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Nitrogen mass balances and denitrification rates in central Ontario Lakes

LEWIS A. MOLOT[1] & PETER J. DILLON[2]

[1] *Faculty of Environmental Studies, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3;* [2] *Ontario Ministry of Environment and Energy, Dorset Research Centre, P.O. Box 39, Bellwood Acres Road, Dorset, Ontario, Canada P0A 1E0*

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Abstract. Nitrogen mass balances for seven unproductive lakes and 20 forested catchments in central Ontario were measured between 1977 and 1989. Average annual lake denitrification rates calculated with the N/P ratio method were strongly correlated with summer anoxic factor (extent of surficial sediment anoxia) whereas denitrification rates calculated with a ^{210}Pb sediment N accumulation method were poorly correlated with the anoxic factor suggesting that the N/P method is superior. Substantial denitrification occurred in all lakes — an average of 36% of TN inputs or 75% of the net gain. On a regional area-weighted basis, 67% of bulk atmospheric TN deposition was stored or denitrified terrestrially, 12% was denitrified in lakes, 4% was stored in lake sediments, and 17% was exported from lakes. N/P ratios were generally less in streams than in precipitation suggesting preferential N retention in catchments, whereas the N/P ratios in lake outputs were slightly higher than lake input ratios, suggesting preferential P retention in lakes. This is consistent with the notion that P-limited lakes can exist adjacent to N-limited forests.

Introduction

Denitrification in lakes has been studied extensively, most often using direct measurement techniques. These methods provide information on controlling environmental factors (Messer & Brezonik 1984), on spatial variation in rates within a lake, or on short-term temporal variation in rates (Keeney et al. 1971; Chan & Campbell 1980; Messer & Brezonik 1983; Seitzinger 1988). Lake denitrification has also been estimated using the mass-balance approach, i.e. as the residual (unmeasured) term in a measured mass balance (Ahlgren 1967; Andersen 1974; Serruya 1975; Messer & Brezonik 1978, 1983). While mass-balance studies are not suited to studies of small-scale spatial or short-term temporal variation, they can provide reliable estimates of longer term denitrification rates over large areas. Hence, mass-balance studies are well suited to estimating the long-term importance of lake denitrification to regional N budgets provided that an appropriate number of lakes are investigated.

Mass-balance studies typically use flux measurements of dissolved and particulate N and P into and out of lakes and N/P ratios in surficial sediments to estimate lake denitrification rates (Ahlgren 1967; Andersen 1974; Messer & Brezonik 1978, 1983; Serruya 1975). This technique is effective because no P is lost via gas phase reactions. However, these studies have often lasted 2 years or less; hence, there is some uncertainty about how representative the flux estimates are of longer time periods because of significant annual variation (Messer & Brezonik 1978, 1983; Serruya 1975; Dillon & Molot 1990; Dillon et al. 1991). Furthermore, surficial sediment N/P ratios represent average accumulation over longer time periods than annual flux measurements. An alternative to the use of sediment N/P ratios is the use of sediment dating techniques, such as the ^{210}Pb method to measure sediment accumulation of N in conjunction with mass balances. Loss of N from the system is then calculated as the residual in the mass balance, i.e. denitrification is equal to total of all inputs less the loss via outflow and to the sediments. Dillon & Evans (1993) used the latter approach to compare retained total phosphorus (TP) to TP accumulation in sediments.

Nitrogen mass balances for seven lakes and 20 forested catchments in central Ontario were monitored between 1977 and 1989 as part of a long-term study of the effects of atmospheric deposition (Dillon & Molot 1990). The objectives of this study were to (1) present long-term (12 year) N flux data over a relatively large region, (2) compare average annual lake denitrification rates using N/P and ^{210}Pb sediment accumulation methods, (3) examine between-lake variation in denitrification rates and (4) compare N/P ratios in precipitation, streams and lake discharges.

Study sites

The seven study lakes are located in south-central Ontario, in the County of Haliburton or the District of Muskoka (Fig. 1). They are headwater lakes with the exception of Red Chalk Lake which receives discharge from Blue Chalk Lake.

The catchments are primarily forested with some cottage development and are underlain by Precambrian metamorphic plutonic and volcanic silicate bedrock. Minor till plains (continuous moraine deposits >1 m thick) and thin till deposits (<1 m thick) interrupted by rock ridges represent the dominant surficial geological characteristics. The depth of

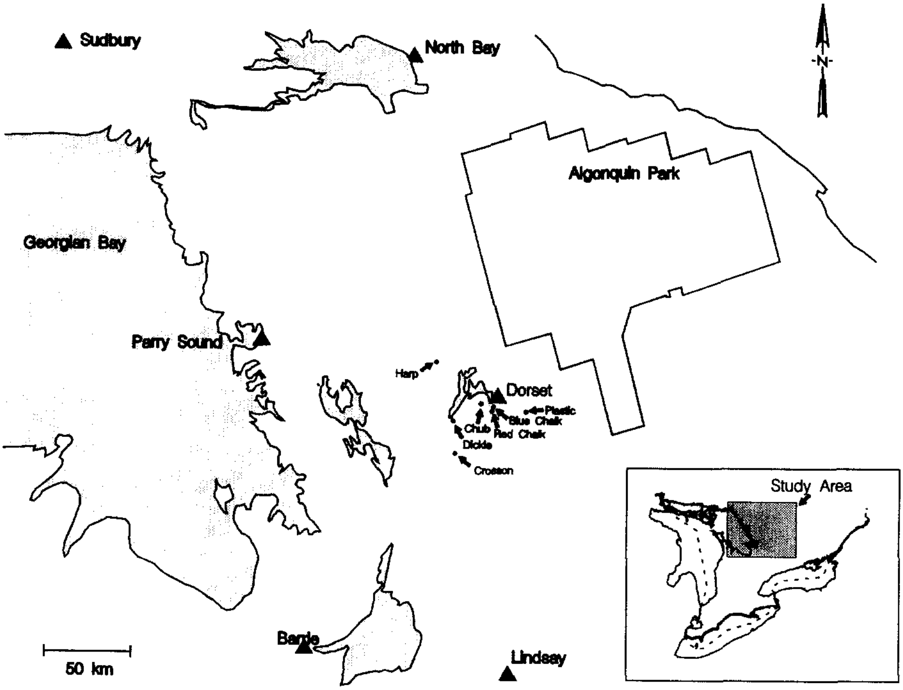

Fig. 1. Map of study area showing location of lakes.

overburden to bedrock ranges from 1 to 10 m in most locations; hence, deep seepage losses are considered negligible. The soil profiles are poorly developed. Detailed descriptions of the geology and physiography of the catchments can be found in Jeffries & Snyder (1983), Girard et al. (1985), Seip et al. (1985), Dillon et al. (1987, 1991) and Reid et al. (1987). The catchments are not in an early successional state, and hence, N fixation is assumed to be negligible (Boring et al. 1988).

The lakes are softwater (mean conductivity ranged from 29 to 38 uS) and oligotrophic to slightly mesotrophic with long-term mean annual whole-lake total phosphorus (TP) concentrations ranging from 5.2 μg L^{-1} in Red Chalk to 10.9 μg L^{-1} in Dickie, long-term mean TP at spring turnover ranging from 5.8 μg L^{-1} in Red Chalk to 12.7 μg L^{-1} in Crosson, and ice-free chlorophyll *a* ranging from 1.9 μg L^{-1} in Blue Chalk to 4.7 μg L^{-1} in Dickie (Molot & Dillon 1991). Long-term mean epilimnetic TN/TP (TN = total Kjeldahl N + NO_3^--N) was greater than 29 (by weight) for all lakes, hence, the lakes are considered P-limited. Mean Secchi depth during summer stratification ranged from 2.8 m in Dickie to

6.8 m in Blue Chalk and Plastic, and mean annual whole-lake dissolved organic carbon (DOC) ranged from 1.75 mg C L^{-1} in Blue Chalk to 5.0 mg C L^{-1} in Dickie (Table 1).

Table 1. Lake surface area (A_o), catchment area excluding lake area (A_d), mean depth ($\bar{z}$), mean whole-lake TP concentration (1977/78—88/89), and mean Secchi depth during summer stratification. Sampling of Crosson began in 1980 and sampling of Plastic began in 1979. The east basin of Red Chalk was not sampled 1980/81—1982/83.

Lake	A_o (ha)	A_d (ha)	$\bar{z}$ (m)	TP (μg L^{-1})	Secchi (m)
Blue Chalk	52.35	105.9	8.5	6.2	6.8
Chub	34.41	271.8	8.9	10.4	3.3
Crosson	56.74	521.8	9.2	10.6	3.6
Dickie	93.6	406.4	5.0	10.9	2.8
Harp	71.38	470.7	13.3	7.4	3.8
Plastic	32.14	95.5	7.9	5.9	6.8
Red Chalk	57.13	532.4	14.2	5.2	5.0

Methods

Water and sediment collection techniques are described in detail in Dillon & Evans (1992). Water samples were filtered through 80-μm polyester mesh into pre-rinsed Nalgene bottles and placed in temperature-controlled containers while in transit to the laboratories.

Bulk precipitation and precipitation depth were 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 fitted with fibreglass window screening to prevent insect contamination leading into 18-L glass bottles (summer) or 43-cm diameter × 63-cm high polyethylene containers (winter) when there was sufficient volume for all chemical analyses. Collection periods ranged from 1 to 40 days, although samples were typically removed weekly.

Stream samples were collected approximately one to four times per month from 1977 to 1989. Sampling began in 1979 in the Plastic Lake catchment and in 1980 in the Crosson Lake catchment. Water level or stage was recorded continuously and measured instantaneously at regular intervals at weirs or flumes installed on the study streams (Scheider et al. 1983). Stage-discharge relationships were constructed for each stream.

One station in each lake was sampled one to four times per month from 1977 to 1989 with the exception of Red Chalk, which has two distinct basins separated by a shallow (<2 m), narrow channel. Both the main and east basins were sampled except for the three-year period 1980/81 to 1982/83, when the east basin was not studied. Sampling began in 1979 in Plastic Lake and in 1980 in Crosson Lake. The samples were collected as integrated volume-weighted epilimnetic, metalimnetic and hypolimnetic samples, with the appropriate depths determined from temperature profiles taken during summer stratification, or in tube composites at all other times of the year. The whole-lake N concentrations on any given sampling day during summer stratification were calculated by mathematically weighting the concentrations in the three strata according to the relative proportions of each strata within the lake. Samples for oxygen analysis were also collected, but the individual samples (generally every 2 m) were not combined (Molot et al. 1992).

Stream, lake and precipitation samples were analyzed for ammonium nitrogen (NH_4^+-N), total Kjeldahl nitrogen (TKN) and total nitrate plus nitrite (NO_3^--N). Analytical methods are described in detail in Ontario Ministry of the Environment (1983). In this report, lake concentrations are annual whole-lake. Total N (TN) was calculated as TKN + NO_3^--N, total inorganic N (TIN) as NO_3^--N + NH_4^+-N and total organic N (TON) as TKN − NH_4^+-N.

The annual deposition of TN from precipitation for each bulk collector was calculated by multiplying the TN concentration in a sample by the cumulative precipitation depth for the sampling period and then adding results for all of the sampling periods. TN loads for the gauged inflow streams and the outflows were calculated by multiplying the TN concentration in the inflows and outflow (measured during the midpoint of a time period) by the total discharge over that time period. Input of TN to the lake from ungauged portions of the watersheds was estimated by extrapolating the output per unit of basin area from the gauged areas of the basins.

As there is extensive shoreline cottage development on two of the lakes (Harp and Dickie Lakes), potential anthropogenic inputs of TN from sewage disposal systems were derived by multiplying estimates of septic TP inputs (Dillon et al. 1992) by an N/P ratio of 6 (Brandes 1978). Because of the uncertainty associated with soil retention of N in the septic effluent, the data are presented as upper (no retention of N in the soil/septic system) and lower (100% retention) estimates of the loading. We considered the potential anthropogenic inputs only in the TN mass balances as the N species in the septic effluents are unknown.

Annual net gain of TN for each lake, TN_{net}, (mg m^{-2} yr^{-1}) was calculated as the difference between the total inputs of TN to the lake (i.e. from precipitation, runoff and septic systems) and the export of TN from the lake, divided by the lake area. Retention, R, is defined as TN_{net}/total input, and in the case of the individual species (NH_4^+-N, NO_3^--N, TON) includes loss via conversion to other species. Net gain and retentions of other nitrogen fractions were calculated analogously. Nitrogen fixation was not measured, but large filamentous or colonial Cyanophyta were typically much less than 10% of the average, ice-free phytoplankton biovolume in the study lakes (Ken Nicholls, Ont. Min. Envir., unpubl. data). The apparent settling velocity, v(m yr^{-1}), was calculated from $R = v/(v + q_s)$, where q_s is the areal water discharge rate (m yr^{-1}) (Reckhow & Chapra 1983). This provides a generalized rate constant for loss of N from the lake by all processes other than via outflow, i.e. v integrates burial in sediments and loss by denitrification.

Between 36 and 94 sediment cores were collected with a K-B gravity corer from the accumulating areas of each lake in 1978, 1979 and 1980 (Dillon & Evans 1993). Replicate cores were taken from each site, sectioned into 1-cm slices to a depth of 20 cm and combined to provide sufficient material for TP, TN, stable Pb and ^{210}Pb analyses. All sediment samples were dried at 100—105 °C for a minimum of 24 hours and ground to a fine powder. Subsamples for chemical analyses were digested in hot sulfuric acid with potassium persulfate. TP and TN were measured after eliminating interfering Fe by precipitation and filtration (Ontario Ministry of the Environment 1983). TN sediment accumulation rates (N_{sed}) were determined for surficial sediments (0 to 3 cm) from average whole-lake sediment accumulation rates and average whole-lake TN concentrations (Dillon & Evans 1993).

Results

Atmospheric deposition

Average atmospheric deposition from 1977—89 for NH_4^+-N, NO_3^--N and TON was 392, 562 and 172 mg N m^{-2} yr^{-1}, respectively, for a total deposition of 1,130 mg N m^{-2} yr^{-1}. TP deposition during the same period averaged 22 mg m^{-2} yr^{-1}; hence, the TN/TP ratio was 51 by weight.

TN inputs in bulk precipitation were at the high end of the range reported by Boring et al. (1988) for selected ecosystems in the United States (110—1240 mg N m^{-2} yr^{-1}). The highest value reported by Boring et al. (1988) occurred in eastern Tennessee in close proximity to coal-fired power plants. Trends in NO_3^--N emissions and deposition in eastern North America have been reported elsewhere (Dillon et al. 1988).

N loading and retention

Annual variation in NO_3^--N, NH_4^+-N and TON input and loss via outflow for any of the study lakes typically varied about two-fold (Tables 2—4), but greater ranges sometimes occurred. For example, NH_4^+-N outflow in 1978/79 in Red Chalk was eight times the annual outflow in 1986/87.

The average long-term loading of TN ranged two-fold from 1550 mg m^{-2} yr^{-1} in Plastic Lake to 3180 mg m^{-2} yr^{-1} in Red Chalk Lake (Table 5). Hence, direct atmospheric deposition to lakes was an important source of TN, accounting for 35% to 73% of inputs to the study lakes, excluding the potential contribution from shoreline development. The annual net difference between input and output via outflow of TN (TN_{net}) includes both accumulation in the sediments and loss from the system via denitrification. This net 'gain', assuming no loading from the septic systems, ranged from 990 mg m^{-2} yr^{-1} in Plastic Lake (64% of input) to 1495 mg m^{-2} yr^{-1} in Harp Lake (48% of input) (Table 5).

The potential contribution of N from the shoreline development (Table 5) was insignificant in 5 cases, representing a maximum of 4% of the total

Table 2. Mean and standard deviation of NO_3^--N inputs and outputs (mg N m^{-2} yr^{-1}) and areal water load, q_s (m yr^{-1}), during 1977/78—1988/89 in the study lakes. L — load, L_o — outflow from lake, v — apparent settling coefficient (m yr^{-1}) calculated as $R \cdot qs/(1 - R)$ where R is retention and q_s is the areal water discharge (m yr^{-1}) and is equivalent to the total discharge from the lake divided by the lake area. Sampling of Plastic began in 1979 and sampling of Crosson began in 1980. Cottage inputs are excluded.

Lake		q_s	L	L_o	R	v
Blue Chalk	mean	1.59	680	88	0.87	12.5
	sd	0.30	105	30	0.05	5.9
Chub	mean	4.41	827	423	0.48	4.2
	sd	0.75	281	108	0.10	1.5
Crosson	mean	5.75	891	623	0.29	2.4
	sd	1.11	167	91	0.06	0.6
Dickie	mean	2.78	646	207	0.67	7.0
	sd	0.59	115	68	0.11	4.2
Harp	mean	4.26	1211	579	0.52	4.9
	sd	0.70	165	130	0.11	2.2
Plastic	mean	2.08	601	119	0.80	9.1
	sd	0.41	64	32	0.05	3.3
Red Chalk	mean	5.77	1128	665	0.38	4.0
	sd	1.03	394	129	0.14	3.5

Table 3. Mean and standard deviation of NH_4^+-N inputs and outputs (mg N m^{-2} yr^{-1}) during 1977/78—1988/89 in the study lakes. L — load, L_o — outflow from lake, v — apparent settling coefficient (m yr^{-1}) defined as $R \cdot qs/(1 - R)$ where R is retention and qs is the areal water discharge (m yr^{-1}). Sampling of Plastic began in 1979 and sampling of Crosson began in 1980. Cottage inputs are excluded.

Lake		L	L_o	R	v
Blue Chalk	mean	429	51	0.88	13.3
	sd	84	19	0.04	4.8
Chub	mean	462	95	0.80	20.1
	sd	122	48	0.06	7.8
Crosson	mean	662	157	0.76	19.2
	sd	85	35	0.05	4.5
Dickie	mean	447	92	0.80	16.9
	sd	90	38	0.07	17.1
Harp	mean	502	66	0.88	37.2
	sd	98	40	0.05	20.1
Plastic	mean	380	73	0.81	10.0
	sd	48	35	0.07	3.6
Red Chalk	mean	616	157	0.76	20.0
	sd	184	88	0.07	7.9

potential input. However, in the cases of Dickie and Harp Lakes, this potential anthropogenic input could constitute 18% of the total input of TN (assuming 0% retention; subsequent calculations are presented with and without this potential component included).

Retention of NH_4^+-N was uniformly high in the study lakes (0.75—0.88, Table 3) whereas TON retention was uniformly low (0.24—0.37, Table 4). Retention of NO_3^--N was more variable, ranging from 0.30 in Crosson to 0.85 in Blue Chalk (Table 2). Settling coefficients were highest for NH_4^+-N and lowest for TON (Tables 2—5).

A representative settling coefficient for the study lakes can be taken as the mean of the individual lake values or as the reciprocal of the slope of the linear regression of 1/R versus q_s (Dillon & Molot 1990). In each case, we used the long-term average measured retention coefficients rather than the data for individual years. The two methods agree quite closely for TN but not for individual fractions (Table 6). Mean v was higher than the regression v for NO_3^- and TIN but was lower than regression v for NH_4^+ and TON. The mean settling coefficient for TN, v_{TN}, was 3.6 m yr^{-1} compared to 3.5 m yr^{-1} using the regression method (Table 6, Fig. 2). The

Table 4. Mean and standard deviation of TON inputs and outputs (mg N m^{-2} yr^{-1}) during 1977/78—1988/89 in the study lakes. L — load, L_o — outflow from lake, v — apparent settling coefficient (m yr^{-1}) defined as R · qs/(1 − R) where R is retention and q_s is the areal water discharge (m yr^{-1}). Sampling of Plastic began in 1979 and sampling of Crosson began in 1980. Cottage inputs are excluded.

Lake		L	L_o	R	v
Blue Chalk	mean	442	277	0.37	1.0
	sd	148	108	0.12	0.4
Chub	mean	1480	1130	0.24	1.4
	sd	298	303	0.10	0.7
Crosson	mean	1900	1430	0.25	1.9
	sd	269	327	0.07	0.6
Dickie	mean	1160	795	0.32	1.3
	sd	290	227	0.11	0.5
Harp	mean	1400	976	0.31	1.9
	sd	303	267	0.07	0.6
Plastic	mean	563	361	0.38	1.3
	sd	84	140	0.11	0.4
Red Chalk	mean	1440	1055	0.26	2.1
	sd	416	289	0.07	1.0

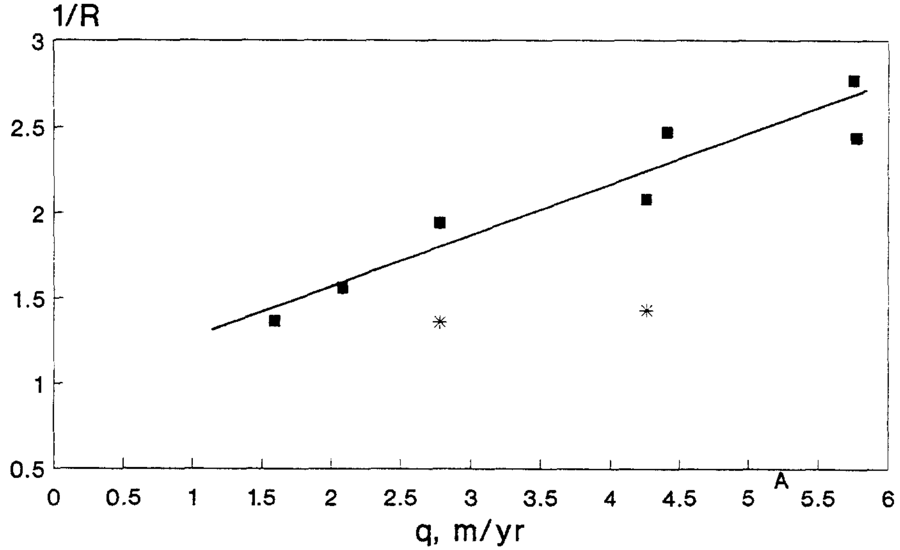

Fig. 2. 1/R for TN versus mean annual areal water discharge (m yr^{-1}) without cottage inputs. Harp and Dickie Lakes are also shown with potential cottage inputs (*).

Table 5. Mean and standard deviation of TN inputs and outputs (mg N m^{-2} yr^{-1}) during 1977/78—1988/89 in the study lakes. L_N — natural load, L_A — potential input from shoreline cottages, L_o — outflow from lake, N_{sed} — sediment N accumulation rate (^{210}Pb method), R is retention, v is the apparent settling coefficient calculated as $R \cdot q_s/(1 - R)$ excluding cottage inputs. Sampling of Plastic began in 1979 and sampling of Crosson began in 1980.

Lake		L_N	L_o	L_A	N_{sed}	R	v
Blue Chalk	mean	1550	415	65	394	0.73	4.5
	sd	294	128	—	—	0.05	1.0
Chub	mean	2770	1650	47	1040	0.40	3.0
	sd	536	367	—	—	0.09	1.0
Crosson	mean	3450	2210	34	1190	0.36	3.2
	sd	330	376	—	—	0.06	0.5
Dickie	mean	2260	1090	498	524	0.51	3.0
	sd	408	257	—	—	0.08	0.8
						(0.60)[1]	(4.2)[1]
Harp	mean	3120	1620	685	574	0.48	4.1
	sd	407	376	—	—	0.08	1.2
						(0.57)[1]	(5.7)[1]
Plastic	mean	1540	553	0	675	0.65	3.9
	sd	175	183	—	—	0.07	0.8
Red Chalk	mean	3180	1880	7	702	0.40	4.0
	sd	776	437	—	—	0.09	1.7

[1] R and v including cottage inputs are shown in brackets for Harp and Dickie Lakes.

Table 6. Comparison of settling coefficients (m yr^{-1}) for NO_3^--N, NH_4^+-N, TON, TIN and TN excluding cottage inputs using mean and regression ($1/R$ versus q_s) methods.

	Mean v	*Regression v*
NO_3^--N	5.5	2.4
NH_4^+-N	16.0	32.6
TON	1.5	3.3
TIN	7.4	5.3
TN	3.6	3.5

y-intercept for $1/R_{TN}$ versus q_s was 1.0 which is identical to the theoretical value of 1 and the coefficient of determination, R^2, was 0.90.

When the potential loading from the septic systems in the cases of Harp and Dickie Lakes was included, the net gain of TN increased from 1495 to 2180 mg m^{-2} yr^{-1} in Harp Lake and from 1160 to 1660 mg m^{-2} yr^{-1}

in Dickie Lake (Table 5). The data suggest that soils may retain significant amounts of N from septic effluent. Soils may also retain significant amounts of TP from the septic systems (Dillon et al. 1992).

Denitrification

^{210}Pb method. Mean annual denitrification rate, DNF, was calculated from,

$$\mathrm{DNF} = \mathrm{TN}_{\mathrm{net}} - \mathrm{TN}_{\mathrm{sed}} \tag{1}$$

where $\mathrm{TN}_{\mathrm{sed}}$ is the sediment accumulation rate of TN. Assuming negligible cottage inputs, the mean annual denitrification rate was 479 mg m^{-2} yr^{-1}, ranging 18-fold from 52 mg m^{-2} yr^{-1} in Crosson Lake (4% of net gain) to 920 mg m^{-2} yr^{-1} in Harp Lake (62% of net gain) (Table 7). Mean annual denitrification rate was poorly correlated with summer anoxic factor ($r = -0.32$, Fig. 3a), a measure of the degree of summer anoxia experienced by sediments (Nurnberg 1984). This measure integrates spatial and temporal anoxia, and is equivalent to the length of time that an area equal to the hypolimnetic sediment area is overlain by anoxic water.

When cottage inputs were included, the mean annual denitrification rate was 670 mg m^{-2} yr^{-1}, ranging 13 fold from 86 mg m^{-2} yr^{-1} in Crosson Lake (7% of net gain) to 1610 mg m^{-2} yr^{-1} in Harp Lake (74% of net gain). The inclusion of septic loads increased the apparent denitrification rate in Dickie and Harp Lakes substantially. However, mean annual denitrification rate was still poorly correlated with summer anoxic factor ($r = -0.30$).

Table 7. Denitrification rate, DNF, calculated with the ^{210}Pb method (mg m^{-2} yr^{-1}), and % net gain denitrified with and without cottage inputs. AF — mean summer anoxic factor (days) from 1977 to 1988. Plastic was not sampled in 1977 and 1978.

	With cottage input		No cottage input		
Lake	DNF	%DNF	DNF	%DNF	AF
Blue Chalk	807	67	742	65	17.0
Chub	131	11	84	8	20.5
Crosson	86	7	52	4	13.3
Dickie	1135	68	638	55	31.3
Harp	1605	74	920	62	1.2
Plastic	316	32	316	32	23.2
Red Chalk	609	46	602	46	11.6
Mean	670	44	479	39	

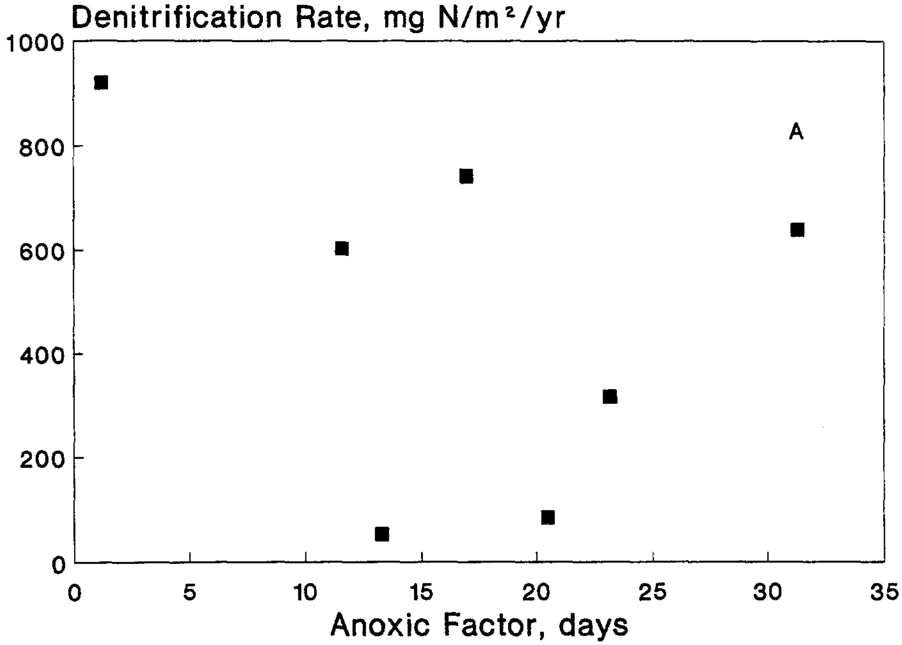

Fig. 3a. Plot of denitrification rate versus summer anoxic factor. Denitrification was calculated using ^{210}Pb method without cottage inputs.

N/P ratio method. Denitrification rates were also estimated from N/P ratios (N/P_{net}) of the retained nutrients (retained nutrient = inputs − outflow) and surficial sediments (N/P_{sed}) (Table 8),

$$DNF = TN_{net}(N/P_{net} - N/P_{sed})/(N/P_{net}) \qquad (2)$$

This method assumes that all retained P is stored in the sediments, and it avoids having to calculate whole-lake sediment and N-accumulation rates. Detailed TP budgets will be presented elsewhere.

Using this approach, the average denitrification rate excluding cottage inputs was 917 mg m^{-2} yr^{-1} with a range of 777 mg m^{-2} yr^{-1} in Dickie to 1210 mg m^{-2} yr^{-1} in Harp. An average of 76% of the net gain, 36% of the total natural loads or 81% of direct atmospheric deposition was denitrified.

Using the N/P ratio method, denitrification rates (without cottage inputs) were strongly correlated with summer anoxic factor, AF (−0.91) (Fig. 3b) and mean depth (0.73). Denitrification was strongly correlated with net gain although this may be a spurious correlation because denitrification is defined as a linear function of TN_{net} (equation 2).

Table 8. Average annual TN/TP ratios (by weight) in total inputs to lake excluding cottages (stream + precipitation + groundwater) (In), lake outflow (Out), net gain (inputs — outflow) and sediments (Sed). Denitrification rate was calculated using the N/P method. TN data from Table 5, TP data from Dillon (unpubl. data).

	TN/TP				Denitrification	
	In	Out	Net gain	Sed	% of net gain	mg m^{-2} yr^{-1}
Blue Chalk	47	47	47	7.9	84	946
Chub	33	41	26	8.7	66	739
Crosson	37	39	34	8.0	78	954
Dickie	27	37	22	7.3	67	777
Harp	37	51	29	5.5	80	1210
Plastic	47	43	49	8.5	83	819
Red Chalk[1]	44	61	31	7.9	75	974
Main				6.8		
East				11.7		
Mean	39	46	34	7.7	76	917

[1] The mean sediment N/P ratios for the east and main basins of Red Chalk were area-weighted to obtain a whole-lake value.

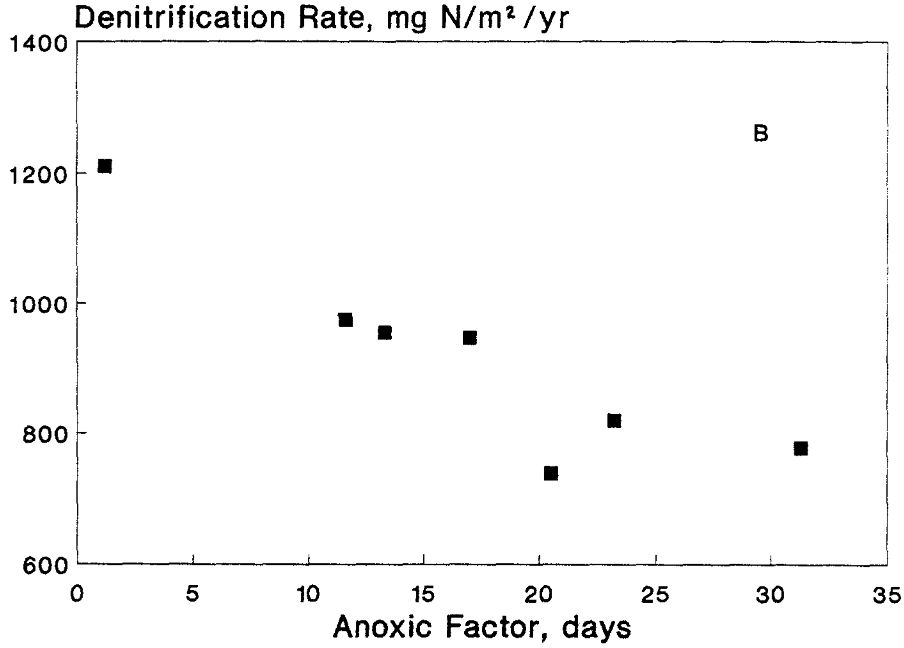

Fig. 3b. Plot of denitrification rate versus summer anoxic factor. Denitrification was calculated using N/P method without cottage inputs.

The average denitrification rate of 76% of the average net gain is much higher than the average of 46% of the net gain calculated using the ^{210}Pb method (Tables 7 and 8). The discrepancy between the two methods is likely due to errors in estimating average whole-lake sediment and N accumulation rates using the ^{210}Pb method rather than errors in estimating sediment N/P ratios.

Surficial sediment N/P ratios were remarkably similar at the 36 sediment collection sites in the 7 lakes. N/P ratios ranged from 4.0 to 11.9 with a pooled mean of 7.9. Mean within-lake N/P ratios ranged from 5.5 in Harp to 8.7 in Chub (Table 8). The mean sediment N/P ratio in the east basin of Red Chalk was slightly higher at 11.7. Since the net gain N/P ratios were substantially higher in all lakes (ranging from 22 in Dickie to 49 in Plastic) than the sediment N/P ratios, the sediment N/P ratios were quite similar, and denitrification using the N/P method was strongly correlated with anoxic factor, we conclude that substantial denitrification occurred in all lakes and the ^{210}Pb method is not as accurate as the N/P method.

On a regional basis, the total mass of N denitrified in the lakes was 12% of bulk deposition in the catchments and lakes. Hence, the lakes were significant vehicles regionally for the return of N to the atmospheric N_2 pool. Catchments retained an area-weighted average of 67% of atmospheric TN deposition (Dillon et al. 1991) but it is not known how much of this was denitrified. Lakes retained 4% of bulk TN deposition in the catchments and lakes.

A linear regression of denitrification rate (without cottage inputs) versus summer anoxic factor (AF) yielded the regression (Fig. 3b),

$$\mathrm{DNF} = 1172.9 - 15.17\,\mathrm{AF}$$

$$R^2 = 0.83, F = 24.1, P > 0.0045. \tag{3}$$

When cottage inputs were included the coefficient of determination was higher (0.90) and,

$$\mathrm{DNF} = 1234.8 - 19.74\,\mathrm{AF}$$

$$R^2 = 0.90, F = 46.0, P > 0.0011. \tag{4}$$

N/P ratios

Streams were somewhat depleted of N relative to P when compared to precipitation. The average long-term, volume-weighted N/P in 18 of 20 tributaries to the study lakes during 1976 to 1984 ranged from 11 to 49 with a mean of 30 by weight (Dillon et al. 1991). The remaining two streams, HP3A and PC1, had ratios of 93 and 175, respectively. The N/P ratio in bulk precipitation was 51.

While N/P ratios were generally less in streams than in precipitation suggesting preferential N retention in catchments, the N/P ratios of average lake outputs were slightly higher than input ratios, suggesting preferential P retention in lakes (Tables 8 and 9).

Table 9. Average annual TN/TP ratios (by weight) in total inputs to lake (stream + cottage + precipitation + groundwater) (In), lake outflow (Out) and net gain (inputs − outflow). Denitrification was calculated using the N/P method. Data from Table 2 and Dillon (unpubl. data).

	TN/TP			Denitrification	
	In	Out	Net gain	% of net gain	mg m^{-2} yr^{-1}
Blue Chalk	37	47	34	77	925
Chub	31	41	23	61	717
Crosson	35	39	31	74	943
Dickie	17	37	12	40	669
Harp	19	51	13	58	1268
Plastic	47	43	49	83	819
Red Chalk	43	61	31	74	972
Mean	33	46	28	67	902

Discussion

Substantial denitrification occurred in all lakes, averaging 36% of TN inputs or 75% of the net gain of TN. On a regional area-weighted basis, 67% of bulk atmospheric TN deposition was stored or denitrified terrestrially, 12% was denitrified in lakes, 4% was stored in lake sediments, and 17% was exported downstream from lakes. Lakes received 27–65% of their TN loading from their surrounding catchments, in spite of apparent N limitation of terrestrial systems.

Denitrification was strongly negatively correlated with anoxic factor, or temporal degree of surficial sediment anoxia, suggesting that denitrification is limited directly by the availability of NO_3^- and indirectly by the availability of O_2 (Messer & Brezonik 1984; Seitzinger 1988).

Denitrification rates in eutrophic systems are much higher than those reported here, suggesting that organic C or N availability may also play a role. Denitrification rates in eutrophic lakes ranged from 1,000 to 46,000 mg N m^{-2} yr^{-1} using the mass-balance approach (Ahlgren 1967; Andersen 1974; Messer & Brezonik 1978, 1983; Serruya 1975) compared to 669 to 1268 mg N m^{-2} yr^{-1} presented here for oligotrophic to slightly mesotrophic lakes.

The N/P method for estimating denitrification rates appears to be superior to the ^{210}Pb method based on the strength of relationships between denitrification and anoxic factor. The ^{210}Pb method may suffer from deviations in ^{210}Pb profiles from the ideal or significant spatial variation in ^{210}Pb accumulation rates whereas sediment N/P ratios were relatively uniform.

The mass-balance model is a black-box model which considers only inputs and outputs and therefore offers limited insight into internal processes. However, one can infer a few things about internal N cycling processes from a consideration of v. First, we note that low R and v for NO_3^--N occurred along with high denitrification rates and low anoxic factors in Crosson and Red Chalk Lakes (Tables 2 and 8), suggesting that significant nitrification must be occurring to support high denitrification rates in these two lakes. This is consistent with the argument above that denitrification is limited directly by the availability of NO_3^--N and indirectly by the availability of O_2 (Fig. 3b).

Second, a low settling coefficient indicates a low pelagic demand whereas a high coefficient indicates strong pelagic demand (Kelly et al. 1990). Hence, the very high NH_4^+-N settling coefficient may be due to a strong algal preference for NH_4^+ over other N fractions. Upon uptake, NH_4^+-N is converted to TON, which is subsequently sedimented, mineralized and nitrified. Finally, v_{TN} is a composite value with less information than the coefficients for individual N fractions. v_{TN} depends on the relative importance of the individual fractions in lake inputs and N cycle pathways.

Undisturbed terrestrial systems are commonly N-limited whereas oligotrophic freshwater systems are typically P-limited (Vitousek & Howarth 1991). Changes in N/P ratios in transit between bulk precipitation and lake outflows provide some support for this argument. N/P ratios were generally less in streams than in precipitation suggesting preferential N retention in catchments, whereas the N/P ratios in lake outputs were slightly higher than lake input ratios, suggesting preferential P retention in lakes (Tables 8 and 9).

Assuming that terrestrial nitrogen fixation was negligible, the decline in N/P ratios between precipitation and stream export suggests that (1) terrestrial productivity was N-limited, (2) significant denitrification occurred in the catchments or (3) there were significant inorganic sources of P in the catchments (weathering). The latter is unlikely because of the prevaof thin tills over most of the region and the resistance of igneous bedrock, in general, to weathering.

Vitousek & Howarth (1991) suggest that aquatic and terrestrial systems have different N/P requirements because of their very different floral communities. If N requirements per unit P are higher in forests than in adjacent freshwater communities, then an N/P ratio of 51 in bulk precipitation could lead simultaneously to N-limited forests and P-limited lakes.

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