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Nitrogen cycling across the sediment-water interface in an eutrophic, artificially oxygenated lake

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ABSTRACT

Processes controlling the nitrogen (N) exchange between water and sediment in eutrophic Lake Sempach were studied using three different independent methods: benthic flux chambers, interstitial water data and hypolimnetic mass balances. The sediments released NH_4^+ (1.1–16.1 mmoles m^{-2} d^{-1}), NO_2^- (0.1–0.4 mmoles m^{-2} d^{-1}) and dissolved organic N (<0.25 mmoles m^{-2} d^{-1}). A net NO_3^- consumption (2.4–11.1 mmoles m^{-2} d^{-1}) related to the NO_3^- concentrations in the overlying water was observed in all benthic chamber experiments. The flux of the reactive species NO_3^- and NH_4^+ was found to depend on hydrodynamic conditions in the water overlying the sediment. For this reason, benthic chambers overestimated the fluxes of inorganic N compared to the other methods. Thus, in short-term flux chamber experiments the sediment may either become a sink or a source for inorganic N depending on the O_2 concentration in the water overlying the sediment and the stirring rate. As demonstrated with a $^{15}NO_3^-$ experiment, nitrate-ammonification accounted for less than 12% of the total NO_3^- consumption. After six years of artificial oxygenation in Lake Sempach, a decrease in hypolimnetic total inorganic nitrogen (TIN) was observed in the last two years. The occurrence of dense mats of H_2S-oxidizing *Beggiatoa sp.* indicated micro-aerobic conditions at the sediment surface. Under these conditions, a shorter distance between the ecological niches of nitrifying and denitrifying bacteria, and therefore a faster NO_3^--transport, can possibly explain the lowering of TIN by enhanced net denitrification.

Introduction

Lake Sempach is an 87 m deep eutrophic, P-limited hard water lake in central Switzerland which has been oxygenated and artificially mixed since 1984 (Gächter, 1987). The goals for artificial oxygenation were to fulfill the requested water quality criterion of 4 mg L^{-1} oxygen everywhere in the lake and to decrease the release of phosphorus from the sediments. The effects of oxygenation and artificial mixing on water quality and phosphorus recycling have been presented elsewhere (Gächter, 1987; Stadelmann, 1988; Gächter et al., 1989).

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The benthic N cycle in Lake Sempach will be emphasized in this chapter. The cycling of N at the sediment-water interface is a field of increasing interest. However, only a limited number of studies on N cycling in lakes have been carried out (Seitzinger, 1988). Because mass balances can be made within the dimensions of lake basins, they offer a good opportunity for studying in situ benthic exchange processes. The objectives of this study were: 1) to compare different approaches of measuring benthic N fluxes in Lake Sempach, 2) to study the mechanisms which control benthic N fluxes, and 3) to investigate the effect of improved oxygen concentrations at the lake bottom on benthic N cycling.

Methods

In situ flux measurements

Benthic chamber flux measurements were conducted at the deepest point of the lake using a large cylindrical flux chamber (1.5 m dia.) described by Gächter et al. (1988). The flux chamber enclosed a water volume of 440 L in the experiments in 1985 or two equal volumes of 220 L in all other experiments. A bottom lander (Devol 1987) with two chambers covering 0.04 m^2 and enclosing 2.9 L was used in one experiment. Great care was taken to avoid any disturbance of the sediment surface. Samples were either pumped through 0.5 cm dia. Tygon tubing to the lake surface (flux chamber) or were drawn from the chamber by spring-actuated syringes (bottom lander). The volume of the sampled water, replaced by water from outside the chamber, was incorporated as a dilution factor in the data presentation. Water enclosed within the flux chamber was circulated continuously with a pump at a flow rate of 5.3 L min^{-1} to ensure uniform mixing. In the bottom lander, the water was mixed by a stirring motor. Resuspended material was never observed in the samples. This indicates that neither the lowering of the chamber or lander, nor water circulation or stirring within the chambers resuspended particulate material from the sediment-water interface.

Flux chamber data are usually interpreted assuming that the fluxes remain constant as long as the incubation time is short. Fluxes were determined by a linear fit to the data, with the initial concentration as an intercept. The slope of this linear fit, multiplied by the volume-to-area ratio of the chamber, was the flux (Berelson et al. 1987). Fluxes determined in this way were defined as "initial fluxes". In cases where the data show a nonlinear change with time, "initial fluxes" depend strongly on the length of the considered time span (Bender et al. 1989).

Determination of benthic fluxes by a hypolimnetic mass balance

The mass of N in the hypolimnion between the 40 m depth and the lake bottom was calculated from concentration vs. depth profiles, taking into account the morphometry of the lake. The 40 m depth was chosen because the vertical eddy-diffusional flux through this hypothetical surface during summer stratification was small compared to sediment fluxes. Maximum losses to the upper layer were estimated using a mean eddy-diffusion coefficient during stratification (1.3 m^2 d^{-1}, Wüest 1987) and the maximum observed concentration gradient (0.15 mmoles N m^{-4}) at the depth of 40 m. Seepage of NO_3^- rich groundwater into Lake Sempach does not occur. Therefore, increases in dissolved N of the water mass below the 40 m depth reflect N which is recycled by sediment mineralization processes.

Interstitial water sampling

Sediment cores were sampled at the deepest location of the lake (87 m depth). Interstitial water was obtained using the centrifugation techniques described by Emerson (1976). Sediment slices were prepared with a vertical resolution of 0.5 cm. In September 1989, an interstitial water sampler based on dialysis techniques (Brandl 1987) was deployed. This sampler, with a vertical resolution between samples of 1.5 cm, was firmly attached to the benthic chamber at a distance of 1 m.

Flux studies using sediment cores

Additional studies were carried out with sediment cores (11 cm dia.) incubated at 5 °C in the laboratory. The water overlying the sediments was replaced at the start of the experiment by filtered lake water from 1 m above the lake bottom, and concentrations were monitored for 2 to 5 days. Different hydrodynamic conditions were induced in the overlying water of parallel sediment cores using magnetic stirrers with different stirring velocities. No visible resuspension of the sediment occurred at any of the stirring velocities. The benthic boundary layer thickness was estimated by the reactive metal method (Santschi et al. 1983): $3.7 \cdot 10^{-3}$ Bq of ^{63}Ni, stabilized in weak acid (10^{-3} M HCl), was added to the cores at the end of each flux experiment. Relative activities were measured with a Packard Liquid Scintillation Counter. The diffusive boundary layer thickness was calculated using a molecular diffusivity of $3.86 \cdot 10^{-6}$ cm^2 s^{-1} for Ni^{2+} at 5 °C (Li and Gregory 1974).

In one experiment, 28 µM $Na^{15}NO_3$ (99 % ^{15}N) was added to the water overlying a sediment core to investigate the end products of NO_3^- reduction in the sediment. After two days of incubation, ^{15}N-content in the overlying water, the interstitial water and the solid phase of the sediment were analyzed using methods outlined in Fiedler and Proksch (1975). ^{15}N was measured with a Statron emisson spectrometer at the Department of Marine Biology, University of Göteborg, Göteborg, Sweden.

Chemical analyses

All filtered samples were passed through prewashed 0.45-µm Sartorius membrane filters. Total dissolved N was digested and measured as NO_3^- after $K_2S_2O_8$ oxidation at 120 °C (Nydahl 1978). NO_3^- was determined with the hydrazine reduction method (Downes 1978). NO_2^- and NH_4^+ were determined according to Bendschneider and Robinson (1952) and Solorzano (1969), respectively. Dissolved organic nitrogen (DON) was calculated as the difference between total dissolved N and dissolved inorganic N.

Results

Typical concentration-time series observed in the benthic chambers are shown in Fig. 1. In all experiments, NH_4^+ concentrations increased steadily, whereas NO_3^- disappeared and NO_2^- remained near zero. Note that the NO_3^- concentration showed a exponential-type decrease with time. DON-fluxes were always small compared to NH_4^+ and NO_3^- fluxes (Table 1). Fluxes (from sediment to water) of TIN, the sum of NO_3^-, NO_2^- and NH_4^+, were always positive in the summer of 1985 varying from 2.6 to 12 mmoles m^{-2} d^{-1} (mean 5.8), whereas in June 1988 and also in September 1989 the mean net TIN fluxes were directed into the sediment.

The amount of inorganic N in the water body below 40 m depth is shown in Fig. 2 for the period from 1979 to 1989. Before artificial oxygenation of the hypolimnetic waters in 1984, the water at 87 m depth became anoxic from July or August to the beginning of the winter overturn in October or November. Since 1984, oxygen concentrations remained above 4 mg L^{-1} everywhere in the lake. In spite of the partly anoxic conditions before 1984, NO_3^- contributed more than 85% to the TIN. Before oxygenation started, NH_4^+ plus NO_2^- accounted for a maximum of 28 tons of N in this water mass, but decreased to less than 3 tons with the onset of permanently oxic conditions. TIN showed a distinct seasonal pattern with maximum in late summer and minimum after the beginning of the winter circulation. A significant accumulation of NH_4^+ during early stratification was observed only before 1986.

The increase of inorganic N from the beginning to the end of the stratification period was fitted with a linear regression equation. The accumulation rate of N divided by the sediment area yields the benthic fluxes listed in Table 1. TIN increased steadily by 1.3 to 2.6 mmoles m^{-2} d^{-1} during all of the observed periods. NH_4^+ accumulation rates ranged up to 0.9 mmoles m^{-2} d^{-1} before 1984. NO_2^- did not accumulate significantly in the hypolimnion.

Concentrations of NH_4^+ as high as 500 µM were observed in the interstitial waters of the sediments at the deepest part of the lake (Fig. 3). DON concentrations ranging up to 100 µM represent about 20% of the total dissolved N in interstitial water (Fig. 3c). NO_2^- and NO_3^- concentrations did not exceed 20 µM in interstitial waters (data not shown). Fluxes calculated from interstitial water data are presented only for NH_4^+ and DON in Table 1. The gradient of NO_3^- across the sediment-water interface could not be resolved adequately to calculate a flux. Estimated NH_4^+ fluxes ranged from 1.1 to 3.5 mmoles m^{-2} d^{-1} and are significantly lower than benthic chamber fluxes (3.9 to 16.1 mmoles m^{-2} d^{-1}). In September 1989, when interstitial water data were collected with a dialysis sampler (Fig. 3c) within 1 m of the benthic chamber, the NH_4^+ flux in the benthic chamber exceeded that estimated from the interstitial water gradient by a factor of 6.

Because of the lack of knowledge concerning fluxes of N_2 and N_2O and the high background concentration of N_2 dissolved in water, a laboratory experiment with ^{15}N-labelled NO_3^- (0.028 mmol L^{-1} $Na^{15}NO_3$) was conducted to trace the end products of NO_3^- reduction in an undisturbed sediment core (Table 2). Of the total

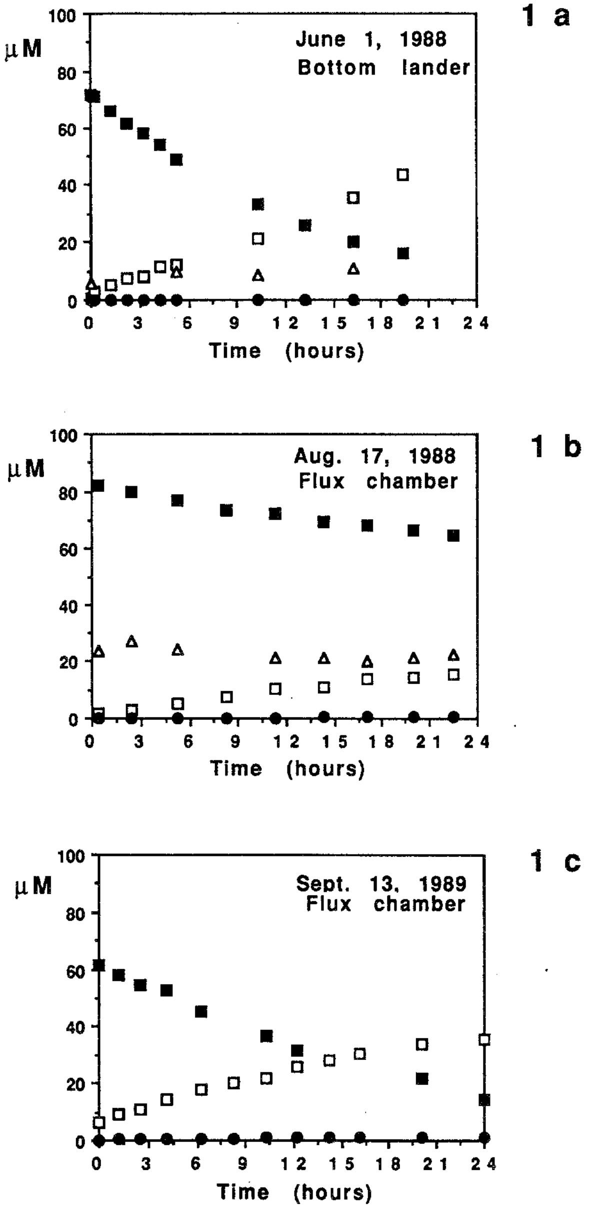

Figure 1. Changes of [NH_4^+] (□), [NO_3^-] (■), [NO_2^-] (●) and [DON] (△) measured with the bottom lander (a) and the benthic flux chamber (b, c) at the deepest point in Lake Sempach

Table 1. Benthic fluxes from the sediments of NH_4^+, NO_3^-, NO_2^-, total inorganic nitrogen (TIN) and dissolved organic nitrogen (DON) measured with different methods in the hypolimnion of Lake Sempach (negative values are fluxes from the water to the sediments)

Method	Period	Fluxes in mmoles m^{-2} d^{-1}				
		NH_4^+	NO_3^-	NO_2^-	TIN	DON
Flux chamber (Water volume: 440 l Circulation rate: 0.72 h^{-1})	May 28, 1985	+7.1	−2.4	–	+4.7	–
	Aug. 19, 1985	+10.3	−3.6	–	+6.7	–
	Sept. 16, 1985	+7.1	−4.6	–	+2.6	–
	Oct. 14, 1985	+16.1	−4.1	–	+12.0	–
	Nov. 11, 1985	+6.4	−3.2	–	+3.2	–
Bottom lander (Water volume: 2.9 l; stirred)	June 1, 1988 [1]	+3.9±0.2	−8.1±0.3	+0.4±0.2	−4.2±0.4	+0.25
Flux chambers (Water volume 220 l Circulation rate: 1.44 h^{-1})	Aug. 17, 1988 [1]	+7.7±2.3	−6.9±0.1	+0.15±0.05	+0.8±2.4	+0.1
	Sept. 13, 1989	+7.2	−11.1	+0.3	−3.6	–
Hypolimnion mass balance	March – Oct. 1979	+0.5	+1.2	<0.1	+1.7	–
	March – Aug. 1980	+0.5	+1.3	<0.1	+1.8	–
	March – Aug. 1981	+0.1	+1.6	<0.1	+1.7	–
	March – June 1982	+0.4	–	<0.1	–	
	March – Oct. 1983	+0.9	+1.3	<0.1	+2.2	–
	March – Oct. 1984	+0.2	+2.4	<0.1	+2.6	–
	April – Oct. 1985	+0.1	+1.5	<0.1	+1.6	–
	March – Sept. 1986	<0.1	+2.5	<0.1	+2.5	–
	March – Oct. 1987	<0.1	+2.0	<0.1	+2.0	–
	March – June 1988	<0.1	+1.3	<0.1	+1.3	–
	April – Sept. 1989	<0.1	+1.3	<0.1	+1.3	–
Calculated fluxes from interstitial water data	May 5, 1988	+3.5	–	<0.1	–	–
	Jan. 19, 1989	+2.6	–	<0.1	–	–
	Sept. 13, 1989	+1.1	–	<0.1	–	+0.2

[1] Mean and standard deviation of 2 chambers at the same location for June 1 and August 17, 1988.

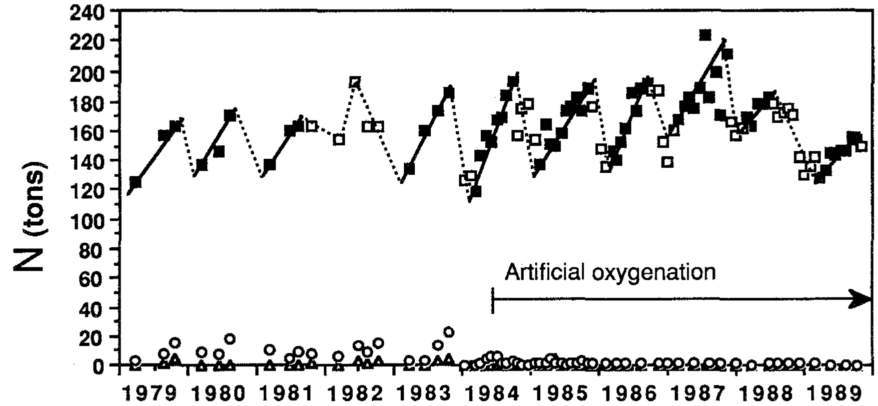

Figure 2. Seasonal accumulation and depletion of total inorganic nitrogen (TIN, ■, □), NH_4^+ (○) and NO_2^- (△), expressed as tons of N, in the waters below 40 m depth. Straight lines (——) represent calculated linear regression lines for TIN data (■) between March and maximum observed TIN accumulation

Table 2. End products of NO_3^- reduction in the sediments of Lake Sempach, traced by ^{15}N-labelled NO_3^-. Missing N indicates a minimum estimate for the relative importance of denitrification compared to other NO_3^- reduction pathways

$^{15}NO_3^-$ diffused into the sediment		Percent 100
^{15}N found:	as NO_3^- plus NO_2^-	<0.5
	as NH_4^+	0.95±0.38
	as particulate N	3.3±3.0
estimated:	as DON	<4
missing ^{15}N	(N_2, N_2O)	>87.9

Table 3. Mean residence times for N compounds in the upper 2 mm of Lake Sempach sediment porewaters. Data are from one sediment core flux experiment in January 1989 with a diffusive boundary layer thickness of 1.8 mm

	Inventory in upper 2 mm	Flux	Residence time in upper 2 mm
	nmoles cm^{-2}	nmoles cm^{-2} hr^{-1}	hr
NH_4^+	57	8.5	6.7
NO_2^-	0.05	0.03	1.7
NO_3^-	<0.2	13	<0.015
DON	8	0.56	14.3

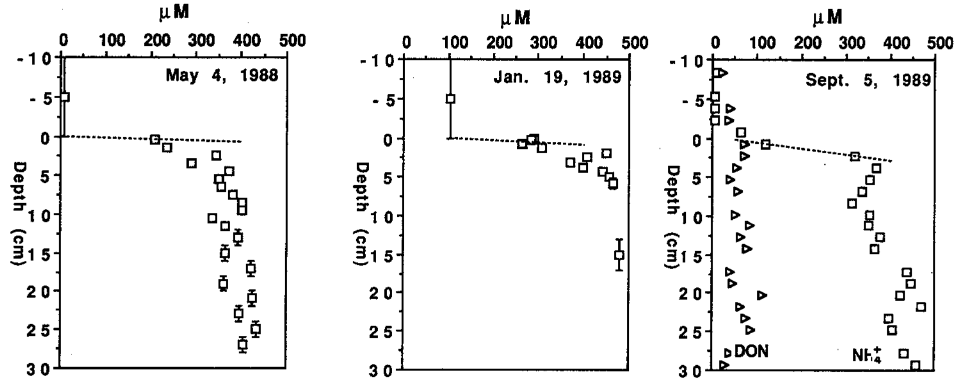

Fig. 3a

Fig. 3b

Fig. 3c

Figure 3a–c. NH_4^+ (□) and DON (▷) concentrations in the interstitial waters of sediments from the deepest point of Lake Sempach: a and b) sediment cores using centrifugation, c) *in situ* dialysis sampling device. Dashed lines represent gradients at the sediment-water interface used for flux calculations (see Table 1)

amount of NO_3^- which diffused into the sediment within two days, less than 4.8% was found as NH_4^+ or particulate N, and less than 4% was measured in the DON pool. The missing ^{15}N must have been lost as gaseous end products (N_2, N_2O). This finding agrees with measured N_2-production in Lakes Michigan (Gardner et al. 1987) and Erie sediments (Fendinger et al. 1987).

Discussion

Comparison of flux measurement approaches

Three independent methods were used to estimate benthic N fluxes in Lake Sempach. Benthic chamber experiments and interstitial water data yield flux rates at well defined locations, whereas mass balances integrate over a large sediment area. As discussed later, each method has advantages and limitations.

Benthic chamber fluxes

Benthic chambers must be calibrated with independent methods to ensure that the processes observed within the chamber reflect the processes taking place outside. As summarized in Table 1, TIN fluxes measured with benthic chambers in 1985 overestimated observed accumulation rates of TIN by the hypolimnetic mass balance approach up to 7-fold. In June 1988 and September 1989, the benthic chambers even suggested net TIN consumption by the sediment, whereas TIN accumulated in the hypolimnion during both summers. NH_4^+ fluxes calculated from interstitial water data were also significantly lower than fluxes observed in benthic

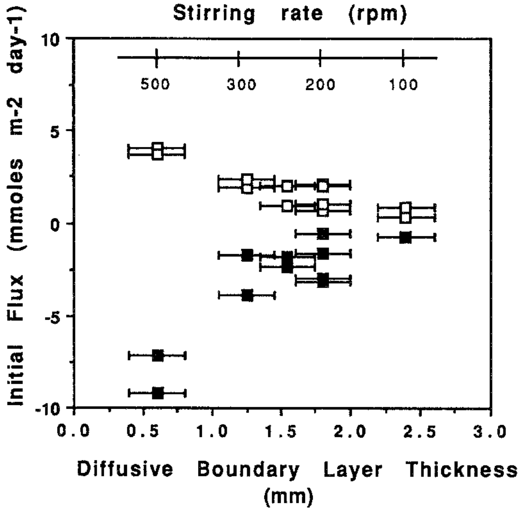

Figure 4. Initial NO_3^- (⊢■⊣) and NH_4^+ (⊢□⊣) fluxes as a function of diffusive boundary layer thicknesses observed in laboratory experiments with different stirring rates in the overlying water. Error bars represent various errors connected with the estimation of the diffusive boundary layer (see Santschi et al., 1983). For definition of "initial" flux see methods

chamber experiments. It is likely that the physical conditions in the chamber do not reflect those on the adjacent lake bottom. As demonstrated in Fig. 4, fluxed of NH_4^+ and NO_3^- across the sediment-water interface depend strongly on the hydrodynamic conditions of the sediment overlying water. Therefore, results obtained from benthic chambers should not be extrapolated to *in situ* conditions without an appropriate calibration. A simple method for estimating bottom stress and diffusive boundary layer (DBL) thickness *in situ* is the alabaster dissolution method (Santschi et al. 1983; Opdyke et al. 1987), which yields an average, time-integrated measure of bottom dynamics during the course of an experiment.

Stirring decreases the diffusive resistance of the DBL, and thus, for purely physical reasons, generally enhances diffusion across the sediment-water interface. However, increased diffusion of electron acceptors and electron donors in opposite directions alters the redox gradient in the sediment. As a consequence, the velocity or even the direction of redox reactions and, hence, the concentration profiles of redox reactive species in the sediment may change depending on the hydrodynamics in the overlying waters. As long as the oxygen flux to the sediment is diffusion controlled, an increase in stirring rate will increase the oxygen uptake by the sediment (Sweerts et al., 1989). As shown in Figure 4, stirring also stimulated the initial NH_4^+ flux from the sediment to the water in experiments with sediment cores. However, after adaptation of the benthic microflora to changed redox conditions and increased nitrification in the sediment surface, a decrease of the NH_4^+ flux from the sediment to the water would be expected.

Conversely, any decrease in turbulence would instantaneously lower the flux of oxygen to the sediment. If, under *in situ* conditions an oxic microlayer existed at the sediment surface, then nitrification in the sediment surface or in the DBL would decrease immediately. As a consequence, an immediate increase in the NH_4^+ flux from the sediment to the water would be expected (Gächter and Meyer 1990). Thus, it is most likely that any change in the hydrodynamics of the water overlying the sediment will instantaneously stimulate an initial NH_4^+ flux from the sediment to the overlying water, leading to a overestimation of the NH_4^+ flux in flux chamber experiments. In other words, a change in DBL thickness does not necessarily exert a proportional change in the fluxes of NH_4^+ and NO_3^- (Fig. 4). As a consequence, the sediments may either become a sink or a source for inorganic N in short term flux chamber experiments, depending on the O_2 concentration in the sediment overlying water and stirring rates (as summarized in Table 1).

Mass balance approach

Long-term averages of fluxes across the sediment-water interface can be determined by mass balances. However, no insight into the mechanisms controlling benthic fluxes can be obtained. The main problem in this approach is its inability to describe chemical and microbiological reactions which may interconvert reactive species in the studied water mass. In the oxic hypolimnion of Lake Sempach, for example, nitrification leads to the oxidation of NH_4^+ and NO_2^- to NO_3^-. As a consequence, the fluxes observed for the reactive species NH_4^+, NO_2^- and NO_3^- determined by the hypolimnetic mass balance should properly be termed "apparent fluxes"'. Reactions other than sediment fluxes which affect inorganic N in the water body below 40 m depth could be denitrification and N uptake or release by settling seston. However, denitrification is not likely to occur in the water column containing more than 10 µM O_2 (Seitzinger 1988), and the difference in PON sedimentation fluxes measured from 1985 to 1987 with two sediment traps in the epi- and hypolimnion, respectively, accounted for a maximum N uptake by settling seston of 0.4 mmoles m^{-2} d^{-1} (Gächter and Meyer 1990). These measurements, along with calculations of maximum estimated losses into the surface waters (0.2 mmoles m^{-2} d^{-1}) support the assumption that accumulation of inorganic N in the water layer between 40 m and the lake botom during summer stratification is a consequence of sediment fluxes.

Data from the benthic chamber experiments, as well as calculations from interstitial water data, indicate that the sediment is an important source for NH_4^+. Since, however, this NH_4^+ does not accumulate in the hypolimnion, it must be oxidized at the sediment-water interface or in the hypolimnion. From the increase of 26 to about 80 tons of NO_3^--N for the spring to September periods during the years 1979 to 1989 (Fig. 2), a minimum volumetric nitrification rate of 0.05–0.11 mmoles m^{-3} d^{-1} or a net release of 1.3–2.6 mmoles N m^{-2} d^{-1} can be estimated. In summary, hypolimnetic mass balances yield accurate long-term flux estimates for TIN, but only limited insight into flux mechanisms.

Flux estimation from interstitial water profiles

This method has been reported to give results in anoxic environments where no bioturbation or nitrification occurs (van der Loeff et al. 1984; Devol 1987). Due to the lack of benthic fauna, bioturbation does not exist at the deepest part of Lake

Sempach. The main limitation of this method in eutrophic lakes with an oxic hypolimnion is that the steep gradient of reactive chemical species across the sediment-water interface cannot be resolved by available interstitial water sampling techniques. Only the use of microelectrodes for O_2 (Sweerts et al. 1989) and for NO_3^- (Sweerts and DeBeer 1989) can circumvent this problem. Fluxes across the interface were calculated from Fick's first law

$$F = \phi \cdot D_s \left. \frac{dC}{dz} \right|_{z=0} \tag{1}$$

where F is the flux, ϕ is the porosity at the sediment surface (0.97), D_s is the diffusion coefficient in the sediment and dC/dz is the concentration gradient at the interface. According to Ullman and Aller (1982) and assuming no adsorption, the diffusion coefficient within the sediment was estimated as

$$D_s = \phi^2 \cdot D_m, \tag{2}$$

where D_m is the molecular diffusion coefficient at interstitial water *in situ* temperature (NH_4^+: $11.8 \cdot 10^{-6}$ cm^2 s^{-1}; Li and Gregory 1974). NH_4^+ fluxes calculated from interstitial water data ranged from 1.1 to 3.5 mmoles m^{-2} d^{-1} and matched the TIN fluxes estimated by the mass balance approach. This estimation is an upper limit for NH_4^+ flux across the sediment-water interface because of adsorption to sediment particles. Hence, diffusion of NH_4^+ may be slower in the interstitial water. Höhener (1990) estimated an apparent diffusion coefficient for NH_4^+ in Lake Sempach sediment of only $3 \cdot 10^{-6}$ cm^2 s^{-1}. Little is also known about the diffusion properties of DON since this fraction is composed of different molecules with different sizes. A maximum diffusion coefficient was estimated to be $5.8 \cdot 10^{-6}$ cm^{-2} s^{-1}, which is the molecular diffusion coefficient for the amino acid alanine (Weast et al. 1985) corrected to 5 °C. Estimated DON fluxes were one order of magnitude smaller than NH_4^+ fluxes.

Mechanisms controlling the benthic fluxes of nitrogen

As previously described, data from benthic chamber experiments may have overestimated N fluxes because turbulence in the benthic chamber did not properly match the average turbulence regime at the lake bottom. The thickness of the diffusive boundary layer (DBL) is a useful concept for comparing different hydrodynamic regimes (Jørgensen and Revsbech 1985; Sweerts et al. 1989). However, the real physical situation may be complicated by the occurrence of a transition zone between turbulently mixed bottom water and the diffusive sublayer (Wimbush and Munk 1970) and also by rapid fluctuations in the friction velocity and bottom stress, which are proportional to the DBL (Opdyke et al., 1987). The influence of hydrodynamic conditions on benthic fluxes has been shown for O_2 in an estuary (Boynton et al., 1981), in rivers (Hickey, 1988), and in lakes (Sweerts et al. 1989). It has also been demonstrated for phosphorus (Fowler et al. 1987; Kairesalo and Matilainen 1988), but not for N. Stirring was also found to play a key role in the transport of reactive trace metals between water and sediments (Santschi et al. 1983; Sundby et al. 1986).

Assuming a mean current speed of 1–2 cm s^{-1} 1 m above the sediment in a similar, stratified lake (Lemmin and Imboden, 1987), DBL thicknesses of 1.7–3.4 mm can be estimated using calculations outlined in Santschi et al. (1990). The range of observed DBL thicknesses in our laboratory experiments matched the range of theoretical thicknesses of the DBL at the lake bottom. However, a DBL thickness of 0.9 mm, measured with alabaster experiments in the bottom lander, indicates that the hydrodynamic conditions in the flux chambers were different from those of the adjacent lake bottom.

Theoretical considerations of the DBL thickness on N cycling

Morse (1974) suggested that diffusive fluxes, calculated from interstitial water gradients, can be considerably erroneous when the boundary condition at the sediment-water interface is violated. The assumption that the concentration of a diffusing substance at the sediment-water interface is equal to the concentration in the overlying mixed water, is not valid and must be replaced by a flux boundary condition:

$$F_{DBL} = D_m (C_{interface} - C_{lake})/z \tag{3}$$

where F_{DBL} is the flux across the diffusive boundary layer, D_m is the molecular diffusion coefficient in water, $C_{interface}$ is the concentration at the sediment-water interface, C_{lake} is the concentration in the mixed lake bottom water and z is the thickness of the diffusive boundary layer. Assuming that the concentration at the interface remains constant during short benthic flux measurements, initial fluxes are directly proportional to the inverse of the DBL thickness as shown in equation 3.

How fast will the concentrations of N compounds at the sediment-water interface change after the onset of new hydrodynamic conditions? Residence times for N compounds in the uppermost 2 mm of sediment were estimated by dividing the total amount found in the interstitial water over that depth range by the initial flux across the interface (Tab. 3). Mean residence times of NH_4^+, NO_2^- and DON in the surface sediment were on the order of 1 to 10 h (Tab. 3), whereas the residence time of NO_3^- is in the order of minutes. Changes in steady state interstitial water profiles, due to disturbance of the flux through the DBL by altering the hydrodynamic conditions, will induce non-steady-state profiles for at least a few mean residence times for each of the diffusing species. This means that after altering the DBL thickness, the NO_3^- interstitial water profile will reach a new steady state within a few minutes whereas the other profiles will change slowly during the entire time span of a benthic chamber experiment. Thus, apparent enhanced fluxes of reduced N compounds can be measured in benthic chambers during an initial phase of several hours in cases where the turbulence within the chamber does not match the conditions outside at the lake bottom. This would explain why NH_4^+ fluxes measured with benthic chambers exceeded fluxes obtained by independent methods (Kemp et al. 1982).

Another feature which can be deduced from equation 3 is that the flux of NO_3^- into the sediment would be linearly related its concentration in the overlying water if the concentration at the sediment-water interface was near zero. All our experiments with benthic chambers and sediment cores revealed a similar relationship between NO_3^- concentration and NO_3^- flux. This pattern means that NO_3^- flux is a first order process with respect to the NO_3^- concentration in the water overlying the sediment and that the NO_3^- flux and not organic substrates would limit NO_3^- reduction processes in the sediments of Lake Sempach.

Impact of artificial oxygenation on N fluxes across the sediment-water interface

During the first two years of artificial oxygenation the concentrations of NH_4^+ and NO_2^- in the hypolimnion, especially near the lake bottom, decreased (see Stadelmann 1988). In contrast, these internal measures seemed to have little effect during the first 4 years on the recycling of inorganic N from the sediments (Fig. 2). However, during 1988 and 1989 less TIN accumulated in the water mass below 40 m depth during the stratification period. This leads to the conclusion that after 4 years of artificial oxygenation in Lake Sempach, hypolimnetic net denitrification has increased during summer stratification.

According to Gächter and Meyer (1990) the average sediment load of particulate N was 2.7 mmoles m^{-2} d^{-1} from 1985 to 1987, and seetling material collected with a sediment trap close to the lake bottom contained 1.13 mmoles PN g^{-1} dry weight. With increasing depth in the sediment the N content of the material decreased to a residual value of about 0.36 mmoles PN g^{-1} dry weight (at 4 cm below the sediment surface). Thus, the deposited material lost about 68% of its original N content during early diagenesis. At an average input of 2.7 mmoles m^{-2} d^{-1} the expected average NH_4^+ production rate was about 1.84 mmoles m^{-2} d^{-1} (0.68×2.7 mmoles m^{-2} d^{-1}).

NH_4^+ fluxes estimated from interstitial water data were 1.1 to 3.5 mmoles m^{-2} d^{-1} (Tab. 1). Considering the inaccuracy of this method, the results agreed reasonably well with the estimate obtained from the hypolimnion mass balance calculation. However, it becomes obvious that benthic chamber fluxes strongly deviated from average *in situ* fluxes. Considering also that dissimilatory NO_3^- reduction to NH_4^+ was shown to be negligible, it is impossible that average NH_4^+ efflux rates exceeded the average particulate N (PN) input rate by 2- to 3-fold.

As previously mentioned, significantly less TIN accumulated in the hypolimnion in 1988 and 1989 than during previous summers (Fig. 2), although PN settling rates did not change and there was no reason to assume a lower NH_4^+ production in anoxic sediment layers during these years. For reasons discussed above, increased flux rates of NO_3^- from the water to the sediment would require increased NO_3^- concentrations in the water overlying the bottom sediments. However, average NO_3^- concentrations at the 85 m depth did not change significantly from 1984 to 1989 (Fig. 5). Even though NO_3^- consumption and NH_4^+ generation were about the same as in previous years, there were still unknown lower net NO_3^- accumulation rates during summer stratifications in 1988 and 1989.

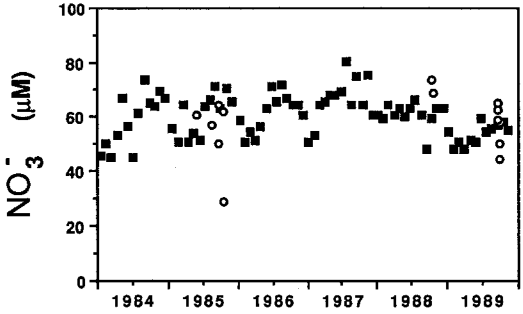

Figure 5. Seasonal variation of $[NO_3^-]$ at 85 m (■) and in 87 m (○) depths in Lake Sempach. The maximum depth is 87 m at this station

Regardless of the permanently aerobic hypolimnion in 1988 and 1989, dense mats of *Beggiatoa* sp. were often observed at the sediment surface. Since *Beggiatoa* are slowly growing organisms which demand a solid substratum and the permanent presence of traces of O_2, these organisms could not exist in the pelagic sediment of Lake Sempach before artificial oxygenation was started in 1984. Since 1988, they are an excellent indicator of improved oxygen conditions at the sediment-water interface. *Beggiatoa* sp. reach their maximum density in a zone where both O_2 and H_2S are present in concentrations of 0 to 10 µmoles L^{-1} (Jørgensen and Revsbech 1983). But in such an environment, growth of nitrifying bacteria is strongly O_2-limited (Henriksen and Kemp 1988) and simultaneously inhibited by H_2S (Srna and Baggeley, 1975). Thus, the zone of optimum nitrification, which requires higher O_2 and lower H_2S concentrations, must be allocated to a layer above the *Beggiatoa* mat. Hence, it is likely that in oxygenated Lake Sempach with *Beggiatoa* at the sediment surface, NH_4^+ is nitrified in the diffusive boundary layer, where sufficient O_2 and simultaneously elevated NH_4^+ concentrations are present.

Beside being a very sensitive redox indicator, as shown in Figure 6 *Beggiatoa* might also influence the nitrification process at the sediment-water interface: *Beggiatoa* mats catalyze H_2S oxidation and thus "detoxify" the environment in the DBL for nitrifying bacteria. Since the sediment is the main sink for NO_3^- it is speculated that the development of *Beggiatoa* sp. after artificial oxygenation of Lake Sempach decreased H_2S concentrations in the diffusive boundary layer overlying the sediments. This provided new ecological niches for nitrifying bacteria in the DBL which are closer to the anaerobic zones where NO_3^- is denitrified. As a consequence, part of the NH_4^+ produced in the sediment since 1988 would have been oxidized and denitrified concomitantly within the pelagic sediment-water interface, either at the sediment surface or within the diffusive boundary layer. The shorter distance between NO_3^- generation and NO_3^- reduction might have enhanced the overall denitrification rate in Lake Sempach. In consequence, less inorganic nitrogen accumulated in the hypolimnion. Recently, Sweerts et al. (1990) confirmed experimentally that removal of NO_3^- was increased when *Beggiatoa* was present at the sediment surface. They suggested that *Beggiatoa* may oxidize H_2S anaerobically using NO_3^- as an electron acceptor. Hence, *Beggiatoa* might not only "detoxify" the environment for nitrifying bacteria but could create an efficient sink for NO_3^-.

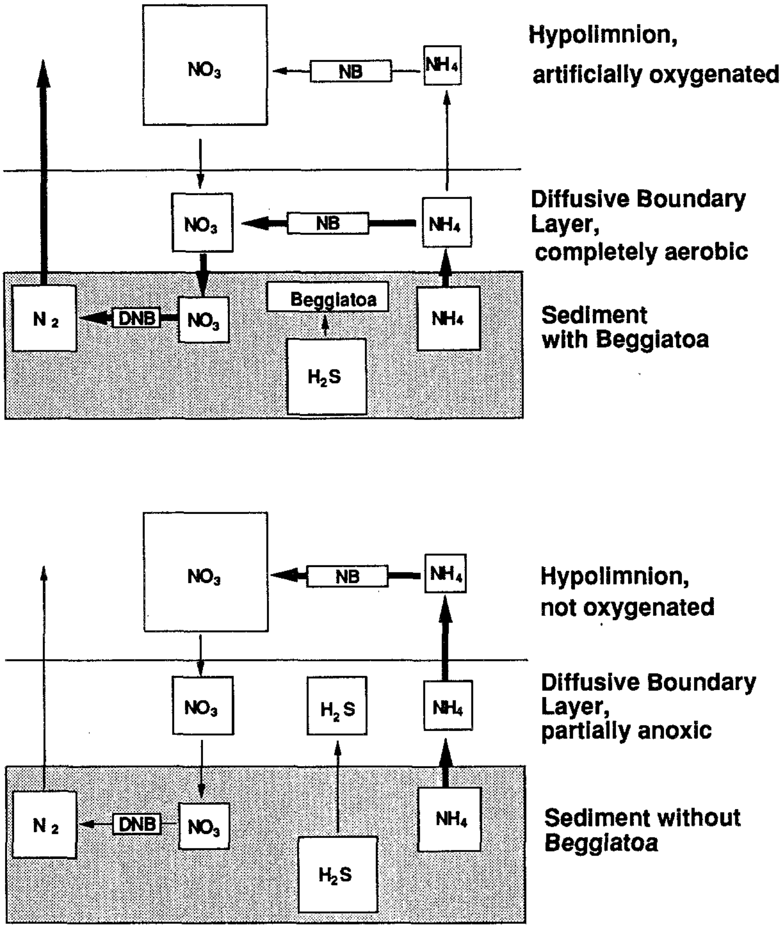

Figure 6. Schematic presentation of nitrogen cycling at the sediment-water interface in the oxygenated (above) and not oxygenated (below) hypolimnion of Lake Sempach (DBL = diffusive boundary layer, NB = nitrifying bacteria, DNB = denitrifying bacteria. Relative flux rates are depicted by arrow sizes)

Summary and conclusions

Lake Sempach is a deep, artificially oxygenated, eutrophic hard-water lake in central Switzerland. Lake water concentrations of TIN (TIN = 0.8 mg L^{-1}) are low compared to those in surface waters entering the lake (average concentrations of TIN = 5.8 mg L^{-1}). In order to study N removal mechanisms in this lake, fluxes of inorganic N species across the sediment-water interface were measured using benthic flux chambers and hypolimnetic mass balance calculations. Microbial reactions and transport processes in the sediment were investigated using $^{15}NO_3$ as a tracer and measurements of TIN concentrations in the interstitial water. It is concluded that 68% of the settled organic N is mineralized during early diagenesis, nitrified at the sediment surface or in the diffusive boundary layer (DBL) and subsequently denitrified in the sediment. Since 1988 much less TIN accumulated in the hypolimnion during summer stratification than in previous years. It is postulated that this was due to the presence of *Beggiatoa* at the sediment surface. This bacterium is known to oxidize H_2S which could effectively detoxify the environment for nitrifying bacteria and increase denitrification near the sediment-water interface. At the same time, it may also use NO_3^- to oxidize H_2S.

It is further demonstrated that the flux of NH_4^+ across the sediment-water interface strongly depends on the hydrodynamics of the water overlying the sediment. Any change in the thickness of the DBL would likely increase the initial NH_4^+ flux for the following reasons: 1) thinner DBL leads to a steeper concentration gradient, and hence, according to Fick's law, to an increased diffusive flux. 2) thicker DBL lowers the flux of O_2 to the oxic microlayer and hence decreases the rate of nitrification. As a consequence, NH_4^+ accumulates at the sediment surface creating a steeper concentration gradient in the DBL. The flux of NH_4^+ to the overlying water would increase. Given this dependence between the thickness of the DBL and the NH_4^+ flux, it is concluded that in environments with oxic sediment surfaces, benthic flux chambers are not suitable instruments to measure fluxes of NH_4^+ across the sediment-water interface.

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