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Dissolved organic and inorganic carbon mass balances in central Ontario lakes

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Abstract. Mass balances of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) based on stream and precipitation inputs and outflows were measured for seven unproductive lakes in central Ontario between 1981 and 1989. Net annual CO_2 evasion occurred in six of the seven study lakes with minor net invasion in the seventh. Atmospheric invasion might have been significant at certain times of the year, particularly during the growing season. Net evasion rates were greater than DIC loading rates, indicating partial mineralization of the terrestrially-derived DOC in the lakes. A steady state mass balance model adequately described the variation in DOC retention between lakes. Net annual carbon accumulation of forest communities based on estimates of net ecosystem production may be overestimated because of significant export of carbon to lakes via streams and groundwater, particularly in catchments with extensive peatlands.

Introduction

The relative importance of terrestrial and atmospheric CO_2 sources in temperate lakes and the role of lakes in regional carbon budgets are not well known (Kurz et al. 1992). Schindler et al. (1975) showed that oligotrophic Lake 239 was oversaturated with CO_2 for much of the annual cycle. Norton and Henriksen (1983) stated that "oligotrophic non-dystrophic waters in North America and Europe are persistently and greatly oversaturated with CO_2 with respect to atmospheric conditions", a result supported by Cole et al. (1994). Persistent CO_2 supersaturation rules out atmospheric invasion and implies that the catchment can be an important source of carbon. Hesslein et al. (1980) measured CO_2 evasion from softwater Lake 224 in northwestern Ontario during late July and August. Both CO_2 invasion and evasion occurred at different times of the summer in fertilized softwater Lake 227 in northwestern Ontario (Schindler & Fee 1973), presumably in response to changing photosynthetic consumption rates. Kling et al. (1991) observed CO_2 supersaturation in 27 out of 29 aquatic systems in arctic Alaska and suggested that transport of dissolved organic carbon from terrestrial to aquatic systems is a significant fraction of annual carbon accumulation. However, Herczeg and

Hesslein (1984), Herczeg et al. (1985) and Hesslein et al. (1991) showed that dissolved CO_2 concentrations in softwaters calculated from pH and DIC measurements may be significantly overestimated compared to direct measurements of pCO_2, particularly in waters with high dissolved organic carbon (DOC). Hence, they question the reported degree of supersaturation in unproductive lakes.

Rao (1978) reported that much of the dissolved inorganic (DIC) in nutrient-poor Findley Lake in Washington state had been previously photosynthetically fixed and subsequently oxidized because it was dissimilar in isotopic composition to atmospheric CO_2. Rao concluded that nonpelagic sites (perhaps terrestrial) were the sources of this DIC.

The relative importance of atmospheric and terrestrial carbon sources on a net annual basis can be determined by means of long-term mass balance studies. This communication presents the results of an intensive 8 year study of annual flux measurements of DOC and DIC in streams, outflows and sediments of seven unproductive, softwater lakes in central Ontario and is the first in a series of papers investigating the export and behaviour of carbon and colour.

Methods

The seven study lakes are located in south central Ontario, County of Haliburton or the District of Muskoka. They are relatively clear, headwater lakes with the exception of Red Chalk Lake which receives discharge from Blue Chalk Lake. The lakes and their catchments are described in more detail in Dillon et al. (1991), Molot and Dillon (1991, 1993) and Molot et al. (1992). Surface areas, mean depth, TP and DOC concentrations are presented in Table 1.

Samples were collected from stream stations from June 1981 to May 1989 at 1 to 4 week intervals, filtered through 80 um polyester mesh into pre-rinsed Nalgene bottles (DOC) or 50 mL pyrex culture tubes (DIC) and placed in temperature controlled containers while in transit to the laboratories (Dillon et al. 1991; Dillon & Evans 1993; Molot & Dillon 1993). Water level or stage was recorded continuously at weirs or flumes installed on the study streams (Scheider et al. 1983). Stage discharge relationships were constructed for each stream.

Bulk precipitation was collected and precipitation depth monitored at up to 12 stations, with never less than 4 stations in operation. Precipitation samples were removed from collectors (0.25 m^2) with Teflon-coated, stainless steel funnels. Collection periods ranged from 1 to 40 days, although samples were typically removed weekly.

Table 1. Lake surface area (A_o), catchment area excluding lake area (A_d), mean depth ($\bar{z}$), mean whole-lake TP and DOC concentrations, and mean Secchi depth during summer stratification from 1977 to 1989. Sampling of Crosson began in 1980 and sampling of Plastic began in 1979.

Lake	A_o (ha)	A_d (ha)	$\bar{z}$ (m)	TP ($\mu g\ L^{-1}$)	DOC ($mg\ L^{-1}$)	Secchi (m)
Blue Chalk	52.35	105.9	8.5	5.0	1.8	6.8
Chub	34.41	271.8	8.9	8.4	4.8	3.3
Crosson	56.74	521.8	9.2	9.17	4.1	3.6
Dickie	93.60	406.4	5.0	10.7	5.0	2.8
Harp	71.38	470.7	13.3	6.7	3.9	3.8
Plastic	32.14	95.5	7.9	4.8	2.3	6.8
Red Chalk	57.13	532.4	14.2	4.4	2.5	6.3

Samples collected for DIC analysis were acidified in the lab with sulphuric acid and CO_2 was colourimetrically determined using an autoanalyzer with phenolphthalein indicator. To estimate DOC, water samples were acidified and flushed with nitrogen to remove DIC, photo-oxidized to decompose DOC to DIC, and then subjected to DIC measurement to determine the amount of carbon. A subset of samples was analyzed before and after filtration through pre-rinsed acid-washed GFC filters; there was no difference in the organic carbon content in filtered and unfiltered pairs, indicating that an insignificant portion of the organic carbon existed in the small particulate fraction. Analytical methods are described in detail in Locke and Scott (1986) and Ontario Ministry of the Environment (1983).

Annual net gain of DOC for each lake, DOC_{net}, ($mg\ m^{-2}\ yr^{-1}$) was calculated as the difference between L, the total inputs of DOC to the lake (i.e., from precipitation and runoff), and the output of DOC from the lake via the outflow, Lo, divided by the lake area. Retention, R, is defined as DOC_{net} /L. The apparent settling velocity, v ($m\ yr^{-1}$), was calculated for each lake from $R = v/(v + q_s)$, where q_s is the areal water discharge rate ($m\ yr^{-1}$). This model can be tested using the reciprocal of the equation, $1/R = q_s/v + 1$, where 1/v is the slope of a plot of 1/R versus q_s. The settling coefficient is, in effect, a generalized, first order rate constant for loss of DOC from the lake by all processes other than via outflow, i.e., v integrates burial in sediments and mineralization. The model ignores internal production of DOC and DIC in the lakes. Calculations were similar for DIC.

Annual sediment C accumulation rates, SED_c, were estimated for the top 1 cm of sediment cores by multiplying sediment C/P ratios by the amount of TP retained annually measured with mass balance studies of total inflows and outflow (Dillon & Evans 1993; Dillon, unpublished data). C/P ratios at each

sampling site were measured and used in the calculations. The difference between TP inputs and outflows is assumed equal to sediment storage (Evans & Rigler 1980; Cross & Rigler 1983; Dillon & Evans 1993). Five to eight cores were taken from each lake at depths ranging from 8.3 m to the lake maximum depths using a KB gravity corer with a 4.8 cm inside diameter core tube. One to three cores were obtained at each station and sectioned using an extruder and plastic collar. Replicate slices were combined, dried at 100°C to a constant mass for a minimum of 24 hrs and ground to a fine powder. Loss on ignition (LOI) was determined gravimetrically after igniting samples at 600°C for 1 hr. The measured LOIs were converted to sediment carbon by multiplying by 0.51 of the dry weight. This factor was based on a subset of 60 samples in which both LOI and total C were measured. Subsamples for TP determination were digested in hot sulphuric acid with the addition of potassium persulphate. TP was measured colorimetrically using an ammonium molybdate-stannous chloride method (Ontario Ministry of the Environment 1983) after eliminating Fe interference by precipitation and filtration.

H_2CO_3* concentrations ($H_2CO_3 + CO_{2aq}$) were calculated from DIC and pH using temperature-dependent measured values for K_1 according to Stumm and Morgan (1981). Equilibrium H_2CO_3* concentration ($H_2CO_3*_{eq}$) was estimated from $H_2CO_3*_{eq} = K_H \cdot P_{CO2eq}$ where K_H is Henry's Law constant and P_{CO2eq} is the partial pressure of CO_2 in lake water at atmospheric equilibrium, which was taken to be $10^{-3.5}$ atm. Ratios of $H_2CO_3*/H_2CO_3*_{eq}$ greater than 1 in lake water indicate supersaturation.

Bodo's (1991) method for robust graphical time series analysis of long term surface water quality records was applied to discrete DIC measurements from 1 m depth. The TRENDS software generates a "de-seasonalized" time series trend, and a "relative seasonality" trend using de-trended series which can be interpreted as a "representative" annual curve. The y scale on the relative seasonality curve is adjusted such that zero is the time-weighted mean trend.

Results

Atmospheric deposition

The average atmospheric DOC and DIC deposition rates from 1981 to 1989 were 0.84 and 0.15 g C m^{-2} yr^{-1}, respectively. Atmospheric DOC deposition ranged from 2 to 13% of total DOC inputs and atmospheric DIC deposition ranged from 1 to 8% of total DIC inputs (Tables 2 and 3) to the study lakes.

Table 2. Mean and standard deviation of DOC inputs and outputs expressed on a lake area basis (g C m^{-2} yr^{-1}) and areal water load, q_s (m yr^{-1}) during 1981 to 1989. L = load, L_o = loss via outflow from lake, R = retention calculated as $(L - L_o)/L$, and v = apparent settling coefficient (m yr^{-1}) calculated as $R \cdot q_s / (1-R)$.

Lake		q_s	L	L_o	R	v
Blue Chalk	mean	1.50	6.54	2.68	0.59	2.2
	sd	0.29	0.66	0.42	0.04	0.3
Chub	mean	4.23	35.4	20.8	0.42	3.0
	sd	0.78	4.0	3.5	0.05	0.3
Crosson	mean	5.60	39.7	24.8	0.37	3.3
	sd	1.09	6.0	4.7	0.05	0.6
Dickie	mean	2.66	31.2	14.2	0.55	3.2
	sd	0.59	4.2	2.9	0.05	0.4
Harp	mean	4.16	28.9	16.9	0.42	2.9
	sd	0.75	4.8	3.4	0.04	0.4
Plastic	mean	2.00	15.1	4.6	0.69	4.6
	sd	0.38	2.4	0.80	0.03	1.0
Red Chalk	mean	5.44	23.5	14.8	0.37	3.2
	sd	0.99	1.8	2.4	0.06	0.7

Table 3. Mean and standard deviation of DIC input and outputs (g C m^{-2} yr^{-1}) during 1981 to 1989 in the study lakes. L = load, L_o = loss via outflow from lake, and R is retention calculated as $(L - L_o) / L$.

Lake		L	L_o	R
Blue Chalk	mean	1.98	2.29	–0.16
	sd	0.32	0.36	0.12
Chub	mean	9.50	4.64	0.52
	sd	1.50	1.19	0.07
Crosson	mean	12.4	4.62	0.63
	sd	2.29	1.09	0.04
Dickie	mean	7.35	2.53	0.66
	sd	1.29	0.65	0.06
Harp	mean	7.85	6.35	0.19
	sd	1.10	1.09	0.05
Plastic	mean	1.91	1.75	0.08
	sd	0.36	0.31	0.13
Red Chalk	mean	7.54	8.34	–0.10
	sd	1.10	1.52	0.06

DOC loading and retention

DOC loading ranged from 6.5 g C m^{-2} yr^{-1} in Blue Chalk Lake to 39.7 g C m^{-2} yr^{-1} in Crosson Lake (Table 2). Annual variations in DOC input

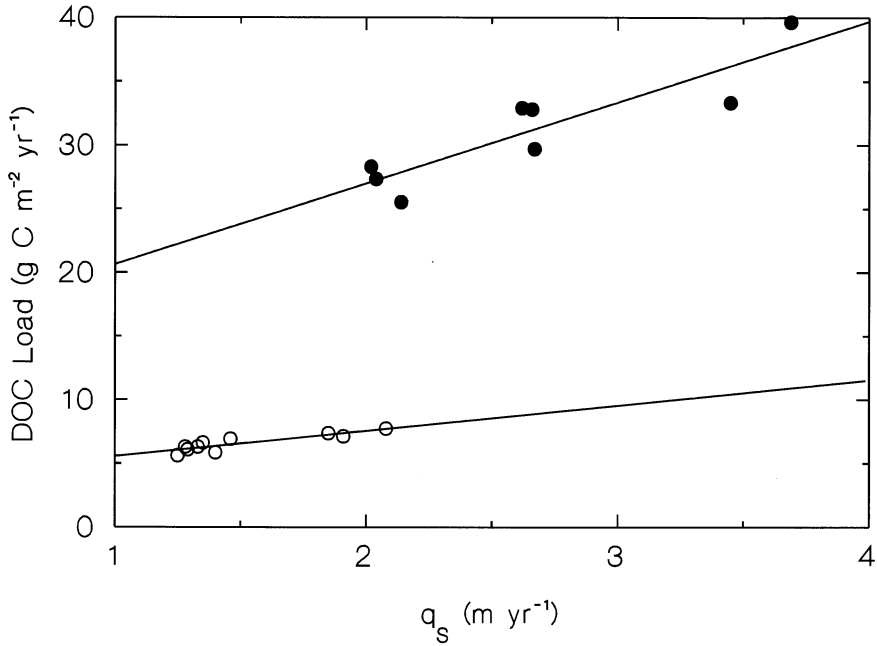

Figure 1. Annual (1981–89) DOC load(g C m^{-2} yr^{-1}) versus q_s (m yr^{-1}) for Dickie and Blue Chalk Lakes. Closed circles = Dickie Lake, open circles = Blue Chalk Lake.

and loss via outflow for the study lakes varied less than two-fold over the eight year period (Table 2). Within a lake, annual differences in DOC loading are explained by differences in q_s (Figure 1). Between lake differences are attributable to catchment differences in the extent of peatlands (Dillon and Molot, submitted).

The relatively high DOC loading rates for these lakes affect their physical properties. Mean, whole-lake DOC concentration (mg L^{-1}) was a strong predictor of Secchi depth (m) in these unproductive study lakes (Secchi = –1.34 DOC + 9.36, R^2 = 0.94, n = 8, data from Table 1) which is consistent with the hypothesis that DOC controls transparency in unproductive lakes (Schindler 1971; Brezonik 1978; Lorenzen 1980; Megard et al. 1980; Canfield & Hodgson 1983; Lind 1986; Schindler 1995).

Retention of DOC varied from 0.37 in Red Chalk and Crosson Lakes to 0.69 in Plastic Lake (Table 2). The reciprocal of R was strongly correlated with q_s, the areal water load, (r = 0.96) (Figure 2) which suggests that the mass balance model described in the Methods section is applicable. The reciprocal of the slope (which is equal to v, the settling coefficient) was 3.4 m yr^{-1}. The settling coefficient ranged about 2-fold from 2.2 m yr^{-1} in Blue Chalk Lake to 4.6 m yr^{-1} in Plastic Lake with the remaining 5 lakes clustered between

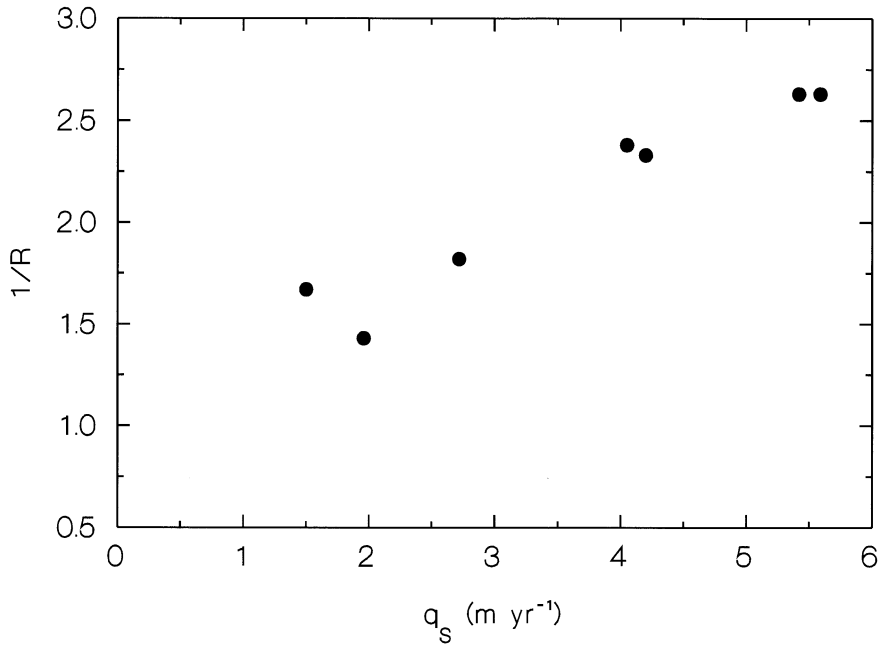

Figure 2. 1/R for DOC versus q_s (m yr^{-1}). Results are 8 year averages (1981–1989) for the 7 study lakes.

2.9 and 3.3 m yr^{-1} (Table 2). The mean v was 3.2 m yr^{-1}. The coefficient of variation for annual values of v ranged from 10% in Chub to 22% in Plastic and Red Chalk lakes. The coefficient of variation for the long term, mean v for all lakes, 3.2 m yr^{-1}, was 22%.

DIC loading and retention

DIC loading ranged from 1.9 g C m^{-2} yr^{-1} in Blue Chalk Lake to 12.4 g C m^{-2} yr^{-1} in Crosson Lake (Table 3). The ratio of DIC to DOC in total inputs was quite constant (range of 0.24 to 0.32) except in Plastic Lake (0.13) (Table 4). The relatively constant ratio in stream fluxes suggests that mineralization of DOC is an important source of DIC in stream waters and that the mineralization rate is a linear function of DOC concentration, with the exception of the Plastic catchment. In the case of Plastic, acidification may have affected the rate of mineralization. The DIC/DOC ratio in output from the lake varied more than in the input (0.18 to 0.85) (Table 4) and is probably affected by various factors such as differing photosynthetic demands, mineralization rates and surface turbulence which affects the rate of gas exchange at the air/water

Table 4. Ratios of DIC to DOC in lake inputs and outputs. Results are averages of annual values measured between 1981 and 1989.

Lake	Input	Output
Blue Chalk	0.30	0.85
Chub	0.27	0.22
Crosson	0.31	0.19
Dickie	0.24	0.18
Harp	0.27	0.37
Plastic	0.13	0.38
Red Chalk	0.32	0.57

boundary (Wannikof et al. 1985; Upstill-Goddard et al. 1990; Wannikof et al. 1991).

DIC retention varied from –0.16 in Blue Chalk to 0.66 in Dickie. Negative retention in some lakes and the low correlation between 1/R and q_s (r = 0.25) indicate that a large in-lake source of DIC was not included in the mass balance calculations. Since particulate organic carbon fluxes from the catchments to the study lakes were very low (Dillon, unpubl. studies), the most likely source is mineralization of terrestrially derived DOC after entry into the lakes.

Sediment storage and Lake Evasion

In all lakes except Blue Chalk, DOC_{net} was greater than SED_c (Table 5), indicating a net annual loss of CO_2 to the atmosphere. Net annual evasion rates ($DOC_{net} - SED_c$) ranged from –0.35 g C m^{-2} yr^{-1} in Blue Chalk to 17.5 g C m^{-2} yr^{-1} in Crosson. When expressed per catchment area rather than lake area, evasion rates ranged from –0.2 to 2.7 g C m^{-2} yr^{-1} (Table 5).

The role of lake acidification in the DOC cycle was evaluated. There was a strong correlation (r = –0.85) between the ratio of evasion to sediment storage and lake pH (Figure 3). Of all the study lakes, Plastic Lake lost the greatest proportion of its retained C to the atmosphere, although the DIC input to Plastic Lake was relatively low (Table 5). The highest DOC "settling" rate also occurred in Plastic Lake which is the lake most affected by atmospheric acidification (Dillon et al. 1987). It is believed that Al-DOC complexation in atmospherically acidified lakes accounts for their low DOC concentration and high transparency. The results of this study suggest that high DOC mineralization or photo-oxidation rates in acidic Plastic Lake or a decrease in *in situ* DOC production compared to the other study lakes could be a cause of high apparent settling (v) and the high ratio of SED_c to net retained total C in Plastic Lake.

Table 5. C/P ratio (by weight) in surficial sediments, annual net TP gain (mg m^{-2} yr^{-1}), surficial sediment C accumulation, net TC (DIC + DOC) gain and lake evasion rates expressed per lake area and catchment area. Units for carbon fluxes are g m^{-2} yr^{-1}. The net gain is defined as total annual inputs – outflow. Lake evasion is defined as net TC gain – sediment C.

Lake	Sediment C/P	TP Gain	Sediment C	TC Gain	Evasion	
					Lake	Catchment
Blue Chalk	112	34.8	3.90	3.55	–0.35	–0.17
Chub	112	53.7	6.01	19.5	13.5	1.71
Crosson	122	41.8	5.10	22.6	17.5	1.90
Dickie	85	119.0	10.1	21.8	11.7	2.69
Harp	84	74.5	6.26	13.4	7.17	1.09
Plastic	108	20.2	2.18	10.6	8.46	2.85
Red Chalk	125	42.8	5.35	7.96	2.61	0.29

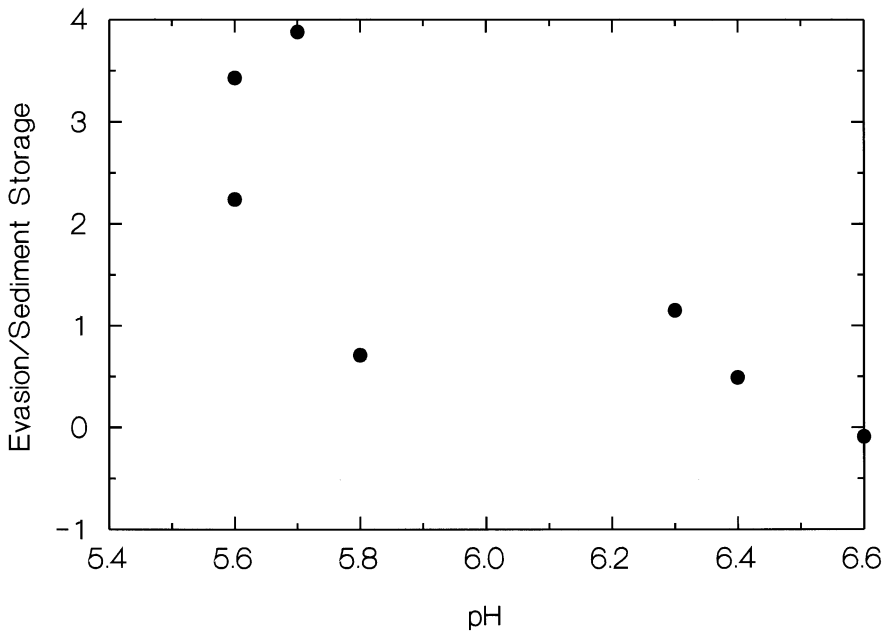

Figure 3. Ratio of carbon loss to atmospheric/sediment C storage versus pH. Results are 8 year averages (1981–1989) for the 7 study lakes.

Seasonal variation in DIC and CO_2 saturation

DIC concentrations at 1 m were high immediately following ice-out, low during summer stratification and high for a brief period during fall turnover probably due to mixing of hypolimnetic CO_2 into upper waters (Figure 4). The

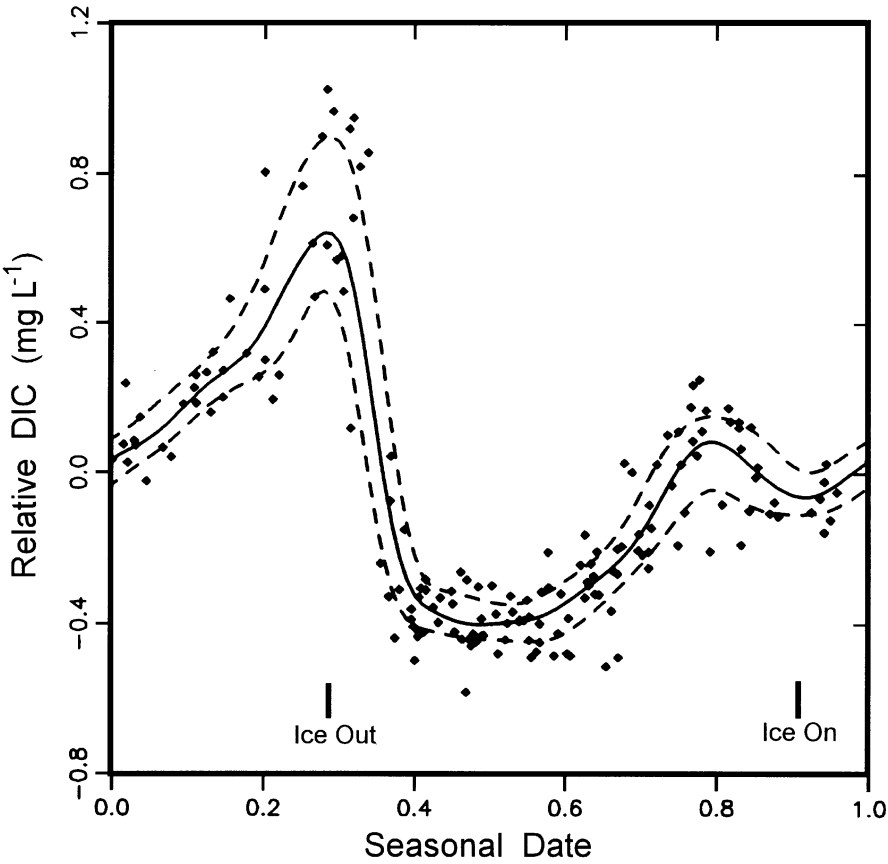

Figure 4. Relative seasonality curve of DIC at 1 m in Dickie Lake using data from June 1981 to May 1989. The median and first and third quartiles are shown.

relative seasonality using detrended time series data (Bodo 1991) was strongly significant. H_2CO_3* concentrations at 1 m were often undersaturated between late May and early August; hence, annual evasion rates estimated as DOC_{net} – SED_c probably underestimated actual invasion rates. Undersaturation was not observed in Harp Lake after early June in 1984.

Discussion

The steady state, mass balance model relating R to $v/(v + q_s)$ described DOC retention well (Figure 2) with coefficients of variation for v ranging from 10% to 22%. The DOC and DIC mass balances also showed that net annual CO_2 evasion occurred in six of the seven study lakes with a minor

amount of invasion in Blue Chalk, the lake with the lowest DOC loading. Evasion levels were probably highest during the early part of spring and fall turnover. Atmospheric invasion might have been significant at certain times of the year, particularly during the growing season. Net evasion rates were greater than stream and precipitation DIC loading rates, indicating partial mineralization of exported DOC in lakes. Net annual evasion may be typical of many unproductive lakes in temperate, boreal and arctic regions (Rao 1978; Hesslein et al. 1980; Kling et al. 1991).

Assessing the role of these lakes in regional carbon budgets depends on estimates of net annual carbon accumulation in biomass and soil. Net annual carbon accumulation rates over short periods of time can be measured as net ecosystem production (NEP) which is the difference between gross photosynthetic production and autotrophic and heterotrophic respiration. The uncertainty associated with NEP is large because small changes in gross photosynthetic production or respiration can result in large changes in NEP. NEP ranged from 56 g C m^{-2} yr^{-1} in a mixed deciduous forest in Tennessee, U.S.A. to 265 g C m^{-2} yr^{-1} in an oak-pine forest in New York, U.S.A. (Edwards et al. 1981; Whittaker et al. 1979). Mean DOC catchment export rates ranged from 1.0 to 8.3 g C m^{-2} yr^{-1} (Dillon, unpublished data) and lake evasion rates expressed per catchment area ranged from –0.2 to 2.7 g C m^{-2} yr^{-1} in this study. Therefore, if the reported NEP range is typical of our study site, forests exported up to 15% of their net annual production downstream and up to 5% was returned to the atmosphere via lakes. The amount exported and mineralized will depend upon the extent of peatlands in the catchments. Stream export of C was approximately 1% of NEP in Hubbard Brook (Whittaker et al. 1979).

Net annual carbon accumulation in the Alaskan arctic based on differences between gross ecosystem photosynthesis and respiration rates may also be overestimated because of significant terrestrial export of dissolved carbon to aquatic systems (Kling et al. 1991).

The major source of the terrestrially-derived DOC in our study lakes is likely peatlands because DOC export rates are readily described by a simple linear function based on the percent of peat coverage in the catchment (Dillon & Molot, submitted). Similar results were reported by Urban et al. (1988). DOC is probably readily leached from peatlands because of the persistent moisture saturation. The exported DOC appears to be of recent origin, because DOC in Harp Lake contains mostly recent, post-nuclear bomb carbon (Schiff et al. 1990). This suggests that buried peat, which can accumulate over thousands of years (Bowville et al. 1983), remains resistant to weathering and mineralization and that the exported DOC is likely derived from recently viable communities near the soil surface.

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References

Bowville BW, Munn RE & Hare FK (1983) The storage of non-living organic carbon in boreal and arctic zones – Canada. United States Department of Energy (DE-AS01-81EV-10688) Washington DC

Brezonik PL (1978) Effect of organic colour and turbidity of Secchi disk transparency. J. Fish. Res. Bd. Can. 35: 1410–1416

Canfield DE Jr & Hodgson LM (1983) Prediction of Secchi disc depths in Florida lakes: impact of algal biomass and organic color. Hydrobiol. 99: 51–60

Cole JJ, Caraco NF, Kling GW & Kratz TK (1994) Carbon dioxide supersaturation in the surface waters of lakes. Science 265: 1568–1570

Cross PM & Rigler FH (1983) Phosphorus and iron retention in sediments measured by mass balance calculations and directly. Can. J. Fish. Aquat. Sci. 40: 1587–1597

Dillon PJ & Evans HE (1993) A comparison of phosphorus retention in lakes determined from mass balance and sediment core calculations. Wat. Res. 27: 659–668

Dillon PJ, Lusis M, Reid RA & Yap D (1988) Ten-year trends in sulphate, nitrate and hydrogen deposition in central Ontario. Atmos. Envir. 22: 901–905

Dillon PJ & Molot LA (1990) The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. Biogeochem. 11: 23–43

Dillon PJ, Molot LA & Scheider WA (1991) Phosphorus and nitrogen export from forested stream catchments in central Ontario. J. Envir. Qual. 20: 857–864

Dillon PJ, Nicholls KN, Scheider WA, Yan ND & Jeffries DS (1986) Lakeshore Capacity Study, Trophic Status. Ont. Min. Municip. Affairs Tech. Report 89 pp

Dillon PJ, Reid RA & deGrosbois E (1987) The rate of acidification of aquatic ecosystems in Ontario, Canada. Nature (London) 329: 45–48

Edwards NT, Shugart HH Jr, McLaughlin SB, Harris WF & Reichle DE (1981) Carbon metabolism in terrestrial ecosystems. In: Reichle DE (Ed) Dynamic properties of ecosystems (pp 499–536). Cambridge University Press, New York

Evans RD & Rigler FH (1980) Measurement of whole lake sediment accumulation and phosphorus retention using lead-210 dating. Can. J. Fish. Aquat. Sci. 37: 817–822

Girard R, Reid RA & Snyder WR (1985) The morphometry and geology of Plastic and Heney lakes and their catchments. Ont. Min. Envir. Data Report DR 85/1

Hengeveld H (1991) Understanding atmospheric change. State of the Environment Report No. 91–2, Environment Canada, Ottawa, Canada

Herczeg AL, Broecker WS, Anderson RF, Schiff SL & Schindler DW (1985) A new method for monitoring temporal trends in the acidity of freshwaters. Nature 315: 133–135

Herczeg AL & Hesslein RH (1984) Determination of hydrogen ion concentration in softwater lakes using carbon dioxide equilibria. Geochim. Cosmochim. Acta 48: 837–845

Hesslein RH, Rudd JWM, Kelly C, Ramlal P & Hallard KA (1991) Carbon dioxide pressure in surface waters of Canadian lakes. In: Wilhelms SC & Gulliver JS (Eds) Air-Water Mass Transfer, Second International Symposium on Gas Transfer at Water Surfaces (pp 413–431). Am. Soc. Civil Eng., New York, NY

Hesslein RH, Broecker WS, Quay PD & Schindler DW (1980) Whole-lake radiocarbon experiment in an oligotrophic lake at the Experimental Lakes Area, northwestern Ontario. Can. J. Fish. Aquat. Sci. 37: 454–463

Jeffries DS & Snyder WR (1983) Geology and geochemistry of the Muskoka-Haliburton study area. Ont. Min. Envir. Data Report DR 83/3

Kelly CA, Rudd JWM, Furutani A & Schindler DW (1984) Effects of lake acidification on rates of organic matter decomposition in sediments. Limnol. Oceanogr. 29: 687–694

Kling GW, Kipphut GW & Miller MC (1991) Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 251: 198–301

Kurz WA, Apps MJ, Webb TM & McNamee PJ (1992) The carbon budget of the Canadian forest sector: Phase I. Information Report NOR-X-326, Forestry Canada, Northwest Region, Northern Forestry Centre, 5320-122 Street, Edmonton, Alberta, Canada, T6H 3S5

Lind OT (1986). The effect of non-algal turbidity on the relationship of Secchi depth to chlorophyll *a*. Hydrobiol. 140: 27–35

Locke BA & Scott LD (1986) Studies of lakes and watersheds in Muskoka-Haliburton, Ontario: methodology (1976–1985). Ont. Min. Envir. Data Report DR 86/4

Lorenzen MW (1980). Use of chlorophyll-Secchi disk relationships. Limnol. Oceanogr. 25: 371–372

Megard RO, Settles JC, Boyer HA & Combs WS Jr (1980) Light, Secchi disks and trophic states. Limnol. Oceanogr. 25: 373–377

Mierle G & Ingram R (1991) The role of humic substances in the mobilization of mercury from watersheds. Wat. Air Soil Pollut. 56: 349–357

Molot LA & Dillon PJ (1991) Nitrogen phosphorus ratios and the prediction of chlorophyll in phosphorus-limited lakes in central Ontario. Can. J. Fish. Aquat. Sci. 48: 140–145

Molot LA, Dillon PJ, Clark BJ & Neary BP (1992) Predicting end-of-summer oxygen profiles in stratified lakes. Can. J. Fish. Aquat. Sci. 49: 2363–2372

Molot LA & Dillon PJ (1993) Nitrogen mass balances and denitrification rates in central Ontario lakes. Biogeochem. 20: 195–212

Molot LA, Dillon PJ & LaZerte BD (1989) Factors affecting alkalinity concentrations of streamwater during snowmelt in central Ontario. Can. J. Fish. Aquat. Sci. 46: 1658–1666

Norton SA & Henriksen A (1983) The importance of CO_2 in evaluation of effects of acidic deposition. Vatten 39: 346–354

Ontario Ministry of the Environment (1983) Handbook of analytical methods for environmental samples. Vols. 1 and 2, Toronto, Ontario, Canada

Rao G (1978) Carbon-13 depletion in a subalpine lake: carbon-flow implications. Science 201: 901–902

Reid RA, Girard R & Nicolls AC (1987) Morphometry and catchment areas for the calibrated watersheds. Ont. Min. Envir. Data Report DR 87/4

Schiff SL, Aravena R, Trumbore SE & Dillon PJ (1990) Dissolved organic carbon cycling in forested watersheds: a carbon isotopic approach. Wat. Resourc. Res 26: 2949–2957

Schindler DW (1971) Light, temperature and oxygen regimes of selected lakes in the Experimental Lakes Area (ELA), northwestern Ontario. J. Fish. Res. Board Can. 28: 157–170

Schindler DW & Fee EJ (1973) Diurnal variation of dissolved inorganic carbon and its use in estimating primary prodution and CO_2 invasion in Lake 227. J. Fish. Res Bd. Can. 30: 1501–1510

Schindler DW, Lean DRS & Fee EJ (1975) Nutrient cycling in freshwater ecosystems. In: Productivity of world ecosystems; proceedings of a symposium. National Academy of Sciences, Washington, DC

Schindler DW, Bayley SE & Parker BR (1995) The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. Limnol. Oceanogr. (in press)

Stumm W & Morgan JJ (1981) Aquatic chemistry, 2nd edition. John Wiley and Sons, Toronto, 780 pp

Upstill-Goddard RC, Watson AJ, Liss PS & Liddicoat MI (1990) Gas transfer velocities in lakes measured with SF_6. Tellus 42B: 364–377

Urban NR, Bayley SE & Eisenreich SJ (1988) Export of dissolved organic carbon and acidity from peatlands. Wat. Resourc. Res. 25: 1619–1628

Wannikof R, Ledwell JR & Broecker WS (1985). Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. Science 227: 1224–1226

Wannikof R, Ledwell JR & Crusius J (1991). Gas transfer velocities on lakes measured with sulfuf hexafluoride. In: Wilhelms SC & Gulliver JS (Eds) Air-Water Mass Transfer, Second International Symposium on Gas Transfer at Water Surfaces (pp 441–458). Am. Soc. Civil Eng., New York, NY

Whittaker RH, Likens GE, Bormann FH, Eaton JS & Siccama TG (1979) The Hubbard Brook ecosystem study: forest nutrient cycling and element behaviour. Ecol. 60: 203–220