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Abstract

A chemical budget analysis for Williams Lake, Minnesota, tracks the seasonal progression of carbon inputs and outputs. CO_2 exchanges with the atmosphere reverse seasonally, with uptake by the lake in summer preceded and followed by larger losses to the atmosphere. Calcium bicarbonate-rich groundwaters seep steadily into the lake, augmented by remobilization of lacustrine marls. Most of the carbon used in summer photosynthesis nevertheless derives from depletion of lake carbon stores, facilitated significantly by plant calcification.

Calcification in summer reduces alkalinity and calcium inventories by 15 and 25%, respectively, while generating equal molar quantities of CO_2. Marl precipitates mainly on submersed macrophytes, several of which calcify in 1 : 1 ratio to photosynthesis when incubated in Ca-supplemented lake water. Despite calcite supersaturation within the epilimnion, there is little authigenic calcification.

From tropical coral reefs to temperate-zone marl lakes and streams, calcareous plants and photosynthetic symbiosis abound in alkaline, hard-water environments and are largely responsible for carbonate sedimentation (Dean and Fouch 1983), raising questions about how calcification and photosynthesis interact. We explore this problem for the case of a mildly alkaline, closed basin, north-temperate lake. In the process, we investigate carbon sources for lake production, including atmospheric and groundwater exchanges and recycling of sedimentary organic and inorganic C. The chemical budget approach follows in the tradition of Otsuki and Wetzel (1974) and Murphy and Wilkinson (1980).

Most of the important characteristics of typical marly lakes have been appreciated for a long time (e.g. Davis 1900). Dissolved calcium and bicarbonate usually derive from dissolution of limestones in up-gradient glacial tills. Davis (1900) argued against authigenic precipitation as the major cause of lacustrine calcification and also observed that snail shells and other animal remains generally comprise a small part of the marl. Instead, aquatic plants, including various angiosperms, cyanobacteria, and especially the alga *Chara*, appeared to be the dominant calcifiers. Davis also noted that some plants calcify far more than others and speculated that simple photosynthetic CO_2 removal from the water was not the only cause of plant calcification.

The induction of calcification by aquatic photosynthesis can be viewed as a consequence of the reaction

$$2HCO_3^- \rightarrow CH_2O + O_2 + CO_3^{2-}, \quad (1)$$

which raises CO_3^{2-} concentrations and therefore $CaCO_3$ saturation levels. Smith (1973), Smith and Veeh (1989), and McConnaughey (1994*a*) discuss some ramifications of this mechanism, and simple calculations illustrate its limits. Starting with water initially saturated with respect to $CaCO_3$ and in CO_2 partial pressure equilibrium with the atmosphere (~350 ppm pCO_2), CO_2 withdrawal can the-

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Acknowledgments

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oretically induce $CaCO_3$ supersaturations of ~40 in freshwater or ~7 in seawater. Photosynthesis seldom produces such high $CaCO_3$ supersaturations in natural waters, however, partly because such intensive CO_2 withdrawal reduces pCO_2 levels to ~1% of atmospheric, which inhibits photosynthesis.

Many calcareous plants, like calcareous animals, also calcify by a mechanism unrelated to CO_2 withdrawal from the medium (McConnaughey 1994*a,b*). These plants characteristically display pH polarization, with distinct alkaline and acidic surfaces. Calcification occurs at the alkaline surfaces, where pH reaches values as high as 10.5 in *Potamogeton* (e.g. Prins et al. 1982) and *Chara* (McConnaughey and Falk 1991). Alkalinization results from proton uptake rather than CO_2 uptake, as evidenced by the ability of the plants to maintain alkaline surfaces in solutions lacking dissolved inorganic C (DIC) and by low rates of carbon uptake at the alkaline surfaces. The plants take up carbon mainly at the acidic surfaces and translocate some carbon to the alkaline surfaces, where it apparently leaks from the cell as CO_2 and precipitates externally as $CaCO_3$ (McConnaughey 1991). Large kinetic isotope effects often accompany the precipitation of $CaCO_3$, providing additional evidence for the use of molecular CO_2 in biological calcification (McConnaughey 1989*a,b*). Chemical modeling suggests that the alkaline surfaces can attain far higher $CaCO_3$ supersaturations than water subjected to CO_2 withdrawal (McConnaughey 1989*c*).

The precipitation of $CaCO_3$ from CO_2 generates two protons at the alkaline surfaces (reaction 2). The plant transports these to the acidic surfaces where they protonate exogenous HCO_3^- to form CO_2 (reaction 3). The resulting high pericellular CO_2 concentrations in the acidic zones (e.g. Smith and Walker 1980; Prins et al. 1982) speed CO_2 uptake and photosynthesis.

$$Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+ \quad (2)$$

$$2H^+ + 2HCO_3^- \rightarrow 2CO_2 + 2H_2O \quad (3)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O. \quad (4)$$

Under mildly alkaline conditions, this physiology generates twice as much CO_2 as it consumes during calcification (McConnaughey 1991). An approximately 1 : 1 ratio of calcification to HCO_3^--dependent photosynthesis often results, not because of chemical changes in ambient waters but rather because reactions 2 and 3 (at the alkaline and acidic surfaces, respectively) are efficiently coupled as part of a bicarbonate-using physiology. Calcareous seaweeds (Pentecost 1978), coccolithophorids (Sikes et al. 1980), and characean algae (McConnaughey 1991) often exhibit ~1 : 1 ratios of calcification to bicarbonate-dependent photosynthesis.

With this as background, we attempt to determine how much plant calcification contributes to growing season net production in a mildly alkaline north-temperate lake. We use a whole-lake chemical budget approach, which requires an analysis of chemical fluxes to and from the lake in addition to the monitoring of chemical changes in the lake.

We chose Williams Lake, Minnesota (46°57′N, 94°40′W; Fig. 1), for this analysis because continuing efforts by the U.S. Geological Survey and its Minnesota cooperators have produced an unusually good data base of lake chemistry and biology, groundwater exchanges with surrounding calcareous glacial terrains, gas exchanges with the atmosphere, and water and energy budgets (e.g. Sturrock et al. 1992; Rosenberry et al. 1993). The choice of Williams Lake does not exaggerate the importance of marl precipitation; the lake is less marly than some other lakes in the region, lacks the obvious groundwater seeps and springs often associated with marl formation, and has lower calcium and alkalinity concentrations than such lakes.

Williams Lake is a closed basin, dimictic lake encompassing 36 ha, having a maximum depth of ~9.3 m and an average depth (volume/area) of 5.2 m. Macrophyte beds occupy about half the lake and usually extend to a depth of 4–5 m (Taylor et al. 1985; Carter et al. 1993). Marginal sediments consist of various mixtures of sand, calcite-rich marl, and organic muck, while organic mucks dominate profundal sediments. The lake lies near the top of a gentle topographic ridge near the northern end of the Park Rapids-Staples glacial outwash plain. The watershed covers 227 ha and is mostly forested with a mixture of coniferous and deciduous trees.

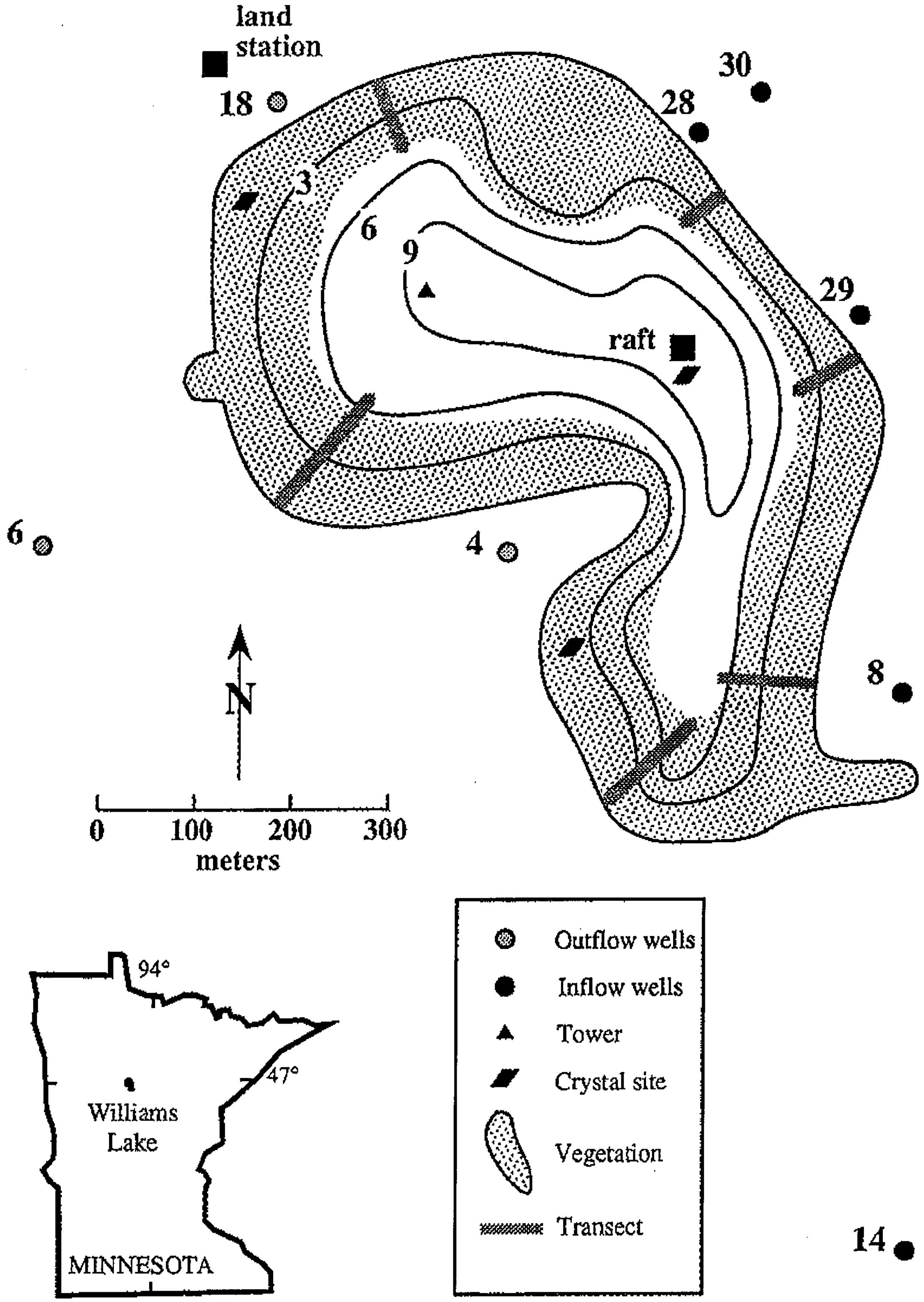

Fig. 1. Map of Williams Lake, Minnesota, showing bathymetry and locations of lake and nearby groundwater sampling sites, macrophyte beds, and macrophyte sampling transects.

Methods

Routine chemical sampling near the deepest part of the lake included in situ measurements of temperature, conductivity, dissolved oxygen, and pH at 1-m depth intervals with a multiparameter probe and retrieval of water samples from 1 and 8 m with a Van Dorn bottle. Sampling was quarterly in 1979, and at approximately monthly (winter) or biweekly (spring–fall) intervals between 1980 and 1990. Results from 191 sampling episodes contributed to this analysis. We used the chemical analysis procedures of Fishman and Friedman (1985). We subsequently edited the chemical data sets, generally excluding data >2 SD from seasonal norms (e.g. two of 191 lake-water alkalinity values). Using sample pH and alkalinity as inputs to the PHREEQE computer program of Parkhurst et al. (1980), we calculated aqueous CO_2, HCO_3^-, and CO_3^{2-} concentrations.

Average monthly chemical concentrations at 1- and 8-m depths were calculated from 11 yr of lake chemical data. Chemistry at other depths was interpolated based on conductivity, and monthly average whole-lake chemical inventories were calculated from the volumes at all depths in the lake.

Eight water-table wells, five hydrologically up-gradient (No. 8, 14, 28, 29, 30) and three down-gradient (No. 4, 6, 18) from the lake (Fig. 1), provided water for chemical analysis of regional groundwaters. Pumping first removed 3–4 well volumes of water or continued until temperature, pH, and specific conductance stabilized. Sediment pore-water equilibrators ("peepers") were also installed in littoral zone sediments of inflow and outflow regions of the lake. Each peeper contained cells at 14 depths spanning 50 cm. The cells initially contained distilled water bounded by a dialysis membrane. Peepers were emplaced from 25 September to 24 October 1992 and from 5 May to 21 July 1993.

CO_2 fluxes across the lake surface were estimated with two versions of a stagnant film gas-exchange model driven by wind velocities measured above the lake. Daily average and maximum windspeeds at 1, 2, and 4 m above the lake were calculated from anemometer readings sampled every minute and logged as hourly statistics during the ice-free part of the year, and the wind at 10 m was estimated by logarithmic extrapolation. Stagnant boundary thickness (h) was estimated by means of Smith's (1985) regression against windspeed.

A relatively standard formulation was used to calculate CO_2 fluxes across the lake–atmosphere boundary in the absence of CO_2 reaction in the boundary layer:

$$F_U = -Dh^{-1}\alpha(CO_2)[P_A - P_W]. \qquad (5)$$

D and α are the diffusivity and solubility of CO_2, and $[P_A - P_W]$ is the CO_2 partial pressure gradient between air and water.

During summer, the probability that CO_2 will react before traversing the stagnant boundary layer increases, due mainly to elevated pH (>8.6) and thick boundary layers (averaging 2×10^{-4} m). This reaction increases the potential CO_2 flux beyond that calculated above. A chemically enhanced CO_2 flux was therefore calculated from Smith's (1985) equation:

$$F_E = -Dr\frac{\cosh(rh)}{\sinh(rh)}\alpha(CO_2)[P_A - P_W]. \qquad (6)$$

$r = \{(k_{H_2O} + k_{OH}[OH^-])/D\}^{0.5}$. k_{H_2O} and k_{OH} are the kinetic constants for CO_2 hydration and hydroxylation. r increases with pH, reflecting faster conversion of CO_2 to HCO_3^-.

Groundwater influx rates were estimated with a flow net analysis based on soil hydraulic conductivities and regional hydrologic gradients. Hydrologically derived groundwater inflow rates agreed fairly well with calculations based on winter accumulations of reactive chemicals and with isotope balance methods applied over limited periods. Groundwater chemistry was measured at five water-table wells hydrologically up-gradient from the lake and at three wells down-gradient from the lake.

Macrophyte biomass was estimated by quadrat sampling along six transects (Fig. 1) in late summer 1991. Plants were separated according to species, decalcified by soaking in acetic acid, dried, and weighed. Photosynthesis and calcification by several submersed macrophytes and plankton were measured in jars containing lake surface water, sometimes supplemented with $CaCl_2$, incubated in shallow water. Calcification (− half the change in alkalinity) and photosynthesis (− change in [DIC] − calcification) were calculated as by

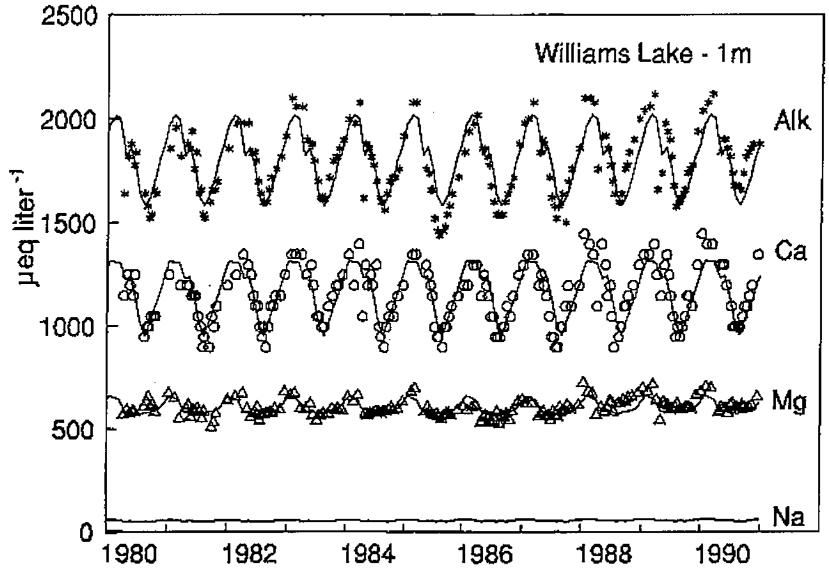

Fig. 2. Variations in dissolved alkalinity and Ca^{2+}, Mg^{2+}, and Na^+, 1980–1990. Average seasonal cycles (for the period 1980–1990) plotted as solid lines.

McConnaughey (1991) from observed changes in pH and alkalinity.

Rates of calcification and photosynthesis in the lake were calculated in an analogous manner, using the monthly mean concentrations observed in the lake and taking boundary fluxes into consideration:

$$\text{Calcification} = -(d/dt)[Ca^{2+}](Mg_{avg}/Mg) + GW(Ca^{2+}) \quad (7)$$

(and similarly, with alkalinity/2) and

$$\text{Photosynthesis} = -(d/dt)[DIC](Mg_{avg}/Mg) + GW\,(DIC) + Atm - \text{calcification.} \quad (8)$$

GW and Atm denote estimated fluxes from groundwater seepage and atmospheric exchange, and Mg_{avg} is the average Mg^{2+} concentration in the lake (311 μM for surface waters). Lake-water Ca^{2+}, alkalinity, and C concentrations were normalized to constant Mg^{2+} concentration for these calculations because dilution of lake waters (mainly in spring, due mainly to melting of winter snow and ice) would otherwise produce the appearance of strong biogeochemical removal at that time. Mg^{2+} was used for normalization because it behaves relatively conservatively in the lake, as discussed below, and because its concentrations were determined with less error relative to seasonal cycles than was the case for Na^+ or Cl^{-1}. Mg^{2+}, Na^+, and Cl^- all show similar seasonal cycles, however.

We examined nonbiogenic calcification in the lake by periodically weighing calcite and aragonite crystals and blocks of limestone suspended inside dialysis bags within the epilimnion near the center of the lake and near the northwest shore.

Results

The chemistry of Williams Lake fluctuates seasonally, with some interannual variability related to regional hydrological changes (Fig. 2). Vertical temperature and chemical stratification develops during both summer and winter (Table 1), but a depth-integrated whole-lake average chemical composition (Table 2) most closely resembles surface waters because most of the lake volume lies above the summer thermocline.

Concentrations of all major dissolved ions increase in winter, then decrease during spring thaw in April (Fig. 3). Following spring thaw, concentrations of Mg^{2+} and Na^+ stabilize, while K^+, Ca^{2+}, and DIC diminish further between May and August. To a first approximation, seasonal fluctuations in Mg^{2+} and Na^+ reflect dilution and can be used to estimate

Table 1. Ionic composition of Williams Lake. Means and standard deviations for samples collected at 1-m and 8-m depths, 1979–1990. Units: μeq liter^{-1} for alkalinity; μM for DIC, Ca, Mg, Na, and K.

	pH	Alk	DIC	Ca	Mg	Na	K
1 m							
Jan	8.0(0.1)	2,007(89)	2,081(112)	668(41)	339(15)	65(3)	28(2)
Feb	7.8(0.2)	2,051(48)	2,180(87)	664(35)	335(15)	65(5)	28(4)
Mar	7.8(0.2)	2,030(110)	2,182(136)	663(43)	328(26)	65(5)	29(4)
Apr	8.0(0.3)	1,859(131)	1,911(156)	626(48)	330(20)	57(7)	24(3)
May	8.3(0.3)	1,902(60)	1,864(123)	633(24)	301(11)	59(4)	24(2)
Jun	8.7(0.3)	1,809(81)	1,740(109)	584(42)	298(12)	58(6)	23(2)
Jul	8.7(0.3)	1,659(89)	1,583(96)	519(46)	296(12)	55(4)	21(3)
Aug	8.5(0.3)	1,616(55)	1,576(78)	487(18)	299(13)	57(4)	22(3)
Sep	8.2(0.3)	1,666(86)	1,671(119)	526(25)	300(15)	56(3)	23(3)
Oct	8.1(0.3)	1,752(69)	1,761(119)	561(24)	302(12)	58(6)	22(3)
Nov	8.1(0.3)	1,836(60)	1,870(66)	587(18)	308(10)	64(8)	24(2)
Dec	8.0(0.2)	1,905(69)	1,963(92)	628(25)	322(15)	64(6)	25(2)
Avg	8.2(0.3)	1,841(141)	1,865(201)	596(59)	311(15)	60(4)	24(2)
8 m							
Jan	7.6(0.1)	2,083(52)	2,235(83)	670(25)	323(12)	66(7)	26(2)
Feb	7.6(0.2)	2,115(37)	2,291(107)	700(32)	330(15)	63(5)	30(2)
Mar	7.8(0.4)	2,140(32)	2,288(151)	710(39)	334(12)	64(5)	29(3)
Apr	7.8(0.3)	2,039(92)	2,133(166)	686(39)	318(21)	60(5)	27(5)
May	8.2(0.3)	1,948(58)	1,944(93)	658(32)	302(13)	57(5)	25(3)
Jun	8.1(0.4)	1,971(58)	1,990(105)	660(22)	303(14)	59(9)	26(2)
Jul	7.6(0.2)	1,977(108)	2,092(137)	665(28)	310(11)	59(7)	26(4)
Aug	7.6(0.4)	1,978(84)	2,183(271)	656(40)	309(10)	58(6)	26(4)
Sep	7.8(0.4)	1,771(120)	1,850(207)	569(50)	303(21)	57(3)	25(3)
Oct	8.1(0.2)	1,790(73)	1,795(96)	582(35)	302(14)	57(4)	24(3)
Nov	8.1(0.2)	1,866(60)	1,894(74)	604(22)	308(13)	59(3)	24(3)
Dec	7.9(0.2)	1,958(74)	2,027(113)	646(28)	319(13)	59(3)	25(1)
Avg	7.8(0.2)	1,970(112)	2,060(163)	651(42)	313(11)	60(3)	26(2)

dilution effects on other, more reactive constituents.

Dilution—Evidence for quasi-conservative behavior by Mg^{2+} and Na^{+} is as follows: lake-water Mg^{2+} and Na^{+} composition falls near a dilution line connecting most up-gradient groundwater samples with meteoric precipitation (Fig. 4). Melting of snow and ~0.5 m of ion-depleted winter ice accounts for much of the ~10% reductions in lake-water Mg^{2+} and Na^{+} concentrations around April. Precipitation, sorption, and biological uptake seem unlikely to be especially important at that time, and calcification (as reflected by Ca^{2+} and alkalinity decrease beyond what would be caused by dilution) occurs later in the year. Marl precipitation and biomass growth in summer do, however, affect lake Mg^{2+} concentrations.

Table 2. Volume-weighted water-column average ionic composition of Williams Lake, 1979–1990. Units as in Table 1.

	Alk	DIC	Ca	Mg	Na	K
Jan	2,015	2,098	668	337	65	28
Feb	2,060	2,195	669	334	65	28
Mar	2,050	2,201	671	329	63	29
Apr	1,884	1,942	635	302	58	24
May	1,897	1,855	630	301	59	24
Jun	1,835	1,780	597	299	58	24
Jul	1,727	1,692	550	299	56	22
Aug	1,647	1,628	502	300	57	22
Sep	1,670	1,677	528	300	56	23
Oct	1,773	1,780	573	302	58	23
Nov	1,841	1,873	590	308	63	24
Dec	1,909	1,968	630	322	64	25
Avg	1,859	1,891	603	311	60	25
SD	133	187	55	14	3	2

Mg^{2+} incorporation into marls can be estimated from the net calcification rate, calculated below, times the Mg : Ca ratio in marls. Carbonate concentrations from four plants (*Chara*, two *Potamogeton* species, and *Myriophyllum*) contain molar Mg : Ca ratios ranging from 0.027 to 0.040, similar to values measured for lake marls elsewhere (Treese et al. 1981). Given a lake-water Mg : Ca ratio of 0.5 and the net calcification rates calculated below,

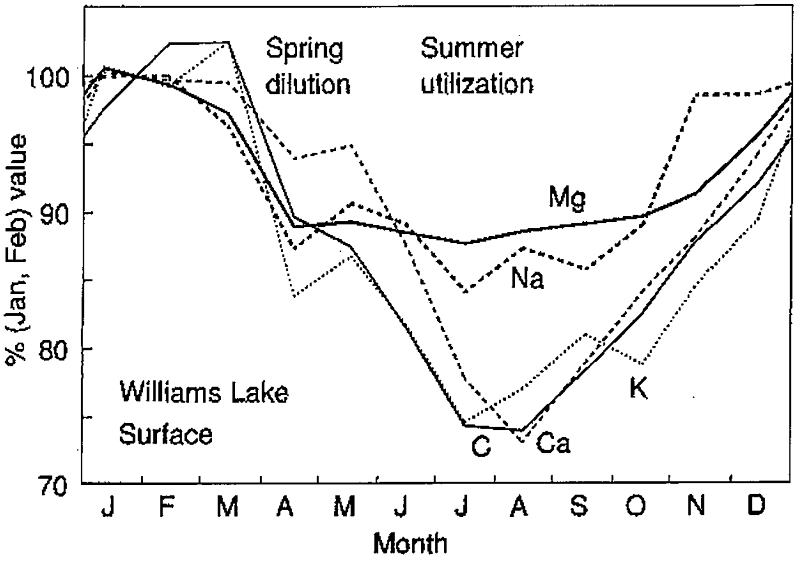

Fig. 3. Seasonal variations in Mg^{2+}, Na^+, Ca^{2+}, K^+, and DIC concentrations at 1 m, plotted as percentages of the average concentrations, January and February.

marl precipitation removes 3 μM Mg^{2+} annually.

Mg^{2+} uptake into biomass can be estimated from the Mg^{2+} content of aquatic plants and phase relationships between lake Mg^{2+} and K^+ cycles. K^+ is the major cation electrolyte in aquatic plants and occurs at low enough concentrations in the lake that plant growth measurably depletes it. K^+ concentrations drop 25–30% between February and July, and much of this decrease occurs after Mg^{2+} and Na^+ concentrations have stabilized. Molar Mg^{2+} : K^+

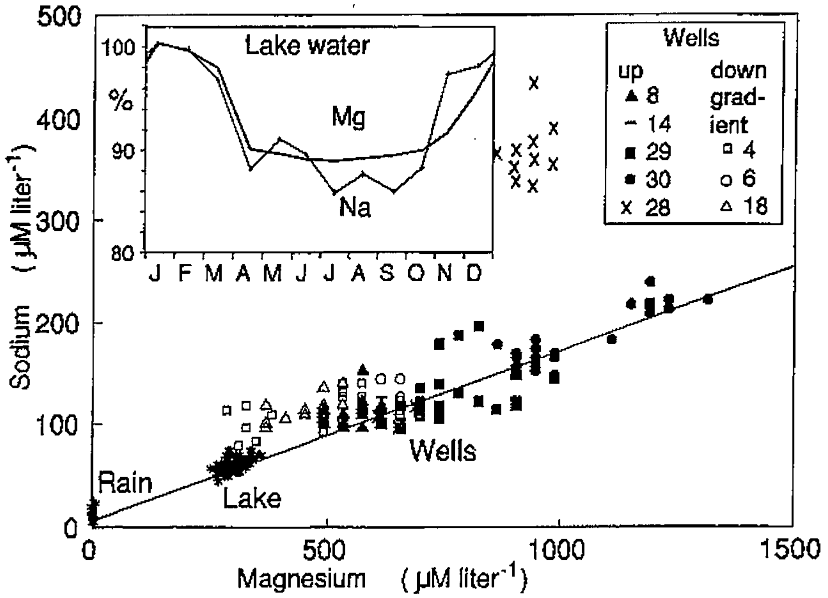

Fig. 4. Mg^{2+} and Na^+ concentrations and hydrologically up-gradient groundwaters. (Well 28 shows evidence of anthropogenic Na^+ augmentation.)

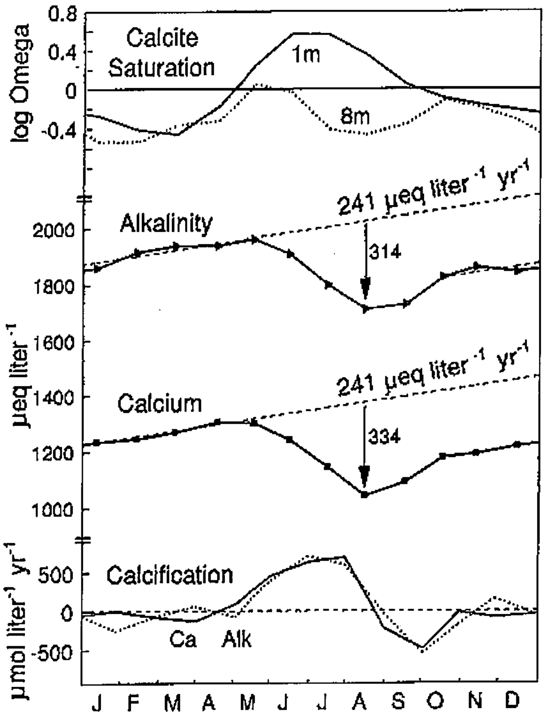

Fig. 5. Calcification in Williams Lake. Top: Calcite saturation state at 1 and 8 m. Middle: Seasonal cycles of dilution-normalized alkalinity and Ca^{2+} in the water column. Regressions covering the period October–April produce slopes of 241 $liter^{-1}$ yr^{-1} for both species. Bottom: Net calcification rate, calculated from monthly changes in Ca^{2+} and alkalinity concentrations.

ratios in several submersed plants from the lake range from 0.2 to 1.0, the higher values probably arising from contamination by plant marls. Net summer Mg^{2+} uptake into plant biomass is then ~0.3 (Mg^{2+} : K^+ in plants) × 3–4 μM (the K^+ decrease not attributable to dilution) or 1 μM.

Marls and biomass therefore appear to account for ~10% of the roughly 40 μM seasonal variation in Mg^{2+}. Treating Mg^{2+} as a strictly conservative element causes overestimation of summertime dilution and underestimation of other biogeochemical fluxes by 10% annually or somewhat more during summer periods of concentrated plant growth and marl precipitation. Mg^{2+} nevertheless offers the best quasi-conservative element measured over the course of the chemical record and is used to estimate dilution.

Figure 4 illustrates two other important points related to groundwater dilution in the lake: up-gradient groundwaters are variable in chemical composition and significantly more concentrated than lake water. The chemical variability both between and within wells complicates estimation of chemical influx to the lake. Depending on which groundwater values are used for comparison, the lake appears to be diluted by a factor of between 1.5 and 4.2 compared to up-gradient groundwaters. Hydrological analyses support a dilution near the lower end of this range.

Calcification—Surface waters are supersaturated with respect to calcite in summer but undersaturated during the remainder of the year and almost always undersaturated at 8 m (Fig. 5, top). Saturation state correlates with pH for both surface and bottom waters. Despite the summertime calcite supersaturation in surface waters, there is little apparent authigenic calcification. Calcite crystals and limestone blocks mounted in dialysis bags suspended in the epilimnion in 1991 showed negligible changes in weight or some dissolution, and similarly deployed aragonite crystals (which are somewhat more soluble) lost weight in summer 1992 (Table 3). Calcification therefore appears to be mainly biogenic and occurs mainly on submersed macrophytes, many of which develop obvious marly coatings in summer.

The annual cycles of dilution-normalized Ca^{2+} and alkalinity are in phase and similar in amplitude (Fig. 5, middle). Regression yields a slope of 0.98 ($r^2 = 0.95$), statistically indistinguishable from the value of 1.0 which would be expected from $CaCO_3$ precipitation and dissolution reactions. Between October and April, lake waters accumulate both Ca^{2+} and alkalinity at a rate of 241 μeq $liter^{-1}$ yr^{-1}. If this rate applies over the whole year, the summer losses correspond to the precipitation of ~160 μM (320 μeq) $CaCO_3$, or about a quarter of the lake calcium inventory (including replenishment). During September and October, lake Ca^{2+} and alkalinity concentrations increase faster than they do between October and April, ultimately restoring about a fourth of the Ca^{2+} and alkalinity that was removed between May and August. This rapid increase in lake-water Ca^{2+} and alkalinity suggests a pulse of $CaCO_3$ dissolution, probably stimulated by plant senescence and heat penetration into lake sediments. Subtracting this dissolution pulse from summer calcification yields a net annual calcification rate of ~120 μmol $CaCO_3$ $liter^{-1}$ yr^{-1}.

Month-to-month rates of calcification can be calculated from the rates of change of Ca^{2+} and alkalinity (again adjusted for dilution and shifted upward by 120 μmol $liter^{-1}$ yr^{-1} to account for net additions) (Fig. 5, bottom). Except around September–October, there seems to be little net marl dissolution, and net calcification rates reach 700 μmol $CaCO_3$ $liter^{-1}$ yr^{-1} in summer.

Groundwater chemical fluxes—Flow net modeling places groundwater inflow rates at 4.3×10^5 m^3 yr^{-1} over the period 1980–1990. Groundwater flow rates vary seasonally and interannually by ~10 and 25%. Groundwater inflow rates calculated from the rate of ^{18}O and ^2H dilution in the lake during winter and in the hypolimnion during summer range from 3.3 to 5.5×10^5 m^3 yr^{-1}. The isotope balance method of Krabbenhoft et al. (1990), based on the preferential evaporation of light isotopes from the lake, yields a preliminary groundwater influx rate of 3.6×10^5 m^3 yr^{-1} between April and September 1991. On the basis of a groundwater inflow rate of 4×10^5 m^3 yr^{-1} and a lake volume of 2×10^6 m^3, the lake-water residence time with respect to inflow is ~5 yr.

For quasi-conservative elements such as Mg^{2+}, groundwater influx rates (per liter of lake water) are then equal to lake concentrations divided by the hydrological residence time with respect to inflow (for Mg^{2+}, 311 μM/5 yr = 150 μM $liter^{-1}$ yr^{-1}). Groundwater influx rates of nonconservative elements (X) such as Ca^{2+} can be calculated as the $X:Mg^{2+}$ ratio in up-gradient groundwaters times the Mg^{2+} influx rate. Groundwater outflux rates for nonconservative elements can be similarly calculated from lake-water $X:Mg^{2+}$ ratios. These circuitous calculations skirt the large chemical variability in up-gradient groundwaters (Figs. 4, 6) and uncertainty in hydrologically calculated outflow rates while taking advantage of the proportionality of nonconservative to conservative elements in up-gradient groundwaters sampled in water-table wells.

Net calcium and carbon additions by groundwater (inflow − outflow) calculated in this manner cannot, however, support the rates of calcification inferred earlier from Fig. 5. This shortfall is also apparent from the fact that lake-water alkalinity and Ca^{2+} concentrations lie only slightly below groundwater dilution lines, as shown on Fig. 6. Additional calcium and carbon therefore appear to be added to the lake through remobilization of sedimentary organic materials and marls. Sediment interstitial waters from the lake littoral zone contain considerably higher Alk : Mg^{2+} ratios than up-gradient water-table wells (Fig. 6), and the same is true for $Ca^{2+} : Mg^{2+}$ ratios. Both up-gradient and down-gradient shores of the lake show this effect, as do some down-gradient water-table wells (No. 4, 18). In summary, sediment recycling of calcium and carbon, in particular, accounts for much of the solute flux entering the lake and helps to replenish the materials used in summer calcification.

Table 3. Weight changes of carbonates deployed in Williams Lake. Locations: raft—near the center of the lake; macrophyte beds—near the edge of the lake. Times: 1—15 April–30 September 1991; 2—20 April–28 July 1992; 3—28 July–23 October 1992.

Exp.	Depth (m)	Time	Wt change (mg)
	Calcite		
Raft	3	1	+0.8
Raft	3	1	−0.5
Macrophyte beds	0.5	1	+2.0
	Limestone		
Raft	3	1	−58.4
Raft	3	1	−128.8
Raft	9	1	−1,000.2
Raft	9	1	−1,092.5
Macrophyte beds	0.5	1	−29.8
	Aragonite		
Raft	3	2	−88.5
Raft	3	2	−47.7
Macrophyte beds	0.5	2	−102.3
Macrophyte beds	0.5	2	−23.6
Raft	3	3	−34.5
Macrophyte beds	0.5	3	−81.5

Atmospheric CO_2 exchanges—The lake accumulates CO_2 under its winter ice cover, reaching pCO_2 supersaturations of several times atmospheric. Springtime CO_2 evasion to the atmosphere and plant uptake subsequently reduce epilimnion pCO_2 values to <70% of atmospheric. The direction of net surface CO_2 exchange therefore reverses seasonally.

We calculated average surface CO_2 flux rates with a stagnant boundary-layer model driven by average wind velocity above the lake. Figure 7 illustrates calculations made with and

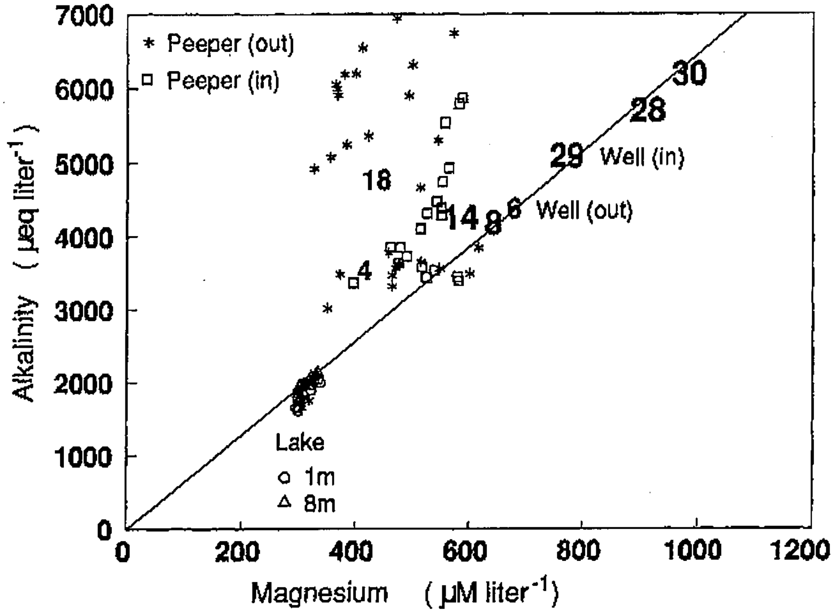

Fig. 6. Alkalinity and Mg^{2+} concentrations, selected littoral zone sediments, and regional groundwaters. Regression line (forced through origin) applies to up-gradient water-table wells (No. 8, 14, 28, 29, 30). Calcification causes lake waters to fall somewhat below this regression line. Dissolution of lake marls contributes to the high alkalinities in littoral zone sediments (peeper data) and some down-gradient water-table wells (No. 4, 18).

without incorporating chemical enhancement of CO_2 diffusion (Smith 1985). This "enhanced diffusion" originates from the reaction of CO_2 to form HCO_3^- within the boundary layer. Chemically enhanced diffusion becomes important when the boundary layer is thick and alkaline because this increases the probability that CO_2 will react before it diffuses across the boundary layer. Incorporating chemical enhancement of CO_2 diffusion in the calculation makes little difference in spring and fall, when CO_2 fluxes are outward from the lake, but in-

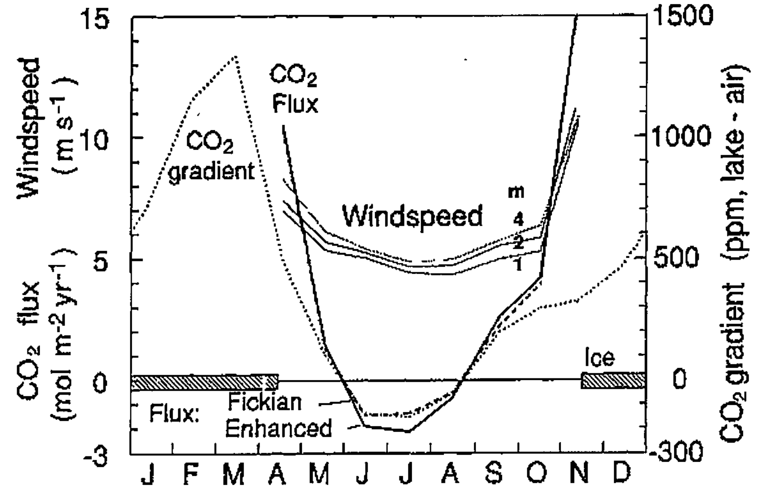

Fig. 7. CO_2 fluxes across the lake–air interface, calculated using a stagnant film model with and without chemically enhanced CO_2 flux. Also shown are average windspeeds and pCO_2 concentrations in the water.

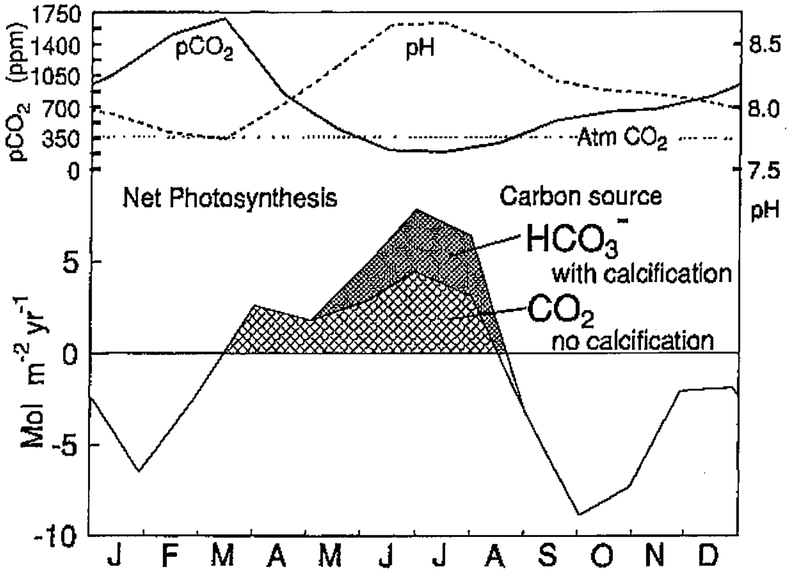

Fig. 8. Photosynthesis in Williams Lake. Top: Seasonal variation of pCO_2 and pH in the epilimnion. Bottom: Calculated rates of net photosynthesis, subdivided into HCO_3^- and CO_2 assimilation (HCO_3^- estimated from alkalinity consumption).

creases summer CO_2 uptake by the lake by as much as 50%.

These calculations may underestimate spring and fall fluxes in particular, since winds then are stronger, more variable, and less measured. But according to these calculations, the lake loses ~0.4 mol CO_2 m^{-2} to the atmosphere during the ice-free part of the year.

Photosynthesis—Having estimated boundary fluxes and rates of carbon removal from the water by calcification, we estimated whole-lake net photosynthesis (photosynthesis-respiration) as the residual carbon imbalance (Eq. 8). Groundwater influx of Ca^{2+} and DIC are estimated as in Fig. 5. These calculations are most reliable in summer, when light winds and a small pCO_2 gradient at the lake surface reduce the importance of atmospheric exchange.

Net photosynthesis prevails from April until August, reaching 7.8 mol C m^{-2} (of lake surface) yr^{-1} in late June (Fig. 8) and totaling 1.9 mol C m^{-2} for the growing season. Atmospheric exchange supplies ~20% of this total; the remainder derives from summertime sediment and groundwater fluxes and drawdown of lake carbon inventories.

A period of strong net respiration follows the summer period of net photosynthesis and coincides with the period of apparent carbonate dissolution discussed earlier. Plant senescence and heat penetration into the sediments probably contribute to this phenomenon. For the year as a whole, respiration appears to dominate, adding a net of 0.7 mol C m^{-2} to the lake. To the extent that this represents a steady state condition and is accurately estimated here, net respiration is presumably supported by the decay of terrigenous detritus and emergent macrophytes, which obtain CO_2 from the air but add CO_2 to the water when they decay.

Submersed macrophytes account for most of the apparent net summer photosynthesis. Daytime pH elevation and pCO_2 depletion are stronger in the macrophyte beds than in the open water, and phytoplankton biomass is ~2% of macrophyte biomass. Carter et al. (1993) estimated above-sediment macrophyte dry weight biomass near the end of the growing season at 6.3×10^7 g, or 6 mol C m^{-2}. This is triple the calculated growing-season net photosynthesis. Overwintering of several dominant macrophytes (including *Megalodonta beckii* and *Chara* sp.) and floating or emergent leaves of other species (which contribute to biomass but not to the calculations of aquatic

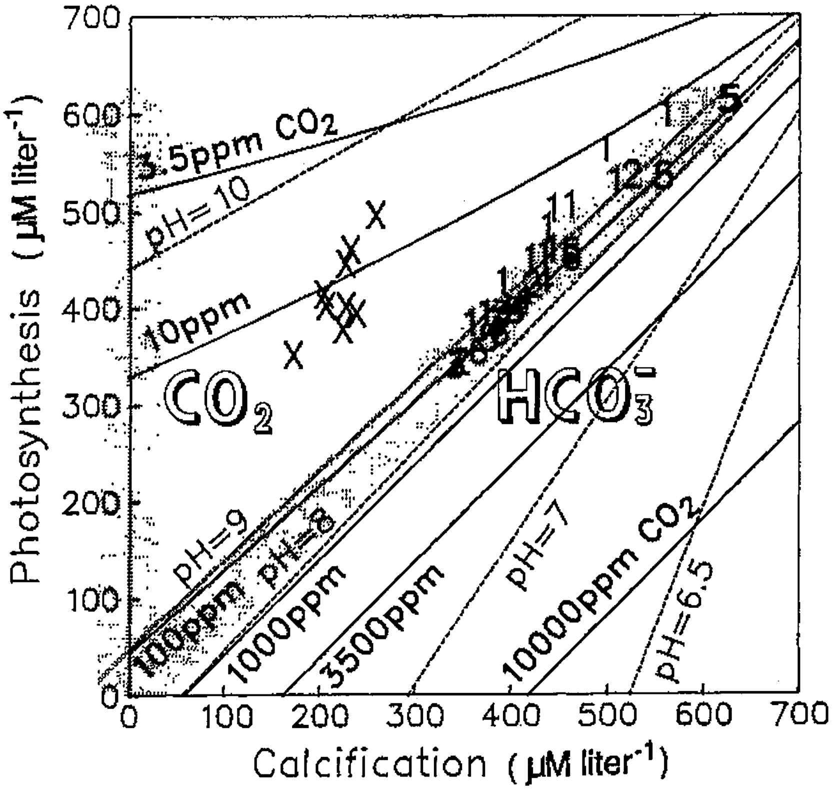

Fig. 9. Net photosynthesis and calcification by *Chara*. Plants were incubated for 2–3 h in lake surface water, with or without Ca^{2+} supplementation; their plotted positions on the graph indicate the cumulative amounts of calcification and photosynthesis which occurred during these experiments. × — No Ca^{2+} supplementation; numbers (1–6) represent mM of Ca^{2+} added. Axes: μM C removed by calcification and photosynthesis during the experiments. Also shown are contours of pH (dashed lines) and pCO_2 (solid lines) calculated as functions of calcification and photosynthesis. Stippled arrows show trajectories of chemical change for CO_2- and HCO_3^--based photosynthesis, where the latter is accompanied by equimolar amounts of calcification. Chemical composition at the origin is typical of Williams Lake surface water in summer.

photosynthesis) presumably contribute to the excess of estimated biomass over summer production.

Despite the summer removal of ~20% of lake DIC, aquatic pCO_2 values usually remain >70% of atmospheric and pH values usually remain <8.7. DIC depletion comes largely at the expense of alkalinity. Bicarbonate-based photosynthesis requires an input of proton equivalents ($HCO_3^- + H^+ \rightarrow CH_2O + O_2$), which, not surprisingly, derive mainly from calcification (Eq. 2). Net photosynthesis can therefore be divided into calcification-dependent and independent components, depending on whether alkalinity is consumed (Fig. 8). Calcification-dependent photosynthesis commences in late May, corresponding approximately with the time that marl coatings appear on submersed plants and lake pCO_2 values drop below atmospheric. It accounts for up to half the total photosynthesis in midsummer.

Many of the submersed macrophytes in the lake, including several species of *Potamogeton*, *Chara*, and *Nitella*, develop obvious marl encrustations in summer. When incubated in jars with lake surface waters, *Chara* sp., three species of *Potamogeton*, *M. beckii*, and *Myriophyllum exalbescens* exhibit high rates of calcification and, when supplemented with 1–6 mM $liter^{-1}$ Ca^{2+} (Fig. 9), approach the 1 : 1 ratio of calcification to photosynthesis described by Eq. 1. Control incubations without macrophytes showed negligible calcification. Although it is not obvious in Fig. 9 (due to variations in plant weights, incubation times, etc.), Ca^{2+} supplementation enhanced photosynthetic rates in all plants tested.

Discussion

The whole-lake chemical budget approach has many limitations. Analytical problems pervade the estimation of boundary fluxes, dilution by meteoric precipitation is hard to measure accurately, chemical stratification of the water column develops during both summer and winter, and gas fluxes by ebullition from sediments and passage through the aerynchyma of emergent plants bypass our computational methods for surface gas exchange. Errors made during the estimation of boundary fluxes, calcification, and dilution corrupt the estimation of photosynthesis. Nevertheless, the whole-lake chemical budget approach provides a reasonably robust method of addressing ecosystem carbon dynamics.

Calcification is one of the more common photosynthetic adaptations in alkaline waters. Calcification raises pCO_2 adjacent to the acidic surfaces of the calcareous plant and substitutes the problems of diffusing CO_2 and proton equivalents toward the plant with the new and often less formidable problems of obtaining HCO_3^- and Ca^{2+} (McConnaughey 1991; McConnaughey and Falk 1991). Many plants also derive structural or defensive benefits from $CaCO_3$ (e.g. Pennings and Paul 1992).

Approximately 1 : 1 ratios of calcification to photosynthesis have previously been reported in several aquatic organisms. In addition to the charophytes, calcareous seaweeds, and coccolithophorids referenced earlier, photosynthetic corals (e.g. Goreau 1963) and foraminifera (Duguay and Taylor 1978; ter Kuile et al. 1989) also approach this stoichiometry at times. In the symbioses, the algae probably benefit from the elevated CO_2 concentrations generated by host calcification. But what is the significance of the 1 : 1 ratio? Presumably it represents a physiological optimization, balancing the benefits to photosynthesis against the costs of calcification. Environmental chemistry imposes additional constraints.

McConnaughey and Falk (1991) observed reductions in the ratio of calcification to photosynthesis at Ca^{2+} concentrations below 1 mM and showed that diffusive limitations of Ca^{2+} uptake were probably responsible. The results from Williams Lake appear analogous. Incubations which were not supplemented with Ca^{2+} began with <0.6 mM Ca^{2+}, and about half of this usually precipitated before the experiments ended. Ca^{2+} depletions this large seldom occur in the lake. Therefore, the 1 : 1 ratios of calcification to photosynthesis observed in incubations with Ca^{2+} supplementation probably characterize bicarbonate-dependent photosynthesis in this lake. The incubation experiments also suggest that Ca^{2+} availability can limit growth rates, perhaps elevating Ca^{2+} to the status of limiting nutrient in alkaline waters with $\lesssim$0.5 mM Ca^{2+}. Without groundwater replenishment of Ca^{2+} (and HCO_3^-), bicarbonate-dependent plant photosynthesis would rapidly become impossible.

pH is of course important. CO_2 is relatively more abundant in neutral to acidic waters, making CO_2 generation from HCO_3^- less attractive. Above pH 9, the calcification-to-photosynthesis ratio in *Chara* increases to values >1 : 1 (McConnaughey 1991) as CO_3^{2-} increasingly competes with HCO_3^- for protonation in the acidic zones of the plant. Many natural waters, including the oceans, have pH values between 8 and 9, so HCO_3^- is the principal proton acceptor in solution, and calcification can be effective in enhancing CO_2 levels. The consequences for aquatic chemistry are interesting. As shown in Fig. 9, large amounts of carbon can be removed from the water with a 1 : 1 stoichiometry of calcification to photosynthesis with only minimal effects on pH or pCO_2. Primary production essentially consumes alkalinity.

Calcification apparently supports between a third and a half of annual net photosynthesis in Williams Lake and up to half of total net photosynthesis during midsummer. Similar values apparently apply, for example, in marine coral-algal reefs (Smith 1973). Calcification helps calcareous plants and symbioses avoid photosynthetic inhibition while keeping environmental pCO_2 values within bounds that sustain other plants. Plant calcification thus contributes to local pH and pCO_2 homeostasis. Calcareous photoautotrophs account for much of the $CaCO_3$ produced globally, and $CaCO_3$ is the dominant form of carbon in the biosphere; hence this concept can properly be extrapolated to global scales. Over geological periods, limestone precipitation therefore reflects photosynthetic physiology and CO_2 concentrations in the hydrosphere–atmosphere system.

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