

Characterization of lake water and ground water movement in the littoral zone of Williams Lake, a closed-basin lake in north central Minnesota

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Abstract:

Williams Lake, Minnesota is a closed-basin lake that is a flow-through system with respect to ground water. Ground-water input represents half of the annual water input and most of the chemical input to the lake. Chemical budgets indicate that the lake is a sink for calcium, yet surficial sediments contain little calcium carbonate. Sediment pore-water samplers (peepers) were used to characterize solute fluxes at the lake-water-ground-water interface in the littoral zone and resolve the apparent disparity between the chemical budget and sediment data. Pore-water depth profiles of the stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were non-linear where ground water seeped into the lake, with a sharp transition from lake-water values to ground-water values in the top 10 cm of sediment. These data indicate that advective inflow to the lake is the primary mechanism for solute flux from ground water. Linear interstitial velocities determined from $\delta^2\text{H}$ profiles (316 to 528 cm/yr) were consistent with velocities determined independently from water budget data and sediment porosity (366 cm/yr). Stable isotope profiles were generally linear where water flowed out of the lake into ground water. However, calcium profiles were not linear in the same area and varied in response to input of calcium carbonate from the littoral zone and subsequent dissolution. The comparison of pore-water calcium profiles to pore-water stable isotope profiles indicate calcium is not conservative. Based on the previous understanding that 40–50 % of the calcium in Williams Lake is retained, the pore-water profiles indicate aquatic plants in the littoral zone are recycling the retained portion of calcium. The difference between the pore-water depth profiles of calcium and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ demonstrate the importance of using stable isotopes to evaluate flow direction and source through the lake-water-ground-water interface and evaluate mechanisms controlling the chemical balance of lakes. Published in 2003 by John Wiley & Sons, Ltd.

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INTRODUCTION

A variety of hydrological tools, including seepage meters (Lee, 1977; Fellows and Brezonik, 1980; Boyle, 1994), portable well points (Lee and Cherry, 1978; Winter *et al.*, 1988), and emplacement of well networks (Schindler *et al.*, 1976; Shaw *et al.*, 1990; LaBaugh *et al.*, 1997) commonly are used to quantify the connection between lakes and ground water. However, owing to the complexity of lake-water-ground-water interaction, complementary tools have been used to refine and corroborate hydrological estimates of the magnitude of flow, including use of chemical tracers (Lee *et al.*, 1980), stable isotopes of water (Dincer, 1968; Krabbenhoft *et al.*, 1990, 1994; LaBaugh *et al.*, 1997), chemical mass balances (Stauffer, 1985; Krabbenhoft and Webster,

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1995), and interstitial pore-water gradients of major ions in the lake bed (Cornett *et al.*, 1989; Mortimer *et al.*, 1999).

Although a variety of hydrological, chemical and isotopic techniques are available to estimate flow between ground water and lakes, rarely are they used in combination, particularly in settings where an extensive well network exists for hydrological context (LaBaugh *et al.*, 1997). Studies in one of the few places where such variety in techniques have been used; Perch Lake, Ontario (Frape and Patterson, 1981; Lee *et al.*, 1980), demonstrated the importance of using the distribution of an isotope, tritium, to interpret chemical profiles of sediment pore water and to understand the processes affecting chemical characteristics of ground water as it flows through the lake bed. Cornett *et al.* (1989) indicated that stable isotope profiles of sediment water might also be useful in calculating the rate of ground-water flow into lakes. Stable isotopes of oxygen ($\delta^{18}\text{O}$) are excellent tracers of water sources because they are constituents of the water molecule itself and they can exhibit large differences with respect to their source (Kendall *et al.*, 1997).

It is useful to know if any chemical changes occur as ground water flows into lakes and lake water flows out into ground water because such chemical changes can affect estimates of ground-water flow derived from interstitial pore-water gradients (Cornett *et al.*, 1989) and confound interpretations of lake chemical budgets based on chemical data from wells alone (Frape and Patterson 1981). Clearly, to assess the impact of ground-water flow, or seepage, to lakes and lake-water flow, or seepage, to the contiguous ground-water system, the physical and chemical properties of these water sources must be understood as they cross the ground-water-lake-water interface.

The Shingobee River headwaters area in Minnesota is another site where the interaction of lakes and ground water have been studied extensively. In this area, a series of lakes have been selected to study how atmospheric, surface and ground water function as an integrated system (Winter, 1997). Williams Lake, a closed-basin lake in the Shingobee River watershed, has been studied for about 22 years using an extensive well network to place the lake in its local and regional ground-water flow system (Winter and Rosenberry, 1997). Ground water represents one-half the annual water input to the lake; the other half is from precipitation (Winter and Rosenberry 1997; LaBaugh *et al.*, 1995, 1997). Hydrological, chemical and stable isotopic information also indicate that the chemical characteristics of Williams Lake are determined primarily by interaction of the lake with ground water. Numerical modelling studies (Siegel and Winter, 1980) indicate that the ground-water flow system interacting with Williams Lake is restricted to the upper part of the surficial aquifer. Owing to the coarse sand substrate, the littoral zone is in direct hydraulic contact with the local ground water system and can be described as a 'hydrological gateway' to and from Williams Lake.

Ground water represents nearly all of the annual input of major chemical constituents to Williams Lake, including calcium (LaBaugh *et al.*, 1995). Calcium precipitates in Williams Lake, primarily mediated by the photosynthetic activity of rooted aquatic plants (McConnaughey *et al.*, 1994). Yet, little calcium carbonate is found buried in modern sediments (Dean and Bradbury, 1997). Thus, the interpretation of chemical mass balances needed to be examined with further focus on movement of water and solutes through the lake bed. To understand the significance of calcium concentrations in sediment pore water, sediment pore-water samplers or peepers (Hesslein, 1976) were used in Williams Lake to determine profiles of major chemical constituents and stable isotopes.

To build on the field and modelling studies, in this study, we focus on the spatial and temporal variation of the stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and selected major chemical constituents in pore-water profiles to characterize the movement of water and solutes across the sediment-water interface. Previous studies of the chemical characteristics of the lake and ground water did not examine interstitial pore-water chemical characteristics as an alternative way to estimate flow nor as a factor influencing the interpretation of lake chemical budgets. Although gradients in ground-water inflow areas have been the focus of studies by others (e.g. Frape and Patterson, 1981; Lee *et al.*, 1980; Cornett *et al.*, 1989; Mortimer *et al.*, 1999), the Williams Lake study also provided an opportunity to present and interpret chemical and stable isotope gradients in lake-water outflow to ground water.

STUDY SITE AND METHODS

Williams Lake is located in north central Minnesota (46°57'N, 94°40'W) (Figure 1). It is underlain by thick, calcareous glacial drift characteristic of ice contact deposits (Siegel and Winter, 1980). The surface area of the lake is 36 ha and it has a maximum depth of 9.8 m. The lake has no channelized surface water inlet or outlet, so the water budget of the lake is controlled by ground-water input, output of lake water to ground water, atmospheric precipitation and evaporation. Water residence time varies from 2.7 to 3.4 years (LaBaugh *et al.*, 1995). Calcium and magnesium are the most abundant cations in the lake, bicarbonate is the most abundant anion, and together these ions represent 95% of the total dissolved ions in the lake. The littoral zone of the lake contains extensive areas of both floating-leafed and submersed aquatic vegetation.

Most of the flow into and out of lakes commonly occurs in the littoral zone (Pfanckuch and Winter, 1984). Thus, to gain a better understanding of water movement in the littoral zone and the significance of calcium concentrations in sediment pore water, sediment pore-water samplers, commonly known as peepers (Hesslein, 1976), were installed at site I and site O in the nearshore littoral zone (Figure 1). These sites were chosen because previous hydrological analyses had indicated these were areas of ground-water inflow and lake-water outflow (Siegel and Winter, 1980) and because of the proximity of these sites to wells from which water had been collected for chemical analysis on a regular basis for more than 10 years. The peepers were constructed from Lucite (the use of trade names is for identification purposes only and does not constitute endorsement by the USGS) blocks 60 cm in length consisting of two rows of 14 cells, each with a volume of 55 ml (Figure 2). Construction and use of these devices were similar to that described by Hesslein (1976). Each peeper was prepared by securing a dialysis membrane to one side, filling each cell with distilled water, and securing a second membrane to the opposite side, sealing the peeper.

The peepers were inserted into the littoral sediments exposing the top two rows of cells to lake water. It is assumed that solute exchange across the membrane occurs over time. Peepers were installed and retrieved in two different seasons during the study, the first in October 1992 and the second in July 1993. The peepers were deployed for at least one month to ensure solute equilibrium between the interstitial pore water and lake water and each peeper cell. Immediately after removal, each cell, containing an equilibrated sample of the sediment interstitial pore water, was sampled by inserting a syringe through the membrane and extracting water for isotopic and chemical analyses.

In addition to collection and analysis of peeper samples, lake water from the middle of Williams Lake and ground water in the vicinity of the lake were collected as part of an effort to understand the relationship of the lake to ground water (LaBaugh *et al.*, 1995). For almost 20 years, lake water has been collected on a monthly basis when the lake is ice-covered and bi-weekly when it is ice-free. Ground water has been collected on a regular basis from observation wells for more than 10 years and detailed chemical analyses have been carried out on more than 300 samples of ground water from these wells. Also, as a follow-up study in May of 1993 and July of 1994, a portable stainless-steel probe (Winter *et al.*, 1988) was used to collect shallow ground water at a 50 cm depth below land or lake sediment surface along 4 m transects perpendicular to the shoreline at areas of ground water inflow and lake flow to ground water.

Oxygen stable isotope ratios were determined using CO₂-H₂O equilibration followed by mass spectroscopy of CO₂ (Coplen, 1988; precision = 0.2‰). Hydrogen stable isotope ratio values were determined using a hydrogen equilibration technique (Coplen *et al.*, 1991; precision = 2‰). Stable isotope ratios are expressed as per mil differences relative to Vienna Standard Mean Ocean Water (VSMOW). Calcium concentrations were determined using inductively coupled plasma spectroscopy as described in Garbarino and Taylor (1979).

RESULTS AND DISCUSSION

Vertical profiles of stable isotopes and chemical constituents in the littoral sediments of Williams Lake are considerably different on the inflow and outflow sides of the lake. Furthermore, the profiles are substantially different seasonally. At the inflow side of the lake (site I), $\delta^{18}\text{O}$ profiles (Figure 3) and calcium profiles

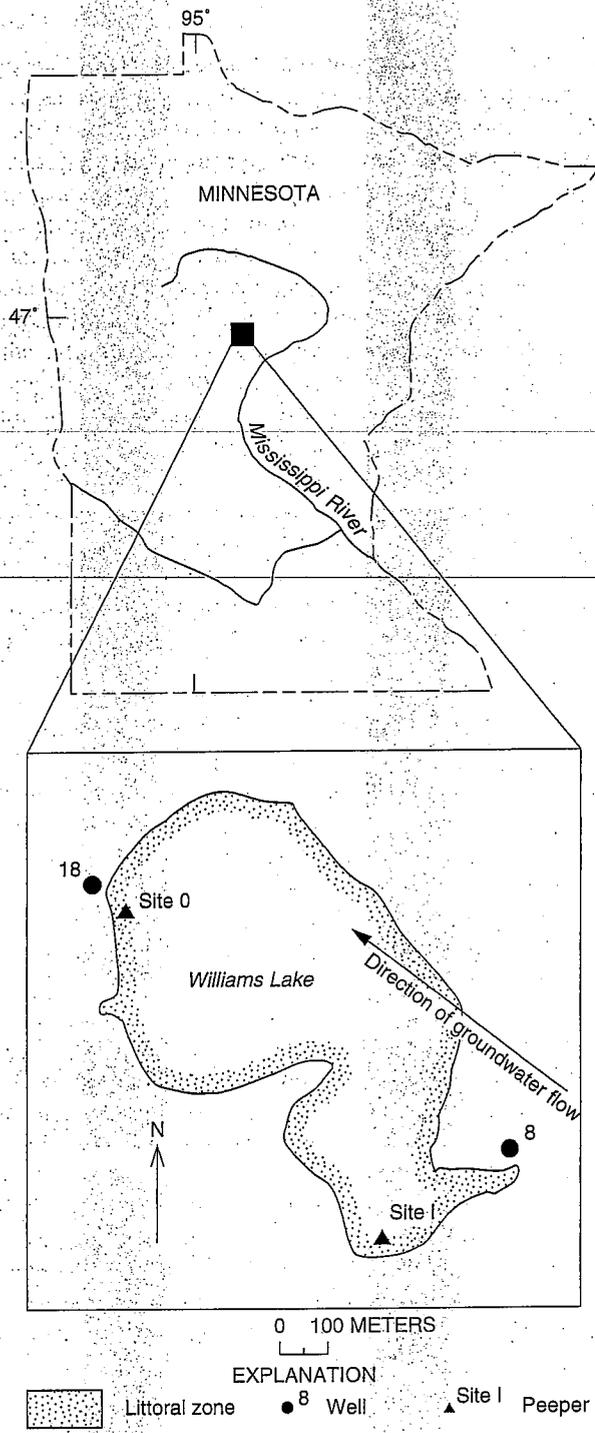


Figure 1. Location of Williams Lake in north-central Minnesota showing the general direction of ground water flow, the estimated area defined as the littoral zone, sampling sites and nearby ground water wells

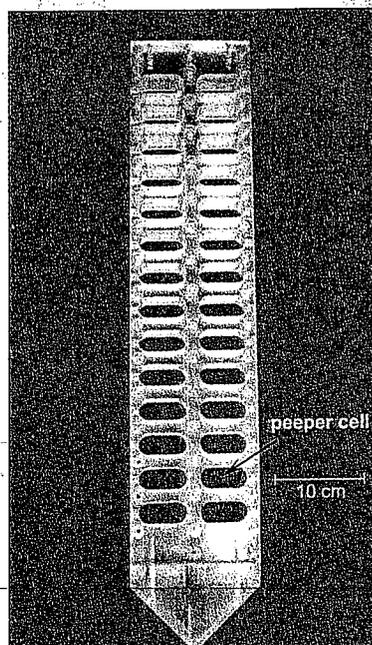


Figure 2. Sediment pore-water sampler commonly known as a peeper (shown here before securing the membrane)

(Figure 4) showed significant variations in concentrations with depth. The $\delta^{18}\text{O}$ profiles at the outflow side (site O) showed much smaller variation with depth. Calcium profiles at site O, however, showed significant variations. Table I provides a statistical summary of the same analytes for the local ground water and Williams Lake (system end members).

Stable isotope profiles

Pore-water profiles for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ indicate that peeper cells located above the sediment–water interface had values similar to those measured in the surface waters of the lake during the time the peepers were in place. At the inflow site, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the upper 10 cm of sediment changed sharply with depth from values similar to lake water to values similar to ground water (Figure 3). At the outflow site, the upper sediment was an area of either little or moderate change in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, none of which at depth approached the values of ground water. Also plotted on Figure 3 are the range of values for Williams Lake, well 8 and well 18 during 1992. Data from well 8 were chosen because they are typical of the ground-water chemistry up gradient of Williams Lake. Data from well 18 are plotted because they are typical of ground water that is influenced by water seeping from the lake to ground water.

Because $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are both components of the water molecule, the profiles of $\delta^2\text{H}$ are nearly identical to those of $\delta^{18}\text{O}$ (Figure 3). Surface-water values for $\delta^2\text{H}$ plot slightly below a plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ generated using precipitation owing to the greater effect of evaporation (Figure 5). This effect can be used to show the mixing between values typical of ground water and that of surface water. Hence the values from the pore waters of the lake lie along a line below that of the local meteoric water line (LMWL), which was determined from water collected from bulk precipitation at the site (Kendall and Coplen, 2000). Figure 5 demonstrates this effect, showing that the pore-water samples from the peepers at site O have undergone a greater degree of evaporation than water from site I. Values from site I lie along the gradient between ground water and lake water, with many values closer to the average value of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in ground water than the values found in lake water, reflecting the input of ground water at site I.

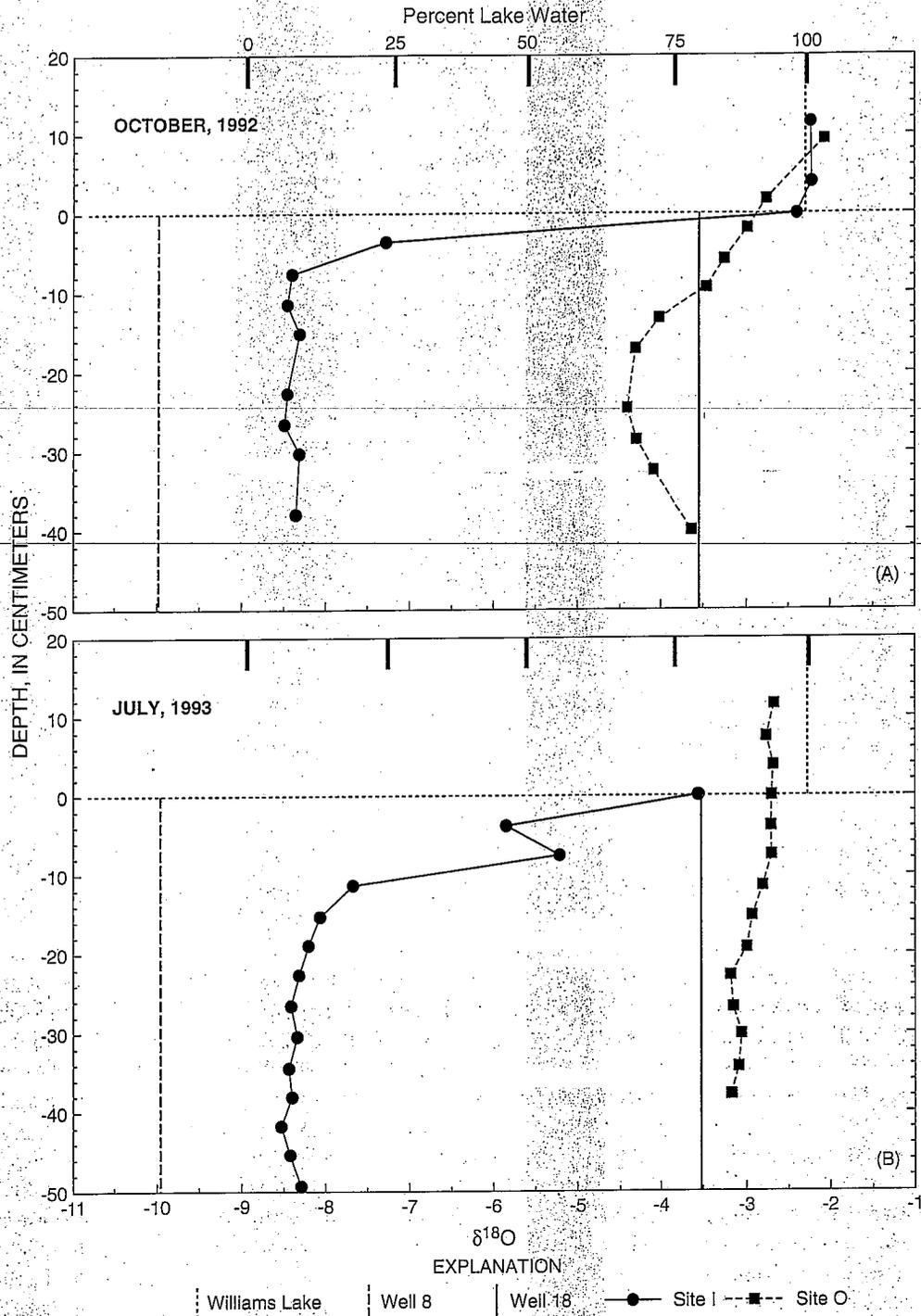


Figure 3. Depth profiles of $\delta^{18}O$ values at site I and site O during (A) October 1992 and (B) July 1993. Also shown are the average lake and ground water values for 1992. Ranges are given in Table I.

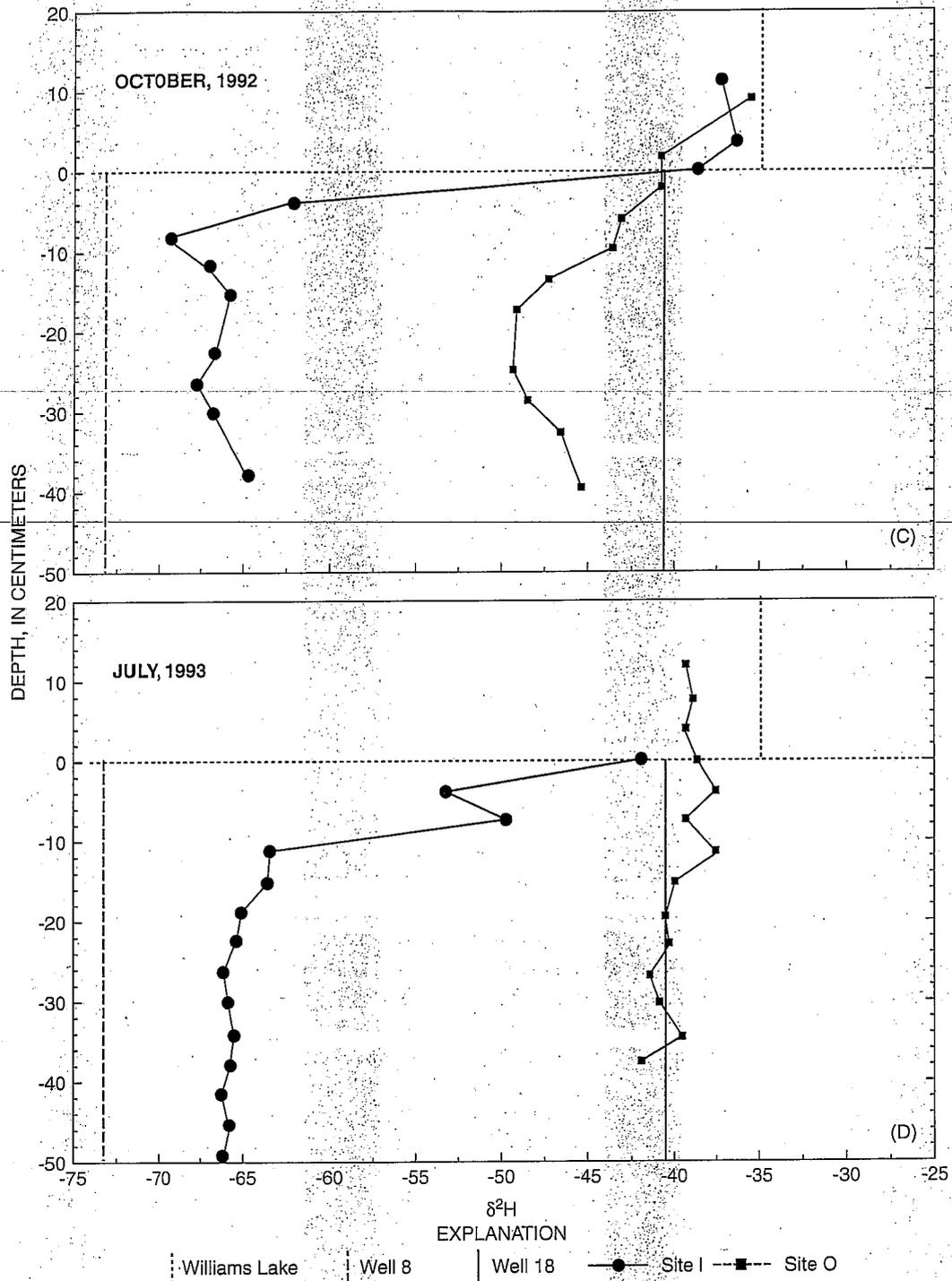


Figure 3. (Continued)

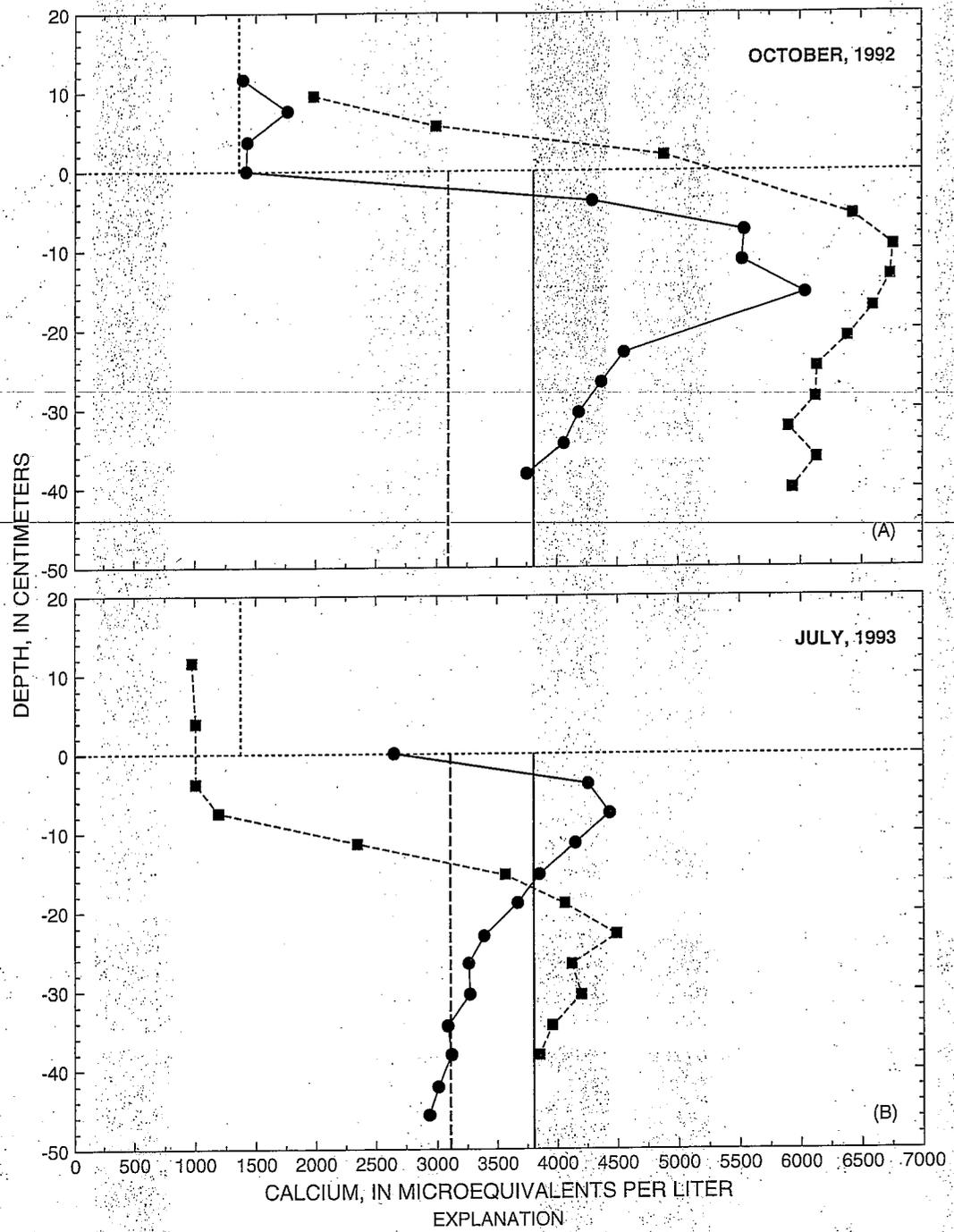


Figure 4. Depth profiles of calcium concentrations at site I and site O during (A) October 1992 and (B) July 1993. Also shown are the average lake and ground water concentrations for 1992. Ranges are given in Table I

Table I. Selected statistics showing the range of values and concentrations for Williams Lake and local ground water during 1992

Variable	Statistic	Well W8	Well W18	Williams Lake
$\delta^{18}\text{O}$ ‰	Mean	-9.98	-3.52	-2.18
	Minimum	-10.10	-3.60	-2.45
	Maximum	-9.90	-3.45	-1.90
	Number	7	7	33
$\delta^2\text{H}$ ‰	Mean	-73.0	-40.5	-35.6
	Minimum	-74.3	-41.2	-38.0
	Maximum	-72.0	-38.5	-33.5
	Number	7	7	33
Calcium $\mu\text{eq/L}$	Mean	3116	3775	1317
	Minimum	3027	3449	1064
	Maximum	3192	3957	1509
	Number	6	6	36

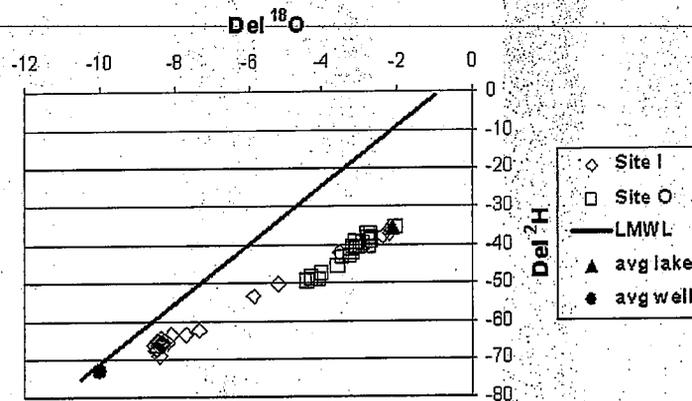


Figure 5. Relation of $\delta^2\text{H}$ to $\delta^{18}\text{O}$ in pore water in sediments of Williams Lake. Also shown are the average lake and well values for 1992. The local meteoric water line is shown for reference.

The gradient of $\delta^{18}\text{O}$ at the inflow site is indicative of advective flow and similar to gradients that result from advective flow observed in the sediments of other inflow lakes (Berner, 1980; Cornett *et al.*, 1989; Mortimer *et al.*, 1999). Measurement of water levels and hydraulic conductivity in wells in the areas of inflow of ground water to the lake between April 1991 and June 1992 indicate that ground water contributed approximately $390\,000\text{ m}^3/\text{year}$, equivalent to a 990 mm rise in lake stage. Isotopic budgets for $\delta^{18}\text{O}$ in the same time period also indicated the lake received considerable water input from ground water (LaBaugh *et al.*, 1997), further corroborating evidence for advective flow based on site I pore-water peeper data.

The gradient of $\delta^{18}\text{O}$ at the outflow site was generally linear with slight to moderate changes in value with depth (Figure 3). The advective-diffusive equations described in Berner (1980) show that uniform concentrations with depth are indicative of a system dominated by diffusive transport and the slope of the profile is related to the degree of diffusivity. However, as noted by Cornett *et al.* (1989), a uniform profile with depth should occur where water is flowing out of the lake through the sediments; hence, at steady state the sediment profile cannot be used to recognize whether diffusive or advective processes are occurring. This profile is consistent with water-table gradients measured in wells in this part of the lake shore (Rosenberry, 1985), indicating it is an area of outflow.

There may be a number of reasons why the October and July profiles for $\delta^{18}\text{O}$ at site O are different; three possibilities are presented here. The first is that the peepers were not placed in exactly the same location each time they were installed. It is possible that the peeper installed in October may have been pushed through a low permeability layer. If this was the case, the water in the low permeability layer may be water that is still in place from an earlier time when lake water that moved into the layer was isotopically heavier, or from an earlier flow reversal from ground water.

The second possibility is that a flow reversal may have taken place during the time the peeper was in place. The process for this possibility would be as follows.

1. Normal lake-water seepage out would cause all of the cells to have a lake-water signature.
2. Following a period of precipitation, focused recharge in the upland adjacent to the lake could cause ground water to flow horizontally into the lake bed in the upper part of the sediments.
3. After the flow reversal dissipates, lake water resumes seeping out of the lake, resulting in a lake-water signature in the uppermost cells in the sediment.

This explanation also would affect the pore-water chemistry by increasing the contact time between the water and the sediments. More than 12 cm of precipitation fell at the site during August and September of 1992. Given the rate of ground-water movement typical for this segment of the lake bed, this freshly recharged water could have reached the location of the peeper during the time it was in place in October of 1992.

The third possibility is evident from data collected at the site using the portable stainless steel probe. Shallow ground water 1 m inland and at the shoreline of the lake in the vicinity of site O during May 1993 had $\delta^{18}\text{O}$ values of -10.78 and -11.48 whereas at 1, 2 and 4 m from the shoreline into the lake shallow ground-water values were -2.49 to -2.53 . In the same area during July 1994, values in shallow ground water were -3.08 at 1 m inland from the shoreline, -2.60 at the shoreline, -2.51 at 2 m and -2.38 at 4 m from shore into the lake. These data are consistent with the fact that site O is an area of lake-water flow to ground water, and the fact that in spring the transition from lake water to ground water may take place along a horizontal distance of a few meters close to the shoreline of the lake. Thus in October of 1992, the mixture of lake water and ground water evident from values in the peeper of -3.0 to -4.5 may simply reflect the fact that the mixing zone between lake water and ground water may have migrated horizontally in response to declining hydraulic gradients on the outflow side of the lake. A similar change along a horizontal gradient was observed in the vicinity of well UM29, which is in an area of flow reversals. Shallow ground water 4 m into the lake from shore near well UM29 during May 1993 had a $\delta^{18}\text{O}$ value of -5.14 , whereas values nearer to the shoreline and 1 m inland ranged from -9.64 to -10.74 . At the same site during July 1993, values were between -2.56 and -3.16 . In contrast, in the vicinity of site I values ranged from -10.68 at 1 m inland to -8.44 at 4 m offshore in May, quite similar to that observed in July when values ranged from -10.73 at 1 m inland to -8.24 at 4 m offshore.

Surface-water and ground-water mixing in the littoral zone

Isotopes of oxygen and hydrogen and selected conservative ions have been shown to be effective tracers for identifying the relative contribution of ground water and lake water to sediment pore water (Frape and Patterson, 1981; Krabbenhoff and Webster, 1995) because these isotopic ratios are not affected by processes occurring in the sediments. To use conservative ions and $\delta^{18}\text{O}$ in this manner, there must be significant differences between water sources (Gat and Gonfiantini, 1981; Kendall *et al.*, 1995).

A mass balance approach utilizing $\delta^{18}\text{O}$ was used to estimate the ground-water and lake-water components of each cell in the peeper using the equation

$$P_{lw} = (C_{pw} - C_{gw}) / (C_{lw} - C_{gw}) / 100 \quad (1)$$

where P_{lw} is the percentage of lake water, C_{pw} is the concentration or value of conservative species, in this case $\delta^{18}O$, in the pore water (peeper cell), C_{gw} is the average concentration of conservative species in a representative ground-water well (well 8) adjacent to Williams Lake, and C_{lw} is the concentration of conservative species in the lake water. This mixing equation was used to estimate the relative contributions of lake water and/or ground water to the interstitial pore water at a known depth in the littoral sediments. Figure 3 shows the relative contributions of lake water and ground water in each peeper cell expressed as percentage lake water. It is clear the peeper cells at site I contain nearly all lake water at the sediment-lake interface and nearly all ground water in the deepest peeper cells. Site O in July indicates lake-water dominance throughout the entire depth profile.

Advection-diffusion model

The use of stable isotope profiles to estimate ground-water flow velocities has been suggested by others (Cornett *et al.*, 1989). Here, the δ^2H profiles of the littoral sediments of Williams Lake were used in an advection-diffusion model to calculate linear interstitial velocity (LIV). This modelling approach has been carried out in other lake studies using tritium and other conservative constituents, such as chloride (Cornett *et al.*, 1989; Mortimer *et al.*, 1999). Use of chloride for this analysis in Williams Lake is not feasible because there is considerable spatial and temporal variability within ground water, probably owing to salt application to roads in the watershed and domestic sources. Furthermore, as a result of having variable sources, the chloride budget was not in agreement with either the hydrological or stable isotope budgets for the lake (LaBaugh *et al.*, 1997).

Typically, one-dimensional advective-diffusion numerical simulation (transport model equations based on analytical solutions of Fick's 2nd Law) are used to estimate ground-water flow velocities (Kolak *et al.*, 1999; Hendry and Wassenger, 1999). This approach requires significant chemical gradients in the pore-water profile. The recent investigation of Mortimer *et al.* (1999) shares similar methods, working scales and site characteristics with those described here. Mortimer *et al.* (1999) utilized an analytical solution of Fick's 2nd Law as proposed by Munk (1966)

$$C_z = \frac{(e^{UzD_s} - 1)}{(e^{UdD_s} - 1)} \times (C_d - C_0) + C_0 \quad (2)$$

where z is the depth from the sediment-water interface, C_z is the pore-water concentration or value of a conservative ion at depth z (in this case, δ^2H), C_0 is the pore-water concentration at the sediment-water boundary, d is the depth at which the ionic strength within the sediment becomes constant (determined from peeper profiles), C_d is the pore water concentration at the point at which the ionic strength becomes constant, U is the linear interstitial velocity (LIV), and D_s is the sediment diffusion coefficient—derived from the equation

$$D_s = \Phi \times D_0 \quad (3)$$

where Φ is the sediment porosity (in this case, 0.27, from Rosenberry (1985)) and D_0 is the diffusion coefficient for H^+ from Li and Gregory (1974).

Because the intention is to estimate the LIV, Equation (2) needs to be solved for U . However, except for a few special cases, it cannot be thus solved in closed form, so Equation (2) was manipulated algebraically to obtain the following recursion relation for U

$$U = (D_s/z) \times \log[(e^{UdD_s} - 1) \times (C_z - C_0)/(C_d - C_0) + 1] \quad (4)$$

The 'log' above is the natural log. Equation (4) contains U on both sides of the equal sign; this therefore can give rise to a sequence U_i ($i = 1, 2, 3, \dots$), where

$$U_{i+1} = (D_s/z) \times \log[(e^{U_i d D_s} - 1) \times (C_z - C_0)/(C_d - C_0) + 1] \quad (5)$$

Either the sequence U_i converges to the true value of U , or it arrives at a degenerate or divergent solution; for practical purposes, however, when $\epsilon U_{i+1} - U_i \epsilon$ becomes small and U is different than zero, Equation (5) has converged. This approach is thus amenable to an iterative approach, needing only a starting or 'seed' value U_0 for the sequence. Erickson (1981), using seepage meters, measured a range of seepage rates for Williams Lake from 4.7 to 243 cm/year. These rates were used as seed values to start the iterative process. At site I during October at a 4 cm depth in the sediment, Equation (4) converged to 316 cm/year. During July, Equation (4) converged to 528 cm/year. At site O during October at a 5 cm depth, the recursion converged to 84 cm/year. There was no $\delta^2\text{H}$ gradient at site O during July.

Another method that can be used to estimate the velocity of water within lake sediments is to divide Darcy fluxes (obtained from the monitoring well network) by porosity (Mortimer *et al.*, 1999). Analysis of lake sediments by Rosenberry (1985) indicated that the porosity of the sediments in the vicinity of site I was 0.27. This resulted in a value of 366 cm/year (99 cm/year/0.27), which compares well with the LIV-determined values (316–528 cm/year).

Water budget analysis for the period April 1991 to June 1992 indicates the water flow from the lake to ground water was approximately 462 cm/year (LaBaugh *et al.*, 1997). It appears the model is underestimating the LIV at site O. Because there is very little or no isotopic gradient at site O, these profiles could not be used to calculate a LIV of water out of the lake and into ground water.

Calcium profiles

Pepper cells in contact with lake water had calcium concentrations similar to concentrations measured in the lake (Figure 4). At or below the lake sediment boundary, concentrations were larger than found in the lake, and similar or greater than concentrations measured in water from wells that represent ground-water inflow to the lake. Concentrations were relatively uniform with depth 25 cm below the lake–sediment boundary in July 1993 but much less so in October 1992. The fact that concentrations between 5 and 25 cm below the lake–sediment boundary at the inflow site were larger than the average concentration in shallow water-table wells in the inflow area was not surprising. Water collected in early August 1991 at two different areas of the ground-water inflow area of the lake using a portable minipiezometer (Winter *et al.*, 1988) indicated that shallow ground water discharging to the lake could vary in calcium concentration from 2400 to 7000 microequivalents per litre.

Unlike the profiles of $\delta^{18}\text{O}$ at the outflow site, calcium concentrations with depth at the outflow site were not relatively uniform. In July 1993, just as at the inflow site, outflow-site calcium concentrations below the lake–sediment boundary increased sharply at depth, and values below 15 cm were similar to values found in ground-water wells. In October 1992, calcium concentrations also increased with depth, but the transition from concentrations similar to lake water to concentrations similar to ground water down gradient of the lake occurred partly above the lake–sediment interface. The relative uniformity with depth of the $\delta^{18}\text{O}$ profiles (Figure 3) and the stable isotope plot (Figure 5) is consistent with the fact that this is a zone of lake discharge to ground water. Yet the calcium profile by itself would suggest this is an area of advective inflow. This discrepancy demonstrates the usefulness of combining stable isotope and major ion data for hydrological interpretation. The potential disparity in interpretation between these data reveals the importance of having an independent conservative tracer such as $\delta^{18}\text{O}$ to aid in the interpretation of chemical profile data from the sediments when analysing flow into or out of a lake. More likely, the profile of calcium at site O reflects the burial and dissolution of calcium carbonate produced in the littoral zone.

Implications for calcium cycling

Knowing the relationship of pore-water gradients to estimates of ground-water inflow to the lake and lake-water outflow to ground water, this information can be used to evaluate other chemical gradients and fluxes through the littoral zone sediments. Williams Lake is a sink for calcium; nearly 40 to 50% of the calcium entering the lake is retained (LaBaugh *et al.*, 1995). Chemical gradients of calcium (Figure 4) suggest the

mechanism for retention is calcium recycling in the aquatic plant system of Williams Lake. Mediated primarily by the photosynthetic activity of rooted aquatic plants, calcium precipitates on the leaves of aquatic plants and sloughs off those leaves in late summer and autumn (McConnaughey *et al.*, 1994). This process of precipitate deposition has been observed around the entire perimeter of the lake. Yet, despite the very visible deposition of this precipitate in autumn, the surficial sediments contain minor amounts (less than 0.8%) of carbonate precipitate (Dean and Bradbury, 1997). Figure 4 provides a possible explanation for the apparent discrepancy between chemical budget and sediment composition data. Calcium concentrations in pore water at depth are generally much greater than concentrations in both lake and ground water. These elevated concentrations suggest processes occur that change calcium from a solid phase, in the form of calcite precipitate, to a dissolved phase.

The absence of significant calcite in the sediments, and presence of elevated calcium concentrations in pore water, may result simply from the seasonal sequence of sediment burial. After the calcite precipitate sloughs off the leaves of aquatic plants, this precipitate is buried under decomposing, senescent plant debris. Decomposition of the plant debris alters the chemical environment of the sediments, thereby causing the dissolution of the precipitate. In response to a lower pH resulting from increased organic acids from decaying aquatic plant matter, calcium returns to solution in the lake and pore waters of the littoral zone. Moreover, other studies have shown that dissolved organic matter (DOM) inhibits calcium precipitation (Hoch *et al.*, 1999), thus offering a possible explanation for the minor amounts of carbonate precipitate in the sediments.

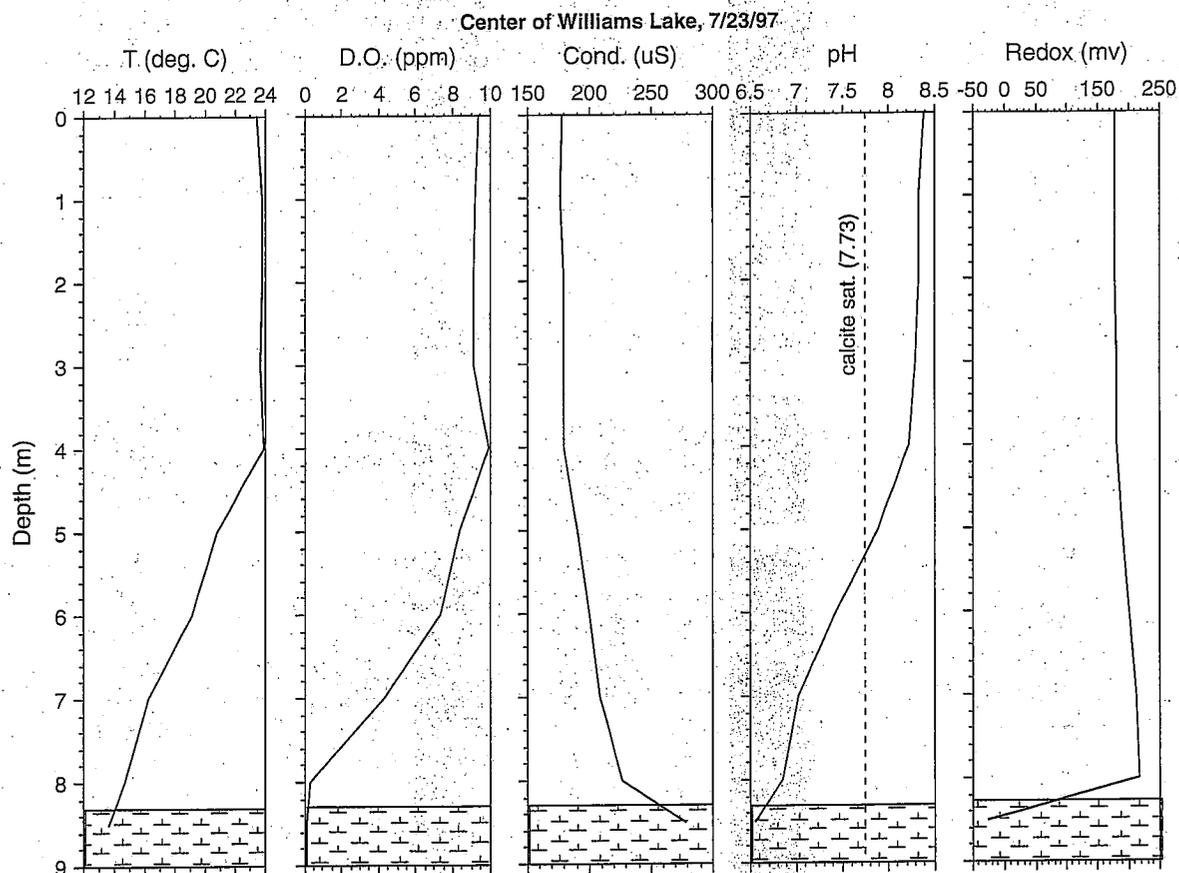


Figure 6. Depth profiles of selected physical and chemical parameters at the centre of Williams Lake during July 1997

The epilimnion of Williams Lake is oversaturated with calcite during late summer. Some calcite precipitation undoubtedly occurs in the open waters of the lake, probably triggered by phytoplankton photosynthesis, just as it does on the leaves of aquatic vegetation. As this pelagic calcite and planktonic organic matter sink into the hypolimnion, decay of the organic matter consumes dissolved oxygen, produces CO_2 , decreases the pH (Figure 6), and leads to the dissolution of calcite and anoxic hypolimnetic conditions in the sediment pore waters. These effects of organic production and decomposition on the precipitation and dissolution of calcite define the 'carbon-pump' as described by Dean (1999) and Dean and Schwab (2002). Thus, calcite dissolution in the sediments is an extension of dissolution that began in the water column. One manifestation of this calcite dissolution is an increase in the calcium concentration in the hypolimnion (unpublished data, Interdisciplinary Research Initiative database, USGS) and in specific conductance of the water (Figure 6). This dissolution process then continues in the sediments as indicated by the large increase in calcium concentration in pore waters (Figure 4). The data for the peeper at site O during October 1992 suggest that at that time calcium was diffusing out of the sediments and affecting the chemistry of the water in the littoral zone for a distance of at least 10 cm above the sediment-water interface. A similar situation must have occurred in the profundal zone of Williams Lake in July 1997, as indicated by the sharp increase in specific conductance just above the sediment-water interface and into the sediments (Figure 6).

The fact that calcite dissolution occurs at depth in both zones of inflow and outflow is supported by the elevated concentrations at depth shown in Figure 4. The seasonality of this input to the sediments is borne out by comparison of the July and October profiles, with larger concentrations evident in October, which is post-deposition of both the calcite precipitate and senescent plant material. The large change in the upper 10 cm profile of the outflow zone between July and October indicates that substantial calcite dissolution takes place in the surficial sediments in an area of lake-water outflow to ground water, providing a readily available source of dissolved calcium for uptake through aquatic plant roots systems in Williams Lake during the next growing season.

CONCLUSIONS

Use of stable isotope sediment pore-water profiles was a useful tool to corroborate the dynamics of ground-water flow into and out of Williams Lake and further evaluate chemical dynamics of the exchange between the lake and ground water. The fact that calcium profiles were the same at inflow and outflow zones of the lake indicates that the profiles of major chemical constituents alone need to be interpreted with caution when additional independent measures of the interaction of lakes and ground water are not available. Interpretation of calcium and stable isotope profiles expanded on the previous understanding that 40 to 50% of the calcium in Williams Lake is retained. The pore-water profiles indicate that calcium is recycled by aquatic plants in the littoral zone and that some calcium is removed from the water by precipitation of calcite in oversaturated waters on the leaves of aquatic vegetation in the littoral zone. All of this calcite is dissolved, however, in the anoxic pore waters in which the pH is lowered to undersaturation by decomposition of senescent plant debris. This littoral-zone organic-carbonate aspect of the carbon pump is complemented in the open water part of the lake by precipitation of calcite triggered by phytoplankton photosynthesis in the epilimnion, followed by dissolution of that calcite in the hypolimnion and profundal sediments rendered undersaturated by decomposition of phytoplankton organic matter.

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