Extraction and seasonal variation of NH_4^+ pools in different types of coastal marine sediments

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ABSTRACT: Seasonal variations in pools of porewater NH_4^+ and exchangeable NH_4^+ desorbed by 1-step (easily desorbed NH_4^+) and multiple KCl extractions (tightly bound NH_4^+) were investigated in sediments from 3 stations in Danish coastal waters. One-step KCl extractions gave higher yields in winter and lower yields in periods of increased sediment activity and temperature. The exchangeable NH_4^+ pool obtained by 1-step extraction was always less than the total pool removed by the multi-extraction technique, independent of sediment type. The multi-extraction technique proved the existence of sediment NH_4^+ pools with different exchange capacities. There was evidence to indicate that the tightly bound pool changed seasonally and entered the normal N cycle. The size and dynamic nature of this pool have not previously been recognized: maximum and minimum integrated values for Aarhus Bay, Norsminde Fjord and Randers Fjord sediments were 32, 36, 25 and 4, 9 and 6 mmol m^{-2}, respectively. A lack of correlation between pool sizes of easily desorbed NH_4^+ and porewater NH_4^+ was not compatible with literature values of the NH_4^+ adsorption coefficient (K-value). K-values varied with station, depth and season (means of all values 3.7 and 11.7 by 1-step and multiple extractions, respectively), and were in general higher than the literature values.

INTRODUCTION

Allochthonous and autochthonous materials suspended in seawater are eventually deposited on bottom sediments. Some of the organic material is decomposed in the sediments, becomes dissolved in the porewater and adsorbed to sediment surfaces, and is ultimately released to the overlying water. By speciating and quantifying sediment nitrogen it is possible to estimate the extent to which diagenesis or degradation of organic nitrogen compounds has occurred, and to model the exchange of nitrogen between the sediment and the overlying water. The predominant nitrogen species in O_2-limited sediments are NH_4^+ in free, adsorbed or fixed forms, organic N and N_2. Berner (1974, 1976, 1977) established the importance of including an adsorption term in his stoichiometric model of nitrogen regeneration. Thus, an estimate of adsorbed NH_4^+ must be considered when calculating the nitrogen budget of organic matter undergoing decomposition.

A literature review revealed that KCl is commonly used to remove exchangeable NH_4^+ from marine sediments (Rosenfeld 1979, Blackburn 1980, Pregnall & Miller 1988, Lomstein et al. 1990). However, there are variations in the use of the technique with regard to the degree of agitation (Terry & Nelson 1975, Haines et al. 1977, Henriksen 1980), the molarity of KCl solution (Bremner 1965, Sørensen 1978, Blackburn & Henriksen 1983, Smith & Patrick 1983), the extraction period (Klingensmith & Alexander 1983, Jenkins & Kemp 1984, Simon & Kennedy 1987, Laima 1991), the extractant to sediment ratio (Laima unpubl. data), and the temperature of extraction (Laima 1991). Recent results demonstrated that 1-step KCl extractions sometimes did not remove all exchangeable NH_4^+ from sediment (Laima 1991).

The objective of the present study was to investigate, on a seasonal basis, the efficiency of 1-step KCl extractions in removing NH_4^+ adsorbed to 3 types of coastal marine sediments. A technique based on multiple KCl extraction was developed for an assay of pools of NH_4^+ more tightly bound to sediment, yet exchangeable by KCl, and to evaluate possible seasonal and depth

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variations in the sediment exchange capacity. During a 6 mo period in 1988, undisturbed cores from 3 sediment types were sectioned and porewater NH_4^+, easily desorbed NH_4^+ (1-step extraction) and total adsorbed NH_4^+ (multiple extraction) were measured. Emphasis was given to seasonal relationships among the various extracted pools.

MATERIALS AND METHODS

Study areas. Sediment samples were collected between January and September 1988 from 3 stations in the southwestern Kattegat, on the east coast of Jutland, Denmark (Fig. 1). Stn 1 was in Aarhus Bay, a 320 km^2 embayment with an average water depth of about 15 m. Sediment was silt/mud with no or very low amounts of visible macrofauna, although the polychaete *Nephtys* sp. and the bivalves *Abra alba* and *Macoma* sp. were sometimes observed. Hydrological characteristics of Aarhus Bay have been described elsewhere (Jensen et al. 1988). Stn 2 was situated in Norsminde Fjord, a shallow estuary of 1.9 km^2 situated on the east coast of Jutland with an average water depth of about 1 m. The fjord receives drainage water, mostly from agricultural waste products and from the town of Odder, leading to great local fluctuations of salinity within the estuary (Muus 1967). The sampling station was situated in the low salinity part of the estuary and was described as station No. 2 by Jørgensen & Sørensen (1985). The sediment was a silt/sand containing Fe hydroxides to a depth of about 4 to 5 cm in winter and about 0.5 to 1 cm in late summer. Benthic microalgae were observed on the sediment surface during spring and the green macroalga *Ulva* sp. was occasionally seen in late

Fig. 1. Location of stations on the east coast of Jutland, Denmark

summer. Benthic fauna, including the polychaete *Nereis* sp. and the crustacean *Corophium* sp., were occasionally observed. Stn 3 was situated near the mouth of Randers Fjord. Salinity changes were low during the year. The sediment was relatively undisturbed and was composed of a fine organic-rich sand containing no visible macrofauna. The depth of the water column was < 1.0 m.

Sampling protocol and extraction procedures. Aarhus Bay sediments were collected with a 'Haps' bottom corer (Kanneworff & Nicolaisen 1973), from which smaller subcores were taken using plexiglass coring tubes (3.6 cm i.d., 20 cm long). At Norsminde and Randers, sediment cores were taken by hand using similar plexiglass coring tubes. Sediment samples with visible fauna were discarded. The sediments were brought to the laboratory within 2 h after sampling. Temperature and salinity were determined in the bottom water (5 cm above the sediment). Overlying water was carefully discarded and the sediment column was sectioned into the following layers: surface to 1 cm, 1 to 2 cm, 2 to 3 cm, and every 2 cm for deeper strata down to 9 cm. Samples from each sediment section were pooled (n = 3), homogenized and sieved through a 1.5 mm mesh to remove gross detritus. Each pooled sample was then subdivided for porosity determinations, removal of porewater and KCl extractions.

Water content was measured as weight loss of the homogenized sediment after drying for 24 h at 105 °C. Specific gravity was measured gravimetrically in duplicate. Sediment porewaters from Stns 1 and 2 were separated from sediments by low pressure N_2 (max. 50 psi, = 3.3 × 10^5 Pa) in closed plastic chambers, with simultaneous filtering of the removed porewater through prewashed sterile Millipore filters (Millipore Corporation Bedford, type HA, 0.45 μm pore size). Because of the low water content of sediments from Randers Fjord, porewater was separated from the sediments by a centrifugation technique, using a double centrifuge tube. Small portions of sediment were placed in the upper vial, and centrifuged (3400 × g, 5 min), to liberate the porewater and collect it in the lower vial. Porewaters were immediately frozen. Sediment samples were mixed with 2M KCl previously bubbled with N_2 and containing 0.5 % zinc acetate to inhibit bacterial activity. The KCl solutions were added at sediment:KCl proportions of 1:1 (w:v). Sediment and KCl were vigorously shaken under N_2 at 0 °C, using a vortex mixer (Ika-Werk VF2). The extraction time was 40 min. Supernatants from this extraction were weighed and recentrifuged (2600 × g, 5 min), to completely clarify. The sediment residues were weighed, and new equivalent amounts of KCl were added. This procedure was repeated until supernatants from 7 KCl extractions were obtained from the
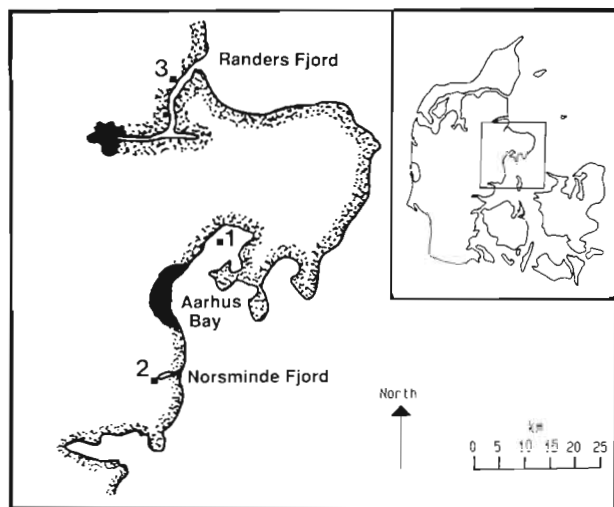
same sediment section. Occasionally, fresh sediments and pellets left after multiple KCl extraction were dried (105 °C, 24 h) for measurements of total N.

Sample analyses. Salinity was measured potentiometrically with a Conductivity Meter CDM 3, total N with a Carlo Erba model NA 1500 Nitrogen Analyser. NH_4^+ was analysed with a Spectronic 70 spectrophotometer fitted with a 300 VA tungsten lamp, using the indophenol method of Kempers & Zweers (1986), with minor modifications (Laima 1991). Prior to NH_4^+ quantification, a few drops of $1M$ $ZnCl_2$ were added to porewaters and KCl extracts, to remove any sulfides. Samples were centrifuged (1700 $\times$ g, <5 min) and NH_4^+ analysed in the supernatants. Absorbance units were read in suitably diluted samples (> 10-fold), to prevent inhibition of colour development (Ngo et al. 1982, Laima 1991). Blank absorbances were low, with optical density typically within the range 0.011 ± 0.005. The sediment porosity was used to convert measured concentrations into appropriate units.

KCl-extractable NH_4^+ was divided into the following pools: (1) A pool of easily desorbed NH_4^+ was calculated by subtracting the porewater NH_4^+ from the pool removed by the 1st KCl extraction. (2) Total adsorbed NH_4^+ was calculated by substracting the porewater NH_4^+ from the sum of NH_4^+ in KCl extracts from multi-extraction. (3) Tightly bound NH_4^+ was calculated as the difference between total adsorbed and easily desorbed NH_4^+. Concentrations were corrected for residual amounts from the previous extraction. The multi-extraction procedure was continued until the NH_4^+ concentration measured in the extract was <5 µM.

RESULTS

One-step versus multiple KCl extractions

Expressed as a percentage of total NH_4^+ desorbed by multiple extraction, 1-step KCl extractions gave low NH_4^+ yields at all stations (Fig. 2). One-step extraction of sediments from Aarhus Bay, Norsminde Fjord and Randers Fjord in May gave 35, 38 and 29 % of the total, compared to 50, 77 and 57 % obtained in January. Increasing the number of extractions resulted in a cumulative increase of the NNH_4^+ yield. The extractability varied with season; NH_4^+ was more easily extractable in January than in May. NH_4^+ yields were maximum after 6 or 7 multiple extractions.

Extraction of unknown N pool

A pool of unknown N, calculated as total (CN analyser) N minus the sum of measured pools (KCl extracts
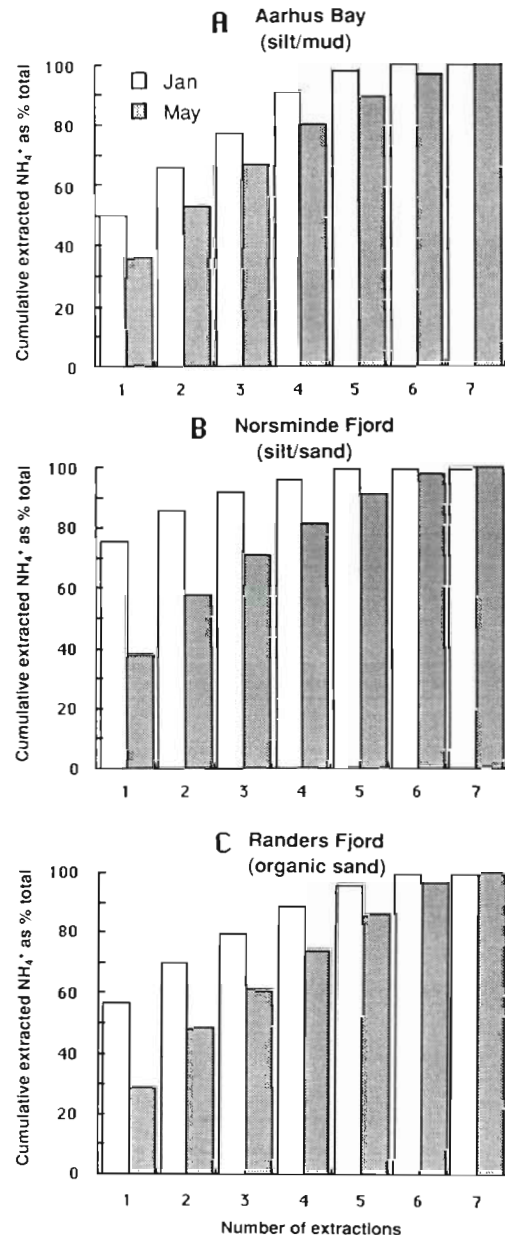

Fig. 2. Cumulative extracted NH_4^+ expressed as % of total KCl-extractable NH_4^+ plotted against number of extractions. Mean values (n = 18) for January (open bars) and May extractions (shaded bars) of the 0 to 4 cm sediment column are shown for each station. Standard errors were <15 % of means (not shown)

+ residual), was extracted from Aarhus Bay and Norsminde sediments, and formed 6 to 26 % and 14 to 48 % of the total N pool, respectively (Table 1). This pool did not correlate with either total N or extractable NH_4^+ (not shown). No such pool was removed during the extractions of the sandy sediment from Randers, where summed pool sizes of KCl-extractable NH_4^+-N and residual N equalled the total N pool (not shown).

Table 1. Effects of multiple KCl extractions on other sediment N pools (January 1988; Stns 1 and 2). The undefined N pool was calculated as total N (A) minus the sum of the NH_4^+-N pool in multiple KCl extracts (B) plus residual N (C). Standard errors were <10 % of average of triplicates (not shown). Measurements of NH_4^+, total N and residual N were performed as described in the text. Pool sizes are expressed in μmol g^{-1} dry wt

Station	Section (cm)	Total N (A)	Total extr. NH_4^+ (B)	Residual N (C)	Undefined N A – (B + C)
1. Aarhus Bay	0–1	238	1.9	222	14
	1–2	238	1.4	222	15
	2–3	239	1.1	218	20
	3–5	235	0.8	163	71
	5–7	199	0.7	219	19
	7–9	144	0.6	105	38
2. Norsminde Fjord	0–1	315	6.1	203	112
	1–2	325	3.6	243	82
	2–3	255	2.2	131	124
	3–5	209	1.4	178	31
	5–7	142	0.8	74	67
	7–9	140	0.6	80	60

Seasonal profiles of porewater NH_4^+

The depth profiles (0 to 9 cm) of porewater NH_4^+ varied with season (Fig. 3). In January and March, there was a net production of NH_4^+ in Aarhus Bay (Fig. 3A), as shown by the convex gradient of the profiles, and a net uptake in Randers Fjord (Fig. 3C). Norsminde sediments were already biological active in January, and a net uptake of NH_4^+ was observed in subsurface layers (Fig. 3B). The activity of benthic macrofauna increased dramatically in April, coinciding with the greatest observed loss in NH_4^+. In May and June, there was a net production of NH_4^+ in Norsminde, whereas losses were observed in Aarhus Bay. In September, a slow build-up of NH_4^+ in the porewater pool occurred in Aarhus Bay and a loss occurred in Norsminde.

Extraction of adsorbed NH_4^+

Significant amounts of adsorbed NH_4^+, differentiated into easily desorbed and total adsorbed NH_4^+, were removed from the sediments throughout the investigation period (Fig. 3). Concentrations were greatest in January, with the largest pools localized in the 0 to 1 cm layer. In March, the sediments were depleted in NH_4^+ from the upper 0 to 1 cm (Norsminde Fjord), 0 to 5 cm (Aarhus Bay) and from the 0 to 9 cm sediment column (Randers Fjord). A new build-up of NH_4^+ followed in March and April, but in June, a decrease in adsorbed NH_4^+ was observed in Aarhus Bay and Randers Fjord. Net uptake was seen in subsurface layers during spring, as indicated by concave concentration gradients.

The partition of NH_4^+ between porewater and adsorbed pools can be better evaluated by investigating the exchangeable:porewater ratios ($NH_4^+{}_{ex}$: $NH_4^+{}_{pw}$) as given by 1-step and multiple KCl extractions (Table 2). There was a 2 to 8-fold increase for multiple KCl extractions compared to 1-step extractions. Ratios were lowest in January and March, and varied little with depth. The highest ratios were obtained in May and June for the 0 to 3 cm sections of Aarhus Bay sediments, where pool sizes of porewater NH_4^+ were negligable (<5 nmol cm^{-3}) compared to the pools of adsorbed NH_4^+ (Fig. 3A).

The tightly adsorbed NH_4^+ pool (total adsorbed minus easily desorbed) changed with season (Fig. 4), indicating that it was in dynamic equilibrium with more readily available pools. The pool was only stable in January and March, whereas in May and June substantial amounts of NH_4^+ were released. This pool tended to gradually increase in September. There was no obvious relationship between seasonal changes in the pools in Aarhus Bay (Fig. 4A) and Norsminde (Fig. 4B) sediments, but there were some common trends in Randers Fjord sediments (Fig. 4C). The relationship of these pools to temperature and salinity will be discussed later (Fig. 4D to F).

DISCUSSION

It was shown (Laima 1991) that KCl is comparable to NaCl or artificial seawater (ASW) in simultaneously removing porewater and adsorbed NH_4^+, provided the sediments are maintained at low temperature during extraction. Quantitative evaluation of these exchangeable pools, particularly the adsorbed pool, is important
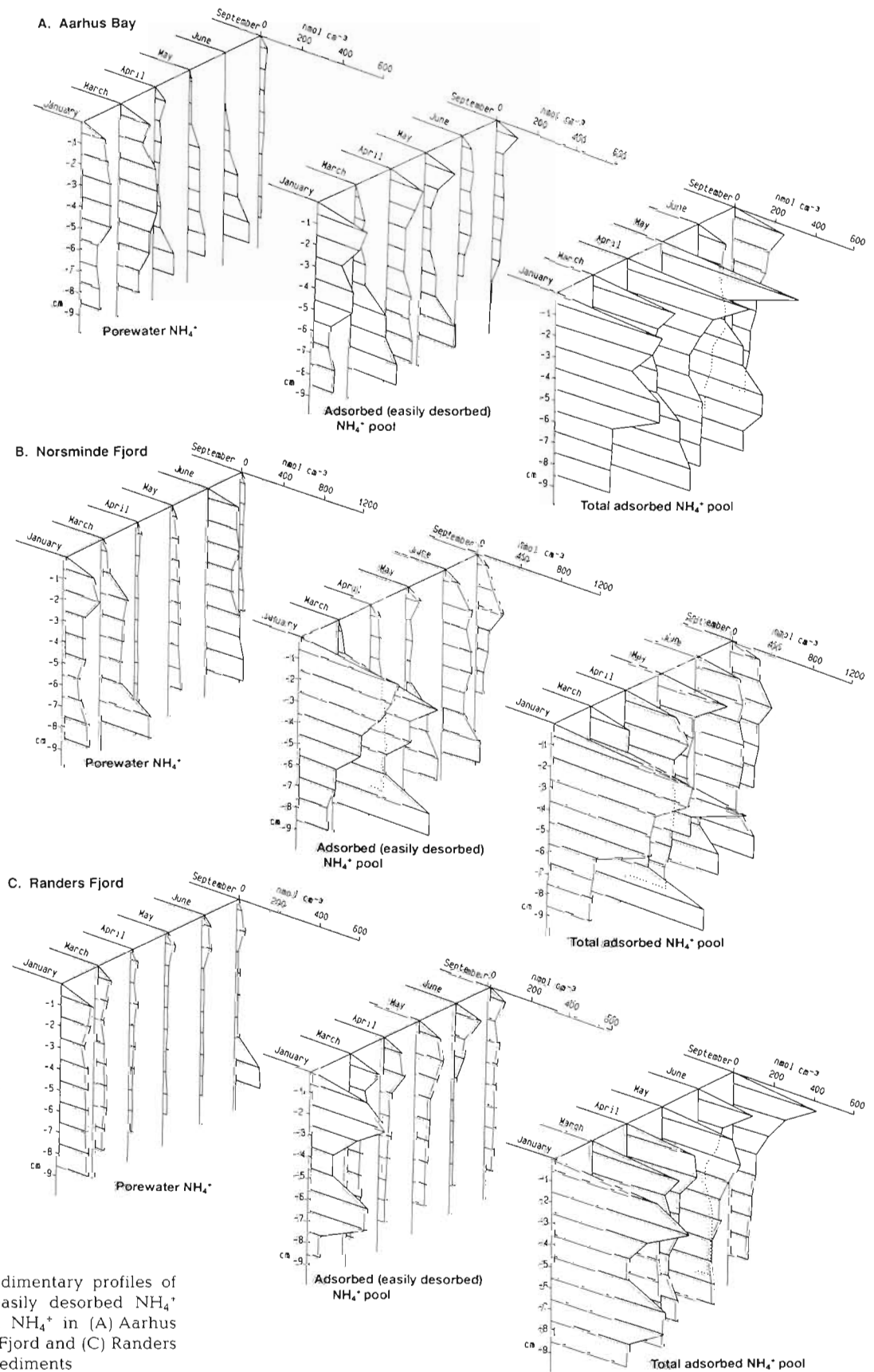
Fig. 3. Seasonal sedimentary profiles of porewater NH$_4^+$, easily desorbed NH$_4^+$ and total adsorbed NH$_4^+$ in (A) Aarhus Bay (B) Norsminde Fjord and (C) Randers Fjord sediments

Table 2. Seasonal variation of $NH_4^+{}_{ex}:NH_4^+{}_{pw}$ ratios (or K-values) for easily desorbed NH_4^+ and total adsorbed NH_4^+ (in parenthesis). Averages are shown (n = 3). Standard errors were < 10 % of mean values (not shown). ND: not determined

Station	Layer (cm)	$NH_4^+{}_{ex}:NH_4^+{}_{pw}$ ratios											
		\multicolumn{2}{c}{Jan}	\multicolumn{2}{c}{Mar}	\multicolumn{2}{c}{Apr}	\multicolumn{2}{c}{May}	\multicolumn{2}{c}{Jun}	\multicolumn{2}{c}{Sep}
1. Aarhus Bay	0–1	2.3	(5)	0.1	(3)	2.9	(10)	9.3	(43)	2.5	(7)	2.9	(7)
(silt/mud)	1–2	1.9	(4)	0.5	(3)	5.6	(20)	14.6	(74)	53.0	(108)	1.5	(7)
	2–3	1.0	(3)	0.0	(2)	2.2	(10)	1.5	(15)	14.7	(33)	2.1	(9)
	3–5	1.4	(4)	0.3	(2)	3.8	(14)	0.6	(8)	2.5	(6)	1.9	(6)
	5–7	1.1	(4)	1.1	(3)	3.5	(10)	1.2	(8)	0.4	(1)	2.3	(5)
	7–9	1.1	(3)	2.2	(5)	1.4	(4)	2.1	(5)	0.0	(0)	0.3	(4)
2. Norsminde Fjord	0–1	3.5	(5)	0.5	(7)	1.7	(15)	4.8	(27)	0.5	(1)	1.7	(5)
(mud/sand)	1–2	2.6	(4)	1.0	(6)	2.5	(19)	0.8	(8)	0.9	(2)	3.3	(6)
	2–3	4.1	(6)	3.9	(6)	2.9	(18)	1.4	(7)	0.7	(1)	8.1	(13)
	3–5	3.2	(5)	3.4	(5)	2.8	(12)	0.6	(4)	1.1	(2)	7.0	(17)
	5–7	2.3	(3)	2.5	(3)	6.8	(22)	3.0	(6)	0.3	(1)	2.1	(7)
	7–9	1.2	(2)	1.9	(2)	8.6	(30)	2.9	(5)	1.0	(1)	ND	ND
3. Randers Fjord	0–1	1.7	(3)	2.4	(7)	4.0	(14)	3.0	(9)	4.3	(9)	4.5	(24)
(organic sand)	1–2	2.6	(5)	1.5	(7)	7.7	(25)	7.9	(24)	1.5	(3)	1.4	(9)
	2–3	1.9	(4)	4.4	(17)	1.2	(8)	7.7	(29)	13.0	(24)	30.1	(98)
	3–5	0.8	(3)	1.9	(8)	2.5	(15)	5.3	(24)	0.8	(4)	8.0	(22)
	5–7	2.0	(4)	1.5	(7)	2.0	(13)	6.4	(30)	1.4	(9)	6.9	(12)
	7–9	0.3	(2)	0.8	(7)	1.9	(14)	3.7	(20)	1.5	(5)	0.5	(1)

in studies of NH_4^+ turnover (Blackburn 1980), and their dynamic nature implies that they might play a significant role in sediment nitrogen cycling, for instance by retaining NH_4^+ that would otherwise rapidly diffuse out of the sediment (Blackburn & Henriksen 1983). The NH_4^+ data (0 to 4 cm) shown in Fig. 2 represent the first reported effect of season on the efficiency of KCl extraction of NH_4^+ in marine sediments. In 3 different sediment types, the extractable NH_4^+ pool (i.e. porewater plus adsorbed) removed by 1-step KCl extraction was underestimated by 34 to 50 % in January and 63 to 71 % in May, relative to the total pool desorbed by multiple extraction. The removal of NH_4^+ from pools not immediately available clearly suggests that NH_4^+ exchanged slowly with added KCl. The extractability of NH_4^+ from bound pools resulted in similar patterns, independent of the sediment type. However, further refinement of the technique is needed in order to define the origin of this NH_4^+. The capacity of K^+ to remove all exchangeable NH_4^+ has been shown elsewhere (Laima 1991).

A drawback of the technique was that an unknown N pool was simultaneously removed from clay sediments (Table 1). Thus, care should be taken in making mass balance calculations for the nitrogen cycle. The suspicion that organic N compounds can be removed during intensive leaching has been reported in soil studies (Azam et al. 1989). In our experiments, the multiple extraction technique was used to investigate and compare the extractability of NH_4^+.

The absence of a common seasonal pattern in the depth profiles of porewater NH_4^+, easily desorbed NH_4^+ and total adsorbed NH_4^+ may reflect changes in the biological and physical processes to which the sediments were subjected throughout the investigation period. In winter, when the bacterial production of NH_4^+ is expected to be small due to low temperature and little input of readily degradable organic material, there were high concentrations of adsorbed NH_4^+, and to a lesser extent, of porewater NH_4^+ (Fig. 2A to C). A possible explanation for the observed lack of gradients of porewater NH_4^+ in subsurface layers (1 to 9 cm) could be sediment resuspension by bioturbation and physical disturbance. Simon (1988) observed a similar lack of porewater NH_4^+ gradient in the 0 to 10 cm layer of Potomac River sediments (USA).

Concentrations of NH_4^+ in the investigated pools changed dramatically in early spring (March). Accumulation of NH_4^+ in the porewater of subsurface layers of Aarhus Bay sediments (Fig. 3A) was in contrast with the observed loss of NH_4^+ from the upper layers of Norsminde Fjord (Fig. 3B) and from the 0 to 9 cm sediment column of Randers Fjord (Fig. 3C). The NH_4^+ profiles in porewater and exchangeable pools seem to be inversely correlated in Aarhus Bay sediments, positively correlated in Randers Fjord sediments and uncorrelated at Norsminde, where the input of freshwater (Jørgensen & Sørensen 1988) and a fall in salinity would release some NH_4^+ from the upper
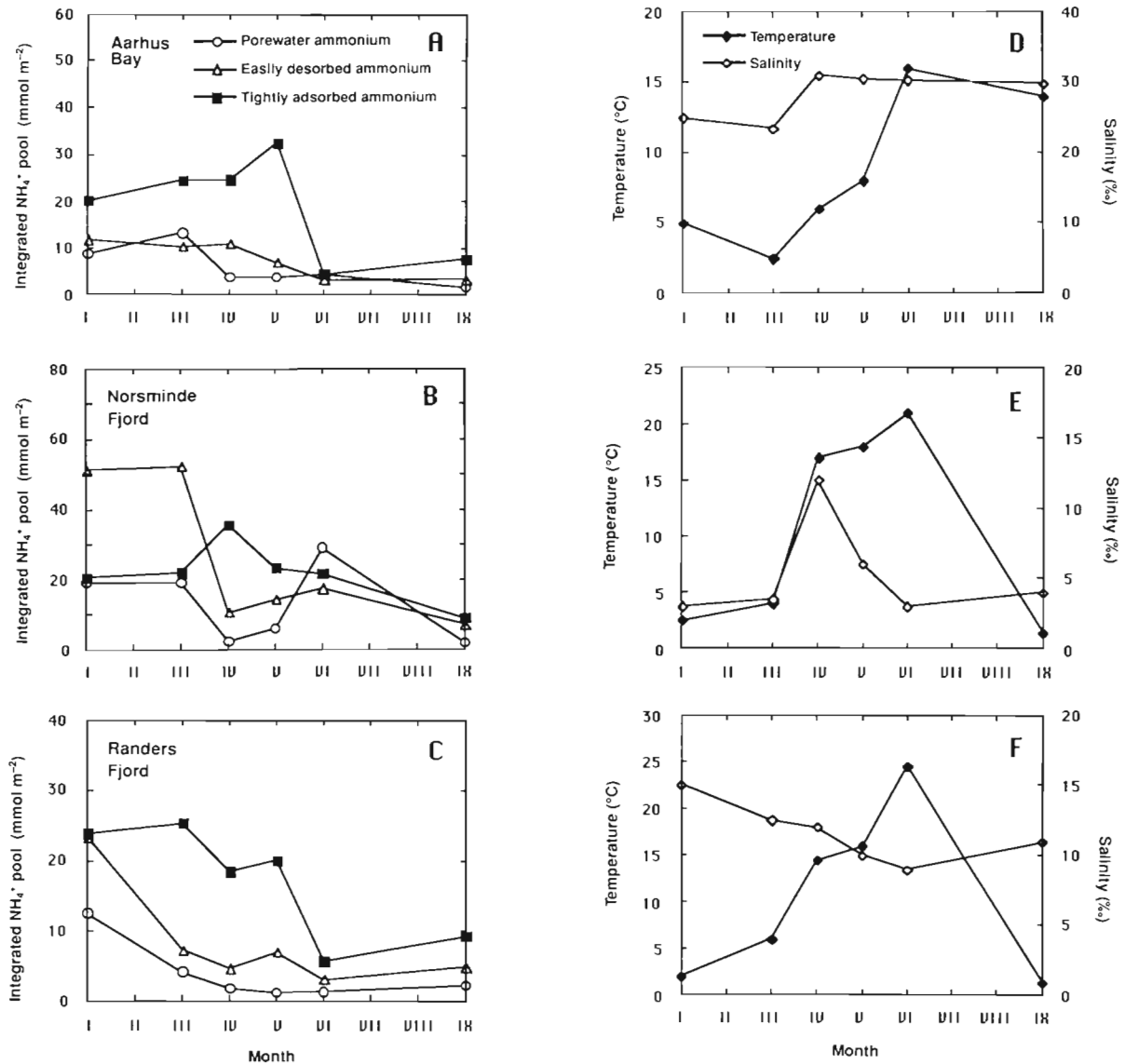
Fig. 4. Depth-integrated profiles (0 to 9 cm) of porewater NH$_4^+$, easily desorbed NH$_4^+$ and tightly bound NH$_4^+$ plotted against month for (A) Aarhus Bay, (B) Norsminde Fjord, and (C) Randers Fjord. Temperature and salinity data are also shown (D, E, and F, respectively)

sediment layers. This suggests a dynamic equilibrium between these pools at the first 2 stations.

A decrease in porewater NH$_4^+$ concentration was commonly observed at the 3 stations during the transition period from March to April-May (Fig. 3A to C). This pattern, suggesting evidence for increased sediment activity during this time of the year, was not apparently balanced by a corresponding decrease in NH$_4^+$ in the adsorbed pools. On the contrary, increasing quantities of NH$_4^+$ were adsorbed to the uppermost 0 to 1 cm of the sediment. Below this layer, common patterns of NNH$_4^+$ loss through bioturbation and/or microbial uptake were observed. This suggests that these NH$_4^+$ losses were counterbalanced by mineral-

ization of recently deposited material. In Aarhus Bay, for example, microscopic observation of the uppermost 5 mm of the sediment showed the presence of a slime of diatoms (including Skeletonema costatum), partially degraded. Thus, the sedimentation of algae might have increased microbial activity at the sediment surface, despite the low temperatures in spring (Fig. 4). This is in agreement with other studies (Graf 1987, Meyer-Reil 1987). Although some of the newly produced NH$_4^+$ may have been denitrified (Jensen et al. 1990), substantial amounts of NH$_4^+$ were simultaneously adsorbed to the sediment (Fig. 3A). It seems thus plausible that such bound pools would compensate for the liberation of NH$_4^+$ to the overlying water, by the

location of NH_4^+ at sites inaccessible to competing cations. The spring increase in NH_4^+ in the bound pools was of a transitory nature. This can be seen in the June profiles, when much of NH_4^+ was lost from almost the entire sediment (except at Norsminde). Again, the convex porewater NH_4^+ profiles indicated that the sediment was highly active. Further, the September profiles suggest that these pools might have been slowly rebuilt in order to reach the concentrations of the winter months. Thus, the sediments behaved dynamically with respect to NH_4^+ pools and adjusted to seasonal events.

The different changes in the NH_4^+ pools will necessarily influence calculated $NH_4^+_{ex}:NH_4^+_{pw}$ ratios at the various sediment depths (Table 2). The increased amounts of NH_4^+ obtained by multiple KCl extractions, compared to 1-step extractions, resulted in a significant increase of the corresponding $NH_4^+_{ex}:NH_4^+_{pw}$ ratios. The high ratios when NH_4^+ was difficult to extract (Fig. 2) suggest an inverse correlation between ratios and extractability. This is to be expected, since exchangeable NH_4^+ was continuously and slowly removed from more tightly bound pools. This kind of correlation would not be predicted if the exchangeable pool was only determined by 1-step KCl extractions. On the other hand, assuming that mineralization of organic matter results in the liberation of a free NH_4^+ pool, a rapid equilibrium between porewater and adsorbed pools would be expected, resulting in an unchanged ratio. This was found to be true in laboratory experiments (Laima 1991). The observed seasonal variation of the $NH_4^+_{ex}:NH_4^+_{pw}$ ratios suggest that these altered ratios might be attributed to variations in the degree of anaerobiosis of the sediments. The high spring-summer ratios were, in fact, associated with high sediment activity (Fig. 3A to C). This is in agreement with Yamada et al. (1987), who found that $NH_4^+_{ex}:NH_4^+_{pw}$ ratios increased with an increase in H_2S concentrations. Large concentrations of adsorbed NH_4^+ compared to porewater NH_4^+ concentrations (5- to 100-fold) were also reported by Simon (1989) in sediments of the Potomac River and Estuary.

In light of the present evidence for an important role of not easily exchangeable NH_4^+ in sediment processes, it is perhaps convenient to isolate this pool from the total adsorbed NH_4^+ pool, and named it 'tightly bound NH_4^+'. There is evidence suggesting that this pool is dynamic, slowly following the patterns observed for porewater NH_4^+ and easily desorbed NH_4^+, particularly the latter (Fig. 4). This time delay might indicate a slow equilibrium with more available pools, thus influencing the calculated $NH_4^+_{ex}:NNH_4^+_{pw}$ ratios (Table 2). Concentrations of this pool were correlated with salinity values, which are expected to influence the degree of NH_4^+ adsorption onto sediment (Boatman
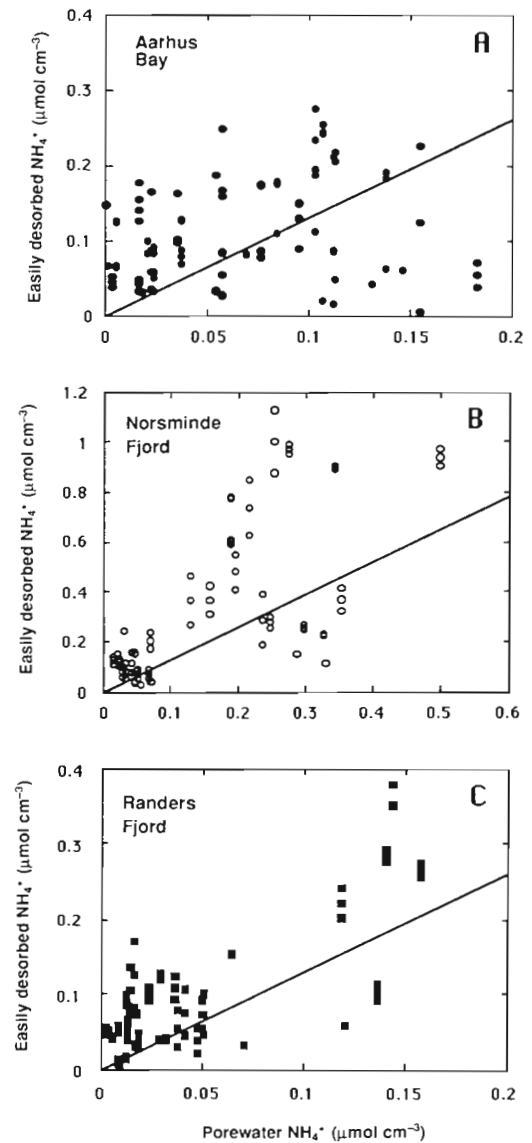

Fig. 5. Plots of easily desorbed NH_4^+ (1-step KCl extraction) against porewater NH_4^+ for (A) Aarhus Bay, (B) Norsminde Fjord, and (C) Randers Fjord; n = 72 at each station. Values were from all sediment depths at all sampling times. Data points were fitted through a 1·1.3 regression line (Mackin & Aller 1984)

& Murray 1982). Moreover, changes in temperature are also known to determine the adsorption of NH_4^+ (Kamyiama et al. 1978).

Mackin & Aller (1984) found a high correlation between porewater NH_4^+ and easily desorbed NH_4^+ in sediments from nearshore and hemipelagic deep-sea areas, and calculated the linear adsorption coefficient (K-value). The K-value is used in most models of porewater NH_4^+ distribution (Berner 1976). A K-value of 1.3 was found to be representative for terrigenous, surface marine sediments (Mackin & Aller 1984). However, a

random distribution of data points along a plot of pore-water NH_4^+ against easily desorbed NH_4^+ suggests that this value could not be applied to our sediment systems (Fig 5). A low correlation between porewater NH_4^+ and adsorbed NH_4^+ was also observed in Potomac River sediments (Simon & Kennedy 1987). The present K-values (i.e. $NH_4^+{}_{ex}$: $NH_4^+{}_{pw}$ ratios) are shown in Table 2. The K-value of 1.3 is only close to the January ratios. The seasonal variation of these ratios has not been predicted in models of NH_4^+ adsorption (Boatman & Murray 1982). Further experiments are needed to evaluate the availability of tightly bound NH_4^+ pools to microorganisms and the extent to which these pools might influence the calculation of NH_4^+ turnover rates in anoxic marine sediments.

LITERATURE CITED

Azam, F., Mulvaney, R. L., Stevenson, F. J. (1989). Transformation of ^{15}N-labelled plant material in three contrasting soils. Biol. Fertil. Soils 8: 54–60

Berner, R. A. (1974). Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus, and silicon in anoxic marine sediments. In: Goldberg, E. D. (ed.) The sea. Wiley, New York, p. 427–450

Berner, R. A. (1976). Inclusion of adsorption in the modelling of early diagenesis. Earth Planet. Sci. Lett. 29: 333–340

Berner, R. A. (1977). Stoichiometric models for nutrient regeneration in anoxic sediments. Limnol. Oceanogr. 22: 781–786

Blackburn, T. H. (1980). Seasonal variations in the rate of organic-N mineralization in anoxic marine sediments. In: Biogéochimie de la matière organique a l'interface eau-sédiment marin. Colloq. Int. CNRS 293: 173–183

Blackburn, T. H., Henriksen, K. (1983). Nitrogen cycling in different types of sediments from Danish waters. Limnol. Oceanogr. 28: 477–493

Boatman, C. D., Murray, J. W. (1982). Modelling exchangeable NH_4^+ adsorption in marine sediments: process and controls of adsorption. Limnol. Oceanogr. 27: 99–110

Bremner, J. M. (1965). Total nitrogen and inorganic forms of nitrogen. In: Black, C. A. (ed.) Methods of soil analysis. American Institute of Agronomy Monograph No. 9, Madison, p. 1179–1237

Graf, G. (1987). Benthic response to the annual sedimentation patterns. In: Rumohr, J., Walger, E., Zeitzschel, B. (eds.) Lecture notes on coastal and estuarine studies, Vol. 13. Seawater-sediment interactions in coastal waters. An interdisciplinary approach. Springer-Verlag, New York, p. 84–92

Haines, E., Chalmers, A., Hanson, R., Sherr, B. (1977). Nitrogen pools and fluxes in a Georgia salt marsh. In: Wiley, M. L. (ed.) Estuarine processes, Vol. 2. Academic Press, New York, p. 241–254

Henriksen, K. (1980). Measurement of in situ rates of nitrification in sediment. Microb. Ecol. 6: 329–337

Jenkins, M. C., Kemp, W. M. (1984). The coupling of nitrification and denitrification in two estuarine sediments. Limnol. Oceanogr. 29: 609–619

Jensen, M. H., Andersen, T. K., Sørensen, J (1988). Denitrification in coastal bay sediment: regional and seasonal variation in Aarhus Bight, Denmark. Mar. Ecol. Prog. Ser 48: 155–162

Jensen, M H., Lomstein, E., Sørensen, J. (1990). Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. Mar. Ecol. Prog. Ser. 61. 87–96

Jørgensen, B. B., Sørensen, J (1985). Seasonal cycles of O_2, NO_3^- and SO_4^{2-} reduction in estuarine sediments: the significance of an NO_3^- reduction maximum in spring. Mar. Ecol. Prog. Ser. 24: 65–74

Jørgensen, K. S., Sørensen, J. (1988). Two annual maxima of nitrate reduction and denitrification in estuarine sediment (Norsminde Fjord, Denmark). Mar. Ecol. Prog. Ser. 48: 147–154

Kamiyama, K., Okuda, S., Kawaii, A. (1978). Studies on the release of ammonium nitrogen from the bottom sediments in freshwater regions. III. Ammonium nitrogen in the sediments in the different water regions. Jap. J. Limnol. 39: 176–180

Kanneworff, E., Nicolaisen, W. (1973). The 'Haps', a frame supported bottom corer. Ophelia 10: 119–128

Kempers, A. J., Zweers, A. (1986). Ammonium determination in soil extracts by the salicylate method. Commun. Soil Sci. Plant Anal. 7: 715–723

Klingensmith, K. M., Alexander, V. (1983). Sediment nitrification, denitrification and nitrous oxide production in a deep Artic Lake. Appl. environ. Microbiol. 46: 1084–1092

Laima, M. J. C. (1991). Ammonium pools in marine sediments. Ph.D. dissertation, University of Aarhus

Lomstein, E., Jensen, M. H., Sørensen, J. (1990). Intracellular NH_4^+ and NO_3^- pools associated with deposited phytoplankton in a marine sediment (Aarhus Bight, Denmark). Mar. Ecol. Prog. Ser. 61: 97–105

Mackin, J. E., Aller, R. C. (1984). Ammonium adsorption in marine sediments. Limnol. Oceanogr. 29: 250–257

Meyer-Reil, L.-A. (1987). Seasonal and spatial distribution of extracellular enzymatic activities and microbial incorporation of dissolved organic substrates in marine sediments. Appl. environ. Microbiol. 53: 1748–1755

Muus, B. J. (1967). The fauna of Danish estuaries and lagoons. Meddr. Danm. Fisk.-og Havunders. 5: 1–316

Ngo, T. T., Pan, A. P. H., Yan, C. F., Lenhoff, H. M. (1982). Interferences in determination of ammonia with the hypochlorite-alkaline phenol method of Berthelot. Analyt. Chem. 57: 46–49

Pregnall, A. M., Miller, S. L. (1988). Flux of ammonium from surf-zone and nearshore sediments in Nahant Bay, Massachusetts, USA in relation to free-living *Pilayella littoralis*. Mar. Ecol. Prog. Ser. 50: 161–167

Rosenfeld, J. K. (1979). Ammonium adsorption in nearshore marine sediments. Limnol. Oceanogr. 24: 356–364

Simon, N. S. (1988). Nitrogen cycling between sediment and the shallow water in the transition zone of the Potomac River and Estuary. I. Nitrate and ammonium fluxes. Estuar. coast. Shelf Sci. 26: 483–497

Simon, N. S. (1989). Nitrogen cycling between sediment and the shallow-water in the transition zone of the Potomac River and Estuary. II. The role of wind-driven resuspension and adsorbed ammonium. Estuar. coast. Shelf Sci. 28: 531–547

Simon, N. S., Kennedy, M. M. (1987). The distribution of nitrogen species and adsorption of ammonium in sediments from the tidal Potomac River and Estuary. Estuar. coast. Shelf Sci. 25: 11–26

Smith, C. J., Patrick, W. H. (1983). Nitrous oxide emission as affected by alternate anaerobic and aerobic conditions from soil suspensions enriched with ammonium sulphate. Soil Biol. Biochem. 15: 693–697

Sørensen, J. (1978). Denitrification rates in marine sediment as measured by the acetylene inhibition technique. Appl. environ. Microbiol. 36: 139–143

Terry, R. E., Nelson, D. W. (1975). Factors influencing nitrate transformations in sediments. J. environ. Qual. 4: 549–553

Yamada, H., Kayama, M., Fujisawa, K. (1987). Seasonal changes of concentrations of inorganic and organic nitrogen in coastal marine sediments. Estuar. coast. Shelf Sci. 24: 585–598