

**NITROGEN MASS BALANCES  
AND  
DENITRIFICATION RATES  
IN  
CENTRAL ONTARIO LAKES**

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IN CENTRAL ONTARIO LAKES**

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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  $^{210}\text{Pb}$  sediment N accumulation method were poorly correlated with 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.

**Key words:** nitrogen, mass balance, denitrification, lake.

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## INTRODUCTION

Denitrification in lakes has been extensively studied, most often using direct measurement techniques. These methods provide information on controlling environmental factors (Messer and Brezonik 1984), on spatial variation in rates within a lake, or on short-term temporal variation in rates (Keeney *et al.* 1971; Chan and Campbell 1980; Messer and 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 and 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 and 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 and Brezonik 1978, 1983; Serruya 1975; Dillon and 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  $^{210}\text{Pb}$  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 and Evans (1992) used in the latter approach to compare retained 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 and Molot 1990). The objectives of this study were to (1) present longterm (12 year) N flux data over a relatively large region, (2) compare average annual lake denitrification rates using N/P and  $^{210}\text{Pb}$  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, County of Haliburton or the District of Muskoka (Figure 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 soil profiles are poorly developed. Detailed descriptions of the geology and physiography of the catchments can be found in Jeffries and 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 soft water (mean conductivity ranged from 29 to 38  $\mu\text{S}$ ) and oligotrophic to slightly mesotrophic with long-term mean annual whole-lake total phosphorus (TP) concentrations ranging from 5.2  $\mu\text{g P L}^{-1}$  in Red Chalk to 10.9  $\mu\text{g P L}^{-1}$  in Dickie, long-term mean TP at spring turnover ranging from 5.8  $\mu\text{g P L}^{-1}$  in Red Chalk to 12.7  $\mu\text{g P L}^{-1}$  in Crosson and ice-free chlorophyll *a* ranging from 1.9  $\mu\text{g L}^{-1}$  in Blue Chalk to 4.7  $\mu\text{g L}^{-1}$  in Dickie (Molot and Dillon 1991). Long-term mean epilimnetic TN/TP (TN = total Kjeldahl N +  $\text{NO}_3^-$ -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  $\text{mg C L}^{-1}$  in Blue Chalk to 5.0  $\text{mg C L}^{-1}$  in Dickie (Table 1).

## **METHODS**

Water and sediment collection techniques are described in detail in Dillon and Evans (1992). Water samples were filtered through 80  $\mu\text{m}$  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  $\text{m}^2$  collectors 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 x 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 ( $\text{NH}_4^+\text{-N}$ ), total Kjeldahl nitrogen (TKN) and total nitrate plus nitrite ( $\text{NO}_3^-\text{-N}$ ). 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  $\text{TKN} + \text{NO}_3^-\text{-N}$ , total inorganic N (TIN) as  $\text{NO}_3^-\text{-N} + \text{NH}_4^+\text{-N}$  and total organic N (TON) as  $\text{TKN} - \text{NH}_4^+\text{-N}$ .

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 were estimated by pro-rating the gross export (i.e., output per unit basin area) data obtained from the hydrologically 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 is unknown.

Annual net gain of TN for each lake,  $TN_{net}$  ( $mg\ m^{-3}\ yr^{-1}$ ) 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 ( $m\ yr^{-1}$ ) and is, in effect, 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 and Evans 1992). 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 and Evans 1992).

## RESULTS

### Atmospheric Deposition

Average atmospheric deposition from 1977-89 for  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and TON was 392, 562 and 172 mg N  $\text{m}^{-2}$   $\text{yr}^{-1}$ , respectively, for a total deposition of 1,130 mg N  $\text{m}^{-2}$   $\text{yr}^{-1}$ . TP deposition during the same period averaged 22 mg  $\text{m}^{-2}$   $\text{yr}^{-1}$ ; 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  $\text{m}^{-2}$   $\text{yr}^{-1}$ ). The highest value reported by Boring *et al.* (1988) occurred in eastern Tennessee in close proximity to coal-fired power plants. Trends in  $\text{NO}_3^-$ -N emissions and deposition in eastern North America have been reported elsewhere (Dillon *et al.* 1988).

### N Loading and Retention

Annual variation in  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -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,  $\text{NH}_4^+$ -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  $\text{m}^{-2}$   $\text{yr}^{-1}$  in Plastic Lake to 3180 mg  $\text{m}^{-2}$   $\text{yr}^{-1}$  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 ( $\text{TN}_{\text{net}}$ ) 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  $990 \text{ mg m}^{-2} \text{ yr}^{-1}$  in Plastic Lake (64% of input to  $1495 \text{ mg m}^{-2} \text{ yr}^{-1}$  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 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  $\text{NH}_4^+$ -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  $\text{NO}_3^-$ -N was more variable, ranging from 0.30 in Crosson to 0.85 in Blue Chalk (Table 2).

Mean apparent settling coefficients,  $v$ , for  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, TON and TN for each lake were calculated from  $R = v/(v + q_s)$  (Reckhow and Chapra 1983) (Tables 2 - 5). Settling coefficients were highest for  $\text{NH}_4^+$ -N and lowest for TON.

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 and 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  $\text{NO}_3^-$  and TIN but was lower than regression  $v$  for  $\text{NH}_4^+$  and TON. The mean settling coefficient for TN,  $v_{\text{TN}}$  was  $3.6 \text{ m yr}^{-1}$  compared to  $3.5 \text{ m yr}^{-1}$  using the regression method

(Table 6, Figure 2). The y-intercept for  $1/R_{\text{TN}}$  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  $\text{mg m}^{-2} \text{yr}^{-1}$  in Harp Lake and from 1160 to 1660  $\text{mg m}^{-2} \text{yr}^{-1}$  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

*<sup>210</sup>Pb Method:* Mean annual denitrification rates, DNF, were calculated from,

$$\text{DNF} = \text{TN}_{\text{net}} - \text{TN}_{\text{sed}} \quad (1)$$

where  $\text{TN}_{\text{sed}}$  is the sediment accumulation rate of TN. Assuming negligible cottage inputs, the mean annual denitrification rate was 479  $\text{mg m}^{-2} \text{yr}^{-1}$ , ranging 18-fold from 52  $\text{mg m}^{-2} \text{yr}^{-1}$  in Crosson Lake (4% of net gain) to 920  $\text{mg m}^{-2} \text{yr}^{-1}$  in Harp Lake (62% of net gain) (Table 7). Mean annual denitrification rate was poorly correlated with summer anoxic factor ( $r = -0.32$ , Figure 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  $670 \text{ mg m}^{-2} \text{ yr}^{-1}$ , ranging 13 fold from  $86 \text{ mg m}^{-2} \text{ yr}^{-1}$  in Crosson Lake (7% of net gain) to  $1610 \text{ mg m}^{-2} \text{ yr}^{-1}$  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 ( $r = -0.28$ ).

*N/P Ratio Method:* Denitrification rates were also estimated from N/P ratios ( $N/P_{\text{net}}$ ) of the retained nutrients (retained nutrient = inputs - outflow) and surficial sediments ( $N/P_{\text{sed}}$ ) (Table 8),

$$\text{DNF} = \text{TN}_{\text{net}} (N/P_{\text{sed}} - N/P_{\text{net}}) / (N/P_{\text{net}}) \quad (2)$$

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

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

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  $\text{N}_2$  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 as denitrified. Lakes retained 4% of bulk TN deposition in the catchments and lakes.

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  $^{210}\text{Pb}$  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  $^{210}\text{Pb}$  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  $^{210}\text{Pb}$  method is not as accurate as the N/P method.

Denitrification rates (without cottage inputs) were strongly correlated with summer anoxic factor, AF (-0.90) 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  $\text{TN}_{\text{net}}$  (equation 2).

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

$$\text{DNF} = 1179.9 - 15.52 \text{ AF} \quad (3)$$

$$R^2 = 0.82, F = 22.57, P > 0.0051.$$

When cottage inputs were included the coefficient of determination was higher (0.89) and,

$$\text{DNF} = 1244.2 - 20.21 \text{ AF} \quad (4)$$

$$R^2 = 0.89, F = 41.8, P > 0.0013.$$

### 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).



## DISCUSSION

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 downstream from lakes.

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  $\text{NO}_3^-$  and indirectly by the availability of  $\text{O}_2$  (Messer and 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  $\text{mg N m}^{-2} \text{ yr}^{-1}$  using the mass balance approach (Ahlgren 1967; Andersen 1974; Messer and Brezonik 1978, 1983; Serruya 1975) compared 669 to 1268  $\text{mg N m}^{-2} \text{ yr}^{-1}$  presented here for oligotrophic to slightly mesotrophic lakes.

The N/P method for estimating denitrification rates appears to be superior to the  $^{210}\text{Pb}$  method based on the strength of relationships between denitrification and anoxic factor. The  $^{210}\text{Pb}$  method may suffer from deviations in  $^{210}\text{Pb}$  profiles from the ideal or significant spatial variation in  $^{210}\text{Pb}$  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  $\text{NO}_3^-$ -N occurred along with high denitrification rates and low anoxic factors in Crosson and Red Chalk Lakes (Tables 2 and 8), and we infer from this 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  $\text{NO}_3^-$ -N and indirectly by the availability of  $\text{O}_2$  (Figure 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  $\text{NH}_4^+$ -N settling coefficient may be due to a strong algal preference for  $\text{NH}_4^+$  over other N fractions. Upon uptake,  $\text{NH}_4^+$ -N is converted to TON, and subsequently sedimented, mineralized and nitrified. Finally,  $v_{\text{TN}}$  is a composite value with less information value than the individual N fraction coefficients.  $v_{\text{TN}}$  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 and Howarth 1991). Changes in N/P ratios in transit between bulk precipitation and lake outflows provides 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 prevalence of thin tills over most of the region and the resistance of igneous bedrock, in general, to weathering.

Vitousek and Howarth (1991) may be correct when they suggested 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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**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 ( $\mu\text{g L}^{-1}$ )	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

**Table 2.** Mean and standard deviation of  $\text{NO}_3^-$ -N input and outputs ( $\text{mg N m}^{-2} \text{ yr}^{-1}$ ) and areal water load, ( $\text{m yr}^{-1}$  during 1977/78-1988/89 in the study lakes. L - load,  $L_o$  - outflow from lake,  $v$  - apparent settling coefficient ( $\text{m yr}^{-1}$ ) calculated as  $R \cdot q_s / (1-R)$  where R is retention and  $q_s$  is the areal water discharge ( $\text{m yr}^{-1}$ ) 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  $\text{NH}_4^+$ -N inputs and outputs ( $\text{mg N yr}^{-1}$ ) during 1977/78 - 1988/89 in the study lakes. L - load,  $L_o$  - outflow from lake,  $v$  - apparent settling coefficient ( $\text{m yr}^{-1}$ ) defined as  $R \cdot q_s / (1-R)$  where R is retention and  $q_s$  is the areal water discharge ( $\text{m yr}^{-1}$ ). 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

Table 4. Mean and standard deviation of TON inputs and outputs ( $\text{mg N m}^{-2} \text{ yr}^{-1}$ ) during 1977/78 - 1988/89 in the study lakes. L - load,  $L_o$  - outflow from lake,  $v$  - apparent settling coefficient ( $\text{m yr}^{-1}$ ) defined as  $R \cdot q_s / (1-R)$  where R is retention and  $q_s$  is the areal water discharge ( $\text{m yr}^{-1}$ ). 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

**Table 5.** Mean and standard deviation of TN inputs and outputs ( $\text{mg N yr}^{-1}$ ) 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, - sediment N accumulation rate ( $^{210}\text{Pb}$  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	$L_o$	$L_A$	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
Harp	mean	3120	1620	685	574	0.48	4.1
	sd	407	376	-	-	0.08	1.2
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

<sup>1</sup> R and v including cottage inputs are shown in brackets for Harp and Dickie Lakes.

**Table 6.** Comparison of settling coefficients ( $\text{m yr}^{-1}$ ) for  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, TON, TIN and TN excluding cottage inputs using mean and regression ( $1/R$  versus  $q_s$ ) methods.

	Mean v	Regression v
$\text{NO}_3^-$ -N	5.5	2.4
$\text{NH}_4^+$ -N	16.0	32.6
TON	1.5	3.3
TIN	7.4	5.3
TN	3.6	3.5

**Table 7.** Denitrification rate, DNF, calculated with the  $^{210}\text{Pb}$  method ( $\text{mg m}^{-2} \text{yr}^{-1}$ ), and % net gain denitrified with and without cottage inputs. AF - summer anoxic factor (days).

Lake	With Cottage Input		No Cottage Input		AF
	DNF	% DNF	DNF	% DNF	
Blue Chalk	807	67	742	65	16.5
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	2.2
Plastic	316	32	316	32	23.2
Red Chalk	609	46	602	46	11.6
Mean	670	44	479	39	

**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).

Denitrification	---- TN/TP ---		% of Net Gain	Sed	Net Gain	mg m <sup>-2</sup> yr <sup>-1</sup>
	In	Out				
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 <sup>1</sup>	44	61	31	7.9	75	974
Main				6.8		
East				11.7		
Mean	39	46	34	7-7	76	917

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



**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).

Denitrification	---- TN/TP ---		% of Net Gain	Net Gain	mg m <sup>-2</sup> yr <sup>-1</sup>
	In	Out			
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

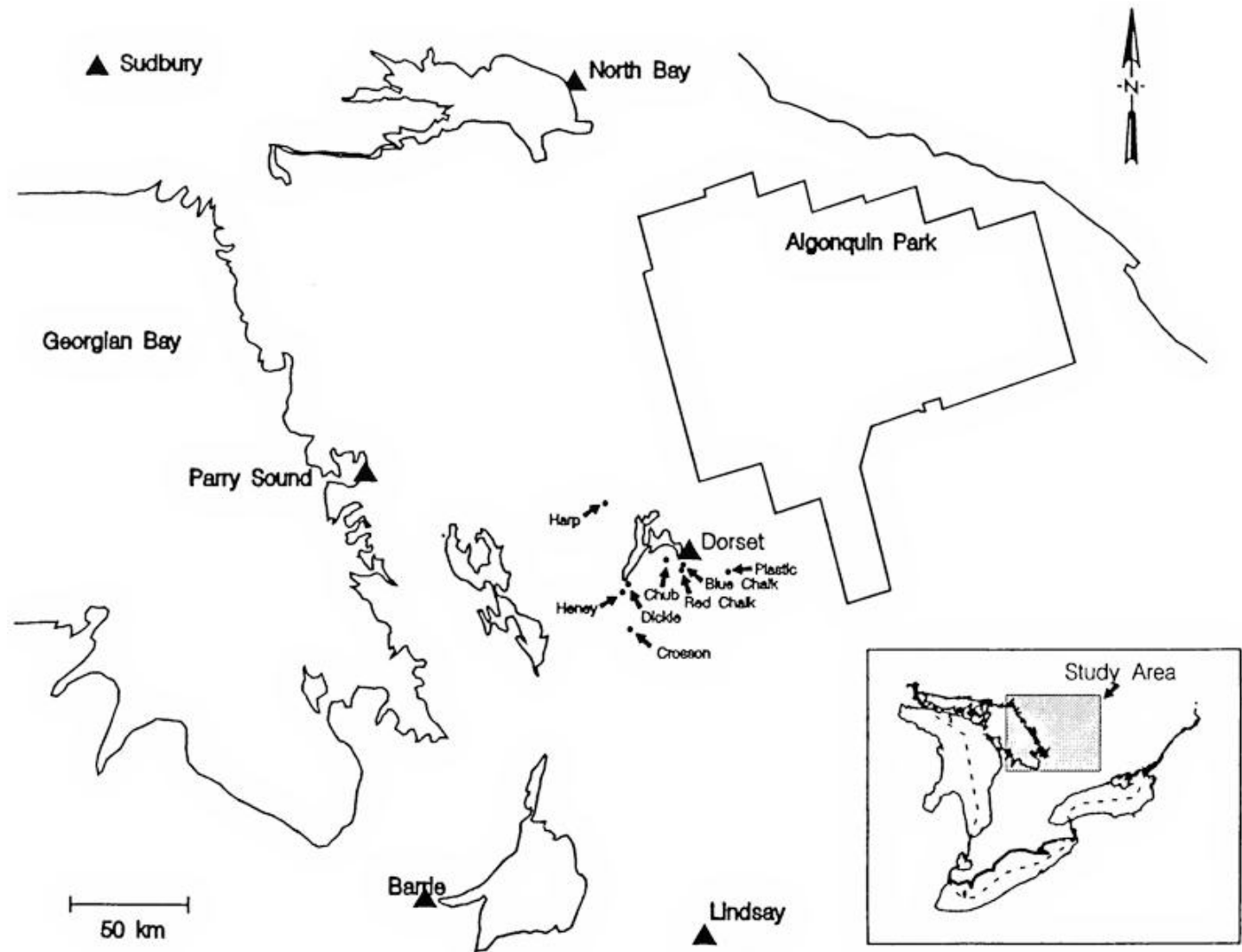


Figure 1

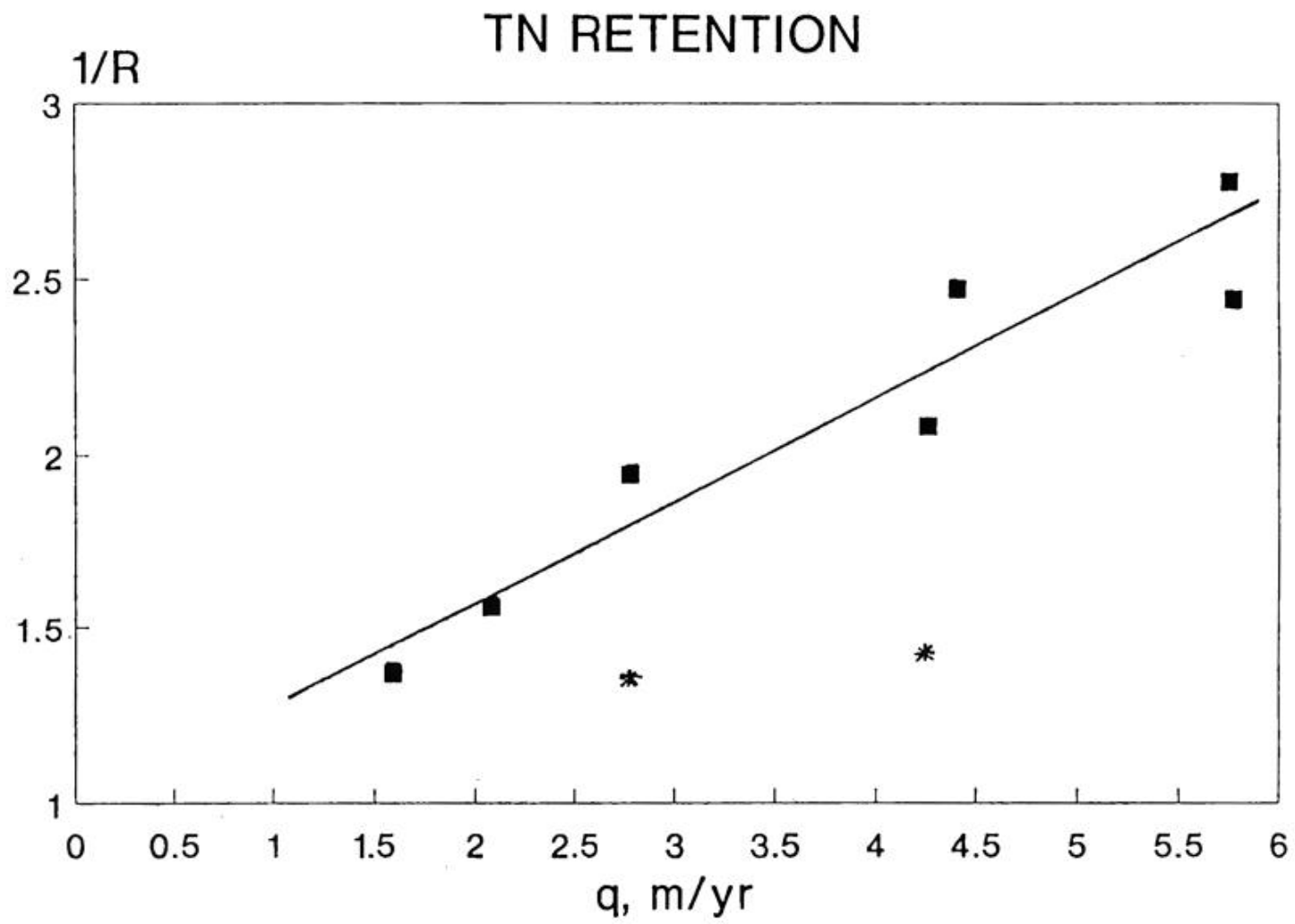


Figure 2

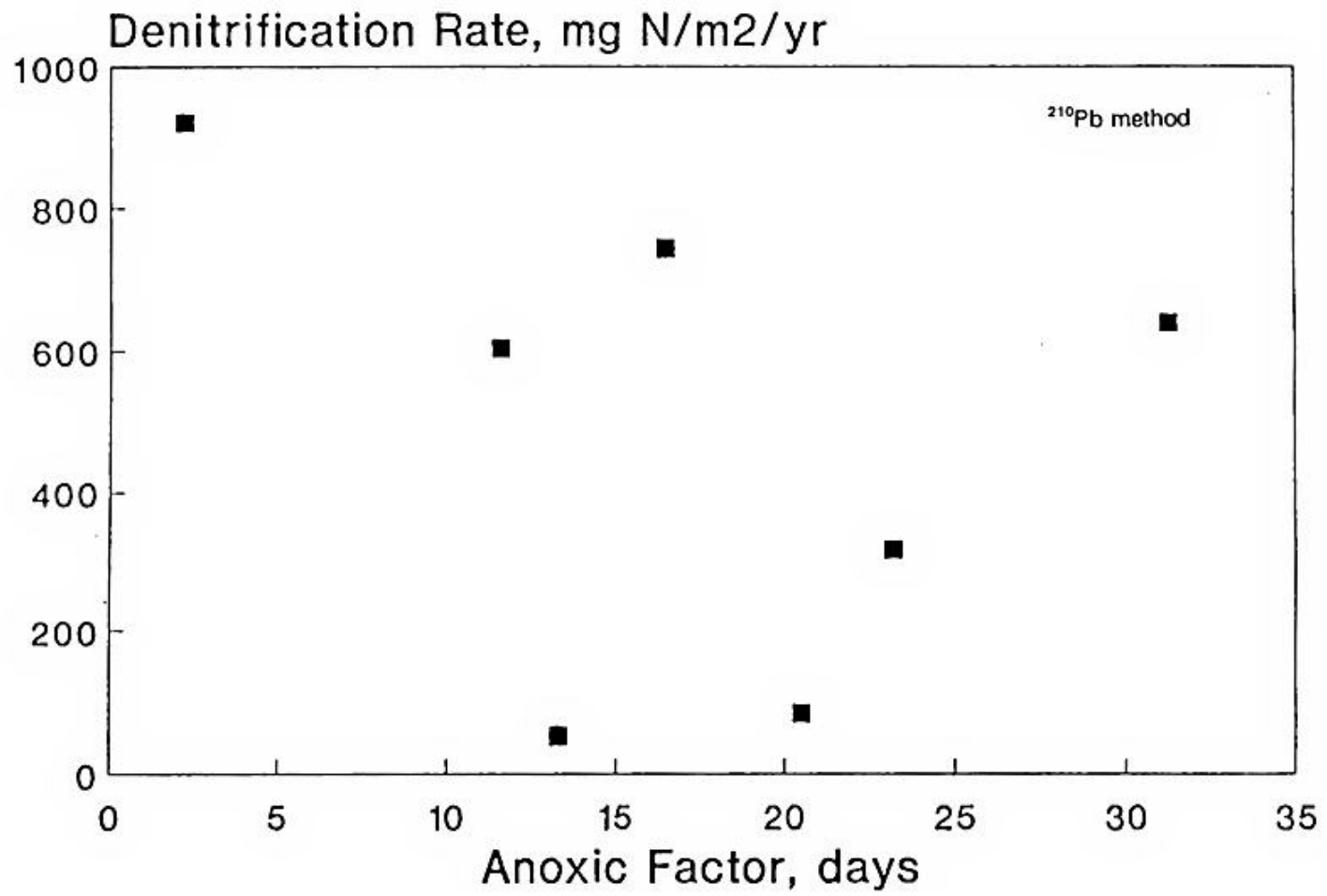


Figure 3a

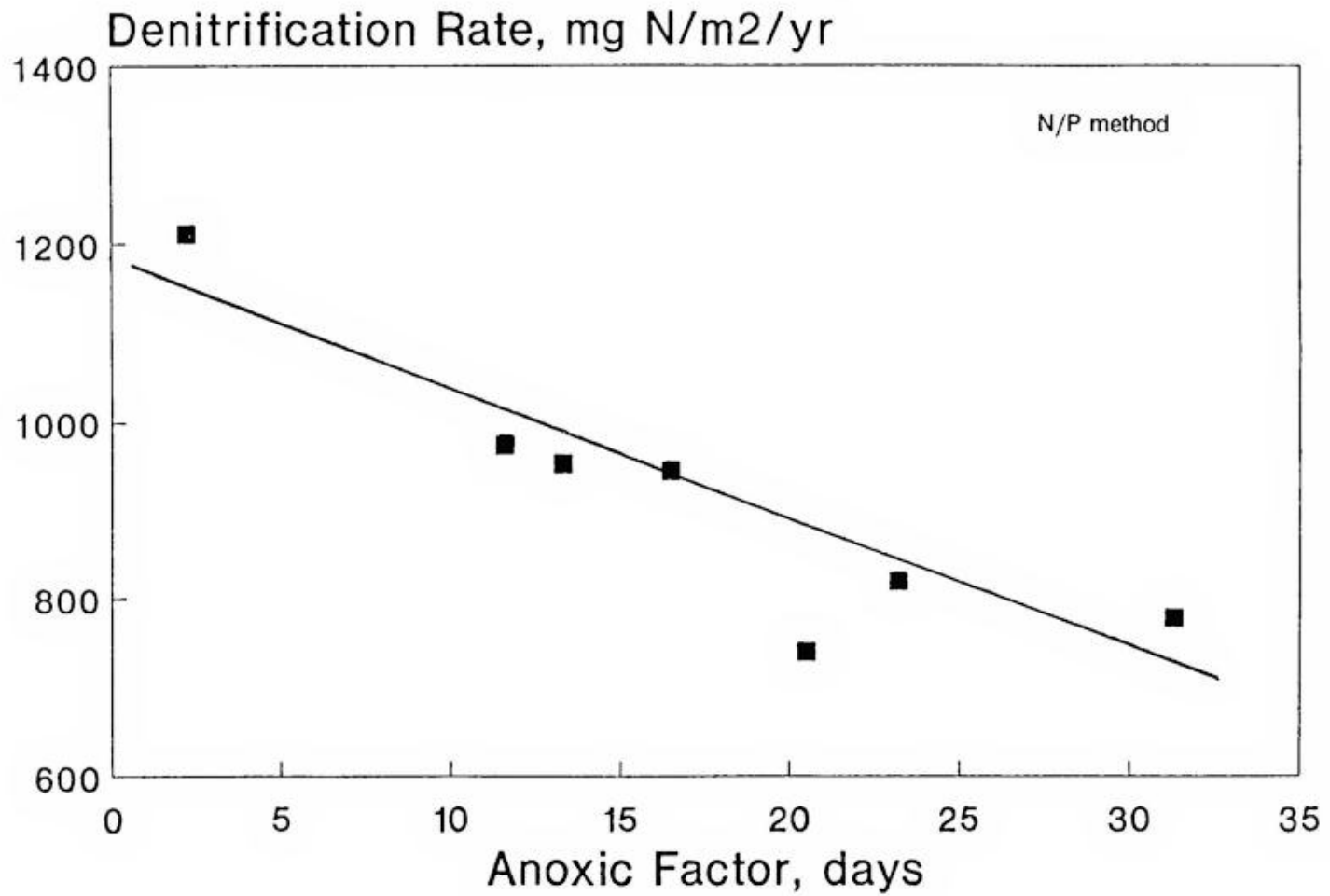


Figure 3b