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Limnology and Oceanography, Vol. 32, No. 6 (Nov., 1987), pp. 1226-1238
Limnol. Oceanogr., 32(6), 1987, 1226–1238
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Nitrogen mineralization and denitrification in Lake Michigan sediments[1]

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Abstract

Organic nitrogen mineralization mechanisms, fluxes, and fates in Lake Michigan sediments were examined by measuring accumulation rates of inorganic nitrogen in laboratory microcosms. Neither ammonium nor nitrate increased substantially in flow-cell or slurry microcosms of offshore, silty sediments. In experiments with gastight chambers containing "intact" offshore, silty sediment cores (sampled at 45- and 100-m water depths), the total fluxes of nitrogen (NH_4^+, NO_3^-, and N_2) across the sediment–water interface ranged from 14 to 51 μg-atoms N m^{-2} h^{-1}. Nitrogen gas accounted for 93–98% of the total inorganic nitrogen flux from the sediment to the water. Inputs of inorganic nitrogen via mineralization processes (mediated by microbial decomposition and invertebrate excretion) appeared to be the major factors controlling the rates of both nitrification and denitrification in these sediments. The overlying water did not serve as a significant net source of nitrate driving the denitrification reaction. These results thus indicate that denitrification is a dominant sink for mineralized nitrogen in these silty Lake Michigan sediments and that this process is closely coupled with the initial mineralization of organic nitrogen in the sediments.

Although primary production provides the biochemical energy that drives upper trophic level food-web dynamics in large lakes and marine systems, the relative importance of various nutrient cycling and energy flow processes in aquatic systems is incompletely known. For example, nutrient regeneration via the mineralization of organic matter is an important process supplying inorganic nutrients to phytoplankton in the Great Lakes (Scavia 1979), but details of food-web energy-loss and nutrient-transformation mechanisms in the lakes are not clear. The mineralization process, mediated mainly by microbes and larger heterotrophs, occurs both in water and sediments, where settling organic material accumulates. Nutrient recycling within the photic zone is important as a short-term nutrient-supply mechanism for phytoplankton (Harrison 1978; Lehman 1980), but the longer term degradation of organic materials in the hypolimnion and sediments is also potentially important, particularly in temperate lakes. It is a primary process controlling the total supply of available nutrients delivered to the epilimnion during periods of destratification when the lakes are mixed. Regeneration and flux of inorganic nutrients mineralized from organic material in lake sediments or the hypolimnion represent important sources of nutrients to Great Lakes phytoplankton on an annual basis (Eadie et al. 1984).

Mechanisms of nutrient transformation and eventual release from Great Lakes sediments are complex, in part because of the heterogeneous composition of the constituent biota. Although both invertebrates and bacteria are involved in sediment–nutrient interactions, nutrient mineralization (i.e. conversion of organic nutrients into inorganic forms) is traditionally thought to be due primarily to activities of bacteria (Wetzel 1975; Aller 1982). Yet, the metabolic activities of benthic invertebrates may also be important to mineralization (e.g. Gallepp et al. 1978; Gallepp 1979; Gardner et al. 1981; Hawkins and Keizer 1982). The quantitative importance of benthic animal excretion, relative to total mineralization in the sediments, has not been established in the Great Lakes. To understand how the various components of the benthic community affect nutrient and biochemical energy cycling processes in the Great Lakes, their respective nutrient mineralization rates should be quantified and the fate of the mineralization products determined. In this paper, we quantify rates of nitrogen mineralization and flux in silty Lake Michigan

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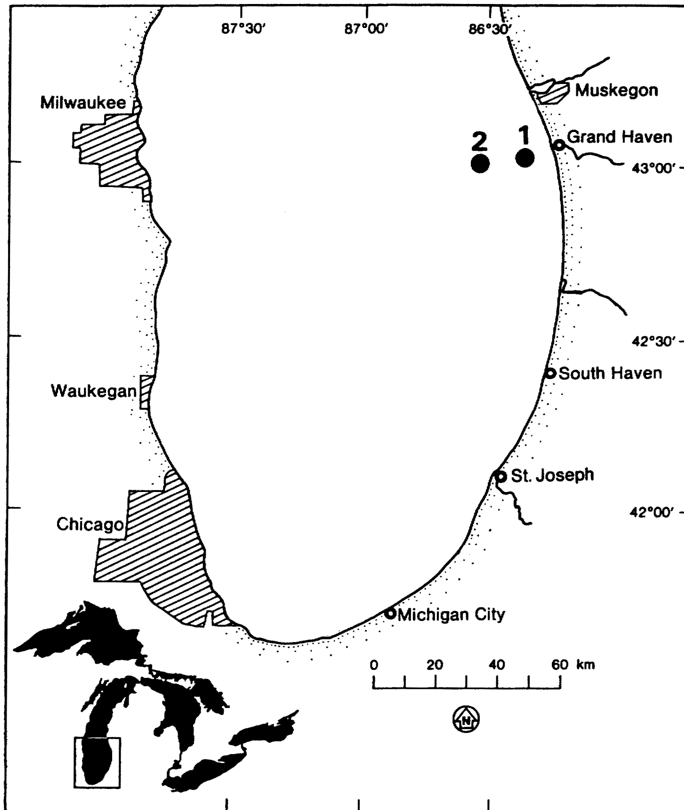

Fig. 1. Locations of sampling sites in southern Lake Michigan. Sites 1 and 2 have respective water depths of 45 and 100 m; both have fine, silty sediments.

sediments, evaluate the contribution of benthic invertebrate excretion to this process, and examine the fate of the mineralized nitrogen.

We thank J. Jones and staff of the Phoenix Memorial Laboratory, University of Michigan, for sediment sterilization; M. Klug, S. Seitzinger, and G. Walker for suggestions on denitrification; W. Burns, J. Grimes, and D. Morse for help in sample collection; P. Landrum for sediments for the slurry experiments; J. Chandler and E. Cichocki for technical assistance; and B. Eadie, M. Quigley, D. Scavia, and S. Seitzinger for suggestions on the manuscript.

Methods

Sampling sites—Sediments with animals were collected on 23 April, 23 May, 20 June, 8 August, and 21 October 1985 from two sites in southern Lake Michigan near Grand Haven, Michigan (Fig. 1). The water depths at sites 1 and 2 are 45 and 100 m. Both sites have silty sediments. The amphipod, *Pontoporeia hoyi,* and the oligochaete, *Stylodrilus heringianus,* are the dominant benthic invertebrates at both sites. Their respective abundances are 10,400 and 2,400 m^{-2} at site 1 and 4,000 and 1,000 m^{-2} at site 2 (NOAA Data Rep. GLERL-28, Ann Arbor; Nalepa unpubl. data).

Nitrogen ion and gas analysis—Ammonium and nitrate (plus nitrite) concentrations in water samples were measured with discrete injection techniques (Gardner 1978; Gardner and Malczyk 1983) after particles were removed by filtration (Gardner and Vanderploeg 1982) or microcapillary high-speed centrifugation (Gardner et al. 1980). Nitrogen gas was analyzed on a Shimadzu gas chromatograph (model GC-8A) equipped with dual Molecular Sieve (5A)

columns, a thermal conductivity detector, and a gas sampling valve (ca. 0.5-ml sampling loop). Further details on gas sampling and analysis are given below with the description of denitrification measurements.

Ammonium excretion measurements—Excretion rates of individual benthic invertebrates were measured as accumulations of ammonium in 2 ml of low-nutrient culture water (NOPN medium; Lehman 1980) containing individual animals over incubation intervals of 2 h by previously described procedures (Paffenhöfer and Gardner 1984).

Flow-cell and slurry experiments—Accumulation of dissolved nutrients in waters of site 1 sediments were examined both with flow-cell and slurry techniques to provide initial insights about nutrient conversions in the sediments. However, these approaches did not eliminate possible effects (e.g. oxygen penetration) caused by disturbing the intact sediments or allow assessment of denitrification rates. Subsequently, denitrification and nutrient flux were measured directly on "intact" cores with gastight chambers (Seitzinger et al. 1980).

Flow cells were constructed from gastight, 5-ml glass syringes equipped with outlet frits and inlet tubes (a large-scale adaptation of the flow cell of Gardner and Scavia 1981) and placed in an adjustable holder constructed to keep the plunger in position. Sediments with and without *P. hoyi* were added to the flow cells, and low-nutrient culture water was pumped slowly (ca. 0.1 ml min^{-1}) through the cells. Flow rates and changes in ammonium and nitrate concentrations in the input vs. output culture water were measured to estimate rates of nitrogen mineralization in the sediments.

Sediments for flow-cell experiments were collected by box corer at site 1 in October 1983. The upper 1–2 cm of sediments were removed from each of five sequential cores and divided into two fractions. Invertebrates were sieved from one fraction and counted. The screened sediments from this fraction and the remaining unscreened sediments were stored at 11°C in large covered beakers until the experiments were conducted (within 4 d). A 3-ml subcore of wet, screened sediments was placed in each flow cell and the plunger was adjusted to enclose the sediments but remove excess water. Each experiment was conducted in pairs with one cell receiving one *P. hoyi,* taken from the unscreened sediment sample, and the other containing only the screened sediments. Temperature-equilibrated culture water was pumped through the cell at a flow rate of about 0.1 ml min^{-1} with high performance liquid chromatographic pumps. The actual flow rate of water coming out of the flow cells was measured by collecting the effluent from the cells over the measured interval between observations. The cells were flushed with culture water for about 17 h to purge dissolved nutrients present in the original pore water. Water samples were taken from the flow-cell outlets and analyzed for ammonium and nitrate at about 17 and 22 h after flow incubations were begun.

Slurry experiments, with time-course measurements of dissolved ammonium and nitrate concentrations in water surrounding untreated and sterilized sediments (site 1), provided additional information about the mineralization or conversion reactions to be expected in silty sediments. Part of the sediments was presterilized before animals were added to prevent microbial transformations of excreted nitrogen and thereby allow quantification of ammonium excretion rates in the presence of sediments. The design of this experiment consisted of four different experimental treatments, i.e. sterilized and nonsterilized sediments with and without *P. hoyi* (4–6 replicates per treatment). In addition, *P. hoyi* excretion rates were measured separately. Upper sediments that had been stored for a few weeks in an aquarium at 4°C were screened into a tray, transferred to a 250-ml beaker, and stored overnight at 4°C to settle. Five-milliliter sediment cores were taken from this beaker and transferred to individual clean scintillation vials containing 5 ml of culture water. Some vials were sterilized by gamma radiation (^{60}Co) at the Phoenix Memorial Laboratory. Except for the period of sterilization, all vials were stored at 4°C until experiments began. Two *P. hoyi* per vial were added to half of the vials for both the sterilized and nonsterilized treatments.

Ammonium and nitrate concentrations were measured 0, 22, and 48 h after incu-

bations began. Before each measurement, the vials were gently inverted several times to remix the pore water with overlying water.

Seasonal studies—Sediment samples were collected with a box corer and subsampled with plastic cylindrical corers (67-mm i.d.) for nitrogen flux and denitrification measurements. The cores (three per site) with overlying water were held in the coring tubes by rubber stoppers and transported in cooled ice-chests back to the laboratory. Additional sediments with constituent animals were collected from the same box cores for animal excretion measurements. Macroinvertebrates were held in their native sediments at about 4°C until animals were removed for excretion incubations (within 5 d of collection). Ammonium excretion rates were measured for *P. hoyi* collected from both sites and for *S. heringianus* from site 1.

Denitrification rates were quantified directly by measuring the concentrations of N_2 gas that accumulated in gastight incubation chambers (after Seitzinger et al. 1980). This direct measurement of N_2 was chosen over nitrogen ion-addition methods to allow estimation of "actual" rather than "potential" denitrification rates (e.g. Kaspar 1985) and over the acetylene inhibition technique so that the nitrification reactions would not be inhibited by acetylene (Anderson et al. 1984). Each chamber was equipped with a single, vertical stopcock to allow purging of the microcosm with $He:O_2$ and withdrawal of gas and water samples for analysis. A suspended magnetic bar stirred the water in each chamber during incubations to enhance gas diffusion and equilibration with the overlying gas layer (Fig. 2).

After each set of samples was brought to the laboratory, the lower parts of the collected cores were extruded by gravity and discarded. The upper 5–6 cm of sediments with overlying lake water were placed in the lower section of a corresponding gastight glass chamber (75-mm i.d.), and the upper chamber section was attached and sealed via a greased O-ring (Seitzinger et al. 1980). Each of the six cores (three per site) was placed in a separate chamber and the lake-water volume was adjusted to give a water volume of about 180 ml. This procedure

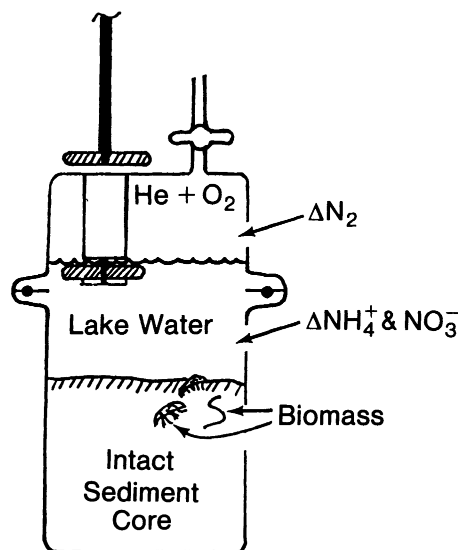

Fig. 2. Schematic diagram of gastight incubation vessels for direct measurement of denitrification (modified from design of Seitzinger et al. 1980).

left a volume of about 230 ml for the overlying gas phase. (Exact volumes were determined for each chamber.) The chambers were sealed and placed in an ice bath; the water and gas phases were then purged for about 1 h with $He:O_2$ (80:20) to remove atmospheric N_2. Purging gas was added to the chamber via a cannula inserted through the vertical stopcock. The chambers were kept in the ice bath during purging to maintain temperatures near the in situ temperature of 4°–6°C. After purging, the chambers were placed in an incubator equipped with an overhead magnetic stirring apparatus designed to continuously drive each of the magnetic stirrers in the respective chambers. All six stirrers were rotated at a speed of 60 rpm by a motor-driven, O-ring drive-belt system.

Chambers were purged with $He:O_2$ every 1–3 d for about 14 d to allow the nitrogen diffusing from the sediments to be replaced with helium. Then, nitrogen flux was measured by gas chromatography over incubation periods of 3–7 d to provide time-course measurements (Seitzinger et al. 1980). At each sampling date, water samples (3 ml) were removed through the stopcock opening via a syringe equipped with a long can-

Table 1. Net fluxes of ammonium and nitrate (ng-atoms N $cell^{-1}$ h^{-1}) from site 1 sediments (3-ml volume) as measured with a flow-cell apparatus at 17 and 22 h after flow of culture water began. For each experiment, a flow cell containing 3 ml of sieved sediments was run in parallel with a similar flow cell with a single *Pontoporeia hoyi* added. Excretion rates were measured on single animals from the same site by incubating them in 2 ml of culture water over 2-h intervals. Incubation temperature, 11°C. Number of replication experiments, four.

Time after flow (h)	Rate of nitrogen release							
	Sieved sediments alone				Sieved sediments + *P. hoyi*			
	NH_4^+		NO_3^-		NH_4^+		NO_3^-	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE
17	−0.6	0.3	4.0	0.6	−0.1	0.1	5.4	1.1
22	−0.7	0.4	3.3	0.8	0.4	1.0	3.8	1.1

Mean excretion rate for *P. hoyi* = 6.3 (SE = 1.2) nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1}
= 4.6 nmol NH_4^+ $animal^{-1}$ h^{-1}

nula, filtered (Gardner and Vanderploeg 1982), and analyzed for ammonium and nitrate (plus nitrite). During sampling, the open end of the vertical stopcock of the gastight chamber was continuously purged with $He:O_2$ to prevent contamination by atmospheric nitrogen. Volume changes in the water and gas phases, as a result of water sample removal, were considered in the flux calculations. To sample the headspace gas, a vertical inlet cannula from the gas-sampling valve was placed in the open end of the vertical stopcock. The sample loop was purged several times with $He:O_2$ by a 10-ml syringe attached to the outlet of the sample loop. After the sample loop was thoroughly rinsed with $He:O_2$, the stopcock was opened and the chamber raised around the inlet cannula for direct sampling of the gas in the chamber. About 5 ml of sample was pulled through the loop with the sampling syringe, and the chamber was then lowered and the stopcock immediately closed. The collected gas sample was injected immediately for analysis. When sampling was completed, each chamber was again purged with $He:O_2$ in preparation for the next measurement.

Incubations and time-course measurements of denitrification and of ammonium and nitrate fluxes were continued over periods of 4–8 weeks. At the end of each incubation, the cores were removed from the chambers and constituent animals were removed, counted, dried (at 60°C for at least 48 h), combusted (at 500°C for 1 h), and reweighed for AFDW determinations.

Results and discussion

Flow-cell and slurry experiments—Changes in ammonium levels were small, erratic, and sometimes not detectable in the flow-cell experiments (Table 1). Nitrate accumulation was measurable, but rates for sediments containing animals were not significantly different from those without animals. This finding indicates that either macroinvertebrate excretion rates were very low and quantitatively unimportant or that part of the mineralized nitrogen was converted to a form other than ammonium or nitrate (e.g. to nitrogen gas via microbial denitrification). The former possibility seemed unlikely, because excretion rate measurements (Table 1) indicated that the animals were releasing ammonium at rates that should significantly elevate nitrogen ion concentrations in incubation cells containing animals relative to those without animals.

However, to consider the possibility that animals may release ammonium slower in the sediment substrates than in sediment-free water, we compared nutrient accumulation in previously sterilized sediments to that in nonsterilized sediments with the slurry technique (Fig. 3). The gamma irradiation treatment released large quantities of ammonium from the sediments into solution, but subsequent changes in ammonium concentration were still measured to estimate ammonium flux in the vials. In the treatment without animals, some of this released ammonium was lost from solution,

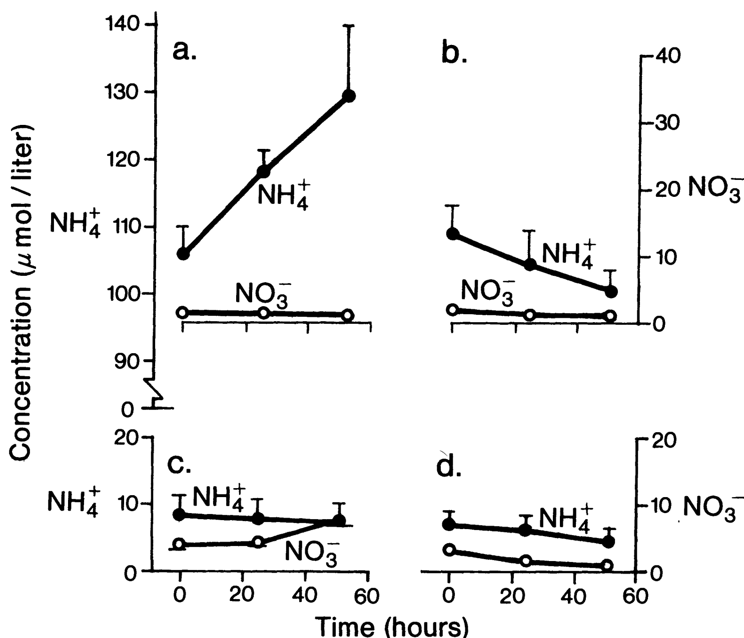

Fig. 3. Changes in ammonium and nitrate concentrations with time for four treatments of Lake Michigan sediments from site 1. a. Sterilized sediments with two *Pontoporeia hoyi* per vial. b. Sterilized sediments without invertebrates. c. Unsterilized sediments with two *P. hoyi* per vial. d. Unsterilized sediments without invertebrates. Range bars = SE.

probably due to sorption, during the 50-h interval of the experiment (Fig. 3). However, in sterilized sediments containing animals, ammonium accumulated during the experiment. If physical removal processes such as sorption are similar in vials with and without animals, animal release rates can be estimated from the increase in ammonium concentration per unit time plus the sorption loss observed in vials without animals. The mean invertebrate release rate calculated in this way [2.3 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1}] was similar to the excretion rates of similar animals incubated without sediments [3.4 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1}; SD = 1.2, N = 13]. As in previous studies of phosphorus release by macroinvertebrates (Nalepa et al. 1983), it implies that the excretion rates of the animals were not affected greatly by the presence or absence of sediments.

In contrast to results from the sterilized sediments, inorganic nitrogen ion accumulations in the nonsterilized samples were less than the inputs expected from animal excretion. As with the flow-cell experiment, ammonium levels did not change significantly (overlapping SE) during the incubations; nitrate concentrations increased slightly in the vials with *P. hoyi,* but much less than would be expected to result from excretion. Nitrate decreased slightly in the vials without animals (Fig. 3). The most reasonable explanation for these results is a coupling of denitrification with nutrient mineralization (Seitzinger et al. 1980; Jenkins and Kemp 1984).

Seasonal studies—To compare denitrification to total nitrogen mineralization and flux in silty sediments, we directly quantified fluxes of N_2, NH_4^+, and NO_3^- (+NO_2^-) from intact cores. Time-course measurements of nitrogen accumulation rates after the initial 10 d of purging and equilibration indicated that about 4 weeks were needed for N_2 accumulation rates to stabilize, i.e. approach constant rates over time, in these sediments. During the interval between 15 and 25 d, the N_2 accumulation rates decreased with time. To establish whether this

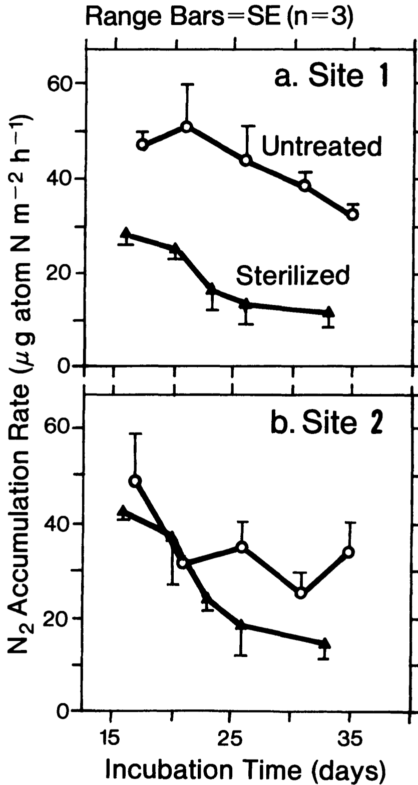

Fig. 4. Accumulation rates of nitrogen in gastight vessels, containing sediments and water from sites 1 and 2 (sampled in October 1985), after the water and gas phases were purged with $He:O_2$ (80:20). The chambers were purged several times during the first 14 d of incubation to allow nitrogen gas to diffuse from the sediments and water in the chamber. Accumulation rates were calculated based on the cross-sectional area of the original cylindrical core. Range bars = SE.

change was due mainly to a long physical equilibration time or to decreasing rates of denitrification in the sediments, we sterilized a supplemental set of cores collected on 21 October 1985. After the rates were measured in unsterilized cores, a second set of cores sampled on the same date and stored at 4°C were placed in the chambers and sterilized so we could observe the time-course of nitrogen depletion in the absence of microbial input and quantify any background diffusive N_2 inputs into the chambers.

The results (Fig. 4) indicated that about 4 weeks of purging and equilibration were needed to achieve constant background rates. After this period, background input rates were approximately constant at about 14 ± 4 (SE) ng-atoms N m^{-2} h^{-1} for site 1 chambers and 18 ± 7 for site 2 chambers. This equilibration time was longer than the 10–13 d needed by Seitzinger et al. (1980), probably because our chambers were not purged as frequently as theirs (>1 d^{-1} during the first week of purging: S. Seitzinger pers. comm.). Because of this slow equilibration with $He:O_2$, we used rates measured 4 weeks after incubations were begun to estimate nitrogen fluxes and transformations. Rates continued to decrease after this period in a few experimental chambers (e.g. Fig. 4a), but remained stable in most chambers examined beyond 4 weeks. The mean background nitrogen inputs observed in the irradiated controls after 4 weeks were subtracted from the measured rates for each site to provide an estimate of actual denitrification rates at each site.

The denitrification estimates may have been affected by the delay between sampling and measurements. For example, if the lability (susceptibility to microbial degradation) of sediment organic nitrogen decreased significantly with time of incubation, in situ mineralization and denitrification rates would be higher than our estimates. On the other hand, if the denitrification reaction was driven mainly by nitrate inputs from the overlying water, denitrification rates could be experimentally enhanced by accumulation of nitrate in the water over the intact core during laboratory incubations. The latter error seems unlikely because net nitrate flux was small (Fig. 5) and denitrification rates were not significantly related to nitrate concentrations in the water ($r < 0.3$, $N = 15$ at each site).

The mean total fluxes of nitrogen compounds (nitrates and N_2) across the sediment–water interface in the gastight chambers for intact cores collected from sites 1 and 2 are presented in Fig. 5. In contrast to previous results from marine coastal systems (Blackburn and Henriksen 1983; Jørgensen and Sorensen 1985; Nowicki and Nixon 1985), measured changes in ammonium concentrations in our chambers were not significantly different from zero and are not shown. Total dissolved nitrogen flux into the overlying water ranged from about 28 to 51 µg-atoms N m^{-2} h^{-1} [mean = 36 ± 5

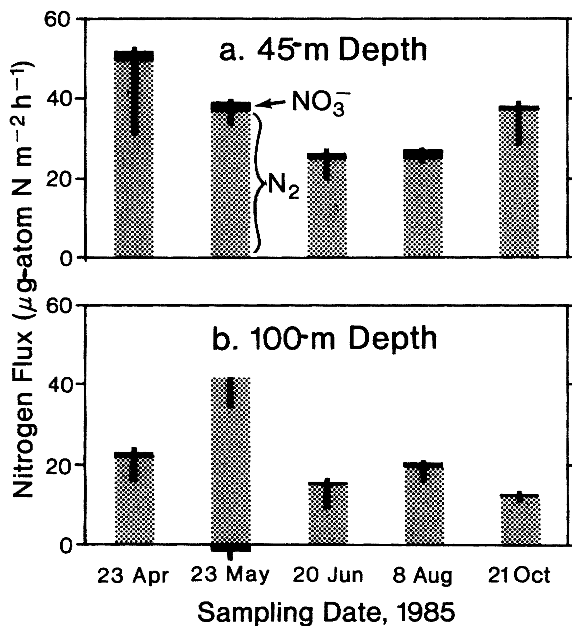

Fig. 5. Areal nitrogen (N_2 and NO_3^-) flux from the sediments to the overlying water on five sampling dates from two sites in southeastern Lake Michigan. Ammonium flux was minimal (not significantly different from zero) and is not included here. Range bars = SE.

(SE)] at site 1 and from about 15 to 42 [mean = 24±5 (SE)] at site 2.

Nitrogen gas production constituted 93–99% of the total nitrogen flux, with nitrate accounting for the rest of the flux (Fig. 5). This result agrees with the hypothesis, suggested above by the sterilization experiment, that most of the nitrogen initially mineralized to ammonium in these silty sediments was ultimately converted to N_2. Likewise, denitrification accounted for 76–100% of total inorganic nitrogen flux in other studies of lakes and rivers (Seitzinger pers. comm.). In contrast, denitrification accounted for only 21–31% of the NO_3^- and NH_4^+ flux from the sediments in Danish coastal waters (Blackburn and Henriksen 1983) and for 35% of the total mineralization in Narragansett Bay (Seitzinger et al. 1984). Values for coastal marine waters are consistently <65% (Seitzinger unpubl. data).

Our fluxes, mostly accounted for by denitrification, were similar but usually slightly lower than denitrification rates reported for Pennsylvania lakes (50–56 µg-atoms N m^{-2} h^{-1}; Seitzinger unpubl. data). They were also similar to in situ denitrification rates reported for New Zealand coastal sediments (Kaspar et al. 1985) but were somewhat lower than denitrification rates in Narragansett Bay (50–100 µg-atoms N m^{-2} h^{-1}: Seitzinger et al. 1980, 1984) or in the Patuxent River estuary (70–89 µg-atoms N m^{-2} h^{-1}: Jenkins and Kemp 1984), probably because of the higher nutrient fluxes into the latter two sites.

Mean fluxes of inorganic nitrogen tended to be higher in April and May than during June through October but seasonal trends were not pronounced for either sites 1 or 2 (Fig. 5). Although changes could reasonably be expected due to varying seasonal inputs of organic compounds from the epilimnion (Scavia and Fahnenstiel 1987), the absence of large seasonal changes was not totally surprising because the temperature was low and relatively constant with season (usually 4°–6°C) at both of these stations.

To evaluate whether our nitrogen flux measurements were reasonable relative to organic nitrogen inputs to the sediments, we compared them to inputs measured at four offshore sites in Lake Michigan as part of a previous sediment-trap study (Eadie et al.

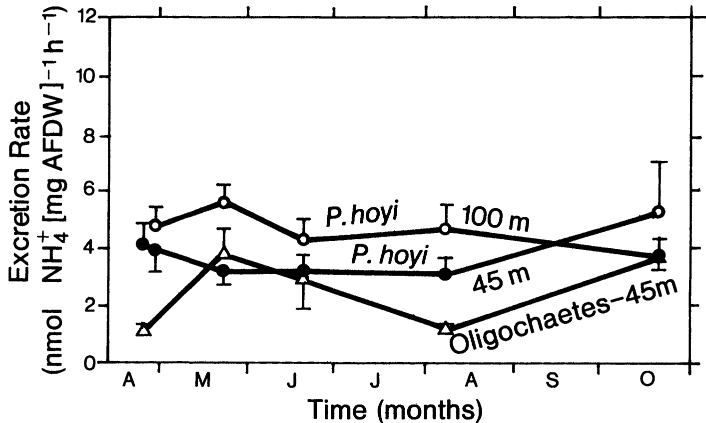

Fig. 6. AFDW-specific ammonium excretion rates for *Pontoporeia hoyi* sampled from sites 1 and 2 and for oligochaetes sampled from site 1 at the same times and locations as the cores taken for nitrogen flux and denitrification measurements (Fig. 5). Range bars = SE.

1984) and to time-series sediment-trap inputs measured near site 2 in 1984 (D. Scavia and G. Fahnenstiel unpubl. data). On the basis of total Kjeldahl nitrogen measurements on summer collections from 35-m-depth traps at the four offshore Lake Michigan sites in 1980, mean net organic input flux was calculated at 19.8±5.5 (SE) μg-atoms N m^{-2} h^{-1} (Eadie et al. 1984). This estimate may be conservative on an annual basis because it does not account for the spring phytoplankton bloom that occurs before the lake becomes stratified. Also, comparisons must be made with caution because the sampling sites were different than ours. However, the influx data agree remarkably well with the mean sediment–water nitrogen flux of 24±5 μg-atoms N m^{-2} h^{-1} that we observed at site 2.

In the time-series study, particulate organic nitrogen (measured with a CHN analyzer) inputs into 10-m traps located near site 2 ranged from 90 to 30 μg-atoms N m^{-2} h^{-1} during the period before lake stratification (23 March to 18 June) and from 10 to 19 μg-atoms N m^{-2} h^{-1} during stratification (18 June to 30 August) (D. Scavia and G. Fahnenstiel unpubl. data). The material collected before stratification is not a good indicator of nitrogen available for mineralization because it includes resuspended refractory materials along with the "new" particles resulting from photosynthesis (Eadie et al. 1984). If summer comparisons are realistic, they indicate that most of the new particulate organic nitrogen reaching the sediments is subsequently mineralized and released back into the water column as N_2 or nitrate. Likewise in Narragansett Bay, denitrification loss rates were about four times larger than calculated losses of fixed nitrogen through burial in the sediments (Seitzinger et al. 1984). The measured offshore inputs were lower than our measured mean flux of 30±8 μg-atoms N m^{-2} h^{-1} at site 1, as may be expected if organic nitrogen inputs from primary productivity (Fee 1973) and other sources (e.g. river inputs) decrease with distance offshore.

Mean ammonium excretion rates ranged from 3 to 5 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1} for *P. hoyi* and from 1 to 4 for oligochaetes over the sampling season (Fig. 6). These excretion rates are lower than those for pelagic zooplankton [e.g. 60–100 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1}: Lehman 1980], but they are similar to rates for nearshore Great Lakes benthic invertebrates [3–15 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1}: Gardner et al. 1983] and slightly higher than rates for benthic invertebrates in Danish coastal systems [0.3–2.1 nmol NH_4^+ (mg AFDW)$^{-1}$ h^{-1} (assuming a wet wt : AFDW ratio of 10 : 1): Blackburn and Henriksen 1983].

The contribution of invertebrate excretion to total nitrogen mineralization was estimated conservatively by multiplying the

biomasses of *P. hoyi* and oligochaetes found in the chambers at the end of the experiments by their mean weight-specific excretion rates for the same sampling date. Biomass measurements were conservative because some mortality occurred during the incubations. If we assume that steady state conditions existed between mineralization inputs and fluxes of inorganic nitrogen from the sediments, these calculations indicate that invertebrate excretion on average accounted for at least 18–42% of total areal nitrogen flux at site 1 and from 9 to 40% of the total flux at site 2 (Table 2). These results are lower than values from coastal marine sediments (Henriksen et al. 1983; Blackburn and Henriksen 1983) but suggest that macroinvertebrate excretion is still quantitatively important to nitrogen mineralization in these sediments. The seasonal averages were 30% of total flux at site 1 and 17% of total flux at site 2, as compared to about 50% of the total mineralization (based on total nitrate accumulation at rates of 33–50 μg-atoms N m^{-2} h^{-1}) that we have observed in slurry experiments with nearshore sandy sediments (water depth, 11 m; unpubl. data). This discrepancy implies that the relative importance of macroinvertebrate excretion to the total mineralization process may decrease with distance from shore.

The above results support the idea that a sizable portion of incoming particulate organic nitrogen may be used directly by detritivores before undergoing extensive microbial degradation (Findlay and Tenore 1982). If we assume a constant C:N ratio in available organic material and microbial growth efficiencies of about 50% (Cole et al. 1982, 1984), the incoming organic particles could support no more than one or two trophic stages of microbial degradation and yet yield the observed "conservative" estimates of total nitrogen excretion by the macroinvertebrates.

Table 2. Percent of total sediment–water nitrogen flux accounted for by macroinvertebrate (*Pontoporeia hoyi* and oligochaetes) ammonium excretion based on invertebrate excretion rates and biomasses of invertebrates in chambers at the end of denitrification-flux experiments on intact cores. *Pontoporeia hoyi* excretion rates were measured for both sites 1 and 2 on all sampling dates (Fig. 6). Site 1 oligochaete excretion rates were combined with biomass measurements from the respective sites to estimate their contribution on each sampling date. Values are conservative because they do not include biomasses of animals that died during the experiment.

1985	Site 1	Site 2
23 Apr	18	10
23 May	27	9
20 Jun	19	14
8 Aug	42	40
21 Oct	42	11

Denitrification and its significance in Lake Michigan—Denitrification occurs in coastal marine and estuarine (e.g. Seitzinger et al. 1980, 1984; Kaspar 1983; Jenkins and Kemp 1984; Kaspar et al. 1985), stream (Chatarpaul et al. 1980), and lake (Goering and Dugdale 1966; Chen et al. 1972; Kaspar 1985) sediments and is important to the global nitrogen cycle (Seitzinger et al. 1980). However, almost no information is available about this process in the Great Lakes, except for limited studies in Green Bay (Chen et al. 1983) and Hamilton Harbour (Klapwijk and Snodgrass 1982), both of which are heavily influenced by tributary and coastal inputs of nutrients.

Although denitrification rates (Fig. 5) were low relative to those observed in more nutrient-rich marine estuarine sediments (e.g. Seitzinger et al. 1980, 1984; Jenkins and Kemp 1984), denitrification appears to be the dominant process controlling the fate of nitrogen mineralized in silty, offshore Lake Michigan sediments. Nitrogen gas was the major form of nitrogen regenerated from the silty sediments at both sites 1 and 2 (Fig. 5). (We did not measure N_2O, but it is usually a quantitatively unimportant, $<10\%$, end product of denitrification: Jenkins and Kemp 1984; Jørgensen and Sorensen 1985.)

Redox conditions in the surface sediments of sites 1 and 2 are apparently well suited for both nitrification and denitrification. Oxygen is required to oxidize ammonium, but denitrification generally requires anoxic conditions. In our study, oxygen concentrations were apparently sufficient in the surface sediments for all of the mineralized ammonium to be quantitatively converted to nitrate. However, conditions were also favorable for quantitative

denitrification of most of the nitrate formed in the sediments. Denitrification probably occurs in small regions of anoxia that are in close physical proximity to the nitrification sites, as reported for coastal sediments (Jenkins and Kemp 1984; Nishio et al. 1983). Although the above results are qualitatively similar to those observed for coastal marine sediments, silty Lake Michigan sediments appear to be a more quantitatively important sink for mineralized nitrogen than are most coastal sediments, where a relatively high percentage of mineralized nitrogen diffuses out of the sediments as NH_4^+ or NO_3^-.

Our results suggest that denitrification is not a significant sink for nitrate dissolved in hypolimnetic water overlying the sediments but that it is a sink for nitrogen that is mineralized in the sediments. Although nitrate concentrations in the water of our experimental chambers ranged from 5 to 83 μM (mean = 48, SD = 20, N = 30) at the times of flux measurement, we did not usually observe net fluxes of nitrate into the sediments from the overlying water. Net flux of nitrate was not significantly related to nitrate concentrations in the overlying water and usually was from the sediments to the water rather than vice versa (Fig. 5). As previously observed in other sediment environments (Koike and Hattori 1978; Seitzinger et al. 1984), it implies that denitrification in Lake Michigan sediments is driven mainly by the nitrate supplied by mineralization reactions in the sediments rather than by influx of nitrogen from the overlying water. This interpretation agrees with the concept of direct coupling nitrification and denitrification reported for some estuarine sediments (Nishio et al. 1983; Jenkins and Kemp 1984). In contrast, overlying waters were a source of nitrate in a Danish estuary (Jørgensen and Sorensen 1985). Sediments with high organic content may be more effective in removing nitrate from overlying water than low-nutrient sediments (Koike et al. 1984). In fact, some measurements of denitrification and nitrification are based on addition of NH_4^+ or NO_3^- to water overlying the sediment (Nishio et al. 1982, 1983; Koike et al. 1984).

If denitrification is quantitatively as important over other offshore regions of the lake as we observed at these sites, much organic nitrogen reaching these sediments must be effectively lost from biologically active pools. However, nitrogen does not appear to limit phytoplankton growth in Lake Michigan; nitrate is abundant in the lake (Bartone and Schelske 1982) and nitrate concentrations seem to be increasing in some of the other Great Lakes (Herdendorf 1984; Lesht and Rockwell 1985). These observations indicate that fixed nitrogen inputs to the lakes must be sufficient to compensate for denitrification losses. Our results document that denitrification must be considered to accurately understand nitrogen dynamics in the Lake Michigan ecosystem.

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Submitted: 5 November 1986
Accepted: 29 July 1987