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Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark

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ABSTRACT: A seasonal study of NH_4^+ and NO_3^- fluxes and concentrations at the sediment-water interface was carried out at a 15 m deep station in Aarhus Bight, Denmark. In winter, NH_4^+ and NO_3^- were released from the sediment at comparable rates (0.20 to 0.40 mmol N m^{-2} d^{-1}). A phytoplankton bloom developed rapidly in early spring. Immediately after mass sedimentation of diatoms, the sediment transiently released NH_4^+ at a high rate (up to 1.5 mmol N m^{-2} d^{-1}) and a dramatic change to a NO_3^- uptake was observed (flux ca −0.80 mmol N m^{-2} d^{-1}). Subsequently both the NH_4^+ release and NO_3^- uptake decreased (summer fluxes ca 0.35 and −0.15 mmol N m^{-2} d^{-1}, respectively). From late summer, NO_3^- was again released from the sediment (ca 0.30 mmol N m^{-2} d^{-1}) and a second, weaker maximum of NH_4^+ release (ca 0.70 mmol N m^{-2} d^{-1}) was observed in fall. Seasonal variation of NH_4^+ and NO_3^- concentrations at the sediment surface (upper 2 mm) and in the bottom water agreed well with observed flux patterns. The high NH_4^+ release and NO_3^- uptake immediately after spring bloom sedimentation indicated rapid increases of mineralization and denitrification. Sediment nitrification seemed to be inhibited, however, probably because the O_2 penetration depth was reduced after sedimentation. Uptake of bottom water NO_3^- rather than nitrification therefore seemed to support the denitrification maximum. Even when calculated for a whole year, about 50 % of the NO_3^- consumed during denitrification was supplied from the bottom water. Annual nitrogen budgets also indicated that denitrification accounted for 25 % of the total inorganic nitrogen release from the sediment.

INTRODUCTION

Nitrogen is generally considered to limit primary production in coastal waters (Ryther & Dunstan 1971), although the subordinate role of phosphorus has recently been discussed (Hecky & Kilham 1988, Howarth 1988). Of major importance in controlling the concentrations of inorganic nitrogen species in shallow waters is their rate of exchange across the sediment-water interface (i.e. benthic fluxes). Release of NO_3^- and NH_4^+ from sediments can thus potentially supply from 30 to more than 100 % of the annual nitrogen requirement for primary producers in coastal areas (Blackburn & Henriksen 1983).

Numerous investigations have dealt with benthic nitrogenous nutrient exchange in various estuarine and coastal sediments; see e.g. reviews by Klump & Martens (1983) and Seitzinger (1988). The multitude of temporal and regional patterns reported indicate a complex relationship between various physico-chemical and biological control factors. Benthic nutrient exchange is largely determined by the rate of detritus sedimentation and decomposition in the sediment and the rate at which the nutrients are transported to or from the overlying water by diffusion and bioturbating infauna (e.g. Goldhaber et al. 1977). Thus, in addition to being important in nitrogen recycling, the benthic flux can also be an indicator of the actual processes involved in sediment nitrogen turnover (Hammond et al. 1985). For instance, interactions between microbial mineralization of organic nitrogen (NH_4^+ production), nitrification (oxidation of NH_4^+ to NO_3^-) and NO_3^- reduc-

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tion, e.g. denitrification (reduction of NO_3^- to gaseous N_2O and N_2), might be inferred from net benthic fluxes of NH_4^+ and NO_3^-. A complete assessment of a sediment nitrogen cycle has been possible when flux determinations have been related to direct measurements of microbial process activities (Blackburn & Henriksen 1983).

The present investigation focuses on the annual pattern of benthic fluxes and interfacial concentration gradients of NH_4^+ and NO_3^- in a coastal bay area characterized by a massive sedimentation of the spring phytoplankton bloom. Sampling was carried out at a site where denitrification was recently found to change dramatically after the rapid sedimentation in spring (Jensen et al. 1988). The inorganic nitrogen fluxes were compared to the previously observed denitrification pattern on a seasonal and annual scale.

MATERIALS AND METHODS

Study area. The investigation was carried out in Aarhus Bight, Denmark, a 320 km^2 embayment in the southwestern Kattegat. The water column of the Kattegat is stratified due to the outflow of low-salinity (< 10 ‰) Baltic water from the south and an inflow of high-salinity (> 30 ‰) Skagerrak water from the north; the mean depth of the halocline is 15 m (Andersson & Rydberg 1988). In the Aarhus Bight the water depth is about 15 m and the stratification periods are here interrupted by periods of mixing once or twice a year (Jensen et al. 1988).

Annual primary production in the Kattegat (above 100 g C m^{-2} yr^{-1} in the Aarhus Bight) seems to be limited by nitrogen (Ærtebjerg et al. 1981). The spring bloom develops in late winter (February–March) and rapidly depletes nutrient pools in the surface water. Due to the shallow water and the absence of grazing zooplankton at this time, a major portion of the algae reaches the sea floor undecomposed (Smetacek 1985, Jensen et al. 1988). The major sedimentation event typically occurs within a month, and less sedimentation may be found during summer (Smetacek 1980, Jensen et al. 1988).

The eutrophication of the Kattegat has become evident during the last decade. Using the extensive set of water column data available from various parts of the Kattegat, Andersson & Rydberg (1988) found a general increase of particulate and dissolved nitrogen pools and a decrease of the O_2 concentration in the Kattegat deep water; from the data they estimated that O_2 consumption had increased by 50 % between 1971 and 1982. In the Aarhus Bight, both the frequency and duration of O_2 deficiency periods have increased during the last 20 yr (Fallesen 1988).

For the present investigation (June 1987 to December 1988), a silty-mud locality was chosen in the central part of Aarhus Bight at a water depth of 15 m. The sediment porosity in the upper 2 mm was 0.89; further description of the site, Stn 16, may be found in Jensen et al. (1988). The sediment was poorly inhabited by macrofauna during the investigation period. However, large specimens of polychaetes *Nephtys* spp. and bivalves *Abra alba* and *Macoma calcarea* were occasionally observed.

Sampling. Water and sediment were sampled at intervals of 5 d to 2 mo with intensive sampling in the spring of 1988, before and after sedimentation of the phytoplankton bloom.

Temperature, salinity, and concentrations of O_2, NH_4^+ and NO_3^- (note: NO_2^- concentrations were always very low in both water and sediment and are included in the NO_3^- data) were determined in samples of surface water (2 m below the surface) and bottom water (0.5 m above the sediment). Samples for determination of O_2 concentrations were taken in 25 ml Winkler bottles. Samples for nutrient analysis were stored frozen at −20 °C in 25 ml polyethylene vials containing 50 µl of chloroform.

Sediment was collected with a 'Haps' bottom corer (Kanneworff & Nicolaisen 1973) taking 12.5 cm (i.d.) cores of the sediment. From the main 'Haps' core, smaller subcores were taken into 3.6 cm (i.d.) wide and 12 cm long acrylic tubes for determinations of in situ NH_4^+ and NO_3^- fluxes and concentrations of pore water NH_4^+ and NO_3^-. All cores were carefully inspected and only those with an undisturbed sediment-water interface were used. Measurements of fluxes and concentration profiles were initiated in the laboratory within a few hours of sampling.

In situ concentrations of NH_4^+ and NO_3^- in the pore water (triplicate cores) were determined in the upper 2 mm section of the sediment; the sample was immediately centrifuged (2900 × *g*, 5 min) and the supernatant frozen at −20 °C for later analysis. Further details are given in Lomstein et al. (1990), a parallel seasonal investigation of in situ profiles of both dissolved and bound NH_4^+ and NO_3^- pools in the 0 to 4 cm depth horizon at Stn 16.

Inorganic N fluxes. From 6 to 8 cores were collected to measure the sediment-water fluxes of NH_4^+ and NO_3^- on each sampling event. The sediment was first adjusted in height so that the acrylic tubes contained about 5 cm of sediment core overlain by 7 cm of water (corresponding to about 70 ml). The water phase was then discarded (except for a few ml to avoid disturbance of the sediment-water interface) and carefully replaced by fresh bottom water collected on the same day. A 10 ml sample from the water overlying each core was saved for determination of initial concentrations of NH_4^+ and NO_3^-. The cores were then completely filled

with bottom water, capped and incubated in the dark at in situ temperature. The caps were equipped with small stirring bars to mix the water phase. Incubation time varied from less than 1 h to about 4 h. Another 10 ml sample from the water gave the final concentrations of NH_4^+ and NO_3^-. After incubation the actual height (volume) of the water phase was noted. The incubated cores were sectioned for a determination of NH_4^+ and NO_3^- in the pore water at 0 to 2 mm depth as described above. No build-up or depletion of either NH_4^+ or NO_3^- in the upper 2 mm of pore water occurred during incubation as judged from the similar concentrations measured before and after an incubation.

During the incubation, 2 ml water samples were taken frequently (2 or 3 times) from the cores and replaced with 2 ml of bottom water; these samples served for detection of changes in flux rates. We observed only constant fluxes of NH_4^+ and NO_3^- during the incubations as judged from linear increases or decreases in concentration over time. Occasionally, the O_2 concentration in the water phase was measured immediately after capping and again at the end of incubation. Initial O_2 concentrations in the cores were close to those measured in the bottom water and the concentrations at the end of the incubations indicated that less than 30 % of the O_2 initially present was consumed.

The sediment was finally sieved through a 1 mm mesh to look for larger macrofauna. Data recorded from such cores were discarded; only few, i.e. 1 or most often none, of the cores were discarded from each incubation series. Flux rates and concentrations are presented as means of 5 to 8 incubated cores. The present study does not include the impact of macrofauna on benthic nitrogen transformations and fluxes.

Sample analyses. Salinity was measured potentiometrically (Conductivity Meter CDM 3, Radiometer, Denmark) and dissolved O_2 concentrations were measured by Winkler titration (Strickland & Parsons 1972). Nutrient concentrations in the various samples were determined by the standard autoanalyzer methods of Solorzano (1969) for NH_4^+ and Armstrong et al. (1967) for NO_3^- plus NO_2^-.

RESULTS

On Figs. 1 to 3, shaded areas indicate the duration of the spring phytoplankton bloom based on the NO_3^- concentration pattern in the surface water. In 1988, NO_3^- consumption began in early March and continued through depletion in early April (Fig. 2B), when also a complete change of the surface sediment was visually observed. Extensive phytoplankton sedimentation had clearly occurred just prior to the sampling event in early April.

Hydrographics

A seasonal temperature minimum of 2 °C in the bottom water was recorded during March (Fig. 1A). In 2 wk, the temperature rose quickly to 5 °C and a strong halocline developed (Fig. 1B), indicating an intrusion of 'new' water into the bight which coincided with the sedimentation of the spring phytoplankton bloom. Thus, a decrease from 25 to 18 ‰ and an increase from 27 to 33.5 ‰ were recorded for the surface and bottom water salinities, respectively; the latter value shows that the intruding bottom water was Kattegat deep water (Andersson & Rydberg 1988). The marked saline stratification continued and the thermal stratification intensified in the following months. After a period with intermittent mixing, the water column finally became thoroughly mixed during October. The major hydrographic events in early spring and fall

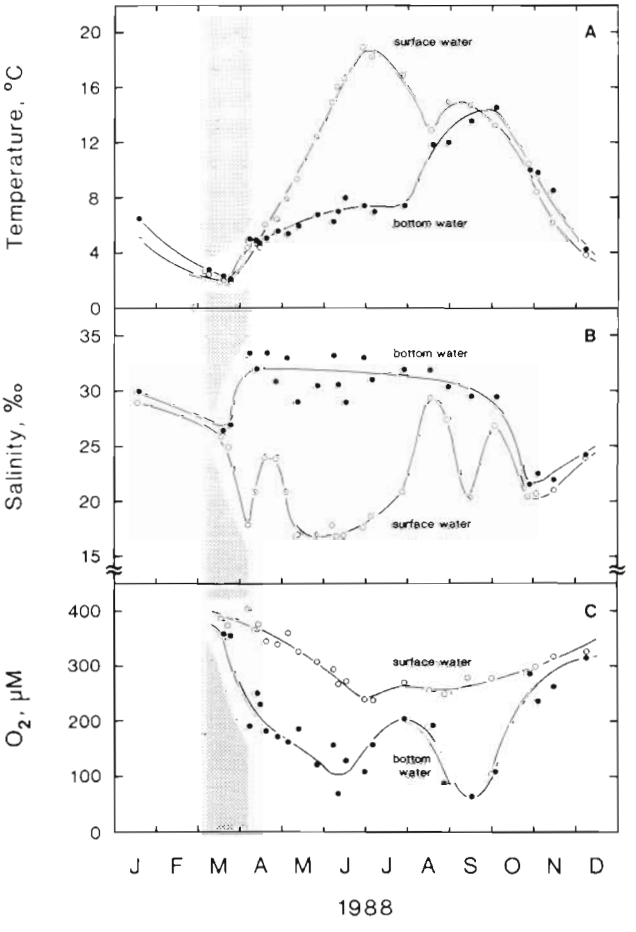

Fig. 1. Water column characteristics from Aarhus Bight (1988): (A) temperature; (B) salinity, and (C) O_2 concentration. ( ) Surface water; (●) bottom water Shaded area indicates the production and sedimentation period of the spring bloom (see text)

were also reflected in the concentration patterns of O_2, NO_3^- and NH_4^+.

The bottom water O_2 concentration decreased from 360 µM (complete saturation) to 190 µM O_2 (60 % saturation) between late March and early April (Fig. 1C), when the saline bottom water intruded the bight. The bottom water remained partially deficient in O_2 (60 to 250 µM O_2 or 22 to 77 % saturation) until the water column was mixed during October.

NH_4^+ and NO_3^- in water and surface sediment

The high winter concentrations of NH_4^+ and NO_3^- (maxima of 3 and 10 to 15 µM, respectively), typical for the relatively well-mixed and oxygenated water column, are evident from Fig. 2. The initiation of the spring bloom resulted in a rapid nutrient consumption, and by early April both NH_4^+ and NO_3^- were almost depleted (< 1 µM) in the surface water. The Kattegat deep water intruding the bight was rich in NO_3^- in addition to being low in oxygen; NO_3^- in bottom water thus returned to a high level in early April (14.7 µM) coinciding with the sedimentation event. Both the NO_3^- concentrations (8 to 10 µM) and NH_4^+ concentrations (3 to 5 µM) were relatively high in the bottom water during the marked summer stratification. As destratification was initiated in August, the water column became depleted of nutrients. The bottom water was occasionally high in NH_4^+ during the early fall. Nitrate reappeared in the water column after the mixing events during October.

The concentrations of dissolved NH_4^+ and NO_3^- in the upper sediment layer (0 to 2 mm) varied considerably during the season (Figs. 2A, B). Sedimentation of the spring bloom induced a significant change in the pool of dissolved NH_4^+, observed as an increase from ca 10 µM to above 40 µM between March and April (Fig. 2A). A steep decrease was observed during May and apart from a weaker peak in early October (ca 30 µM), the concentration remained in the 10 to 20 µM range during the rest of the year. The concentration of pore water NO_3^-, which always peaked at 0 to 2 mm depth, increased from fall to winter and a maximum concentration of ca 25 µM was found in March (Fig. 2B); during the rest of the year, the NO_3^- concentration did not exceed 15 µM. Between spring bloom sedimentation and depletion of bottom water NO_3^- (April to July), the concentrations were generally higher in bottom water than in pore water, although within similar ranges (8 to 15 µM and 6 to 12 µM, respectively). Lowest pore water concentrations, ca 5 µM, were found in the early fall (September–October), when NO_3^- was depleted in the bottom water.

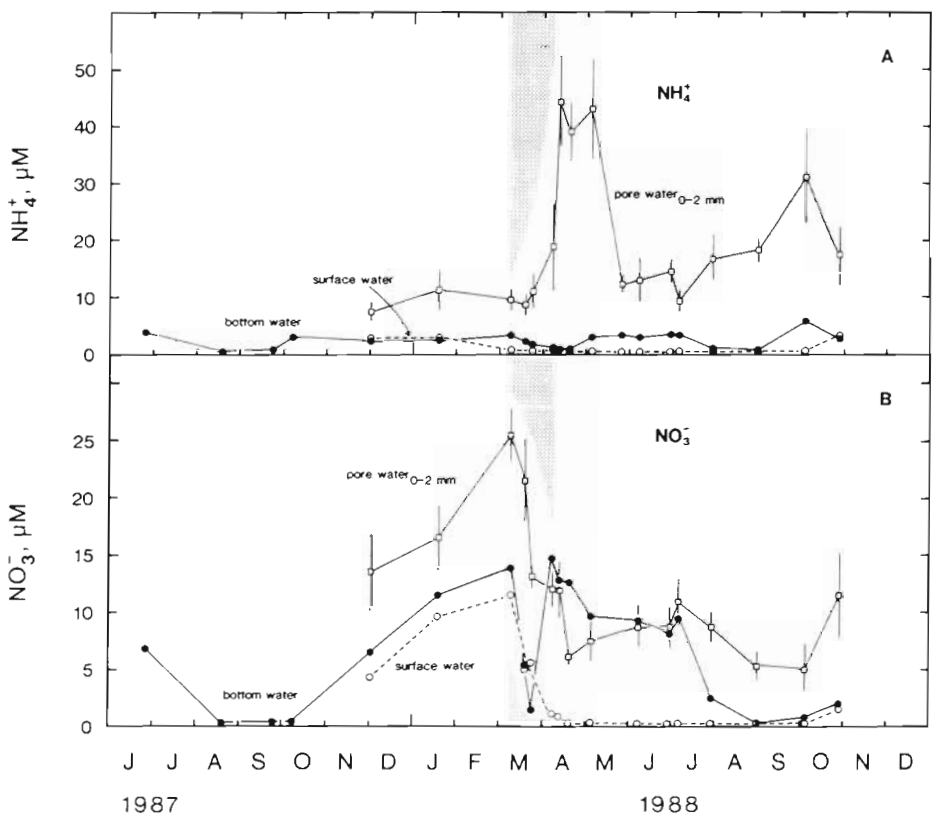

Fig. 2. Seasonal patterns of (A) NH_4^+ and (B) NO_3^- concentrations in water and surface sediment at Stn 16 in Aarhus Bight (1987 to 1988). (○) Surface water; (●) bottom water; (□) pore water at 0 to 2 mm depth (mean and SE values indicated; n = 5 to 8). Shaded area as in Fig. 1

Fluxes of NH_4^+ and NO_3^-

Lowest NH_4^+ fluxes, ca 0.20 mmol N m^{-2} d^{-1}, were measured in March (Fig. 3A). A dramatic increase was observed following the spring bloom sedimentation and a seasonal maximum of ca 1.5 mmol N m^{-2} d^{-1} was recorded in April. Shortly after, NH_4^+ release decreased abruptly and rates were only ca 0.35 mmol N m^{-2} d^{-1} in May to July. In September–October they were somewhat higher, 0.60 to 0.70 mmol N m^{-2} d^{-1}. The highest fluxes coincided with the steepest interfacial NH_4^+ gradients and generally, the seasonal patterns of fluxes and concentration gradients corresponded remarkably well (Figs. 2A and 3A).

From late summer and throughout the winter (August to March), NO_3^- was released from the sediment at rates between 0.10 and 0.35 mmol N m^{-2} d^{-1} (Fig. 3B). A sudden change to a high uptake by the sediment was observed between late March and early April when the intrusion of NO_3^--rich bottom water and the bloom sedimentation took place, resulting in negative NO_3^- fluxes between −0.60 and −0.80 mmol N m^{-2} d^{-1}. The uptake rate declined rapidly and the flux was only about −0.15 mmol N m^{-2} d^{-1} in May to July, when the bottom water still was rich in NO_3^-. In the whole period from April to July, the rate of NO_3^- uptake was apparently proportional to the NO_3^- concentration in the bottom water (r^2 = 0.88, n = 8). As NO_3^- disappeared from the bottom water in August, a net release of NO_3^- was again recorded. The shifts in the direction of the NO_3^- flux in early spring and late summer could generally be predicted from the changes in concentration gradients at the sediment-water interface (Figs. 2B and 3B).

DISCUSSION

Sedimentation and benthic metabolism during spring

The spring bloom of primary production occurs in late winter/early spring when ambient light is sufficient and the water column is rich in nutrients. When

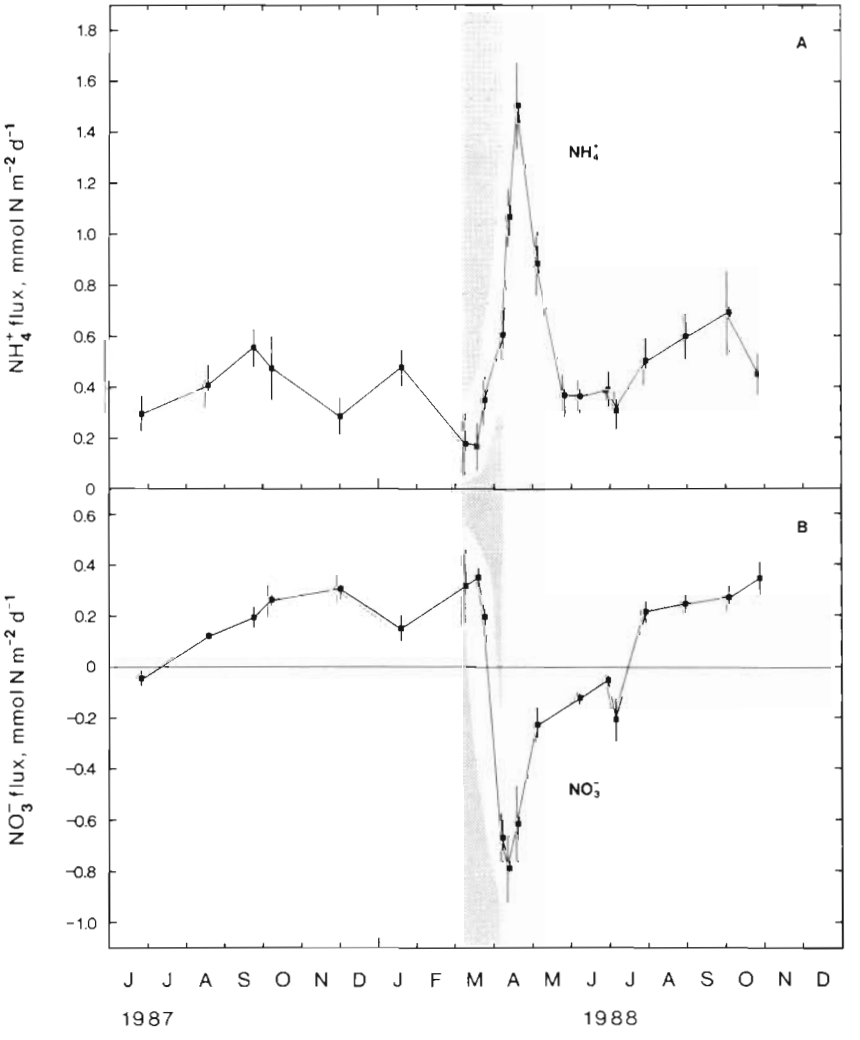

Fig. 3. Seasonal patterns of (A) NH_4^+ and (B) NO_3^- fluxes (mean and SE values indicated; n = 5 to 8) at Stn 16 in Aarhus Bight (1987 to 1988). Negative flux indicates uptake by the sediment. Shaded area as in Fig. 1

the nutrient stock in the surface water were depleted in early April, a brownish flocculent layer, 1 to 2 mm thick, containing an abundance of diatoms (notably *Skeletonema costatum*) was clearly visible on the sediment surface indicating that mass sedimentation had occurred within a 2 wk period between sampling occasions in late March and early April. Although sedimentation probably continued on a smaller scale throughout April, the major sedimentation event gave a pulse input of organic matter to the sea floor.

Others have found that the rapid input of labile organic matter to the sea floor immediately triggers increased microbial activity at the sediment surface despite low temperatures in early spring (Graf 1987, Meyer-Reil 1987). One consequence of the sedimentation was a sudden decrease of the penetration depth of O_2 in the sediment; while the oxic zone at Stn 16 was ca 5 mm deep in late March, it was only 1.5 mm in early April (Rasmussen 1989). This was probably due to an increased O_2 consumption immediately after sedimentation, although the decrease of the bottom water O_2 content (Fig. 1C) also contributed to the lower O_2 penetration. Enoksson (1987) similarly found a spontaneous doubling of the O_2 consumption rate (mineralization rate) after undisturbed sediment cores were spiked with algal detritus.

After the sedimentation event, we frequently observed a dark-colored band of ca 1 mm thickness just below the flocculent diatom layer at the surface. The dark coloration was due to FeS precipitation and originated from SO_4^{2-} reduction immediately below the oxic zone (L. Moeslund pers. comm.). The sudden deposition of phytodetritus depleted O_2 and apparently resulted in development of a very narrow SO_4^{2-} reduction zone which was clearly separated from the deeper, conventional SO_4^{2-} reduction zone. A similar surficial zone with SO_4^{2-} reduction (and low O_2 penetration), related to accumulation of organic aggregates, has been demonstrated in a soft-bottom sediment in the Skagerrak (Sørensen & Jørgensen 1987). Later in summer, the black zone was gradually displaced downwards in the sediment and was observed with much lower frequency in the cores; it completely disappeared in June–July.

Both nitrification and denitrification might be affected by the transient appearance of a discrete, reduced layer in the surface sediment. Both the sediment NO_3^- profiles showing a maximum at 0 to 2 mm depth and a depletion below 1 cm (Lomstein et al. 1990), and the N_2O accumulations in depth-sectioned, C_2H_2-inhibited sediment from Stn 16 (Jensen et al. 1988), indicated that all nitrification and denitrification activity is located within the upper 1 cm. The brownish surface floc as well as the dark band underneath had variable size and distribution on the sediment surface, and could in some cores be absent. Hammond et al. (1985) suggested that only certain areas (patches) of surface sediment may be sufficiently oxidized to favour nitrification, while others showing rapid O_2 consumption may act as NO_3^- sinks. This may also have been the case at Stn 16 in the period following sedimentation, and Jensen et al. (1988) assigned a considerable core variability of denitrification rates to sediment heterogeneity.

Seasonal variations of fluxes and concentrations of NH_4^+ and NO_3^-

During winter, the O_2 penetration depth was at its seasonal maximum (Rasmussen 1989) and the NH_4^+ flux and NH_4^+ concentrations in the pore water were relatively low. The organic matter at the sediment surface is probably relatively refractory and N-deficient during winter (Blackburn 1987). A likely low NH_4^+ formation from mineralization was apparently met by relatively efficient NH_4^+ oxidation by nitrifying bacteria; hence, the NH_4^+ and NO_3^- releases were in the same range (0.20 to 0.30 mmol N m^{-2} d^{-1}). Marked NO_3^- accumulation in the surface sediment and a release of NO_3^- to the overlying water also indicated that nitrification was important during winter. Nedwell et al. (1983) suggested that sediment nitrification prevents a release of NH_4^+ from Baltic sediments during winter, and there, NO_3^- accounted for as much as 92 % of the total NH_4^+ plus NO_3^- flux. The low winter denitrification measured in the present sediment, ca 0.1 mmol N m^{-2} d^{-1} (Jensen et al. 1988), must be supported by sediment nitrification and by the NO_3^- pool in the bottom water when the latter was large. A net efflux of NO_3^- due to nitrification in the surface sediment does not necessarily imply that denitrification is supported by nitrification alone unless NO_3^- is absent from the overlying water (Christensen et al. in press).

Fluxes and concentrations of NH_4^+ and NO_3^- changed dramatically after sedimentation of the spring bloom (Figs. 2 and 3). Such a distinct and rapid response in sediment metabolism occurring after a bloom sedimentation in a coastal area has, to our knowledge, not previously been reported from in situ measurements. The increases of both the pore water NH_4^+ concentration and the NH_4^+ flux were apparently due to the sudden increase in availability and rapid mineralization of a labile organic nitrogen pool. However, suppression of nitrification activity may also be important. The 7.5-fold increase measured for the in situ NH_4^+ flux is in accordance with a 6- to 10-fold increase found in sediment core microcosms in which a sedimentation event was mimicked (Kelly & Nixon 1984, Enoksson 1987). Garber (1984) similarly observed rapid release of

$^{15}NH_4^+$ to pore water and overlying water after adding ^{15}N-labelled organic matter to the surface of undisturbed sediment. By comparing low and high additions of organic matter, Kelly & Nixon (1984) found slowly and rapidly increasing NH_4^+ fluxes, respectively The steep increase of NH_4^+ release at Stn 16 indicated that the bloom sedimentation event was rapid, in accordance with our visual observation of a brown diatom layer being deposited on the sediment in less than 2 wk. During May, the NH_4^+ flux decreased to almost winter levels, corresponding with the decline to background levels within 1 to 2 mo observed in Kelly & Nixon's (1984) microcosms. The rapid decline of the NH_4^+ release may represent exhaustion of the labile fraction of the detrital nitrogen pool.

The combination of bloom sedimentation and intrusion of NO_3^--rich bottom water was responsible for the rapid change from a modest release in winter to a high NO_3^- uptake in early spring. At similar bottom water concentrations of NO_3^- in early March and early April (13.9 and 14.7 µM, respectively), totally different fluxes were thus recorded (0.30 and −0.70 mmol N m^{-2} d^{-1}, respectively). This observation alone is sufficient to imply that the processes involved in NO_3^- turnover changed dramatically after the sedimentation, and a marked stimulation of denitrification in early spring has in fact recently been found in Aarhus Bight sediments (Jensen et al. 1988); the denitrification rates at Stn 16 were similar, if not identical, to the present NO_3^- uptake rates both in April and May to July which suggests a low nitrification activity following sedimentation. Even though the onset of rapid mineralization and NH_4^+ release after deposition of the phytodetritus is expected to stimulate volume-specific nitrification (Kemp et al. 1982, Henriksen & Kemp 1988), overall nitrification might in fact be suppressed because the O_2 concentration and penetration depth decreased dramatically after bloom sedimentation. Nitrifiers compete poorly with heterotrophs at low O_2 availability (Belser 1979), and Hansen et al. (1981) suggested the depth extension of the oxic zone to be a major controlling factor of nitrification in sediments. The transient decrease of nitrification activity following rapid spring bloom sedimentation was already suggested in our previous work (Jensen et al. 1988), and is strongly supported by the present observations of a change in the direction of the interfacial NO_3^- gradient, a sudden change to a high sediment uptake of NO_3^-, a significant NH_4^+ accumulation in the surface sediment and a highly increased NH_4^+ release. Comparable results were obtained by Enoksson (1987) from incubation of cores in a continuous flow-through system; firstly, the NO_3^- flux immediately changed direction from a release to a net uptake after algal cells were added to the sediment surface, and secondly, nitrification seemed to cease completely due to O_2 limitation because the highly increased NH_4^+ flux equalled the calculated NH_4^+ production.

It seems likely that diffusion from the water phase was the predominant NO_3^- source for denitrification from the onset of sedimentation until depletion of the bottom water NO_3^-, since the NO_3^- uptake rate was proportional to the NO_3^- concentration in the bottom water during the whole period (April to July). If a partial or complete inhibition of nitrification took place, the spring maximum of denitrification may have been further facilitated by the reduced depth of the oxic surface zone. The thickness of the oxic zone (i.e. the diffusion barrier for NO_3^-) is a major controlling factor for denitrification, when the NO_3^- concentration is lower or equal to the O_2 concentration in the overlying water (Nielsen et al. in press). The denitrification maximum in the spring could thus have been due to an increase of the diffusion supply of NO_3^- occurring after the oxic surface zone became narrower, although a direct stimulation of the process by the input of labile organic substrate cannot be excluded.

The results suggest that denitrification was the predominant NO_3^- -consuming process in the sediment. An algal uptake of NO_3^- following the spring sedimentation at Stn 16 was possible, however, since a fraction of the diatoms deposited in the early spring were viable (mainly *Skeletonema costatum*) and contained considerable amounts of intracellular (particulate) NH_4^+ and NO_3^- (Lomstein et al. 1990). These intracellular pools persisted in the surface sediment throughout summer, and the deposited microalgae might have continued their assimilation of nutrients, taking up NH_4^+ and NO_3^- from the bottom water and pore water (Lomstein et al. 1990). Results from other light-limited Kattegat sediments at similar depth (Blackburn & Henriksen 1983, Sundbäck & Granéli 1988, Sundbäck & Jönsson 1988) indicated that sufficient light prevails from early spring to late summer for microphytobenthic primary production by both pelagic and benthic species, and that O_2 production and nutrient assimilation by the microalgae are presumably important for the direction and magnitude of the benthic inorganic nitrogen flux. Even though our flux measurements were performed in the dark, a possible microalgal assimilation of NH_4^+ and NO_3^- might have continued during incubations (e.g. Andersen & Kristensen 1988).

The variations of both NH_4^+ and NO_3^- fluxes from August onwards were relatively small and showed no significant trends. There was perhaps a small, secondary maximum of NH_4^+ release (0.60 to 0.70 mmol N m^{-2} d^{-1}) at high temperatures during fall (12 to 15 °C, September–October). Such maxima coinciding with seasonal temperature maxima have occasionally been reported (e.g. Nixon et al. 1976, Boynton et al. 1980,

Klump & Martens 1981, Nowicki & Nixon 1985, Boucher & Boucher-Rodoni 1988, Teague et al. 1988). The NO_3^- fluxes demonstrated a release, which was relatively constant from August when the interfacial NO_3^- gradient again changed direction. This was a result of both NO_3^- depletion in the bottom water and nitrification in the sediment. Denitrification activities were also low and constant during this period (Jensen et al. 1988), and when NO_3^- was absent from the bottom water (August–October), the process was solely supported by nitrification.

Based on the stoichiometry of benthic O : N fluxes (e.g. Boynton & Kemp 1985) and from measurements with ^{15}N technique (Nishio et al. 1983, Jenkins & Kemp 1984, Horrigan & Capone 1985), the relative importance of nitrification and denitrification is shown to change on a seasonal as well as a regional scale. From the present study we suggest that nitrification may temporarily cease after rapid sedimentation events and that in such cases nutrient-rich bottom waters may be the chief NO_3^- source for denitrification.

Seasonal and annual estimates of NH_4^+ and NO_3^- fluxes in relation to denitrification

In Table 1, seasonal and annual estimates of the present inorganic nutrient fluxes are compared to previous estimates of denitrification (Jensen et al. 1988). The 2 chosen periods, April to mid July and mid July to March, are characterized by the direction of the NO_3^- flux (Fig. 3B).

The annual net NH_4^+ release (181 mmol N m^{-2} yr^{-1}) was a factor of 6 higher than the net NO_3^- release (29 mmol N m^{-2} yr^{-1}), the latter being low due to considerable NO_3^- uptake in April to July. During the rest of the year, when NO_3^- was released from the sediment, the NH_4^+ flux was only higher by a factor of 2 or less. Denitrification (70 mmol N m^{-2} yr^{-1}) annually accounted for 25 % of the total inorganic nitrogen flux, which is within the ranges, 15 to 75 % and 7 to 26 %, for various coastal marine sediments compiled by Seitzinger (1988) and Blackburn & Henriksen (1983), respectively; the latter authors reported 22 % for the western Kattegat area which is close to our estimate. The value was higher, 55 %, during April to July when denitrification activity was high and controlled by the NO_3^- influx, but was only 15 % during the rest of the year when the average daily denitrification was 3 times lower.

The water column supplied as much as 85 % of the NO_3^- required for denitrification during the 3.5 mo period following sedimentation. Nitrification could potentially supply all NO_3^- for denitrification during the rest of the year if the 2 processes were completely coupled, as NO_3^- was consistently released from the sediment (i.e. nitrification exceeded NO_3^- consumption). However, in periods with high NO_3^- concentrations in the bottom water (November to March; Fig. 2B) this pool will, as previously mentioned, also contribute to the denitrification. For that reason, the 0 % value in Table 1 as well as the 47 % value for the annual proportion of denitrification fed by bottom water NO_3^- are minimum estimates.

Since about half or more of the annual denitrification was supplied by NO_3^- diffusion from the bottom water, the present sediment might represent an exception to the general suggestion, made by Seitzinger (1988), that sediment nitrification is by far the major NO_3^- source for denitrification in coastal marine sediments with oxic bottom waters. This conclusion was based on data compiled from several studies, showing either a NO_3^- release from the sediments or a NO_3^- uptake much lower than the measured denitrification. However,

Table 1. Benthic fluxes of NH_4^+ and NO_3^-, denitrification activity, and total inorganic nitrogen flux (Σ inorg. N) in Aarhus Bight (Stn 16). Units are mmol N m^{-2} for indicated period; values in parentheses are daily averages in mmol N m^{-2} d^{-1}. Also shown are percent of total inorganic N flux due to denitrification, and percent of denitrification supported by NO_3^- diffusion from bottom water (Negative flux indicates uptake by the sediment)

Period	Flux[a]				% of total inorg. N flux due to denitrification	% of denitrification supported by NO_3^- diffusion from bottom water
	NH_4^+	NO_3^-	Denitrif.[a]	Σ inorg. N		
April – mid July	66 (0.62)	−33 (−0.32)	39 (0.36)	72 (0.67)	55	85[b]
Mid July – March	115 (0.45)	62 (0.24)	31 (0.12)	208 (0.81)	15	> 0[c]
Annual	181 (0.50)	29 (0.08)	70 (0.19)	280 (0.77)	25	> 47[d]

[a] Denitrification data from Jensen et al. (1988)
[b] (NO_3^- uptake rate in April – mid July)/(denitrification rate in April – mid July) × 100
[c] Minimum estimate (see text)
[d] (NO_3^- uptake rate in April – mid July)/(annual denitrification activity) × 100. (Minimum estimate; see text)

none of these studies were apparently based on frequent seasonal sampling, and specific temporal patterns of inorganic nitrogen flux and denitrification might have been overlooked. On the other hand, various characteristics of the Kattegat area such as the significant spring sedimentation and the strongly stratified water column with occasional intrusion of nutrient-rich bottom water may impede a direct comparison with many of the investigated areas cited by Seitzinger (1988). This study shows that there is no reason to expect a consistently strong nitrification-denitrification coupling in highly fluctuating areas like Aarhus Bight.

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