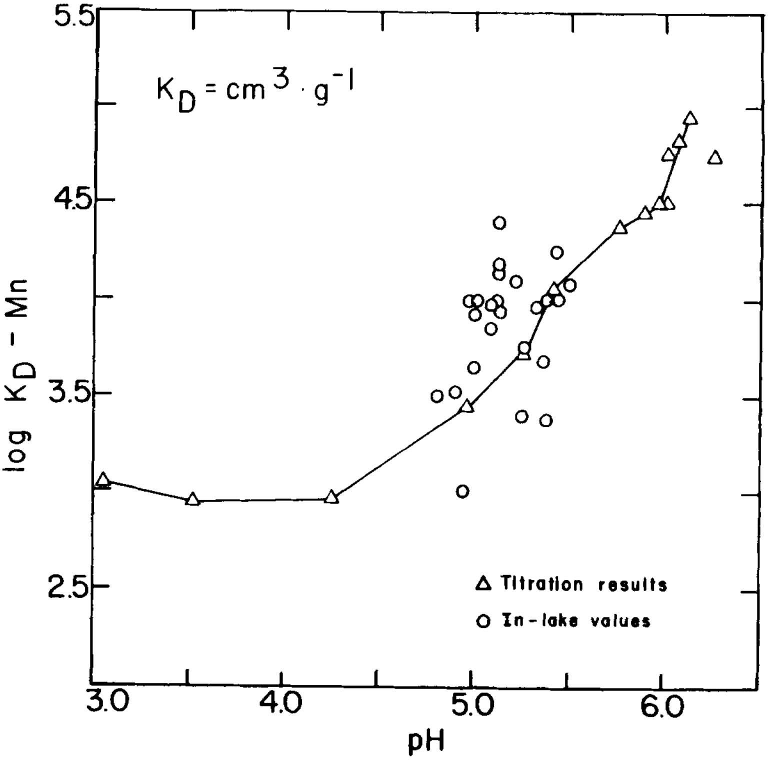


Figure 7. In-lake and titration results for manganese distribution coefficients (K_D) as a function of pH.

Within the present hydrologic and pH regime of Dart's Lake, evidence based upon low specific deposition rates, low distribution coefficients (K_D – Mn), and water column observations were consistent with the fact that Mn is a relatively conservative element with respect to solution/surface interactions and vertical deposition. The flux of Mn to Dart's Lake sediments as determined by sediment cores also suggests a very low rate of retention. Al and Fe flux rates were 700 and 350 times Mn, respectively, as determined by sediment cores (White, 1984). The disparity is even greater for Big Moose Lake sediments, where Al and Fe flux rates were 500 and 1000 times Mn, respectively (see Charles, *et al.*, 1987). The calculation of Fe and Mn flux rates based on sediment cores should be viewed with caution since Fe and Mn are subject to recycling and surface enrichment in sediments. Nevertheless, the limited retention of Mn in Dart's Lake is also supported by the general conditions of undersaturation with respect to the solubility of MnOOH and the fact that the rate of Mn(II) oxidation in acidic waters is extremely slow (Handa, 1970; Stumm and Morgan, 1981).

The conservative nature of Mn has implications for acidic lake systems. The quantity of Mn deposited in sediment traps was very low relative to organic carbon, Al and Fe. The molar ratio of Mn to C, Fe, and Al deposited in 14 m traps on average was $10^{-3.5}$, $10^{-2.2}$ and $10^{-2.1}$, respectively. Therefore it is unlikely that Mn is an important adsorbent in acidic surface waters. Also because sediment pools of Mn were low, reduction of Mn was not a significant mechanism for the generation of acid neutralizing capacity within Dart's Lake (Driscoll and Schafran, 1984). Finally elevated water column concentrations of soluble Mn are more available for uptake by aquatic biota than particulate-bound Mn, and may result in physiological problems (Harvey and Fraser, 1982).

Conclusions

Changes in Mn concentrations within Dart's Lake, although slight, were related directly to dissolved oxygen concentrations and indirectly to thermal stratification patterns, as well as to the pH of drainage inputs. Despite the high rates of soluble Mn influx to the lake, little retention of Mn occurred in this acidic system. Manganese deposition to the sediments was affected by significant temporal and spatial changes in D.O. and pH, however, the rate of particulate deposition was a minor component of Mn cycling. Under the present conditions, Mn is a highly conservative element in this system. Significant increases in pH, through liming for example. are however likely to reverse this behavior and enhance depositional losses and retention of Mn in Dart's lake.

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