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The cycling of nutrients in a closed-basin antarctic lake: Lake Vanda

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Abstract. Lake Vanda is a permanently ice covered, meromictic, closed basin lake, located in the Dry Valley region of Southern Victoria Land, Antarctica. A unique feature of the lake water column structure is that the bottom lake waters exist as a natural diffusion cell. The diffusive nature of these waters allows rates of sulfate reduction, nitrification and denitrification to be calculated from nutrient concentration gradients. Calculation reveals that sulfate reduction is by far the most important anoxic process acting to oxidize organic material. In addition, rate calculations reveal that bottom water nutrient profiles are in steady state. One argument in support of this conclusion is that the calculated rate of nitrification balances the flux of ammonia from the anoxic lake waters. The flux of phosphorus from the reducing waters is several times less than would be predicted from the nitrogen and phosphorus content of decomposing lake seston. Solubility calculations show that phosphorus may be actively removed at depth in Lake Vanda by the formation of hydroxyapatite. It is found that estimated rates of nitrogen and phosphorus removal in the bottom lake waters and sediments roughly balance the riverine input flux. This suggests that throughout the lake a nutrient steady state may exist, and that the anoxic zone may be the most important loci for nutrient removal. Finally, the ratio of nitrogen to phosphorus entering Lake Vanda by riverine input is less than the 'Redfield' ratio of 16/1; in contrast to the lake waters which are strongly phosphorus limited at all depths. This curious aspect of the lake's nutrient chemistry is explained by the presence of preformed nitrogen, which has been concentrated in the deep brine due to several episodes of evaporative concentration.

Introduction

A series of east-west striking, glacially carved, ice-free desert valleys cut inland from McMurdo Sound toward the Polar Plateau. These valleys are maintained ice free by the desiccating action of pervasive, low moisture katabatic winds, which sweep down from the Polar Plateau. Since 98% of the Antarctic continent is ice covered, the 'Dry Valleys' are uniquely exposed bedrock environments. A prominent feature of these valleys is a group of permanently ice-covered, closed-basin lakes.

Lake Vanda is 5.6 km long, 1.4 km wide, and has a maximum depth of 68 m (Nelson and Wilson, 1972). The lake is fed by the Onyx River, which

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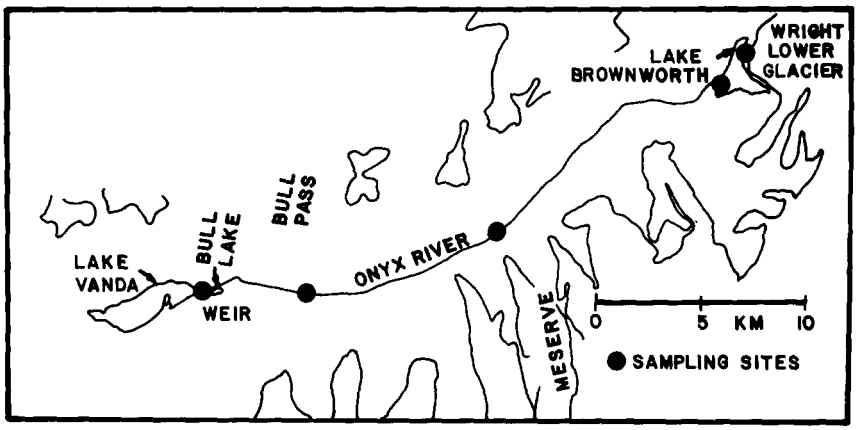

Figure 1. A generalized map of Wright Valley showing various sampling locations along the Onyx River.

flows for about 6–8 weeks during the austral summer. The river has its origin at Lake Brownworth and ultimately at the Wright Lower Glacier (see Figure 1) located about 27 km to the west of Lake Vanda. Since it occupies the deepest depression in Wright Valley, there is no riverine outflow from the lake. At present, Lake Vanda is maintained at a relatively constant depth (Chinn, 1981), with water input from the Onyx River being balanced by sublimation and wind abrasion from the lake's 4 m-thick permanent ice cap (Ragotskie and Likens, 1964). This hydrologic scheme acts as an effective mechanism for concentrating ions within the water column of the lake.

Studies of major ion chemistry (Angino et al., 1965; Jones and Faure, 1967; Green and Canfield, 1984) reveal that Lake Vanda is meromictic. From just under the ice surface, down to about 48 m, the waters are relatively fresh and cool, with an average salt content of about 900 mg l^{-1} and an average temperature of about 7 °C (Angino et al., 1965). Within this region a convecting current of 1 cm s^{-1} has been detected (Ragotski and Likens, 1964). It is likely that this current is responsible for the relative chemical homogeneity found within the upper waters. Below 48 m, steep thermal and chemical gradients develop which continue to the lake bottom. By 67 m, the salt content has increased to 123 g l^{-1} and the water temperature has risen to 25 °C (Wilson and Wellman, 1962). Below 60 m the water is anoxic. Within the region of the sharp chemocline, the water column is extremely stable and molecular diffusion is the most important mass transfer process for dissolved species (Wilson, 1964; Matsubaya et al., 1979; see appendix).

The great stability of the lower waters has allowed Wilson (1964) to model the major ion profiles and to determine the diffusion age of the chemocline. Briefly, Wilson proposed that the present water column structure is the result of a multistage process where, first, owing to colder paleoclimatic conditions, the Onyx River stopped flowing. As a result, the ice surface of the lake was

continually sublimated and abraded, concentrating ions into a progressively smaller volume, and finally into a shallow brine pool. A warm period followed during which the Onyx River began to flow, eventually overlaying the dense brine with dilute melt water. Molecular diffusion ensued and modeling of the resulting major ion profiles using Fick's second law gave an age for the filling event of 1200 years B.P. (Wilson, 1964; Toth and Lerman, 1974; Matsubaya et al., 1979). Evidence supporting this model is found in the sediments underlying the deepest portion of the lake (Wilson et al., 1974; present study), where three distinct and two less distinct calcite-gypsum bands are found, suggesting that three or more cycles of evaporative concentration have occurred in the past.

During the 1980–1981 austral summer, samples were collected and analyzed for the nutrient species nitrate, nitrite, ammonia, dissolved orthophosphate, and total phosphorus. In addition, the Onyx River was sampled throughout its flow season, and the concentrations of the same nutrient species were analyzed.

This study has several objectives, namely, to quantify the rates of sulfate reduction, nitrification, and denitrification in the permanently stratified waters below the chemocline; to examine the cycling of nutrients within and between various compartments of the lake; to determine the sources as well as the sinks for lake nutrients; and finally to explain, in terms of the lake's recent geologic history, the observation that Lake Vanda is strongly phosphorus limited whereas its major inflow contains roughly the Redfield ratios of N to P.

In what follows, we wish to emphasize the importance of diffusion as a mechanism of nutrient transport in this system, and to call attention to the significance of past evaporation events in explaining the present nutrient distributions in the lake.

Review of lake biology

The biology of Lake Vanda has recently been described by Vincent and Vincent (1982). The lake is recognized as one of the clearest and most oligotrophic in the world (Goldman et al., 1967; Vincent and Vincent, 1982), and our determination of the secchi depth as 22 m is consistent with this assessment. Low algal standing crops as well as low rates of primary productivity are observed at all depths, except for a narrow band located just above the anoxic zone. At this location in the water column, a low-light adapted, active population of phytoplankton (Goldman et al., 1967; Vincent and Vincent, 1982) has been observed. It is likely that the enhanced biological activity in the region is due to a diffusional input of nutrients from the anoxic zone below (Vincent and Vincent, 1982; Canfield and Green, 1983). Of additional interest, Vincent et al. (1981) found a band of nitrifying bacteria coinciding with the nitrate maximum (50–58 m) and a very narrow

band of denitrifying bacteria located between 59 and 62 m in depth. These results are summarized in Figure 2.

Photosynthetic carbon uptake is not restricted to the water column. Recently, a population of blue-green algae has been discovered on the lake bottom (Love et al., 1983), and it is likely that this mat material covers an extensive area of the benthos (Love et al., 1983). Though these living stromatolites exist as prominent features of the lake's biological community, their importance in the cycling of carbon and nutrients within the lake is unknown.

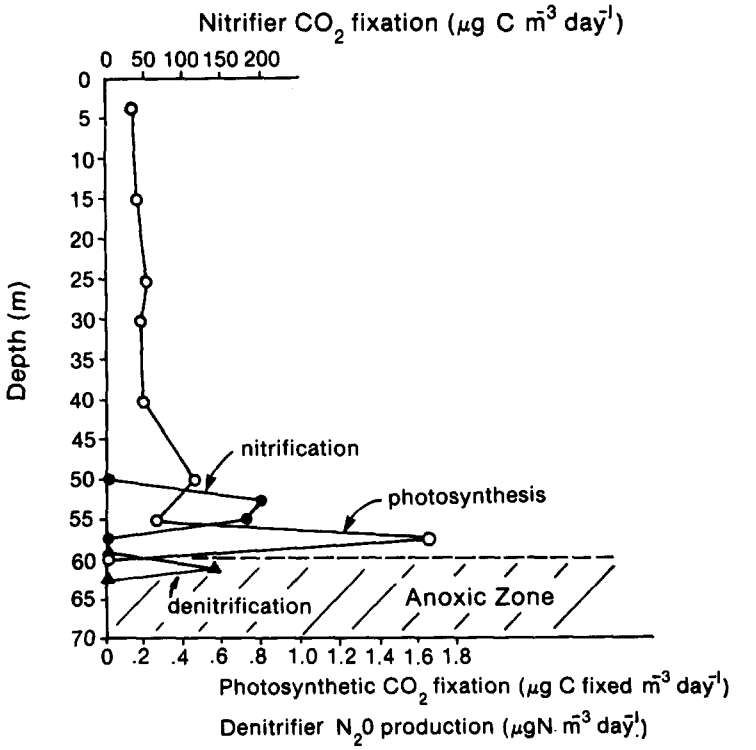

Figure 2. The magnitudes of several important biological processes are shown as a function of depth in Lake Vanda. The data are after Vincent et al. (1981).

Materials and methods

Lake Vanda was sampled for nutrients on December 17, 1980. Water was collected in an all-plastic Kemmerer bottle and samples were transferred into acid-cleaned, 1-liter "nalgene" (LPE) bottles. As standard practice, sample bottles were rinsed two times with the lake sample before filling. Lake water was filtered for "dissolved" nitrients immediately upon collection,

through a 0.45 μ millipore filter. All samples except those used for the determination of ammonia were frozen within a few hours after collection, and transported to the Eklund Biological laboratory at McMurdo Station for analysis.

Samples were collected from the Onyx River at the permanent weir site established by the New Zealand Ministry of Works. This site is located approximately 1 km upstream of Lake Vanda (see Figure 1). The weir height was recorded at each sampling time, and flow rates were calculated from the measured weir heights using a calibration table supplied to us by the New Zealand Ministry of Works. For chemical analysis, Onyx River waters were treated in an identical manner as described below for the lake samples.

Ammonia was analyzed using the indophenol blue method as described by Grasshoff (1976). The analysis was performed in the field within two hours after sample collection. The technique is sensitive to about 0.1 μmol l^{-1} and the analytical precision is about 5%.

Dissolved orthophosphate was determined using the ascorbic acid method of Strickland and Parsons (1968). However, due to extremely low water column concentrations, the resulting molybdate complex was concentrated by extraction into isobutanol. All samples were run in duplicate. The sensitivity of the method is about 3 nmol l^{-1}, with an analytical precision of about 10%. Total phosphorus was determined in a similar manner except that all phosphorus species were first oxidized to orthophosphate using sodium persulfate as described in Standard Methods (APHA, 1975).

Water concentrations of nitrate were determined by first reducing the nitrate using a cadmium reduction system (Grasshoff, 1976). The resulting nitrite was analyzed using the azo dye method (APHA, 1975). Nitrite concentrations were determined on unreduced water samples using the same chemistry as described for nitrate. The analytical precision for both nitrate and nitrite determinations was about 2%.

Results

Nutrient chemistry of the Onyx River

The Onyx River was sampled and analyzed for various phosphorus and nitrogen species throughout its flow season. The results of this sampling are presented in Figures 3 and 4. Quite high concentrations of both nitrate and total phosphorus were observed during the initial flow period. During this time, nitrite was also detected. The initially high nutrient concentrations decreased rapidly after a few days,and after a week, concentrations became relatively constant, with nitrite dropping below the detection limit. Three times during the sampling period, Onyx River water was analyzed for ammonia, but none was detected.

Using the above nutrient data and the Onyx River discharge values obtained at the time of sample collection (as well as several other times

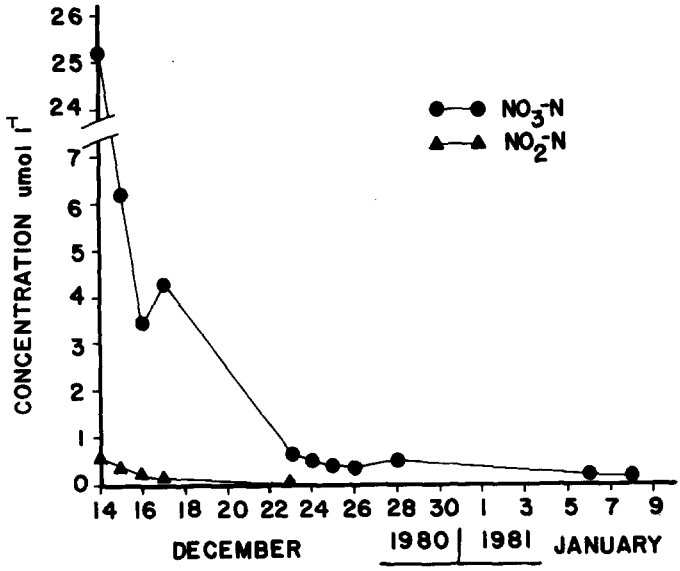

Figure 3. The concentrations of nitrate and nitrite are shown as a function of time within the Onyx River.

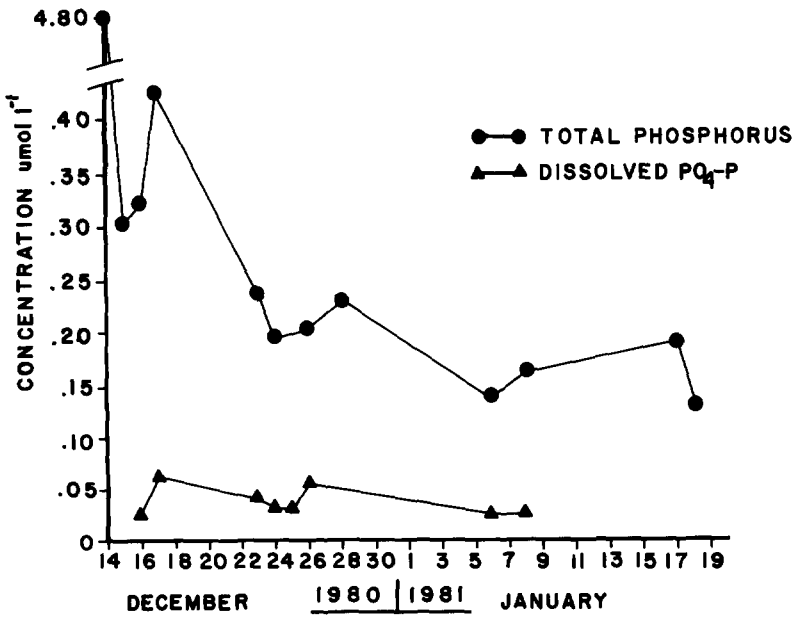

Figure 4. Time variations in Onyx River phosphorus species are shown.

Table 1. Average concentrations of nutrients in the Onyx River (μmol l^{-1})

PO_4-P	Total P	NO_3-N	NO_2-N	NH_4-N
0.039	0.20	0.59	*[a]	N.D.[b]

[a]None detected after 12/17/80 (see Figure 2)
[b]N.D. = none dected

throughout the flow season), the total mass of each nutrient species delivered to Lake Vanda during the 1980–81 austral summer was determined. Seasonal concentration averages were obtained by dividing the total mass of nutrient discharged to the lake by the annual water discharge. Results are given in Table 1.

Onyx River data can be used to compute the relative rates with which both nitrogen and phosphorus are delivered to Lake Vanda. From the above data (Table 1), dissolved nutrients enter the lake with a molar nitrogen to dissolved orthophosphate ratio of 15/1, very near the ratio (16/1) with which these nutrients are incorporated into marine plankton (Redfield et al., 1963). The ratio of nitrogen to total phosphorus entering Lake Vanda is 2.9/1. As some fraction of the particulate phosphorus may be available for uptake by the lake biota (Medine and Porcella, 1982), the input ratio of biologically available nitrogen to phosphorus lies somewhere between 15/1 and 2.9/1. These ratios imply an excess of phosphorus in the riverine input relative to the Redfield uptake ratio of 16/1. This appears to be the general trend in Dry Valley lakes and streams where nitrogen limitation is commonly observed (Vincent, 1981; Green, unpublished data).

On January 6, 1981, nutrient concentrations were determined at various points along the Onyx River in order to discern their sources and sinks. For this purpose, water samples were collected at approximately 10 km intervals beginning at the Wright Lower Glacier and ending at the weir site (Figure 1). The results are shown in Figure 5. It is apparent that over much of the river's course, nitrogen and phosphorus have quite different geochemistries. Whereas the concentration of nitrate is roughly constant between Lake Brownworth and Bull Pass, the concentrations of both dissolved and total phosphorus increase, much in the same way as is observed for the major ions (Green and Canfield, 1984). Considering the high nitrate concentrations found in the ice of the Wright Lower Glacier, it appears that this glacier acts as the source for nitrate in the Onyx River. Though no phosphorus species were measured in the glacial ice, the trend of increasing concentration with distance down river indicates that the source for this nutrient is valley rocks and soils.

A striking feature of the transect is the precipitous drop in both nitrate and phosphorus concentrations between Bull Lake and the Vanda weir. The loss of dissolved orthophosphate between these two points is 0.075 μmol l^{-1} and the loss of nitrate is 1.15 μmol l^{-1}. The ratio, $\Delta N/\Delta P$, is 15/1, which is

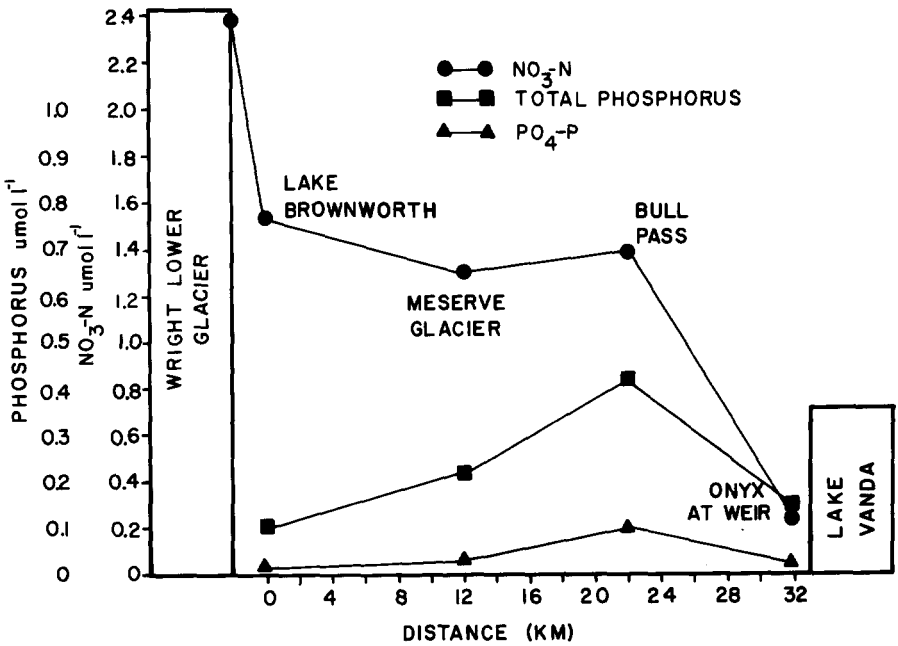

Figure 5. Concentrations of nitrogen and phosphorus species in the Onyx River along a transect beginning at the river origin (Wright Lower Glacier) and ending at the Onyx weir.

very close to the 'Redfield Ratio.' This suggests that the deficiency in nitrogen and phosphorus between Bull Pass and the Vanda weir is caused by their incorporation into biological material. The observed nutrient scavenging probably occurs in Bull Lake, a small (approximaely 100 m by 200 m by 2 m deep) waterbody located about 200 m upstream from the weir site (see Figure 1). Thus, it is likely that the high concentrations of nitrogen and phosphorus seen in the early flow season represent the contribution of winter-long regenerated nutrients from this small lake.

Nutrient distributions in Lake Vanda

Water column nutrient data from Lake Vanda are presented in Figures 6 and 7, and are summarized in Table 2. Lake concentrations for dissolved oxygen, hydrogen sulfide (Torii and Yamagata, 1981), and chloride are given in Figure 8. Briefly, nitrate concentrations are reasonably constant in the upper 45 m of the lake. Below 45 m, nitrate increases to a maximum at 54 m and then quickly falls to zero at the oxic-anoxic interface, located at 60 m depth. Nitrite behaves in a similar manner. By contrast, the concentrations of total and dissolved phosphorus are relatively constant well into the diffusional zone, and these concentrations do not begin to increase until a few meters above the oxic-anoxic boundary. Ammonia, a product of anoxic, biological respiration, behaves in a manner similar to phosphate; that is, it exhibits low

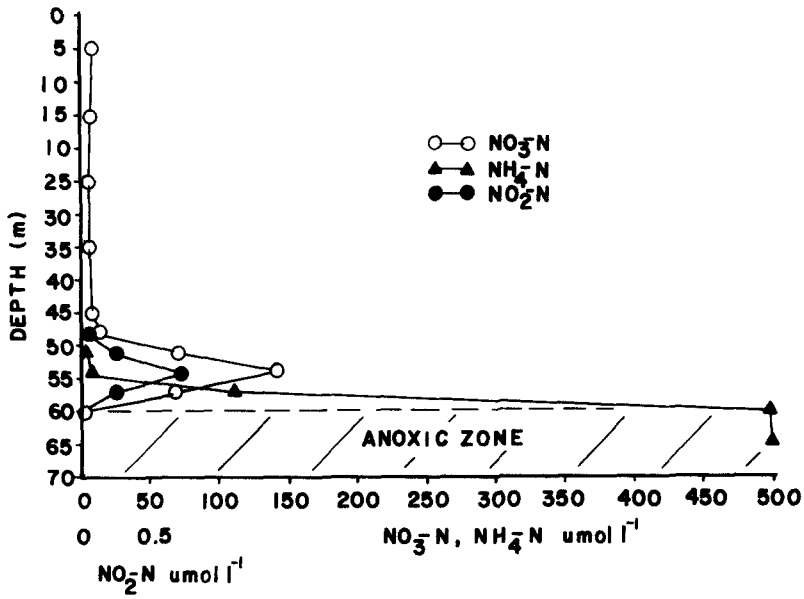

Figure 6. Concentrations of dissolved nitrate, nitrite, and ammonia are shown as a function of depth in Lake Vanda.

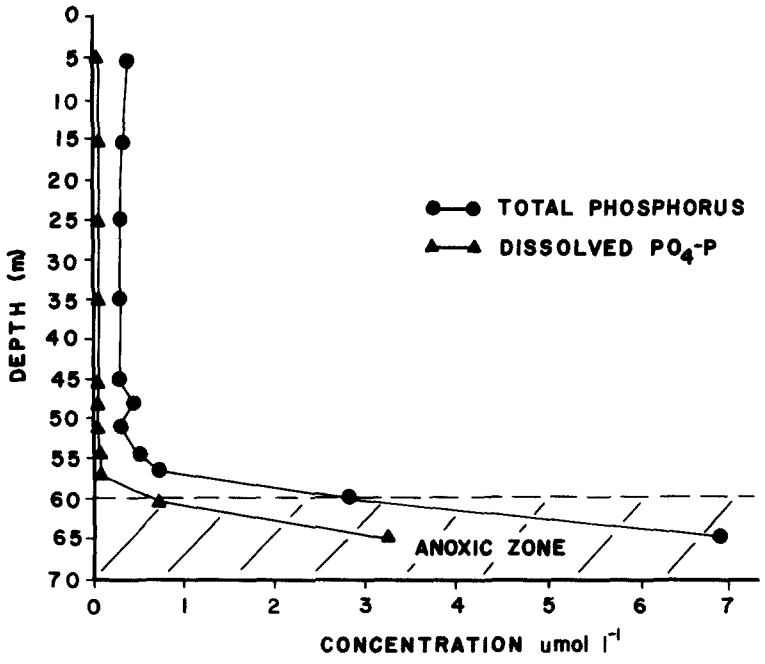

Figure 7. Lake Vanda concentrations of phosphorus species are shown.

Table 2. Nutrient distributions in Lake Vanda

Depth (m)	Concentration (μmol l^{-1})				
	Total P	PO_4-P	NO_3-N	NH_4-N	NO_2-N
5	0.35	0.019	6.05	[a]	0.046
15	0.32	0.025	5.76	0.43	0.043
25	0.24	0.028	4.56	[a]	0.031
35	0.23	0.024	4.49	0.00	0.027
45	0.23	0.013	6.86	[a]	0.030
48	0.40	0.013	10.9	0.23	0.031
51	0.24	0.003	72.0	0.11	0.22
54	0.51	0.021	143	4.14	0.76
57	0.72	0.042	67.9	111	0.21
60	2.8	0.66	0.00	507	0.00
65	6.9	3.20	0.00	507	0.00

[a]Not analysed

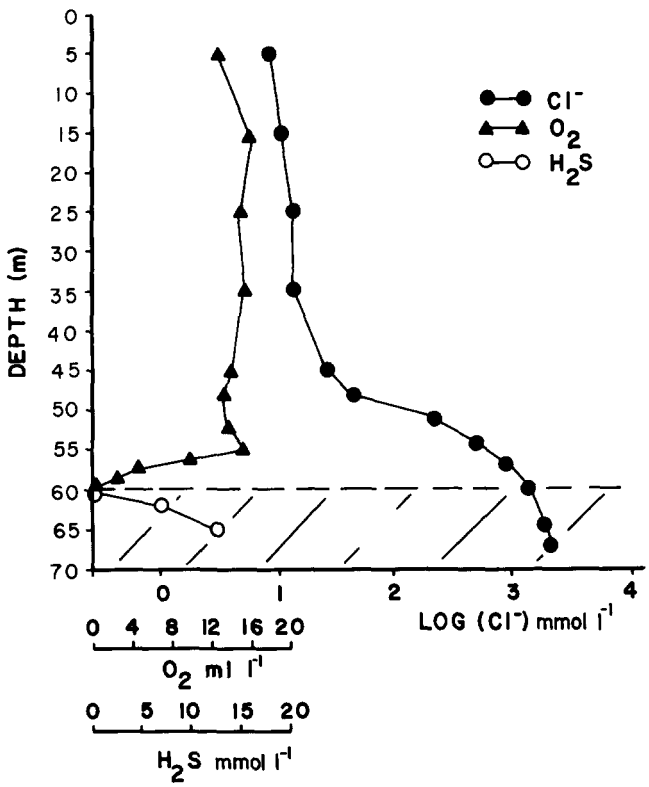

Figure 8. The concentrations of dissolved oxygen, H_2S, and chloride are shown with depth. Note the sharp chemical gradient separating Lake Vanda into a well-mixed upper zone and a diffusionally dominated lower zone.

Table 3. Diffusion information for calculation of nutrient fluxes

Species	Diffusion coefficient[a] 10^{-6} cm^2 sec^{-1}	Depth interval (m)	Gradient (μm cm^{-4})
H_2S	10.3	65–60	3.13×10^{-3} [b]
NH^-_4	16.8	60–57	1.28×10^{-3} [c] 1.28×10^{-3} [d]
$H_2PO^-_4$	7.15	65–60	5.16×10^{-6} [c] 16.8×10^{-6} [d]
NO^-_3	16.1	54–60	2.36×10^{-4} [c] 5.29×10^{-4} [d]
NO^-_3	16.1	54–48	2.40×10^{-4} [c] 4.30×10^{-4} [d]

[a]Diffusion coefficients at 18 °C from Li and Gregory (1974)
[b]data from Torii and Yamagata (1981)
[c]data from present study
[d]data from Vincent et al. (1981)

concentrations throughout the upper lake, and high concentrations beginning just above the oxic-anoxic interface and increasing into the anoxic zone. In contrast with the Onyx River, Lake Vanda waters are strongly phosphorus-limited at all depths. This curious aspect of the lake's nutrient geochemistry will be discussed below.

In the modeling that follows, a great deal of emphasis will be placed on the gradients of nutrient concentrations within the diffusional zone. In addition to our own, the only other complete set of nutrient values for Lake Vanda is presented by Vincent et al. (1981). These data were also collected during the 1980–81 austral summer. A comparison between the data from Vincent and from the present study is made in Table 3, where nutrient gradients are given over various depth intervals of interest. For ammonia, the data sets agree. However, for both phosphate and nitrate, gradients calculated from our data are roughly a factor of two lower than those calculated from the data of Vincent et al. (1981). Regardless of the data set used, however, the conclusions generated from the modeling below remain qualitatively unchanged.

Discussion

The distribution of various nutrient species (Figures 6–8), coupled with rate measurements (Figure 2) show that, not unlike a sediment column, the waters of Lake Vanda are comprised of vertically discrete zones of sulfate reduction, nitrification and denitrification. An intriguing aspect of the lake's physical limnology is that in the lower stable region of the lake, dissolved species transport is by molecular diffusion (Wilson, 1964; Matsubaya et al., 1979; see

appendix), the rates of which are reflected in the concentration gradients. Hence, the lower lake distributions of nutrients and H_2S may be used to quantitatively assess the rates of nutrient liberation, removal and transformation by the above processes. Much of the following discussion will be aimed at determining these rates. The information gained will prove valuable in the discussion of nutrient steady state, nutrient regeneration efficiencies in the oxic lake waters, and in exploring the loci of nutrient removal within the lake.

Rates of sulfate reduction and denitrification

The distribution of ammonia (Figure 6) indicates that there is a substantial flux of this nutrient out of the anoxic portion of the lower lake. In principle, under steady state conditions, the flux of ammonia from the anoxic zone equals the rate with which ammonia is liberated into solution by the decomposition of organic matter under anoxic conditions. Below 60 m depth, the only microbial processes which are likely to be quantitatively significant in organic matter oxidation are denitrification and sulfate reduction. Methanogenesis is unlikely since the sulfate concentration in the anoxic zone is quite high ($\sim 10\,\text{mmol}\,l^{-1}$; Angino et al., 1965) and the presence of sulfate reducing bacteria (as suggested by the high sulfate concentrations) appears to inhibit microbial methane production (Fenchel and Blackburn, 1979).

From the data in Table 3 and the area of the plane through which ions are diffusing at the oxic-anoxic interface ($1.3 \times 10^{10}\ \text{cm}^2$), the flux of ammonia out of the anoxic zone is calculated to be 8.8×10^6 mmoles yr^{-1}. This value may be compared to the rates with which ammonia is liberated by the processes of denitrification and sulfate reduction. The rate of denitrification is estimated by considering the concentration gradient of nitrate below 54 m. The slope of the profile (Figure 6) indicates that nitrate is diffusing into the anoxic zone, and the shape suggests that reaction does not occur until very near the oxic-anoxic interface. This is consistent with the presence of the narrow band of denitrifying bacteria found by Vincent et al. (1981) between 59 and 62 m depth. The rate of denitrification should be limited by the diffusional supply of nitrate to this zone. The diffusional supply is obtained by combining the diffusion coefficient and slope data from Table 3 with the area (60 m) through which ions are diffusing. With these data a denitrification rate of 1.6×10^6 mmols $NO_3\ yr^{-1}$ is obtained. Assuming Redfield ratios (Redfield et al., 1963) for the decomposing organic matter (C/N = 106/16) and also assuming no secondary oxidation of ammonia, the following reaction may be written (Richards, 1965):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_x + 84.8HNO_3 \leftrightharpoons$$
$$106CO_2 + 42.4N_2 + 148.4H_2O + 16NH_3 + xH_3PO_4.$$

From the above stoichiometry, the reduction of 1.6×10^6 mmoles of nitrate should liberate 0.3×10^6 mmoles of ammonia into the anoxic zone.

Sulfate reduction is given by the following reaction:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_x + 53SO_2^{2-} \rightleftharpoons$$

$$106CO_2 + 53S^{2-} + 16NH_3 + 106H_2O + xH_3PO_4$$

and rates of sulfate reduction may be calculated by first assuming the anoxic zone to be at steady state with respect to hydrogen sulfide. That is, the input of H_2S by sulfate reduction is balanced by the outputs, which include diffusion and reaction. The diffusion of H_2S out of the brine is calculated by using the sulfide data of Torii and Yamagata (1981) (Figure 8). At the pH of the anoxic zone (5.5–6.0) the dominant sulfide species is H_2S and the appropriate diffusion coefficient for H_2S is given in Table 3. From these values, the yearly mass flux of sulfide from out of the anoxic zone is calculated to be 2.3×10^7 mmoles $H_2S\,yr^{-1}$. Sulfide may also be removed by the formation of metal sulfides, of which iron sulfide is the most important. Owing to the low concentrations of iron found in the upper waters of Lake Vanda (Green and Canfield, in press), it is inferred that the upper lake is at steady state with respect to inputs from the Onyx River and thus yearly riverine iron inputs can be used to estimate iron removal rates in the anoxic zone. Using the iron input data from Green and Canfield (In press), it is found that the removal rate of sulfide as FeS is small when compared to the diffusional flux, and a steady state sulfate reduction rate of 2.3×10^7 mmoles yr^{-1} is calculated.

The amount of ammonia liberated due to sulfate reduction may be estimated by again assuming the decomposing organic material to exhibit Redfield ratios. The stoichoimetry dictates that the given rate of sulfate reduction should liberate 7.0×10^6 mmoles of ammonia to the anoxic zone each year. If this result is compared to the 0.3×10^6 mmoles of ammonia liberated yearly by denitrification, it is seen that sulfate reduction is by far the most important anoxic process acting to decompose organic matter. Summing the ammonia contributions from both sulfate reduction and denitrification yields a total input to the anoxic zone equal to 7.3×10^6 mmoles yr^{-1}. This agrees very favorably with the calculated yearly diffusive flux of ammonia out of the anoxic zone (8.8×10^6 mmoles). The close agreement demonstrates that nutrient diffusional profiles are good quantitative indicators of the rates of biological processes in the lower waters of the lake. A steady state between anoxic organic matter oxidation rates and the flux of ammonia from the anoxic zone is also indicated.

The organic carbon which is oxidized by anaerobic microbial processes must ultimately be derived from carbon fixation occurring in the oxic lake waters. Of interest would be the efficiency with which nutrients are cycled and contained within these waters, as well as the rates with which nutrients are delivered to the anoxic zone. Nakai et al. (1975) report that the sediments underlying the anoxic waters are extremely sparse in organic carbon, con-

taining only about 0.03% wt, suggesting that these sediments are a relatively insignificant sink for organic carbon. It would appear, then, that the rate of anoxic organic matter oxidation, as determined above, would equal the rate of organic matter supply to the anoxic zone. This rate, coupled with the rate of carbon fixation in the oxic waters above, would yield the rate of nutrient loss, and conversely, the efficiency of nutrient regeneration.

From the data of Vincent et al. (1981) (Figure 2) we calculate the 3×10^8 mmoles of carbon are photosynthetically fixed per year within a column of lake water (area equal to 1.3×10^{10} cm^2) extending from the oxic-anoxic interface to the lake surface (assuming photosynthesis to occur for the 180 days of Antarctic sunshine). It is found that this carbon fixation is equally divided between the upper convecting portion of the lake (3–48 m) and the lower diffusion zone (48–60 m). From the above data, 18% of the yearly productivity overlying the anoxic zone settles and is oxidized by anoxic processes. If both the upper and lower lake lose nutrients equally to the anoxic zone, then 18% of the primary productivity within both layers is lost to the anoxic waters. If upper lake nutrients are more efficiently recycled (as might be expected due to the convective nature of the upper lake waters), then between 18% and 36% of the lower lake productivity is yearly lost.

Steady state nitrification model

Between 48 and 60 m, the distribution of nitrate (Figure 6) suggests the presence of a band of nitrifying bacteria (Vincent et al., 1981). The overall rate of nitrification within this zone should be limited by the supply of ammonia from below. Diagenetic modeling of the nitrate profile can be used to assess this claim and to add further evidence to the steady state nature of nutrient distributions in the lower lake.

It was determined above that between 18% and 36% of the organic matter that is biologically fixed between the depths of 48 and 60 m settles and is oxidized by anoxic microbial processes. For the purpose of the present calculation it will be assumed that the loss rate for organic carbon and nutrients is 25% of the total fixed. This is not a crucial assumption since it generates an uncertainty of about 20% in the model calculation relative to the extreme values of 18% and 36% for loss rates. Data from Vincent et al. (1981) (Figure 2) show that throughout most of the nitrification zone the photosynthetic rate is reasonably constant at a value of about 29 μmoles C fixed m^{-3} yr^{-1}. When this photosynthetic rate is coupled with the 25% loss rate of fixed carbon, a loss rate for nitrate, from the nitrification zone, of 1.2×10^{-8} mmoles nitrate m^{-3} s^{-1} is calculated. This calculated loss rate assumes that nitrate is acting as the preferred nitrogen source in this region.

Nitrification rate data from Vincent et al. (1981) (see Figure 2) can be approximated as a linear function which increases from zero at 50 m to a maximum at 54 m. The rate then decreases symmetrically to 58 m where it is again zero. The concentration profile for nitrate shows a similar symmetry

around 54 m and because of this symmetry, only the top halves of the profiles will be modeled. A schematic of the idealized nitrification profile and the nitrate profile is shown in Figure 9.

The nitrification profile is divided into two layers: layer A and layer B. In layer A, the processes of nitrification, molecular diffusion, and biological removal are important in affecting the distribution of nitrate. In layer B, the nitrification rate is reduced to zero and, hence, only the processes of molecular diffusion and biological removal are important. The following diagenetic equations may be used to describe the nitrate profile in each layer. Assuming steady state:

$$\text{Layer A:} \quad D_N \frac{d^2C}{dX^2} = PX - P_m + R$$

$$\text{Layer B:} \quad D_N \frac{d^2C}{dX^2} = R$$

where D_N = molecular diffusion coefficient for nitrate at 18 °C, C = concentration of nitrate, P = constant of proportionality between height and nitrification rate, P_m = maximum nitrification rate, X = height (positive upwards), $P_m - PX$ = linear function used to describe nitrification, and R = removal rate of nitrate due to biological incorporation.

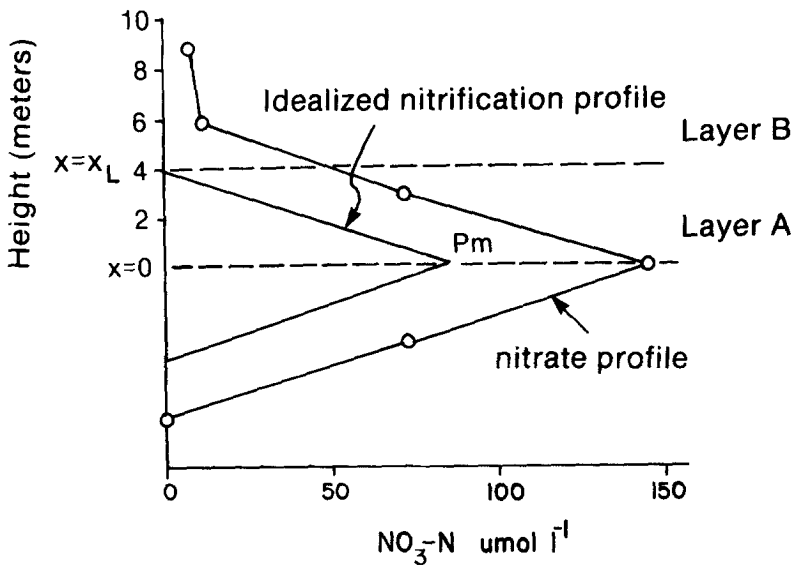

Figure 9. The nitrification model is diagrammatically expressed. Included with our nitrate data is a curve which schematically shows the idealized nitrification rate profile (compare to Figure 2). In Layer A, the processes of nitrification, biological removal, and diffusion are considered important in establishing the nitrate profile. In Layer B, nitrification is negligible, and only diffusion and biological removal are modeled. See the text for a full description of the symbols.

The two equations are solved with the following boundary conditions:

$$X = O; \quad C = C_m$$

$$X = 0; \quad \frac{dC}{dX} = 0$$

$$X = X_L; \quad C_A = C_B$$

$$X = X_L; \quad \frac{dC_A}{dX} = \frac{dC_B}{dX}$$

where C_m is the maximum nitrate concentration and X_L is the height where the nitrification rate goes to zero (boundary between layer A and layer B). Since at $X = X_L$ the nitrification rate is zero, $P_m = PX$ at this height. With these conditions, the following solutions are obtained:

$$\text{Layer A:} \quad C_A = \frac{PX^3}{6D_N} - \frac{PX_L X^2}{2D_N} + \frac{RX^2}{2D_N} + C_m$$

$$\text{Layer B:} \quad C_B = \frac{RX^2}{2D_N} - \frac{PX_L^2 X}{2D_N} + \frac{PX_L^3}{6D_N} + C_m$$

with the following values: $R = 1.2 \times 10^{-8}$ mmoles $NO_3\ m^{-3}\ s^{-1}$, $D_N = 1.61 \times 10^{-9}\ m^2\ s^{-1}$, $C_m = 143$ mmoles m^{-3} and $X_L = 4$ m.

The value of P is obtained by curve-fitting the measured nitrate profile and is determined to be 11.5×10^{-9} mmoles $m^{-4}\ s^{-1}$. The form of the solution is that of a trinomial. Though only suggested from our data, a nitrate distribution resembling that of a trinomial is demonstrated by the close interval sampling of Vincent et al. (1981).

The above nitrification proportionality constant corresponds to a maximum nitrification rate of 4.6×10^{-8} mmoles $m^{-3}\ s^{-1}$ at 54 m and a yearly average rate of 8.7×10^6 mmoles nitrate produced. The estimated flux of ammonia out of the anoxic zone is calculated to be 8.8×10^6 mmoles yr^{-1}, which agrees remarkably with the calculated nitrification rate. The agreement is certainly better than the uncertainties in the data. However, these results strongly suggest that the lower water column in Lake Vanda is a steady state system where the rate of nitrification is balanced by the supply of ammonia from the anoxic zone below.

The above model assumes that nitrate is acting as the preferred nitrogen source in this region and that all of the ammonia diffusing from the anoxic zone is available to the nitrifying bacteria. It is possible that ammonia may also be acting as a source of planktonic nitrogen, especially in the region between 55 and 60 m where the concentration of ammonia is large. Using the primary productivity data from Vincent et al. (1981), it is calculated that between 55 and 60 m depth, photosynthesis consumes (assuming Redfield

ratios) 11.6×10^6 mmoles $N\,yr^{-1}$. Since about 25% of the biologically fixed nutrients are lost and not regenerated within this region of the lake, 2.9×10^6 mmoles of the diffusional ammonia flux may be yearly removed and not available to nitrifying bacteria. Hence, the supply of ammonia out of the anoxic zone should be bracketed between 5.9×10^6 mmoles yr^{-1} and 8.8×10^6 mmoles yr^{-1}. This range of values is still in good agreement with model-predicted results.

The results from this model may be compared with rates measured in situ by Vincent et al. (1981) (Figure 2). Nitrification rates were measured by comparing carbon-14 uptake in dark bottle experiments where one of the bottles was spiked with the nitrification inhibitor nitrypyrin. The results were reported as rates of nitrifier CO_2 fixation (μg C fixed m^{-3} day^{-1}). Billen (1975) reports that nitrifying bacteria fix 0.12 μmole of bicarbonate for each μmole of ammonia oxidized to nitrate. With this conversion factor, the nitrification data of Vincent et al. (1981) translate into a yearly oxidation of 3.9×10^8 mmoles of ammonia to nitrate. This value is roughly 50 times greater than model-predicted results, and the estimated diffusional flux of ammonia to this zone. The reasons for this discrepancy are not clear, though the conversion factor proposed by Billen (1975) may be inappropriate for this system.

Nutrient removal in the anoxic lake waters

Results thus far reasonably demonstrate that the lower lake distributions of nitrogen (48 m to the lake bottom) are in steady state. One argument in support of this claim is that the flux of ammonia from out of the anoxic zone (based on the concentration gradient for ammonia) closely matches the flux predicted from the calculated rates of anoxic organic matter oxidation. One may also expect that the flux of phosphorus from this zone should be predicted on the basis of anoxic organic matter decomposition rates. From the data in Table 3, the flux of nitrogen from the anoxic zone is between 580 (using our data) and 180 (using data from Vincent et al., 1981) times greater than the phosphorus flux. The delivery ratio of nitrogen to phosphorus into the anoxic zone is uncertain. However, in no portion of the lake's oxic waters are sestonic N/P ratios as high as those above (Vincent and Vincent, 1982). The high nitrogen to phosphorus flux would indicate that there is either a nonstoichiometric release of nitrogen and phosphorus from the organic matter decomposing in the anoxic zone, or that mineral formation removes phosphorus and hence the anoxic zone operates as a phosphorus trap. A likely explanation is that phosphorus is sequestered in the lower, most concentrated portions of the brine, by the formation of hydroxyapatite, $Ca_5(PO_4)_3OH$. At 65 m depth the concentration of calcium is 0.63 moles l^{-1}, the pH is 5.6 (Green and Canfield, in press), and the concentration of dissolved phosphorus is 3.2×10^6 moles l^{-1}. With activity coefficients calculated by the method of Nesbitt (1984) and the dissociation constants for phosphoric acid given by Nriagu (1983), the ion activity product (IAP) for hydroxy-

apatite is $10^{-53.6}$. This value is several orders of magnitude greater than the equilibrium constant (10^{-58}) (Nriagu, 1983) and suggests that mineral formation may indeed be an important removal mechanism for phosphorus in the anoxic zone.

Assuming that during denitrification nitrate is reduced to nitrogen gas, the lake's bottom waters may be an important locus for the removal of both nitrogen and phosphorus. The rate of nitrate removal by denitrification has been previously calculated and was found to equal 1.6×10^5 mmoles yr^{-1}. The rate of phosphorus removal within the anoxic waters is equal to the delivery rate from the oxic lake waters minus the rate of diffusion from out of the anoxic zone. Combining our nutrient results with the diffusion coefficient for $H_2PO_4^-$ (Table 3), the diffusive flux of phosphorus from the reducing waters is 0.15×10^5 mmoles yr^{-1}. The delivery flux is estimated using sestonic N/P ratios obtained by Vincent and Vincent (1982). The average sestonic N/P found in the oxic waters of the lake is 62/1. Within the lower diffusional portion of the lake (between 48 and 60 m), the ratio of N/P is 88/1. From previous discussions steady state has been established between the nitrogen flux from the anoxic zone and the rate of delivery of reduced carbon and nutrients from settling plankton. Hence, the flux of ammonia from the reducing waters (88×10^5 mmoles yr^{-1}) multiplied by the P/N ratio of the decomposing organic material should yield the delivery rate of phosphorus to these waters. Using the above values for sestonic N/P ratios, the delivery flux of phosphorus to the anoxic zone is bracketed between 1.42×10^5 mmoles yr^{-1} (N/P = 62) and 1.0×10^5 mmoles yr^{-1} (N/P = 88). Subtracting the diffusive flux from these values, it would appear that between 1.27×10^5 mmoles and 0.85×10^5 mmoles of phosphorus are removed yearly in the lake's anoxic waters. This would suggest that most of the phosphorus delivered to the deepest lake waters is removed and only a small fraction (~ 15%) is free to diffuse back into the oxic portion of the lake. The above data are summarized in Table 4.

Table 4. Nutrient balance sheet[a]

	N	P
Onyx River input[b]	12×10^5	4.0×10^5 (total P) 0.8×10^5 (dissolved ortho-P)
Diffused from anoxic zone	88×10^5	0.15×10^5
Supplied to anoxic zone	88×10^5	1.42×10^5 (N/P = 62) 1.00×10^5 (N/P = 88)
Removed in lower lake	16×10^5	1.27×10^5 (N/P = 62) 0.85×10^5 (N/P = 88)

[a] All values in mmoles yr^{-1}

[b] Calculated by combining input data from Table 1 with average Onyx River flow rate (2×10^9 l yr^{-1}; Chinn, 1981)

Bottom water removal rates may be compared with Onyx River input rates (Table 4). Though the biologically available riverine input flux of phosphorus is uncertain, it is striking that bottom water removal mechanisms appear to remove both nitrogen and phosphorus at rates comparable to their input rates. The results would indicate that an overall nutrient steady state exists in Lake Vanda, where nutrient inputs from the Onyx River are balanced by nutrient outputs to the lake's bottom waters and sediments. This conclusion, however, must remain tentative, since the importance of the lake's benthic algal community in the removal and cycling of nutrients is not known.

Origin of lake nutrients

The origin of nutrients within Lake Vanda may be addressed by calculating 'apparent' residence times for nitrogen and phosphorus within the lake waters. The calculation is conducted in the same manner as outlined by Barth (1952) for oceanic residence times. Though Lake Vanda may at present exist in steady state with respect to nutrient inputs and outputs, this is not certain. The steady state assumption, however, is not crucial to the following interpretation. Rather, the calculation is meant to point out any inconsistencies between calculated 'apparent' residence times and what is known about the lake's recent past.

The total mass of nitrogen and phosphorus in Lake Vanda is obtained by multiplying the volume of successive conic sections, e.g., between 5 and 15 m, by the average nutrient concentrations at these depths, and then summing over the entire lake. Conic section volumes were computed from the detailed bathymetric map presented by Nelson and Wilson (1972). The results obtained are a total mass of nitrogen equal to 7.5×10^9 mmoles and a total mass of phosphorus equal to 9.3×10^7 mmoles. The total mass of each nutrient is divided by the present Onyx River delivery rate (Table 4) and the 'apparent' residence time is thus obtained. The results are an 'apparent' residence time for nitrogen equal to 6400 years and 'apparent' residence times for phosphorus of 1100 years for dissolved phosphorus inputs and 220 years for total phosphorus inputs. The 'apparent' residence time for nitrogen is longer than the 1200 years spanned since the most recent lake filling event (Wilson, 1964), and shows that more nitrogen exists in Lake Vanda than could be accounted for by the past 1200 years of Onyx River flow. This would suggest that preformed nitrogen, probably as the ammonium ion, existed in the Lake Vanda brine prior to this filling episode. The 'apparent' residence times for phosphorus are much shorter and are consistent with the possibility that the bulk of the phosphorus presently found in the lake has entered in the past 1200 years. These observations help to explain the apparent inconsistency involved in a nitrogen-limited river feeding a strongly phosphorus-limited lake, especially since the removal ratios of N/P do not appear much different from the Onyx River delivery ratios. The explanation would appear to be that an ancient source of preformed nitrogen – a remnant

of past evaporation cycles – has been available to diffuse into the upper lake and to affect the nitrogen-to-phosphorus ratios throughout the lake. We are unaware of any other natural waterbody whose nutrient chemistry has evolved in this manner.

Conclusions

This conclusion calls attention to the critical importance of the lake's recent geologic history in establishing the behavior of nutrients. Twelve hundred years before present, Lake Vanda existed as a shallow brine pool. Within this salty layer, nitrogen (probably as the ammonium ion) was in abundant concentration, whereas phosphorus may have been nearly absent. At this time the Onyx River began to flow, overlaying the dense brine with dilute glacial melt water. Molecular diffusion ensued and the preformed nitrogen was free to diffuse into the upper lake. The result of this early nutrient behavior is still seen today in the pronounced phosphorus limitation observed throughout the lake. Phosphorus limitation within the lake is in contrast to the riverine input, where nitrogen appears to be the limiting nutrient.

Modeling has demonstrated several important aspects of lake nutrient behavior. Lower lake nutrient distributions appear to exist in a steady state. This is demonstrated by the equivalence in the rates of ammonia release by anoxic organic matter oxidation and the flux of ammonia from the anoxic zone. In addition, calculated rates of ammonia oxidation are balanced by the diffusive flux of ammonia to the nitrifying bacteria. Within the lake bottom waters, both phosphorus and nitrogen removal are observed; nitrate by denitrification and phosphate, probably, by mineral formation. In order to maintain a lower lake nutrient steady state, a continuous supply of upper lake-derived nutrients is required. Consistent with this claim, high nutrient loss rates are calculated from the lake's oxic waters. Modeling results indicate that nitrogen and phosphorus are delivered to the anoxic lake waters in a ratio much greater than their bottom water removal ratio. As a result, nitrogen is observed to diffuse high into the water column and into the upper lake, whereas phosphorus is retained and recycled within a few metres of the oxic-anoxic interface. Lastly, it is found that the rates of nitrogen and phosphorus removal in the bottom lake waters are roughly equivalent to Onyx River input fluxes, suggesting tentatively that the whole lake may presently exist in a nutrient steady state.

Appendix

Concern may arise regarding the possibility that preformed ammonia is largely responsible for establishing the concentration gradient of ammonia out of the anoxic zone. Evidence exists which suggests that this is not the

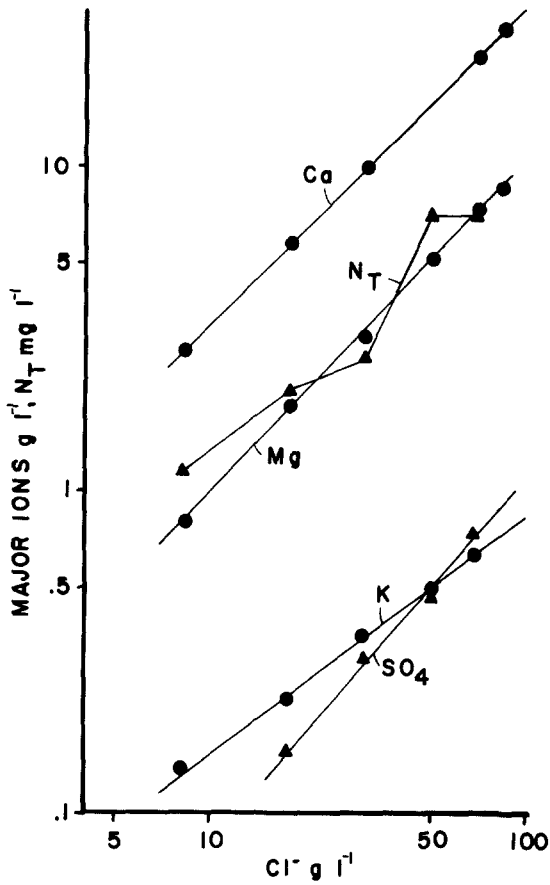

Figure 10. Log concentration of chloride ion is plotted against the log concentration of various major ion species and total nitrogen. The data are from concentrations in the diffusion zone (51 m to the lake bottom). The slopes of the lines represent the ratios of the diffusion coefficient for chloride with the ion of interest.

case. In Figure 10, the log concentration of chloride ion is graphed against the log concentration of several major ion species and total nitrogen. For chemical species that behave conservatively, the log-log plot generates a straight line whose slope represents the ratio between the diffusion coefficients for the ions of interest and chloride. The theoretical justification for this relation is developed by assuming that the current diffusion profiles began as a salt layer overlain by a thick lens of fresh water (Wilson, 1964). If cylindrical geometry is assumed (with a flat bottom), the distribution of a chemical species within the water column at any time is given by

$$C(t, h) = \frac{m}{(\pi Dt)^{1/2}} \exp(-h^2/Dt)$$

where: t = time, h = height above bottom, C(t, h) = concentration of a diffusing species, which is a function of both time and height above the bottom, m = mass per unit area of a chemical species in the original salt layer, and D = molecular diffusion coefficient.

The logarithm of this expression is:

$$\log C = \tfrac{1}{2} \log \frac{m^2}{\pi Dt} - \frac{h^2}{Dt}$$

At a given time, the concentration is a function of only the height, and the slope of the line resulting from a log-log concentration plot as in Figure 10 would be given (in its simplified form) as:

$$\frac{\log C_A(h_1) - \log C_A(h_2)}{\log C_B(h_1) - \log C_B(h_2)} = D_B/D_A$$

where h_1 and h_2 are two different heights above the bottom and the subscripts A and B denote different chemical species. In Table 5, calculated diffusion coefficients (corrected for cross-coupled diffusion) (Ben-Yaakov, 1972) are compared with those predicted from the slopes in Figure 10. The agreement is satisfactory, especially considering that no attempt was made to correct for either ion-pairing (Lasaga, 1979) or ionic strength. The important point is that compared with the conservative major ions, nitrogen clearly behaves nonconservatively. Thus, rapid nutrient cycling (with respect to diffusion), particularly in the 54–60 m region, is indicated. Data from Vincent et al. (1981) yield the same results. These trends suggest that nitrogen distributions within the lower waters of the Lake Vanda are not controlled by simple unperturbed diffusion (as with the major ions) but instead, are being substantially modified by the lake biota. In addition, the agreement in Table 5 supports the contention that the lower waters of Lake Vanda represent an unperturbed diffusion cell.

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Table 5. Diffusion model summary

Ion	$\frac{\log Cl}{\log Ion}$	$\frac{D_{Cl}}{D_{Ion}}$[a]
Ca	1.00	1.00
Mg	1.04	1.05
K	0.75	0.45
SO_4	1.17	1.85

[a]Calculated by method of Ben-Yaakov (1972)

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