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Porewater acid/base chemistry in near-shore regions of an acidic lake
The influence of groundwater inputs

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Abstract. Sediment porewaters in the near-shore region (within 1 m of the shoreline) of an acidic lake (Dart's Lake) were monitored during the summer of 1983 to investigate whether spatial variations in porewater acid/base chemistry were significant in this region of the lake. Previous investigations of Dart's Lake porewaters have indicated that within deeper waters (> 2 m depth), sediment porewaters are elevated in alkalinity relative to overlying lake water. Within the near-shore region, porewaters both considerably more and less acidic than the lake water were observed. Both reduction of strong acid anions (SO_4^{2-}, NO_3^-) and the mobilization of base cations were significant mechanisms of alkalinity production in porewaters exhibiting reducing conditions. In sediments reflecting oxic conditions, porewaters were generally more acidic than the lakewater. Measurement of groundwater seepage into the lake at the near-shore sites indicated that oxic sites exhibited elevated inputs of groundwater when compared to sites where reducing conditions existed. The acidic porewaters associated with high groundwater flows suggests that groundwater inputs to the lake may be a source of acidity (not alkalinity) on a whole-lake basis.

Introduction

Acidic surface waters have been observed in many regions of the world and have been related to the atmospheric input of strong acids (LaZerte & Dillon 1984; Driscoll & Newton 1985). As a consequence, deleterious effects to aquatic organisms have been related to both chronic and episodic surface water acidification (Baker 1984; Henriksen et al. 1984). Although surface waters have become acidified, it has been reported that sediment porewaters of these systems largely remain circumneutral (Kelly & Rudd 1984; Carignan 1985; Rudd et al. 1986a). In these sediments microbial reduction of SO_4^{2-}, NO_3^-, Fe, Mn, and the production of NH_4^+ neutralize H^+ inputs causing sediment porewaters to remain circumneutral even near the sediment-water interface (Schiff & Anderson 1986). In addition, these reactions neutralise acidity in overlying lakewater and may be a quantitatively important source of alkalinity in whole-lake alkalinity budgets (Baker et al. 1986; Schindler et al. 1986). As a result of these alkalinity producing reactions which maintain a relatively neutral pH environment, there apparently has been little change in sediment microbial activity following acidification of lakes (Kelly et al. 1984).

Studies of porewater chemistry in acidic lakes have occurred within both hypolimnetic (Carignan 1985; Cook et al. 1986) and in epilimnetic sediments (Cook et al. 1986; Rudd et al. 1986a; Schiff & Anderson 1986). Common among these studies have been the occurrence of considerable sediment microbial activity that generally results in porewaters having higher alkalinity than the lake water column. These results suggest that independent of the spatial location within an acidic lake, sediment porewaters will be less acidic and a potential source of alkalinity to the water column.

To date, the porewater chemistry for near-shore (within several meters of the shoreline) sediments of lakes acidified by atmospheric acid inputs has been poorly documented and the relationship of these waters to porewaters from deeper regions of lakes is unknown. The potential for the chemistry of near-shore sediment porewaters in lakes to be considerably different than deep water sediments is likely due to differences in sediment chemistry (e.g. differences in mineral and organic matter content) as well as spatial variation in advective fluxes from the terrestrial groundwater system. In studies of nutrient loading to lakes from groundwater inputs, considerable variation in near-shore porewaters was attributed to groundwater inputs (Brock et al. 1982; Belanger & Mikutel 1985). Considerable spatial variation in both the rate of groundwater inputs and porewater chemistry in the near-shore lake regions was well documented in these studies and groundwater inputs to these lakes were determined to significantly control lake water chemistry.

For groundwater inputs to lakes, the highest rate of seepage is generally observed nearest to the shoreline (McBride & Pfannkuch 1975). Thus, the chemistry of near-shore porewaters may be significantly influenced by groundwater inputs and the flux of water through this zone will generally represent the highest loading (on a per area basis) for groundwater inputs to a lake. If the chemistry and inputs of groundwater to lakes are spatially variable then substantial variations in porewater acid/base chemistry may occur in acidic lakes in regions impacted by atmospheric acid inputs. It is likely that if variations in the acid/base chemistry of near-shore porewaters exist then these variations will influence the distribution of benthic organisms, fish spawning, and aquatic vegetation.

We report here the results of a study in which spatial variations in acid/base chemistry of porewaters in the near-shore zone of an acidic lake were examined.

Study site and methods

The study site, Dart's Lake (43°47′N, 74°51′W), is a drainage lake located in the Adirondack Mountain region of New York State, USA. Dart's Lake has one major inlet, a single outlet, drains a watershed of 107 km^2 and has a surface area of 0.58 km^2. Due to the large watershed area, drainage inputs to the lake represent the largest water source and have been estimated as greater than 95% of the lake budget. Bedrock geology of the region is characteristically crystalline

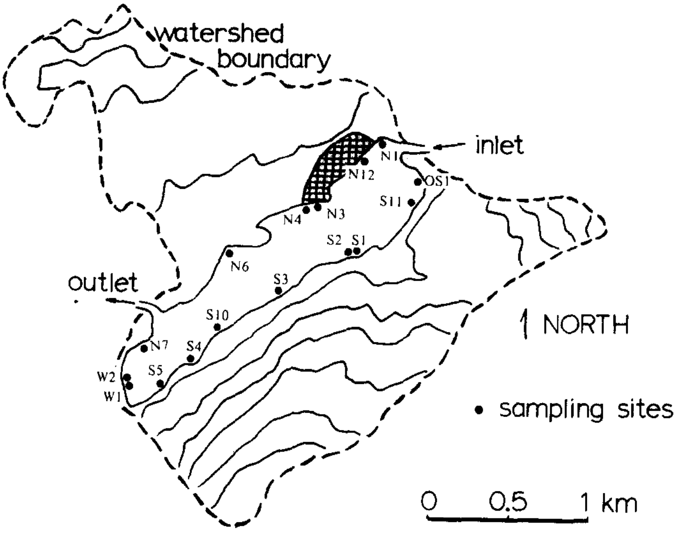

Fig. 1. The Dart's Lake study site and the watershed area directly surrounding the lake. The watershed boundary includes only that region of the watershed that is a potential source of groundwater directly to the lake. Porewater sampling sites are indicated by ●; the cross-hatched area indicates a region occupied by a summer youth camp.

granitic gneiss and surficial till is generally thin ($< 3\,m$) (Newton et al. 1987). The watershed is predominantly forested and consists of a mix of coniferous and deciduous vegetation. The watershed area immediately surrounding the lake is undisturbed except along the northwest side of the lake (Fig. 1).

Lake water (surface) pH values vary seasonally from approximately 4.8 in spring to 5.6 in the summer. pH depressions that occur at spring snowmelt are largely associated with increased inputs of nitrate (Driscoll & Schafran 1984). Aluminum concentrations are elevated (5–$15\,umol\,l^{-1}$) in the lake and are well correlated to variations in pH. Sulfate is the dominant anion, but has minor seasonal variations. During periods of stratification, hypolimnetic sediment microbial activity is evidenced by decreases in concentrations of strong acid anions (SO_4^{2-} and NO_3^-) and increases in Fe, Mn, and NH_4^+ in the hypolimnion. These changes cause an increase in alkalinity and decreases in H^+ and Al within this region of the lake (Schafran & Driscoll 1987a). Microbial activity of epilimnetic sediments in the lake has been studied directly and porewaters of these sediments have been observed to be circumneutral (Rudd et al. 1986a). Consequently, both hypolimnetic and epilimnetic sediments appear to be sources of alkalinity to the lake.

A survey of near-shore sediment porewaters of Dart's Lake was conducted from May to November 1983 at 16 locations around the perimeter of the lake (Fig. 1). To collect sediment porewaters a sampler similar to a minipiezometer was used (Lee & Cherry 1980). The porewater samplers consisted of acrylic tubing with polyethylene screened openings near one end of the tube and a septum covering the other end. Porewater samplers were permanently installed by inserting the sampler slowly into the predominately sandy sediments of the near-shore regions of the lake; sample depths ranged from 20 to 30 cm below the sediment-water interface and samplers were installed within 1 m of the shoreline. Porewater samples were withdrawn by piercing the septum with a needle connected to a polyethylene syringe. Following withdrawal (and wasting) of water already present in the sampler, a 70 ml sample was collected for chemical analysis. Water in the syringe was gently expelled from the syringe into a sample bottle that was filled to the rim and then tightly capped. Samples were stored on ice during transport and at 4°C during laboratory storage.

Seepage meters (Lee 1977) were periodically used during the study to measure groundwater seepage at the different sites. Determinations of groundwater flux were made on a flux or no flux basis during this period to determine whether groundwater movement into the lake was occurring. To assess the relative groundwater flux (quantitatively) among the study sites, seepage fluxes were measured at 11 of the study sites in the early summer of 1986. Further description of equipment and sampling is available elsewhere (Schafran 1988).

Porewater samples were measured for pH potentiometrically by glass electrode. Sulfate, NO_3^-, and Cl^- were measured by ion chromatography and base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were measured by flame atomic absorption spectrophotometry (AAS). Dissolved inorganic carbon (DIC) was measured by acidification and syringe stripping of CO_2 and detection with a gas partitioner (Stainton 1973). Dissolved organic carbon (DOC) was determined by persulfate oxidation of filtered, acidified, and N_2 purged samples followed by CO_2 detection with a gas partitioner (Menzel & Vaccaro 1964). Ammonium was measured by the alkaline phenol method and dissolved silica was determined by the ammonium molybdate procedure both using an auto analyzer. Iron was measured by flameless AAS on a 1.5 ml aliquot of sample that was acidified with ultrex nitric acid to pH 2 in the field. Two operationally defined fractions of Al, labile monomeric Al and nonlabile monomeric Al, were measured by extraction with 8-hydroxyquinoline and analysis by flameless AAS. Nonlabile Al is believed to represent the fraction of dissolved Al complexed by organic ligands while the labile Al fraction represents the dissolved aquo (Al^{3+}), hydroxide and inorganically complexed Al (Driscoll 1984). Due to the limited sample size, direct measurements of alkalinity were not made. Instead, porewater alkalinities were calculated (Eq. 1) using a chemical equilibrium model (ALCHEMI; Schecher & Driscoll 1987) that determines the speciation of inorganic carbon and the partial pressure of CO_2 (P_{CO2}). Due to electroneutrality constraints, alkalinity is also equivalent to the difference between the major cations and strong acid anions in solution not included in Equation 1 (Eq. 2); the relative difference in concentrations of the major cations and anions were examined to evaluate the processes that contributed to the generation of alkalinity in these waters. ALCHEMI was also used to determine the speciation and equivalent concentration of Al (Al^{n+}) in waters studied.

$$ALK = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad [1]$$

$$= 2[\mathrm{Ca}^{2+}] + 2[\mathrm{Mg}^{2+}] + [\mathrm{Na}^{+}] + [\mathrm{K}^{+}] + [\mathrm{NH}_4^{+}] + n[\mathrm{Al}^{n+}] + n[\mathrm{Fe}^{n+}] + 2[\mathrm{SO}_4^{2-}] - [\mathrm{NO}_3^{-}] - [\mathrm{Cl}^{-}] - [\mathrm{F}^{-}] \qquad [2]$$

where: [ ] indicates the molar concentration of the major solutes in the porewaters.

Note for the alkalinity calculations, the contribution of protolytic organic anions is not considered. Weak organic acids can contribute to the alkalinity of water and can be a significant source of alkalinity at low pH values (Sullivan et al. 1989). In this paper we examine the apparent contributions of base cation mobilization and strong acid anion removal to porewater alkalinity.

Results

Near-shore regions influenced by groundwater seepage

The movement of water through the sediments at the study sites was determined for a limited number of sites during the course of this study. Although quantitative fluxes were measured on only a few dates and at only a few sites during the period of chemical sampling, determinations of groundwater inputs indicated that each site was under the influence of advective transport into the lake. A subsequent survey of groundwater fluxes at 11 of these sites was conducted on 15 May and 5 June of 1986 to determine the relative magnitude of groundwater fluxes. At all sites, groundwater movement was detected into the lake and an approximately two order of magnitude difference in groundwater flux was observed (Table 1).

Table 1. Groundwater seepage* into Dart's Lake.

Site	Redox condition**	Seepage rate	
		May 15, 1986	June 5, 1986
N1	Reducing	2.8	2.8
N7	Reducing	1.2	1.3
W2	Reducing	0.8	0.4
S5	Reducing	6.1	0.3
S4	Reducing	3.5	1.5
S10	oxic	9.5	5.5
S3	oxic	13.4	31.9
S2	oxic	70.6	64.0
S11	oxic	40.8	19.3
N4	oxic	8.5	14.8
N6	oxic	14.7	22.8

* Seepage rate in liters $\text{meter}^{-2}\ \text{day}^{-1}$.

**Porewater oxygen condition as characterized in the 1983 study (see text).

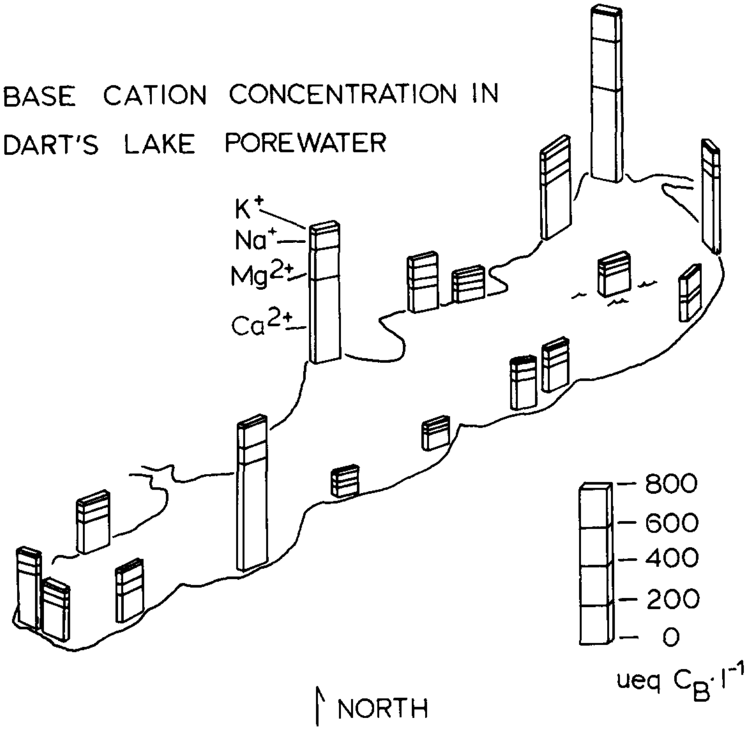

Fig. 2. Distribution of base cations in the near-shore porewaters of Dart's Lake. Concentrations depicted represent mean values over the period of study. The bar located in the middle of the lake represents the mean annual concentration from a prior study (Schafran & Driscoll 1987a).

Patterns in Base Cation Concentrations in Near-Shore Porewaters

The sum of base cations ($C_B = Ca^{2+} + Mg^{2+} + Na^+ + K^+$; eq l^{-1}) exhibited considerable variability in near-shore porewaters of Dart's Lake (Fig. 2). Values ranged from 91–865 ueq l^{-1} with many sites significantly different than lake water concentrations (C_B = 180 ± 15 ueq l^{-1}; lakewater mean ± s.d.). This trend in C_B concentrations suggests that the alkalinity production due to base cation release varies substantially among the near-shore porewaters. Temporal variations in C_B were generally minor (coefficient of variation ranged from 2–20% at each site) and no seasonal trends were evident. Base cation concentrations were positively correlated with dissolved silica concentrations ($p < 0.0001$, $r^2 = 0.57$) and is consistent with weathering of silicaceous minerals as the predominant source. Base cation concentrations were also significantly correlated with P_{CO2} in porewaters ($p \pm 0.0001$; $r^2 = 0.67$) suggesting that mineral weathering and associated release of C_B is mediated by microbial production of CO_2 in groundwaters/sediments.

As reported for surface waters of the region, Ca^{2+} was the dominant base cation (at all but one site) and contributed 27–74% of the C_B charge. Mag-

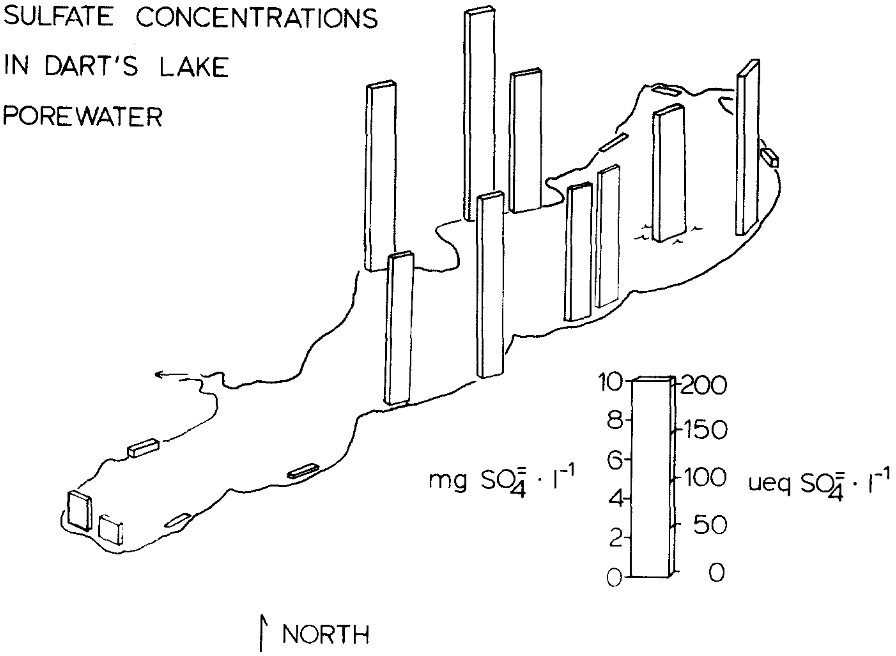

Fig. 3. Sulfate concentrations in Dart's Lake porewaters. Concentrations depicted represent mean values over the study period.

nesium and sodium concentrations were of secondary importance as a percentage of C_B. The percentage contribution of each base cation varied among sites with sodium being the dominant cation at one site. Potassium contributed the lowest charge to C_B at all but one site.

Effects of oxidizing/reducing conditions on patterns of strong acid anions and ammonium

Sulfate was the dominant strong acid anion at half the sites monitored. High porewater concentrations of SO_4^{2-} are consistent with the atmospheric inputs of SO_4^{2-} to the area and are similar to conditions in the lake (Fig. 3). The intersite variation suggests that SO_4^{2-} can be influenced by biogeochemical processes occurring within the sediments or at some location prior to groundwater emerging to the sediments. It was apparent from measured SO_4^{2-} concentrations and from supporting chemistry (NO_3^-, NH_4^+, Fe) that reducing conditions influenced porewater chemistry at sites exhibiting low SO_4^{2-} concentration. At eight of the sixteen sites, mean (over the period of study) concentrations of SO_4^{2-} were below 40 ueq l^{-1} with six sites below 10 ueq l^{-1}. At the remaining sites, SO_4^{2-} concentrations were approximately equal to or greater than the mean annual lake concentration (138 ueq l^{-1}; Schafran & Driscoll 1987b). We use the dichotomy of SO_4^{2-} concentrations henceforth to classify these sites as either "reducing" or

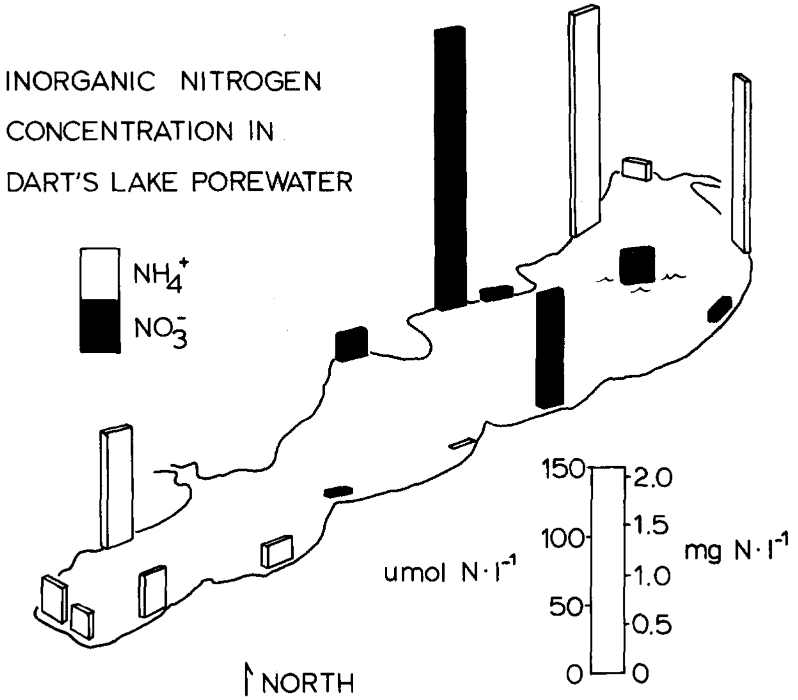

Fig. 4. Concentrations on NO_3^- and NH_4^+ in Dart's Lake porewaters for the 25 August 1983 sampling date.

"oxic" sites. This designation is applicable for the period of study but may not indicate the oxygen status for other periods of the year or over longer periods of time.

Nitrate concentrations at the reducing sites were generally low ($< 2\,\mathrm{ueq\,l^{-1}}$) or below the analytical limit of detection (Fig. 4). These conditions reflect the sediment microbial use of NO_3^-, in the absence of O_2, as an electron acceptor or low NO_3^- inputs to porewaters. Nitrate concentrations in oxic porewaters were generally higher and showed more temporal variability (not shown). For a number of oxic sites, elevated NO_3^- concentrations observed in May (e.g. sites S11, S10, N6 = 48, 28, 34 ueq $\mathrm{l^{-1}}$, respectively) were substantially reduced in June (1, 3, 15 ueq $\mathrm{l^{-1}}$). Consequently, low sediment porewater concentrations of NO_3^- evident during the biologically active summer period are not solely associated with reducing conditions.

Ammonium was measured for only one sampling date (25 August, 1983) during the study (Fig. 4). For this date, NH_4^+ was generally below detection at oxic sites. Ammonium was readily detected at reducing sites although the concentrations varied substantially. Nitrate was not evident at any of the sites where NH_4^+ was present however the absence of NO_3^- was not indicative of the presence of NH_4^+. At one oxic site neither NO_3^- or NH_4^+ were detectable. These results manifest that total dissolved inorganic nitrogen concentrations vary considerably in the near-shore porewaters of Dart's Lake.

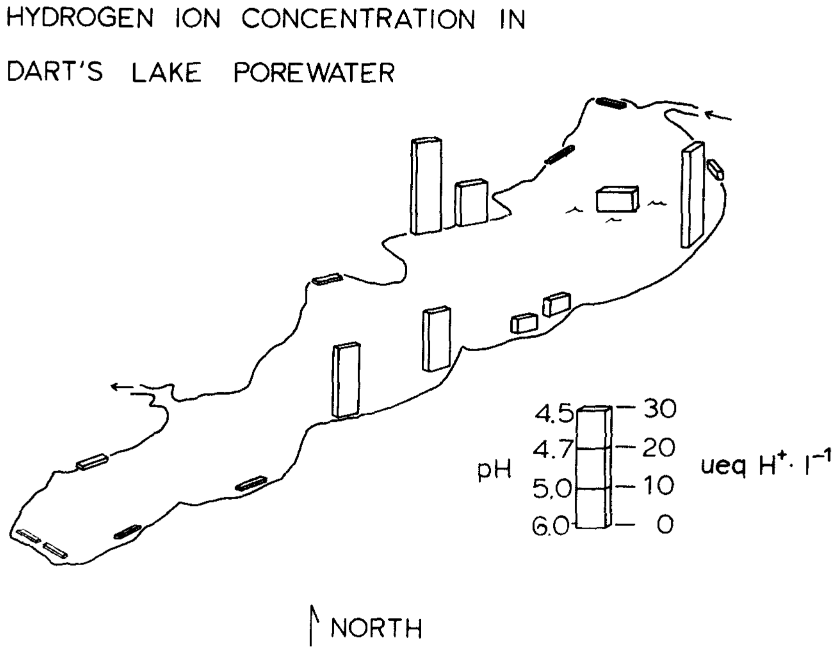

Fig. 5. Hydrogen ion concentrations in Dart's Lake porewaters. Concentrations depicted represent mean values over the study period.

Within the lake water column, NO_3^- is the dominant form of inorganic nitrogen (excluding N_2) and is seasonally influenced with elevated concentrations in the winter and spring and lower concentrations in the summer (range 13–43 ueq l^{-1}; Driscoll et al. 1987). Ammonium concentrations within the lake are much lower in comparison and generally follow the same temporal variation as NO_3^- (range < 1–6 ueq l^{-1}).

Spatial variation of hydrogen ion and aluminum

Hydrogen ion concentrations varied by approximately 2 orders of magnitude within the near-shore porewaters and represent water that was considerably more and less acidic than the lake water (Fig. 5). Acidic porewaters ($pH < 5.5$) were confined to oxic sites (7 of the 9 oxic sites) while pH values > 5.5 were observed at all reducing sites. Elevated labile monomeric Al (Al_l) concentrations were observed at sites of elevated H^+ concentrations and reflect the pH dependent solubility of Al (Fig. 6). Due to the circumneutral pH values at reducing sites, Al_l concentrations were very low in these porewaters (< 2 umol l^{-1}). The Al_l concentrations were elevated at five highly acidic sites relative to lakewater concentrations (range = 14–75 umol l^{-1}). This occurrence implies that the sediment porewaters were active sources of Al to the lake under either groundwater inflow (advective transport of Al) or no flow (diffusive transport of Al) conditions at these sites. If seepage from the lake occurred at any of these sites

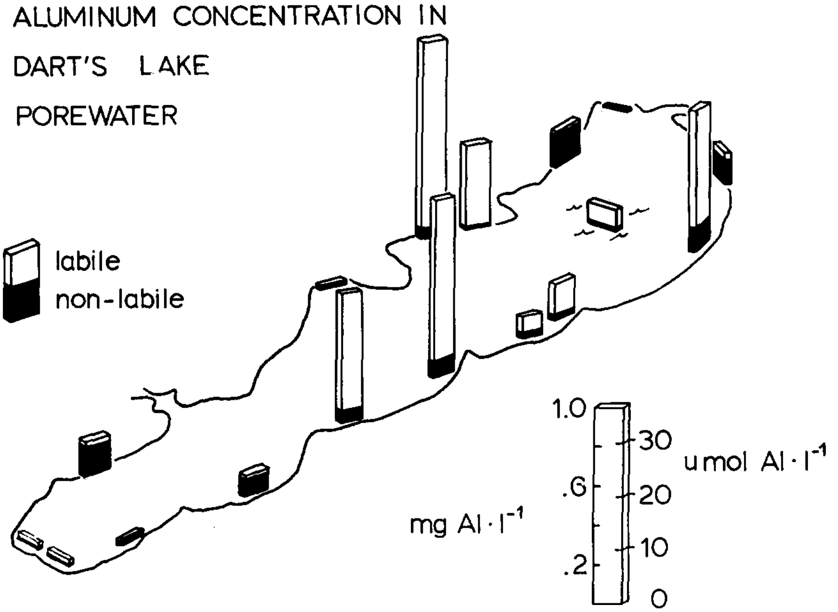

Fig. 6. Dissolved aluminum concentrations in Dart's Lake porewaters. Concentrations depicted represent mean values over the study period.

then input of porewater elevated in Al to the lake would be unlikely. From limited analysis of non labile monomeric Al it was evident that concentrations of this fraction were generally low ($< 5\,\mathrm{umol\,l^{-1}}$) and comprised a significant fraction of dissolved porewater Al only at sites having circumneutral pH values.

Discussion

Acid/base chemistry of porewaters

Considerable variability in water chemistry was observed among porewater solutions implying that the porewaters were under the influence of substantially different biogeochemical processes (Fig. 7). As a consequence, the concentration of H^+ was highly variable. For all sites the variation of C_B was the most significantly correlated parameter to variations in alkalinity. When reducing and oxic sediment porewater composition of C_B and alkalinity were analyzed independently by linear regression analysis, significantly different intercepts were observed but not significantly different slopes (reducing sites $ALK = 0.97(C_B) + 40$, $r^2 = 0.77$, $n = 31$; oxic sites $ALK = 0.88(C_B) - 160$, $r^2 = 0.79$, $n = 49$; C_B and ALK in $\mathrm{ueq\,l^{-1}}$). At a given C_B concentration it is apparent that the alkalinity of a reducing site porewater would be substantially greater ($\approx 200\,\mathrm{ueq\,l^{-1}}$) than an oxidizing site. This variation is largely a result

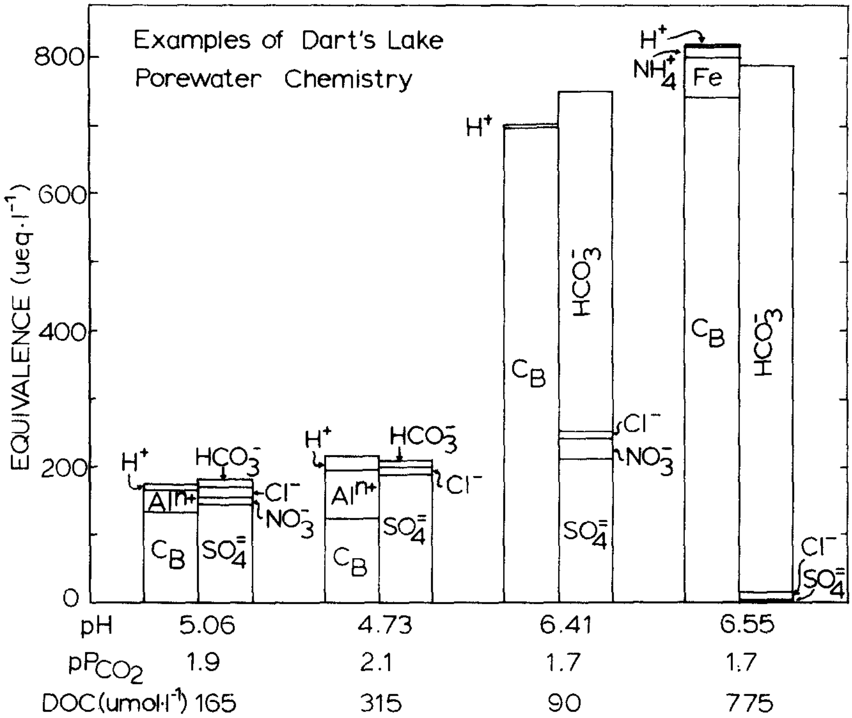

Fig. 7. Examples of the porewater chemistry in near-shore regions of Dart's Lake. Samples represented are (left to right) N3 (10/7/83), S3, N6, and S4 (9/23/83).

of the elevated concentrations of SO_4^{2-} and NO_3^- (188 ± 53 ueq l^{-1} SO_4^{2-}, 34 ± 45 ueq l^{-1} NO_3^-; mean ± s.d.) in oxic waters when compared with the very low concentrations of SO_4^{2-} and NO_3^- under reducing conditions (10 ± 14 ueq l^{-1} SO_4^{2-}, 0.4 ± 1.0 ueq l^{-1} NO_3^-; mean ± s.d.).

Under oxic conditions, strong acid anions were elevated and H^+ neutralized by the solubilization of C_B and Al. Under highly acidic conditions Al comprised a significant portion of the cationic equivalence. At acidic porewater sites the capacity for base cation mobilization was either substantially lower than other nonacidic sites or the reaction time between the porewater solutions and minerals was shorter. Since Al is a protolytic, cation, its release from soil/sediment results in a temporary increase in alkalinity. However, if porewaters are neutralized, aqueous Al will hydrolyze consuming an equivalent amount of alkalinity. Consequently, inflow of acidic porewaters containing elevated Al concentrations to the lake will consume lakewater alkalinity. In addition, Al is toxic to aquatic organisms (particularly in a hydrolyzed form) and the elevated concentrations in the porewaters could negatively impact aquatic organisms in the vicinity of these sites. Fish spawn in regions of high groundwater flow (e.g. lake trout, brook trout) and young life history stages could particularly be affected by these conditions.

Microbial reduction of strong acid anions (SO_4^{2-}, NO_3^-) which has been observed in the epilimnetic sediments and evidenced in hypolimnetic waters of Dart's Lake (Rudd et al. 1986a; Schafran & Driscoll 1987a) appears also to occur in certain regions of the near-shore sediments. Nearly complete removal of SO_4^{2-} and NO_3^- likely contributes in excess of 140 ueq l^{-1} alkalinity at reducing sites (Fig. 7); the amount of alkalinity that may be generated by SO_4^{2-} and NO_3^- removal in these sediments is estimated by the difference between the sum of SO_4^- and NO_3^- concentrations in oxic and reducing sediments. At reducing sites concentrations of C_B, Fe, and NH_4^+ are often elevated such that both the removal of strong acid anions and the mobilization of these cations contribute to the production of substantial amounts of alkalinity. The generation of alkalinity that may be directly attributable to reducing conditions appears to be approximately 200 ueq l^{-1}. This value represents the difference in alkalinity at a C_B concentration of zero for the base cation-alkalinity regression equations for the reducing and nonreducing sites. The mobilization of both Fe and NH_4^+ represent sources of alkalinity in sediment porewaters but probably contribute little to lakewater alkalinity since oxidation of Fe in oxic regions and biological assimilation/oxidation of NH_4^+ would offset alkalinity production from these reactions.

Slow exchange of sediment porewater with the lake could be responsible for limiting O_2 fluxes into the sediment causing sediment conditions to exist. Porewaters under reducing conditions exhibited higher CO_2 concentrations which suggests a slow release to the lake. However, elevated CO_2 at these sites could also be due to enhanced biological activity when compared to oxic sites. Variations in sediment organic matter content could potentially be responsible for variations in sediment microbial activity. However, a comparison of sediment organic content of sediment cores collected at sites of oxic and reducing conditions revealed no statistically significant difference (paired-sample t-test, $\alpha = 0.10$) between these two groupings (mean sediment organic matter concentration for all sediment samples = 4.4%, s.d. = 10.6%; Schafran 1988).

Groundwater influence on porewater chemistry

The influx of groundwater from the terrestrial system may have a significant impact on the chemistry of near-shore porewaters. Where a lake and the surrounding groundwater system are hydraulically linked, such that a hydraulic gradient in the direction of the lake exists, groundwater will flow to the lake with the highest inputs near the shoreline (McBride and Pfannkuch, 1975). The chemistry of this water which is influenced by terrestrial processes could significantly affect the chemistry of near-shore porewaters particularly where the rate of seepage is high.

The influence of groundwater flow on near-shore porewater chemistry is suggested when the seepage flux rates and the chemistry of the near-shore sites are examined. Sites of reducing porewaters exhibited low seepage rates while porewaters exhibiting oxic conditions had higher seepage rates in comparison (Table 1). Although the flux rates and porewater chemistry were collected at

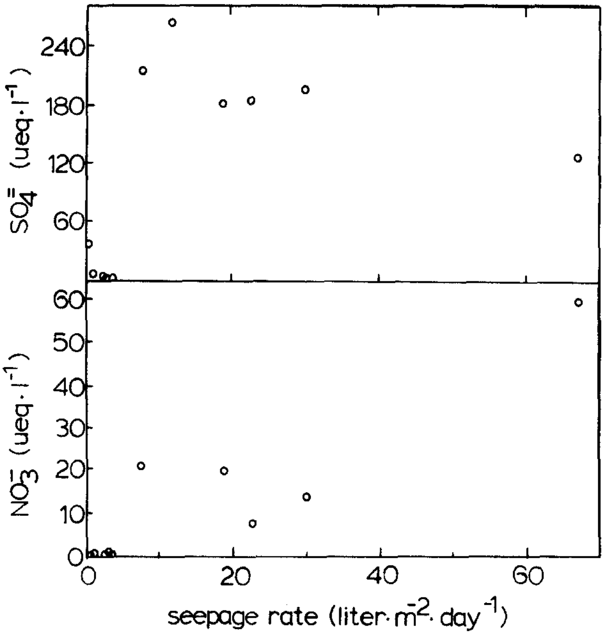

Fig. 8. Scatter diagram of (a) mean SO_4^{2-} concentrations and (b) NO_3^- concentrations versus mean seepage velocities from Table 1.

different times, it is likely that the relative flux among sites does not change drastically over the course of a year (i.e. sites of high flow are always higher than low flow sites even though temporal variation in flow occurs at all sites; Schafran 1988). This assumption is based on the fact that all sites experience the same hydraulic head (lake surface) in the zone of discharge and that the height of the groundwater table above each site is likely to fluctuate over an annual period in generally the same pattern (Chen et al. 1984) due to similar precipitation inputs.

If groundwater flow is a significant factor controlling the oxidizing/reducing (redox) conditions in the sediment, then concentrations of redox-sensitive solutes (SO_4^{2-}, NO_3^-) should exhibit a pattern consistent with this relationship. Sulfate and NO_3^- concentrations in near-shore porewaters were influenced by the groundwater flux occurring at each site. Sites of low groundwater flux were sites of low NO_3^- and SO_4^{2-} concentrations while elevated concentrations appear to be associated with higher flows (Fig. 8). Similarly, Fe and NH_4^+ concentrations reflected the same apparent influence of the groundwater seepage rate (not shown).

The relationship between the apparent porewater redox conditions and the groundwater flux is likely the result of the associated flux of O_2 with groundwater. In regions of high groundwater input to the sediments, the flux of O_2 probably exceeds the sediment microbial demand and thus the porewaters remain oxic. When groundwater flow is low the associated flux of O_2 would be low and inadequate for sediment microbial requirements. Under conditions of O_2 depletion, sediment microbes are likely to use alternate electron acceptors (NO_3^-, SO_4^{2-}, Fe, Mn) for respiration. It is not known whether reducing conditions existed at shallower sediment depths (i.e. closer to the sediment-water interface) at these oxic sites since microbial activity closer to the sediment water interface may have completely removed all O_2 before groundwater reached the lake. If microbial activity consumed the available O_2 within this depth interval then conditions for alkalinity production by NO_3^- and SO_4^{2-} would have existed and groundwater entering the lakes at these sites could have been sources of alkalinity to the lake. However, this would not be a long-term/permanent influx of alkalinity as sulfate sequestered in the sediments could presumably reoxidize during less biologically active periods of the year (when oxygen would again be present in the porewater solutions) causing acidification of the porewater solution. During subsequent monitoring (October 1984–September 1986) at one of the oxic sites (S3), oxic conditions were observed up to the shallowest depth sampled (10 cm below the sediment-water interface; Schafran 1988).

Sulfate concentrations in oxic porewaters of Dart's Lake showed considerable spatial variation compared to the relatively constant concentrations that occur among surface waters of the region (Driscoll et al. 1987). Sulfate concentrations in all oxic porewaters were generally equal to or higher than within lake concentrations. The variation of SO_4^{2-} concentrations among oxic porewaters suggests that abiotic or biotic reactions involving SO_4^{2-} occur within the terrestrial system or deeper within the sediments. Within terrestrial systems microbial activity can significantly affect the sulfate content of water draining through soils. Microbial decomposition of organic sulfur followed by oxidation to sulfate readily occurs in the forest floor (Alexander 1983) resulting in increased sulfate concentrations of water passing through this layer (Cole & Johnson 1977). These elevated concentrations are often not apparent in waters draining through thicker till as adsorption within lower mineral soils can remove sulfate from solution (Fuller et al. 1986). Consequently, waters draining through thicker overburden/soils could exhibit lower sulfate concentrations than waters originating and passing through predominately thin organic soil horizons.

It is possible that during the study period SO_4^{2-} was mobilized from the oxic sediments by oxidation of reduced sulfur species previously sequestered in the sediment (under previously reducing conditions) and was partly responsible for the elevated and variable SO_4^{2-} concentrations observed. Sulfur oxidation events have been previously reported in the sediments of acidified lakes (Rudd et al. 1986a; Sweerts et al. 1986; Schiff & Anderson 1986). We believe, however, that terrestrial influences on porewater SO_4^{2-} were probably responsible for the elevated and spatially variable concentrations given the sustained period of time (>4 months) over which they were observed. In addition, this study occurred during the most biologically active period of the year in which, if seasonal variations in redox status occur, reducing conditions should have predominated. Thus, it is probable that these oxic sites remain oxic year round and the SO_4^{2-} observed in these porewaters is due to transport through the terrestrial system.

The spatial variability of the total inorganic nitrogen content (NO_3^- + NH_4^+) concentrations in the porewaters was considerable (Fig. 4). Mechanisms controlling the mobilization/immobilization of N are likely to be predominantly biological in nature. The nutritional requirements of both terrestrial vegetation within the adjacent watershed and sediment microbes for N may influence the chemistry of near-shore porewaters. Terrestrial vegetation undoubtedly have a marked effect on N concentrations in near-shore lake porewaters for sites which exhibit higher rates of groundwater seepage (i.e. where NO_3^- predominates). It would be expected that during periods of elevated terrestrial biological activity (summer), terrestrial N requirements would reduce the NO_3^- transported to near-shore porewaters while during nonbiologically active periods, NO_3^- would be more readily transported from the terrestrial system to the porewaters. This assumption would be consistent with the seasonal variation in the transport and loss of NO_3^- that is generally observed within soil solutions and drainage waters of northern temperate forested systems (Likens et al. 1977; Foster et al. 1989). This seasonal trend is similarly observed within Dart's Lake (Driscoll & Schafran 1984) and within surface waters of the surrounding region (Driscoll et al. 1987). For all oxic porewaters that were sampled in May, NO_3^- concentrations had decreased by over 75% by mid July. This observation suggests that for sites of high groundwater input, terrestrial biological activity may be the most important factor controlling seasonal variations in inorganic NO_3^- concentration in porewaters.

Near-shore porewaters as lakewater alkalinity sources and sinks

In many recent studies, microbial reactions occurring in lake sediments have been identified as sources of alkalinity to overlying acidic lake waters (Kelly et al. 1982; Carignan 1985; Cook et al. 1986; Rudd et al. 1986a; Schindler et al. 1986; Baker et al. 1986). These studies have generally been conducted in sediments of deeper regions of lakes (than conducted in this study) where diffusion of alkalinity from the sediment porewaters serves as an internal alkalinity source for the lake. It appears that in most chronically acidic lakes that sediment concentrations of base cations are low and consequently the mobilization of base cations generally contributes little to porewater and subsequent lakewater alkalinity (Rudd et al. 1986a). Sediments within Dart's Lake observed at 2 and 14 meter water depth exhibit high rates of SO_4^{2-} and NO_3^- reduction which contribute to alkalinity in the overlying lake water while release of C_B appears to be minimal (Rudd et al. 1986a; Schafran & Driscoll 1987a).

For near-shore porewaters exhibiting reducing conditions, mobilization of C_B was generally a larger component of the total alkalinity production than either SO_4^{2-} or NO_3^- reduction and the converse of patterns evident in deeper water reducing sediments. Because of the higher porewater C_B concentrations, these near-shore reducing sites should supply alkalinity at a higher areal rate to the lake than deep water sediments. Additionally, advective movement in the near-shore regions should enhance porewater transport of alkalinity to the lake relative to the diffusion-dominated flux occurring from deep water sediments. However, the areal predominance of deeper water (organic) sediments relative to the sandy near-shore sediments in the lake is likely to dictate that a greater flux of alkalinity (generated from SO_4^{2-} and NO_3^- reduction) will occur from deeper water sediments than the near-shore reducing areas. A mass balance previously conducted on the lake (Schafran & Driscoll 1987a) supports this contention as decreases in SO_4^{2-} and NO_3^- between the inlet and outlet of the lake were observed while base cations were relatively conservative in the lake.

Due to the study sampling design, changes in porewater chemistry may have occurred between the sediment depths monitored and the sediment-water interface, and not been observed in our results. Microbial activity near the sediment-water interface may have consumed available O_2 resulting in the establishment of vertically narrow anoxic zones near the sediment-water interface. Within these zones microbial reduction of NO_3^- and SO_4^{2-} could have produced alkalinity resulting in groundwater inputs to the lake having positive alkalinity. Additionally, base cations may have been mobilized from the shallow sediments resulting in alkalinity generation in the shallow porewaters.

It is unlikely that either of these processes would result in substantial alkalinity generation and flux to Dart's Lake. In laboratory simulations of groundwater fluxes through Dart's Lake near-shore sediments using intact sediment cores (20 cm depth), little capacity to neutralize acidic groundwater inputs through base cation mobilization was observed (Schafran, unpublished data). Although alkalinity production by NO_3^- and SO_4^{2-} reduction could generate (assuming complete removal) $> 100\,\mu\mathrm{eq}\,\mathrm{l}^{-1}$ alkalinity (Fig. 7), the majority of this production would be due to sulfate reduction. The alkalinity produced by SO_4^{2-} reduction would be permanent only if the reduced S remained in the sediment. One condition for reduced S to remain in this shallow sediment region, would be for redox conditions to remain perpetually anoxic/reducing at these shallow depths. Within Dart's Lake, reducing conditions in the shallow sediments are unlikely to occur for long periods of time as O_2 in groundwater would likely be transported through the sediment and into the lake during periods of reduced biological activity (October–May). The reintroduction of O_2 to these sediments could reoxidize the reduced S, consuming alkalinity resulting in no net alkalinity generation within the porewaters.

The form of reduced sulfur formed in the sediments largely will dictate whether sulfur would be remobilized and alkalinity consumed. If reduced sulfur is retained as an iron sulfide fraction, this fraction would be susceptible to significant reoxidation and concomitant alkalinity consumption under oxic conditions. Sulfur retained as organic sulfur (particularly carbon bonded sulfur) is less likely to reoxidize under oxic conditions and hence could accumulate within the sediment resulting in net alkalinity generation to the porewaters and lake. Within Dart's Lake, sulfur analysis of cores retrieved from epilimnetic sediments (water depth = 2.5 M) showed that the major end product of SO_4^{2-} reduction was organic sulfur (> 90%; Rudd et al. 1986b); the sulfur fraction in the near-shore sediments under groundwater influence is unknown. Thus, there would appear to be some potential for production of permanent alkalinity in shallow sediments that cycle between oxic and reducing conditions. It is probable that given the relatively short time period over which SO_4^{2-} reduction might occur (if it occurs) at these shallow sediment depths, that groundwaters observed as being acidic in this study would constitute acidic (alkalinity consuming) inputs to the lake for the majority of the year.

The removal of NO_3^- by microbial reduction is a permanent source of alkalinity and may have contributed to porewater alkalinity (at shallower sediment depths than sampled) and lake alkalinity. However, this alkalinity contribution would be limited to the short time period during which these narrow anoxic zones might establish. This occurrence would be a seasonal source of alkalinity and during non biologically active periods would not contribute to porewater alkalinity. Therefore, the acidic porewaters under the influence of groundwater movement observed in this study can be accurately viewed as a sink for lake water alkalinity.

Near-shore acidic ($pH < 5.5$) porewaters appear to coincide with areas of elevated groundwater flow to the lake. Acidic conditions probably exist at these sites due to a short hydraulic retention time for w ater passing through the watershed which limits the extent of neutralization by terrestrial biogeochemical processes. If the random survey conducted here is representative of the near-shore regions of the lake as a whole, then groundwater inputs are a source of acidity to the lake (i.e. consume lake water alkalinity). This observation is in contrast with many modeling studies where groundwater inputs have been characterized as sources of alkalinity to lakes (Anderson & Bowser 1986; Lin & Schnoor 1986; Baker & Brezonik 1988; Eshleman & Hemond 1988). In many lake-groundwater systems this is likely an accurate depiction (Kenoyer & Anderson 1989), however, for Adirondack region lakes this may not be representative.

The rapid transport of precipitation through the terrestrial system is likely responsible for the acidic groundwater inputs to Dart's Lake. Other lake-watersheds within the Adirondack region similarly exhibit quick lateral transport of groundwater through shallow soils (Chen et al. 1984; Staubitz & Zariello 1989) and probably have similar acidic groundwater inputs. Acidic groundwater containing elevated concentrations of Al has also been reported in Europe (Hultberg & Johansson 1981). The influence of acidic groundwater inputs is not solely linked to lakes as Yuretich et al. (1989) have observed stream acidification due to spatially variable acidic groundwater inputs.

It would be imprudent at present, due to the limited data, to estimate the potential effect of groundwater inputs and diffusion of alkalinity from near-shore sediments on lake water chemistry. In fact, the spatial variability present at Dart's Lake suggests that determining groundwater inputs of aqueous solutes to lakes is difficult even when groundwater inputs and chemistry are measured directly.

This work serves to indicate that near-shore sediment porewaters can not be viewed solely as a source of alkalinity to the lake. It remains to be examined to what distance acidic porewaters extend from the lake shoreline and what proportion of lake sediment porewaters are acidic; a subsequent investigation at one site has indicated that acidic porewaters ($pH < 5.5$) existed at a distance of greater than 5 m from the shoreline (Schafran 1988). Because there have been few studies of biogeochemical transformations in near-shore regions of acidic lakes, the extent of this condition within acid-sensitive regions is unknown. Further investigation is needed to determine the extent of acidification in shallow water lake sediments and the effects that this condition has on aquatic flora and fauna in the near-shore region of lakes.

Conclusions

The near-shore sediment porewaters of Dart's Lake were substantially more variable than observations of sediment porewaters in deeper parts of the lake. Inputs of groundwater appear to be responsible for much of this variability particularly with regards to porewater redox conditions. Acidic porewater solutions elevated in Al have not previously been observed in deeper water sediment porewaters of the lake but were observed in some of the near-shore sites. Movement of elevated concentrations of H^+ and Al into the lake from these sediments appears likely under the conditions observed in this study and would result in lakewater alkalinity consumption. The occurrence of acidic, Al-rich groundwater inputs may influence fish spawning, the distribution of near-shore sediment dwelling and epipelic organisms, as well as the distribution of aquatic vegetation.

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