Reports

Zinc Deposition in Acid Lakes: The Role of Diffusion

Abstract. *Steep negative concentration gradients of dissolved zinc are present between the overlying waters and the anoxic pore waters of two acid lakes. In the anoxic pore waters, the low zinc concentrations can be explained as due to the formation of relatively insoluble zinc sulfide minerals. Downward diffusive fluxes of dissolved zinc account for at least 50 to 75 percent of the recent zinc deposition to the sediments of these lakes. This downward diffusion occurs to a depth of 2 to 3 centimeters below the sediment water interface, where pronounced maxima in total zinc are observed. These subsurface peaks in total zinc have been interpreted as an indication of recent lake acidification. The present observations indicate that such subsurface peaks may also result from a diagenetic activity unrelated to recent changes in lake acidity.*

A recent increase in anthropogenic zinc deposition to the sediments of lakes has been documented in many studies (*1–3*). Two different mechanisms could account for zinc accumulation in lake sediments: (i) the sedimentation and burial of particulate zinc (*4*) and (ii) the diffusion of dissolved zinc from lake water to a sedimentary sink. Although previously neglected, the second mechanism appears to be potentially important. Zinc is relatively soluble in acidic to slightly alkaline lake waters (*5*) but is expected to be much less soluble in sulfide-bearing anoxic pore waters (interstitial waters); therefore, significant zinc concentration gradients and diffusive fluxes may exist at the sediment-water interface of such lakes. In this report we estimate the relative importance of the diffusion mechanism in two lakes by comparing the present-day rates of zinc accumulation to the calculated diffusive fluxes across the sediment water interface.

Duplicate sediment cores (*6*) were obtained at a depth of 20.2 m in Clearwater Lake, Ontario (46°22′N, 81°03′W) (hypolimnetic *p*H, 4.5 to 5.5; $[SO_4^{2-}]$, 150 to 200 μmol liter^{-1}) and at 15.5 m in Tantaré Lake, Québec (47°04′N, 71°32′W) (hypolimnetic *p*H, 5.3 to 5.5; $[SO_4^{2-}]$ = 40 to 50 μmol liter^{-1}). The cores were sectioned at 1-cm intervals within 1 hour of collection, lyophilized, and analyzed (*7*) for total zinc (Zn_t) and ^{210}Pb (*8*). Pore water samples were obtained in duplicate by in situ dialysis (*9*) within 2 m of the coring sites. Pore water aliquots were collected, within 5 minutes of sampler retrieval from the sediments, for the measurement of $[\Sigma CO_2]$ (*10*), *p*H, and $[H_2S]$ (*11*), [Zn] (henceforth designated as Zn_p), [Ca], [Mg], [Fe], $[SO_4^{2-}]$, and $[NH_4^+]$ (*12*).

The observed [Zn] of the overlying water appears typical of that of southeastern Canadian lakes (*13*). The Zn_p profiles (Fig. 1) are characterized by steep concentration gradients between 0 and ~2 cm, an indication that zinc is diffusing below the sediment water interface. Below 2 cm, the low Zn_p concentrations (1×10^{-9} to 11×10^{-9} mol liter^{-1}) are associated with the presence of measurable pore-water sulfide. The pore water of Clearwater Lake is at saturation with respect to amorphous ZnS just below the interface (Table 1). In both sediments, the pore waters are slightly oversaturated with respect to sphalerite; this result suggests that the formation of this mineral is a plausible reaction controlling Zn_p. Owing to the uncertainty in the published solubility product (K_s) values (*14*) and to the fact that Zn_p and $[H_2S]$ are close to their detection limits, the uncertainty in the saturation indexes is probably of the order of ±2. These results are in contrast to the large oversaturations reported for zinc (*15*) in anoxic marine waters and pore waters.

The sediment Zn_t profiles (Fig. 1) show a maximum at 2.5 to 3.5 cm, with a nearly linear decrease to a constant level at 9 to 10 cm. Such profiles are common in acid lakes (*1–3*). The recent increase in Zn_t has been attributed to increased an-

Table 1. Distribution of major zinc and sulfur species and saturation indexes for three common zinc sulfide minerals in the pore waters of Clearwater and Tantaré lakes. $\Sigma[H_2S]$ and $\Sigma[Zn]$ are analytical concentrations; we computed $\{HS^-\}$, $\{Zn^{2+}\}$, and $[Zn(HS)_2^0]$ by using WATEQ2 (*14*) and analytical [Ca], [Mg], [Fe], [Mn], $[HCO_3^-]$, $[SO_4^{2-}]$, ΣH_2S and ΣZn. The saturation index is defined as log (IAP/K_s) where IAP, the ion activity product, is equal to $(\{Zn^{2+}\}\{HS^-\})/\{H^+\}$, and K_s is the solubility product of each mineral at in situ temperature corresponding to the reaction $ZnS_{(s)} + H^+ \rightleftharpoons Zn^{2+} + HS^-$. The temperature-corrected K_s^{25} values used for amorphous ZnS, sphalerite, and wurtzite are $10^{-9.02}$, $10^{-11.62}$, and $10^{-9.68}$, respectively (*14*).

Depth (cm)	*p*H	$\Sigma[H_2S]$	$\{HS^-\}$	$\Sigma[Zn]$	$\{Zn^{2+}\}$	$[Zn(HS)_2^0]$	Saturation index		
		(mol liter^{-1})					ZnS_{am}	Sphalerite	Wurtzite
				Clearwater Lake					
1	6.14	2.8×10^{-6}	2.31×10^{-7}	1.01×10^{-7}	2.11×10^{-9}	9.74×10^{-8}	0.01	2.74	0.69
4	6.31	9.3×10^{-6}	1.15×10^{-6}	2×10^{-9}	1.73×10^{-12}	1.99×10^{-9}	−2.21	0.52	−1.53
8	6.27	3.8×10^{-6}	4.39×10^{-7}	1×10^{-9}	5.92×10^{-12}	9.93×10^{-10}	−2.13	0.60	−1.45
12	6.24	2.9×10^{-6}	3.15×10^{-7}	1×10^{-9}	1.14×10^{-11}	9.86×10^{-10}	−2.02	0.71	−1.34
				Tantaré Lake					
1	6.22	1×10^{-7}	8.90×10^{-9}	3×10^{-9}	2.49×10^{-9}	1.71×10^{-10}	−1.21	1.58	−0.51
4	6.22	4×10^{-7}	3.55×10^{-8}	3×10^{-9}	1.36×10^{-9}	1.48×10^{-9}	−0.87	1.92	−0.17
8	6.20	5×10^{-7}	4.26×10^{-8}	2×10^{-9}	7.41×10^{-10}	1.17×10^{-9}	−1.07	1.72	−0.37
12	6.20	4×10^{-7}	3.39×10^{-8}	4×10^{-9}	1.88×10^{-9}	1.89×10^{-9}	−0.77	2.02	−0.07

thropogenic zinc fallout since the turn of the century. The decrease in $\mathrm{Zn_t}$ frequently observed at the sediment surface in these lakes has been attributed to a leaching of either the bottom sediments or the suspended solids by recently acidified surface waters (*2, 3*).

The downward diffusive flux (J, in micrograms per square centimeter per second) of $\mathrm{Zn_p}$ across the sediment water interface of both sites was estimated from Fick's first law, corrected for the electrical coupling (J_e) of the zinc flux to the fluxes of major ions (*16*):

$$J = -D_t\frac{dC}{dx} + J_e \qquad (1)$$

where D_t is the coefficient of molecular diffusion (in centimeters squared per second) at in situ temperature, and dC/dx is the concentration gradient (in micrograms per cubic centimeter of pore water per centimeter) at the interface. We assumed that porosity and tortuosity effects, normally taken into consideration when treating diffusion in porous media (*17*), were negligible here because of the high porosity (>0.96) of the top 2 cm of both sediments. Since $\mathrm{Zn^{2+}}$ is the only important dissolved zinc species expected to occur in dilute acidic waters that are low in dissolved organic carbon, we used a temperature-corrected D_{25} value of 7.15×10^{-6} cm^2 sec^{-1} for $\mathrm{Zn^{2+}}$ (*18*). According to Eq. 1, the downward diffusive $\mathrm{Zn_p}$ fluxes for Clearwater and Tantaré lakes are thus 1.71 and 0.96 μg cm^{-2} year^{-1}, respectively. The coupling effect appears relatively small in both lakes and results in a correction of −11 percent for Clearwater Lake and +7 percent for Tantaré Lake. Equation 1 does not take into consideration the possibly important effect of benthic irrigation in the transport of solutes across the interface. Consequently, the true $\mathrm{Zn_p}$ diffusive fluxes may be higher than calculated from Eq. 1.

In order to evaluate the relative importance of diffusion in zinc deposition, an estimate of the accumulation rate of $\mathrm{Zn_t}$ in the sediments is needed. This accumulation rate was derived from $\mathrm{Zn_t}$ and bulk sediment accumulation rates inferred from ^{210}Pb geochronology. The 5- to 15-cm region of the ^{210}Pb profiles (Fig. 1) of sediments for both lakes shows the log-linear unsupported ^{210}Pb decrease expected in environments where compaction is negligible and where sediment and ^{210}Pb deposition have been constant with time. The change in slope occurring in the topmost 5 cm of the profiles can be attributed either to a recent increase in deposition or to bioturbation (*19*). In Tantaré Lake, a recent increase in sediment deposition is very unlikely as the lake's watershed has not been disturbed by forest fire, road construction, or wood harvesting for at least the last 100 years. In Clearwater Lake, sediment deposition may have recently increased owing to the extensive deforestation of the watershed that occurred 40 to 50 years ago as a result of $\mathrm{SO_2}$ emissions from nearby smelters. However, the fact that well-developed mixed layers of constant ^{210}Pb activity have been observed by Dillon and Smith (*3*) at a nearby site and at other sites in Clearwater Lake as well as the lack of evidence for recently increased deposition (also measured with ^{210}Pb) in nearby lakes (*20*) similarly affected by deforestation suggest that the change in the ^{210}Pb slope occurring at 5 cm is also a mixing feature. Since the ^{210}Pb profiles of the top 5 cm of both sediments appear to be influenced by bioturbation (or by some other mixing phenomenon), we calculated bulk sediment accumulation rates between 5 and 15 cm from the least-squares fit of a plot of unsupported ^{210}Pb activity versus cumulative sediment dry weight, assuming a constant initial ^{210}Pb activity at the lower boundary of the mixed layer. The average ($n = 2$) sedimentation rates thus obtained are 7.60 mg cm^{-2} year^{-1} (0.75 mm year^{-1}) for Clearwater Lake and 4.13 mg cm^{-2} year^{-1} (0.83 mm year^{-1} for Tantaré Lake; duplicate values were within 10 percent of each other.

If postdepositional mobility was as-

Table 2. In situ temperature, coefficient of molecular diffusion (D_t) for zinc, estimated diffusive flux (J, a mean value obtained from two $\mathrm{Zn_p}$ profiles in Clearwater Lake and four in Tantaré Lake), total zinc accumulation rate in the sediments, and percent relative contribution of diffusion in Clearwater and Tantaré lakes.

Lake	Temperature (°C)	D_t (10^{-6} cm^2 sec^{-1})	J (μg cm^{-2} year^{-1})	$\mathrm{Zn_t}$ accumulation (μg cm^{-2} year^{-1})	Diffusion (%)
Clearwater	11.9	4.91	1.71	3.28	51.8
Tantaré	5.1 to 6.5	4.12	0.96	1.26	76.2

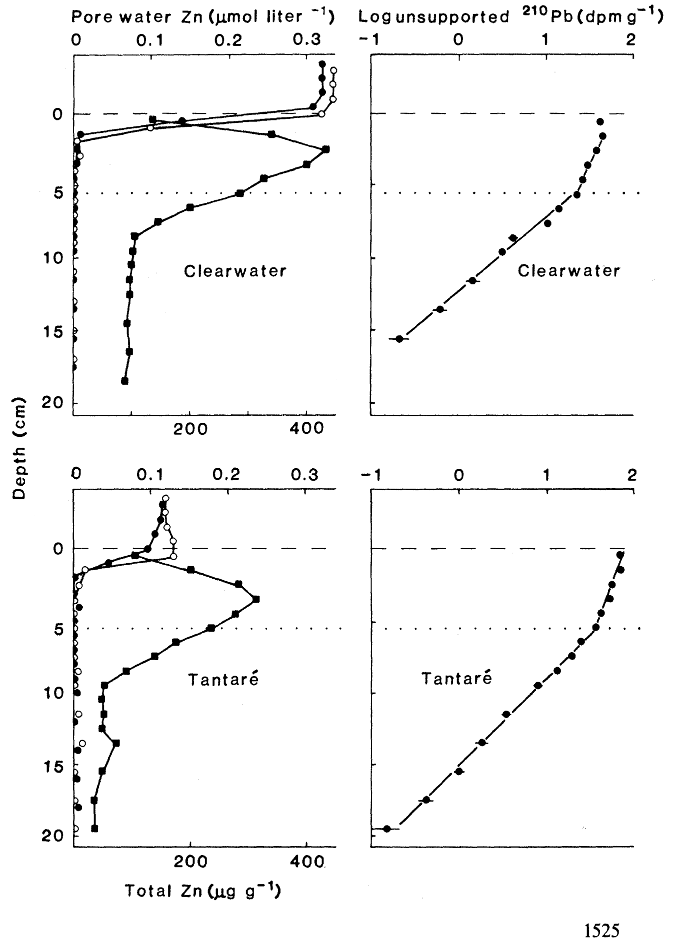

Fig. 1. Pore water zinc ($\mathrm{Zn_p}$; ● ○) and total zinc ($\mathrm{Zn_t}$; ■) (left panels) and unsupported ^{210}Pb (right panels) in the sediments of Clearwater and Tantaré lakes. The cores were taken in June 1984; the pore water profiles were obtained in June 1984 for Clearwater Lake and in June or September of 1984 for Tantaré Lake. The two pore water profiles chosen for Tantaré Lake represent the most different profiles encountered. The dashed lines indicate the sediment water interface, and the dotted lines indicate the lower limit of the ^{210}Pb-defined mixed layer. The error bars represent ±1 σ of the counting errors.

sumed to be negligible and if sedimentation was constant in time, the present rate of zinc accumulation in the sediments could be estimated directly from the product of surface Zn_t and the present deposition rate of bulk sediment. However, the Zn_p profiles indicate that a significant downward postdepositional diffusive Zn_p flux occurs to a depth of 2 to 3 cm. In other words, the accumulation of Zn_t by a given sediment layer does not end until it is buried below 2 to 3 cm. Moreover, the subsurface Zn_t peaks of both sediments are located well within the ^{210}Pb-defined mixed layer (Fig. 1). In the two sediments, the slope of the ^{210}Pb profiles between 0 and 5 cm suggests a biodiffusion coefficient (K_b) of 6×10^{-9} to 10×10^{-9} cm^2 sec^{-1} for the sediment solids when a mixing model with constant K_b (*19*) is used. A considerable biodiffusional transport of Zn_t may therefore occur in the upward direction in the region of positive Zn_t concentration gradient (above the peak) and in the downward direction below the peak. Zinc may thus be rather mobile in these sediments, and the recent Zn_t accumulation rates would likely be erroneous if estimated as the product of surficial Zn_t and recent accumulation rates of bulk sediment. To minimize the possibility of underestimation, we calculated the present Zn_t accumulation rates from the maximum Zn_t concentrations, which occur between 2 and 3 cm in Clearwater Lake ($\bar{x} = 432$ μg g^{-1}, $n = 2$) and between 3 and 4 cm in Tantaré Lake ($\bar{x} = 306$ μg g^{-1}, $n = 2$). A major (51.8 to 76.2 percent) portion of the sedimentary Zn_t appears to have a diffusive origin (Table 2). The importance of this flux suggests a diagenetic origin for the observed Zn_t peaks; the 1-cm vertical discrepancy observed (Fig. 1) between the depth of Zn_p precipitation and the position of the Zn_t peaks may reflect seasonal variations in the Zn_p profiles. The Zn_p fluxes are probably underestimated since molecular diffusion only was assumed in the flux calculations. In situ tracer diffusion experiments (*21*) conducted in September 1984 at the coring site in Tantaré Lake show that the benthic irrigation transport coefficient is on the order of 5×10^{-6} to 6×10^{-6} cm^2 sec^{-1} for the top 4 to 5 cm. However, it is not yet known whether this value is also representative for other times of the year. Nevertheless, this result suggests that Zn_p diffusion may actually be higher than estimated.

The importance of diffusion as a transport mechanism for zinc has several implications for our understanding of zinc dynamics in acid lakes. The transport of trace metals from the water column to the sediments has generally been regarded as a sedimentation process controlled by the extent of trace metal association to the suspended solids and by the rate of sedimentation of the suspended solids (*4*, *20*). The present results suggest that such a model may not be applicable for zinc in acid lakes, and perhaps for other elements (for example, cadmium, nickel, and cesium) that are present in the water column in relatively high concentrations but are efficiently scavenged in the sediments. In addition to the historic increase in anthropogenic zinc deposition, several other factors including the downward molecular plus irrigation transport of Zn_p, the biodiffusion of Zn_t within the mixed layer, and the local chemical equilibria between sediment solids and pore water constituents may have contributed to the shape of the observed Zn_p and Zn_t profiles. Subsurface Zn_t peaks have often been interpreted as evidence for recent lake acidification. Our results provide an alternate explanation for such peaks: they appear to result from an important postdepositional diffusive transport of dissolved zinc below the sediment water interface. As a direct consequence of the importance of the diffusion mechanism, historical reconstructions of zinc deposition (and related freshwater acidification inferences) based on sediment deposition chronologies and total zinc profiles appear questionable for acid lakes. Because of the nonsteady state nature of anthropogenic zinc influx in lakes, it may be advisable to use nonsteady-state numerical methods in the interpretation of sedimentary zinc profiles and in the modeling of the early diagenesis of this element and other transition metals in acid lakes (*22*).

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10. The 5-ml Vacutainers had been flushed with helium and evacuated to remove a variable CO_2 contamination; 50 μl of a saturated $HgCl_2$ solution was added as a preservative. Within 3 days of collection, the samples were acidified, and the CO_2 was measured (after a vigorous, 30-second agitation) by gas chromatography. We calculated pore water $[HCO_3^-]$ from ΣCO_2 and *p*H, using the first dissociation constant of carbonic acid at in situ temperature.
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12. The samples were injected into 7-ml Teflon vials preacidified with 30 μl of 1*N* (Ultrex) HCl. Pore water metals were measured by flame or graphite-furnace atomic absorption spectrometry, $[SO_4^{2-}]$ by ion chromatography, and $[NH_4^-]$ by an automated colorimetric method. Zinc was usually undetectable ($<10^{-9}$ mol liter^{-1}) in the blanks for storage times not exceeding 2 to 3 weeks.
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