

# Distribution of adsorbed ammonium pools in two intertidal sedimentary structures, Marennnes-Oléron Bay, France

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**ABSTRACT:** The 1-step and multiple-step KCl extraction technique was used to evaluate quantitatively the distribution of adsorbed  $\text{NH}_4^+$  in the 0–5 cm strata of 2 intertidal muddy structures from Marennnes-Oléron Bay, France. KCl extraction efficiency was higher in the reconstituted sediment slurries and decreased significantly in the presence of porewater ions, leading to underestimations of the size of the pool of adsorbed, easily desorbed  $\text{NH}_4^+$ . Various pools of adsorbed  $\text{NH}_4^+$  were displaced from the sediment after reaction with KCl in multiple steps. Pools of tightly bound  $\text{NH}_4^+$  were much larger in runnels as opposed to ridges, and accounted for up to 32% (ridge) and 40% (runnel) of the  $\text{NH}_4^+$  desorbed from the sediment. These pools have important implications for the calculation of the  $K_D$  value, the dimensionless  $\text{NH}_4^+$  distribution coefficient. Differing relationships between easily desorbed  $\text{NH}_4^+$  or tightly bound  $\text{NH}_4^+$ , on the one hand, and the sediment grain size,  $\text{CaCO}_3$  and N content, on the other, suggest multiple origins for particulate matter in the sediment.

**KEY WORDS:** Ammonium · Adsorption · Mudflat · Ridge · Runnel

## INTRODUCTION

An important fraction of the organic matter produced in coastal ecosystems is deposited and decomposed in sediments. Ammonium, which is regenerated by deamination of this organic matter, can be found dissolved in pore water, adsorbed onto the surface of clay particles and organic matter, or fixed within the clay structure. There is a dynamic equilibrium between  $\text{NH}_4^+$  pools and, in addition, there is a rapid exchange between the adsorbed pool and the porewater pool. Ammonium which is not nitrified in the oxic layers of sediment is ultimately released to the overlying water and may influence primary production (Boynton et al. 1982). As the adsorbed pool may represent a substantial part of total  $\text{NH}_4^+$  in sediments, the adsorption process must be considered when model-

ling nitrogen diagenesis in coastal sediments (Rosenfeld 1979). Indeed, Berner (1976, 1977) established the importance of including an adsorption term in his stoichiometric model of nitrogen regeneration, and Blackburn (1980) showed that the assessment of this exchangeable  $\text{NH}_4^+$  is necessary for studying nitrogen turnover.

The assessment of adsorbed  $\text{NH}_4^+$  is usually achieved through KCl extraction, but Laima (1992b,c) has shown that a 1-step procedure protocol is not sufficient to release the total adsorbed pool and that it is necessary to proceed through a multiple KCl extraction method of up to 6 or 7 successive steps. Thus, he found that 1-step extractions removed only 29 to 77% of the total adsorbed  $\text{NH}_4^+$  pool, depending on the sediment type and season. This 'tightly bound  $\text{NH}_4^+$ ' (the sum of additional KCl extractions), as opposed to the 'easily exchangeable  $\text{NH}_4^+$ ' fraction (the amount released by a 1-step KCl extraction minus porewater  $\text{NH}_4^+$ ), can

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represent the dominant form of  $\text{NH}_4^+$  and may strongly influence the calculation of the sediment exchange capacity and the  $\text{NH}_4^+$  turnover rate. Therefore, it is of prime importance to assess this pool quantitatively and to appraise the effect of the factors controlling it.

Intertidal mudflats are areas of intensive organic matter production and deposition, and thus also of mineralization. These mudflats play an important role in benthic regeneration in estuaries and associated bays. Although their importance in primary productivity (Pinckney & Zingmark 1993) and as a food source for benthic invertebrates (Montagna et al. 1995, Riera et al. 1996) has been recognized, their role in the whole ecosystem is not fully understood. Such mudflats are frequently characterized by major sedimentary structures known as 'ridges and runnels', i.e. a parallel succession of crests and troughs normal to the shore (Dyer 1998). These features are likely to act as a prominent structuring spatial factor, however, and their influence on the distribution of most geochemical and biological variables is still unknown.

It is therefore our goal (1) to test the methodology for the measurement of the different adsorbed  $\text{NH}_4^+$  pools and (2) to show that the 'ridges and runnels' structures strongly influence the distribution of sediment ammonium pools and the efficiency of ammonium extractability. Finally, we shall provide a budget of ammonium distribution as a function of these intertidal sedimentary structures.

## MATERIALS AND METHODS

**Study area.** Marennes-Oléron Bay is an estuarine zone occupying an area of about 170 km<sup>2</sup> between Aix Island and the Maumusson Channel in south-west France (Fig. 1). Bedforms extend over most of the mudflat, and they represent permanent structures in which ridges occupy  $\frac{2}{3}$  and runnels  $\frac{1}{3}$  of the surface area (Sauriau et al. 1997). There is a major contribution of autochthonous material to the sediments, essentially composed of microphytobenthos (Cariou-Le Gall & Blanchard 1995), of which the most abundant are

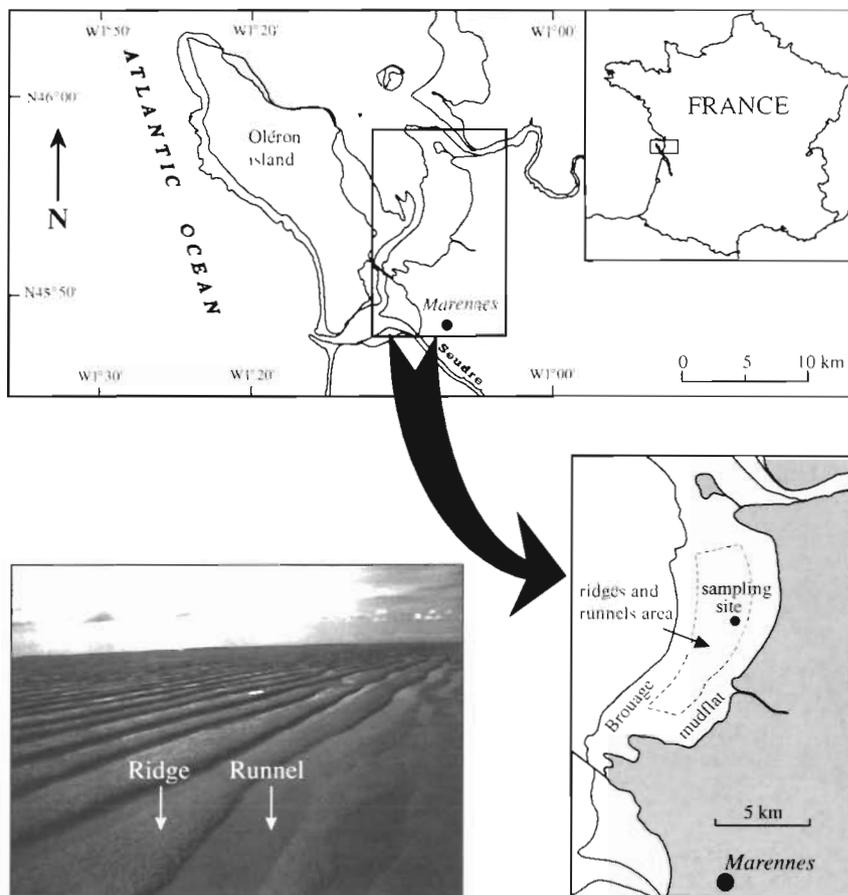


Fig. 1. Photograph of ridges and runnels at the study site, and maps showing the site location in the middle of an intertidal mudflat in Marennes-Oléron Bay, France

diatoms (particularly *Navicula*, *Nitzschia* and *Gyrodinium*). Macrofauna assemblages on Brouage mudflats belong to the *Macoma balthica* community (Thorson 1957). However, there is some difference between the species abundances on ridges and runnels (Sauriau & Gouleau unpubl. data). Thus, *Hydrobia ulvae* is more numerous in the runnels. This is a surface and/or a subsurface deposit feeder that can easily crawl on and dig into the fluid mud of runnels. In contrast, *Scrobicularia plana*, a deposit-feeder, is more numerous on ridges: its biomass can be over 30 g ash-free dry weight (AFDW) m<sup>-2</sup>. Polychaetes species are also more numerous in ridges as against runnels. *Tubificoides benedini*, *Tharyx marioni*, *Streblospio shrubsolii* benefit from the more stable conditions on the ridges compared to runnels. *M. balthica*, a suspension/deposit-feeder bivalve, and *Nereis ombergii*, a carnivorous polychaete, are equally distributed over both bedforms. The hydrobiological characteristics of the bay have been described elsewhere (Héral et al. 1983). Recent work has studied the role of the microtopography on diffusive  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes (Gouleau

unpubl. data) and on its ability to trap nutrients and to regulate geochemical fluxes (Feuillet-Girard et al. 1988, 1997).

**Sampling protocol and extraction procedures.** Sampling took place in the upper part of the middle slikke where the ridge-and-runnel system spreads over a 30 km<sup>2</sup> area of the mudflat, see Fig. 1 and Germaneau & Sauriau (1996). Twelve sediment cores (5.4 cm diam., 20 cm long) were collected randomly by hand at low tide (tidal coefficient = 36) on April 16, 1997, 6 covering about 3 m<sup>2</sup> of surface area on a ridge and similarly a further 6 in an adjacent runnel. Based on previous tests on site variability of porewater nutrient concentration, this sampling strategy was found to give a good representation of the study area (Feuillet-Girard unpubl. data). Sediment cores were stored at 0°C and quickly transported to the laboratory. Overlying water was carefully discarded, the sediment was then cut into five 1 cm thick slices. Samples were sieved through a 1.5 mm mesh to remove gross detritus and macrofauna. Specific density was measured gravimetrically in triplicate. A portion of wet sediment was sieved (50 µm mesh); some coarse fraction was used for grain size determinations and some was dried and decarbonated with HCl for the determination of the CaCO<sub>3</sub> content. Water content was measured as weight loss after drying for 72 h at 60°C and corrected for salt effects. The C-N composition of sediment organic matter was determined in duplicate using a CHN analyzer Carlo Erba 1500 using acetanilide (N = 10.39% and C = 71.09%) as standard. Prior to the C-N analysis, 100 mg of sediment were acidified with HCl 1 N to remove carbonates. This decarbonation was increased by sonification. Then the samples were dried under vacuum to eliminate HCl vapours, after which 1 ml of Milli-Q H<sub>2</sub>O was added and the samples were homogenized by sonification and freeze-dried.

Some sediment characteristics are shown in Table 1.

**Collection of porewater and KCl extracts.** Moderate to intensive extraction assays were designed to point out the likely effect of porewater ions on KCl efficiency for displacement of NH<sub>4</sub><sup>+</sup> from the sediment, and to desorb at least 3 exchangeable NH<sub>4</sub><sup>+</sup> pools. In Series A (Fig. 2, left-hand side) slices from different depths were purged in N<sub>2</sub> and centrifuged in gas-tight containers. Porewater extracts were filtered through GF/C Whatman filters (0.45 µm pore size), and stored at -20°C for further treatment. Sediment pellets from which pore water had been removed (about 30% remained) were mixed together with de-ionized H<sub>2</sub>O in a double wash, and left on ice. The suspension was centrifuged and NH<sub>4</sub><sup>+</sup> was measured in the supernatant. This procedure was repeated until the NH<sub>4</sub><sup>+</sup> concentration in the supernatant was below 5 µmol l<sup>-1</sup>. When necessary, de-ionized H<sub>2</sub>O was added to these pellets to regain the original H<sub>2</sub>O content. Reconstituted sediments were pooled and extracted at 0°C with 2 M KCl which was bubbled with pure N<sub>2</sub> immediately before use (Laima 1994). In Series B (Fig. 2, right-hand side), slices from each level were pooled together, and KCl extracts incorporating both pore water and the easily desorbed pool were obtained as before. Finally, pellets were weighed and new equivalent amounts of KCl were added, always keeping the sediment to extractant ratio constant. Multiple extractions were carried out until 6 additional supernatants were obtained from each depth.

**Analyses and calculations.** Salinity was measured using a microprocessor conductivity meter LF 320 WTW and a standard conductivity cell Tetracon 325. Ammonium was measured using the salicylate method with minor modifications (Laima 1992a). Reagents were added to 10- to 20-fold diluted water samples, and absorbance units (AU) were read in a Uvikon 722 LC spectrophotometer fitted with a quartz halogen

Table 1. Some characteristics of ridge and runnel structures. Marennes-Oléron Bay, April 1997

| Layer (cm)     | H <sub>2</sub> O (ml g <sup>-1</sup> ) | Porosity (ml cm <sup>-3</sup> ) | Salinity <sup>a</sup> (‰) | N (µg mg <sup>-1</sup> dw) | C (µg mg <sup>-1</sup> dw) | Grain > 50 µm (%) | CaCO <sub>3</sub> <sup>b</sup> (%) |
|----------------|--|---------------------------------|---------------------------|----------------------------|----------------------------|-------------------|------------------------------------|
| <b>Ridges</b>  |  |                                 |                           |                            |                            |                   |                                    |
| 0-1            | 0.57                                   | 0.71                            | 44.7                      | 1.7                        | 11.5                       | 1.9               | 21.3                               |
| 1-2            | 0.51                                   | 0.58                            | 45.0                      | 1.6                        | 10.8                       | 4.3               | 16.9                               |
| 2-3            | 0.49                                   | 0.61                            | 40.0                      | 1.6                        | 10.6                       | 4.7               | 15.1                               |
| 3-4            | 0.54                                   | 0.68                            | 39.0                      | 2.0                        | 12.6                       | 2.2               | 16.9                               |
| 4-5            | 0.56                                   | 0.70                            | 37.7                      | 1.6                        | 10.7                       | 1.9               | 25.5                               |
| <b>Runnels</b> |  |                                 |                           |                            |                            |                   |                                    |
| 0-1            | 0.66                                   | 0.81                            | 35.3                      | 1.7                        | 12.0                       | 1.9               | 48.9                               |
| 1-2            | 0.66                                   | 0.85                            | 35.7                      | 1.9                        | 14.2                       | 2.8               | 55.8                               |
| 2-3            | 0.62                                   | 0.79                            | 35.3                      | 2.2                        | 15.2                       | 1.8               | 59.1                               |
| 3-4            | 0.61                                   | 0.80                            | 35.0                      | 2.1                        | 12.8                       | 1.9               | 53.7                               |
| 4-5            | 0.60                                   | 0.80                            | 32.8                      | 1.8                        | 12.1                       | 5.6               | 39.8                               |

<sup>a</sup>Porewater data. <sup>b</sup>Measured in the coarse fraction (>50 µm)

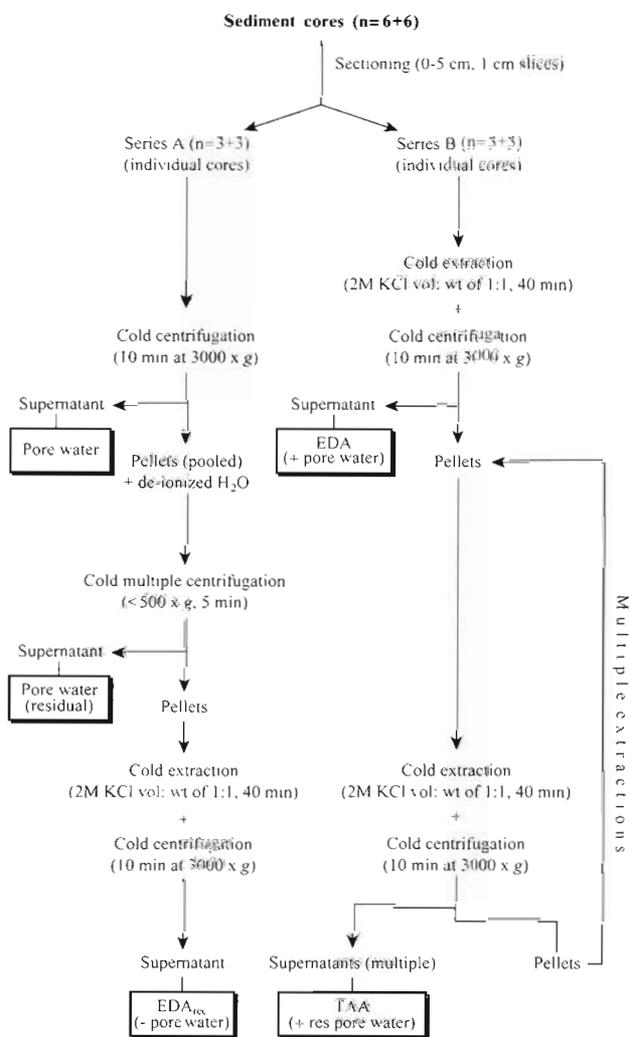


Fig. 2. Extraction scheme for removal of porewater, easily desorbed  $\text{NH}_4^+$  (EDA), reconstituted EDA ( $\text{EDA}_{\text{rec}}$ ) and tightly adsorbed ammonium (TAA) pools. All steps were performed under a stream of  $\text{N}_2$

lamp and a R 928 PM detector. Detection limits lie in the  $-0.3$  to  $4$  AU range, the photometric accuracy is better than  $\pm 0.004$  AU at  $1$  AU. Unknown factors present in extracts from marine sediments are known to interfere with colour development of the salicylate method (Ngo et al. 1982). We tested these effects by calculating  $\text{NH}_4^+$  recovery in 10- to 20-fold diluted samples that were spiked with internal standards. A good recovery ( $\sim 99\%$ ) was obtained, so possible interfering factors on colour development were absent in the used dilution range. Adsorbed, easily desorbed  $\text{NH}_4^+$  (EDA) is the pool desorbed in the normal 1-step extraction of fresh sediment (Series B), minus the  $\text{NH}_4^+$  dissolved in pore water. Reconstituted, easily desorbed  $\text{NH}_4^+$  ( $\text{EDA}_{\text{rec}}$ ), is the fraction desorbed after 1-step KCl

extraction of reconstituted sediment (Series A). Total adsorbed  $\text{NH}_4^+$  is obtained by subtracting porewater  $\text{NH}_4^+$  (as measured in Series A) from the total  $\text{NH}_4^+$  in multiple KCl extractions (Series B), after correction for residual pore water and residual KCl. Tightly adsorbed ammonium (TAA) is obtained by subtracting the EDA pool from the pool desorbed in 6 residual extractions. Analyses of variance and correlation analysis at 95% confidence interval were performed using STATISTICA (StatSoft Inc. 1993).

## RESULTS AND DISCUSSION

Pool sizes of easily desorbed  $\text{NH}_4^+$  depended on whether or not pore water had been removed prior to addition of KCl. Fig. 3 shows relationships between EDA and  $\text{EDA}_{\text{rec}}$  in the 0–5 cm strata of ridges and runnels. In both structures, measurements of the reconstituted pool yielded more  $\text{NH}_4^+$  compared to the original pool. It is not likely that the higher  $\text{NH}_4^+$  yield found in  $\text{EDA}_{\text{rec}}$  is due to exposure of new organic binding sites to added  $\text{K}^+$  since we did not observe more coloured waters in these rinses. An explanation for a lower  $\text{NH}_4^+$  yield in EDA compared to  $\text{EDA}_{\text{rec}}$  is a  $\text{K}^+$  effect in the presence of porewater (pw) ions, in moving the equilibrium  $\text{NH}_4^+_{\text{pw}} \rightleftharpoons \text{NH}_4^+_{\text{exch}}$  towards sites with poor access to cation exchange (exch). Depressive effects of  $\text{K}^+$  on  $\text{NH}_4^+$  exchange have also been reported in other coastal environments (Laima 1994) and in soil studies (Nõmmik & Vahtras 1982). This hypothesis is further supported by Fig. 4, where cumulative  $\text{NH}_4^+$  concentration data obtained from multiple extractions of intact sediments (pore water included) are plotted against the number of

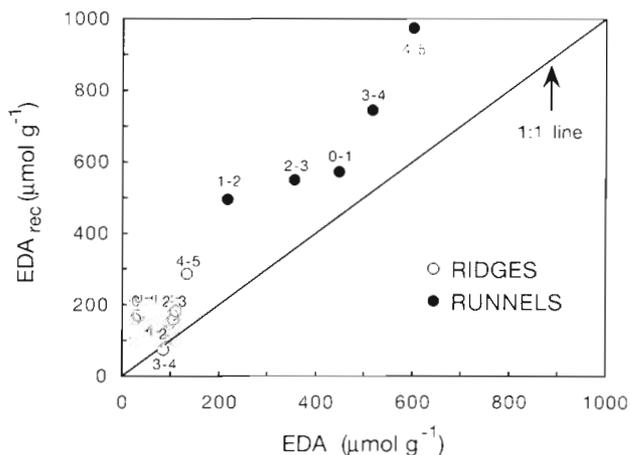


Fig. 3. Effect of the extraction procedure on the measurement of the EDA pool

Table 2. Average distribution of  $\text{NH}_4^+$  pools in the 0–5 cm strata of ridge and runnel structures and linear relationships between dissolved and adsorbed  $\text{NH}_4^+$ 

|  | $\text{NH}_4^+$<br>( $\text{nmol g}^{-1}$ ) | $\text{NH}_4^+$<br>(% total) | Linear regression<br>( $r^2$ ) | p     |
|--|---|------------------------------|--------------------------------|-------|
| <b>Ridges</b>                              |   |                              |                                |       |
| <b>Pools</b>                               |   |                              |                                |       |
| Pore water                                 | 51  | 22                           |                                |       |
| EDA <sub>rec</sub> (1-step KCl extraction) | 108   | 46                           |                                |       |
| TAA (6 extra KCl extractions)              | 74  | 32                           |                                |       |
| Total extractable pool                     | 233   | 100                          |                                |       |
| <b>Relationships</b>                       |   |                              |                                |       |
| Pore water vs EDA <sub>rec</sub> (n = 20)  |   |                              | 0.92                           | <0.05 |
| Pore water vs TAA (n = 20)                 |   |                              | 0.73                           | >0.05 |
| <b>Runnels</b>                             |   |                              |                                |       |
| <b>Pools</b>                               |   |                              |                                |       |
| Pore water                                 | 80  | 7                            |                                |       |
| EDA <sub>rec</sub> (1-step KCl extraction) | 587   | 53                           |                                |       |
| TAA (6 extra KCl extractions)              | 447   | 40                           |                                |       |
| Total extractable pool                     | 1114  | 100                          |                                |       |
| <b>Relationships</b>                       |   |                              |                                |       |
| Pore water vs EDA <sub>rec</sub> (n = 20)  |   |                              | 0.17                           | >0.05 |
| Pore water vs TAA (n = 20)                 |   |                              | 0.09                           | >0.05 |

extractions. Extraction of  $\text{NH}_4^+$  increased initially, following a progressive dilution of the porewater pool and a simultaneous increase of excess  $\text{K}^+$  concentration. However, if the  $\text{NH}_4^+$  yield were only a result of volumetric effects, dilution curves would be comparable. This was not the case. It is more likely that  $\text{NH}_4^+$ , which moved towards non-exchangeable pools during the first extraction step, had re-entered the exchangeable pool. The decrease in yield during the remaining extractions was probably caused by exhaustion of  $\text{NH}_4^+$  adsorbed to the sediment matrix. It is clear that the TAA pool represented a substantial fraction of  $\text{NH}_4^+$  in these intertidal sediments: 32% in ridges and 40% in runnels (Table 2).

Differences between ridges and runnels were also found in the porewater  $\text{NH}_4^+$  distribution along the sedimentary profile (Table 3). Variation among cores was high (CV up to 56%). Porewater salinity was higher in ridges (mean [ $\pm$  SE] =  $41 \pm [3]$  PSU) than in runnels (mean [ $\pm$  SE] =  $35 \pm [1]$  PSU) (Table 1). However, pooled salinity and porewater  $\text{NH}_4^+$  (n = 30) were inversely correlated (Fig. 5A). A salinity rise in the upper horizons of ridges is likely due to water losses through evaporation during emersed conditions. On the other hand, when the tide is in, flushing due to gravitational drainage may also induce  $\text{NH}_4^+$  losses in these horizons. Exposure to rain and wave-pumping can also alter salinity and porewater  $\text{NH}_4^+$  concentrations. Essentially, runnels represent waterlogged micro-environments in which nutrients are better retained than in the ridges.

The dimensionless  $\text{NH}_4^+$  distribution coefficient  $K_D$  is calculated as (Krom & Berner 1980):

$$K_D = (1 - \Phi/\Phi) p_s K^* \quad (1)$$

where  $\Phi$  is porosity (porewater volume/sediment volume),  $p_s$  is dry sediment density (assumed  $2.65 \text{ g ml}^{-1}$ ) and  $K^* = C_N^*/C_N$ , where  $C_N^*$  is the rapidly exchangeable  $\text{NH}_4^+$  concentration in  $\mu\text{mol g}^{-1}$  dry wt sediment and  $C_N$  is the porewater concentration in mM relative to porewater volume. Usually,  $K_D$  values range from 1 to 20 in marine sediments (Seitzinger et al. 1991, Raaphorst & Malschaert 1996). The term  $C_N^*$  in Eq. (1) was improved to account for the multiple-extractable pool. The adsorbed pool obtained in this way undoubtedly gives a better estimate of this coefficient (Table 2) and therefore should be used in models of  $\text{NH}_4^+$  adsorption (Boatman & Murray 1982).

Plots of adsorbed  $\text{NH}_4^+$  (in 1-step or multiple-step extraction protocols) against porewater  $\text{NH}_4^+$  were not significantly correlated ( $p > 0.05$ ), except the relationship  $\text{NH}_4^+$  pw versus EDA<sub>rec</sub> that correlated significantly in ridges (Table 2). Some inverse correlations were found between porewater  $\text{NH}_4^+$  and the improved  $K_D$  values (Fig. 5B). Indeed, both consistency and non-consistency in these relationships have been reported (Mackin & Aller 1984, Simon & Kennedy 1987). Mayer & Rice (1992) suggest that this inverse correlation is due to saturation of high-energy sorption sites with

Table 3. Porewater  $\text{NH}_4^+$  data (mM) and calculated distribution coefficients ( $K_D$ ) using Eq. (1). Rapidly exchangeable  $\text{NH}_4^+$  ( $C_{\text{ex}}^*$ ) is given by the EDA<sub>rec</sub> pool.  $C_{\text{tot}}^*$  is obtained by adding the TAA pool to  $C_{\text{ex}}^*$ .  $\text{NH}_4^+$  pw: porewater  $\text{NH}_4^+$ ;  $K_{D1}$ : data from using EDA<sub>rec</sub> in Eq. (1);  $K_{D2}$ : data from using (EDA<sub>rec</sub> + TAA) in Eq. (1)

| Section (cm)   | $\text{NH}_4^+$ pw | $K_{D1}$      | $K_{D2}$       |
|----------------|--------------------|---------------|----------------|
| <b>Ridges</b>  |                    |               |                |
| 0–1            | $0.095 \pm 0.03$   | $1.2 \pm 0.4$ | $1.3 \pm 0.4$  |
| 1–2            | $0.037 \pm 0.01$   | $2.9 \pm 0.9$ | $10.7 \pm 0.9$ |
| 2–3            | $0.087 \pm 0.06$   | $2.1 \pm 1.5$ | $3.8 \pm 2.5$  |
| 3–4            | $0.085 \pm 0.01$   | $1.9 \pm 0.3$ | $2.5 \pm 0.4$  |
| 4–5            | $0.166 \pm 0.02$   | $1.0 \pm 0.1$ | $1.0 \pm 0.1$  |
| <b>Runnels</b> |                    |               |                |
| 0–1            | $0.127 \pm 0.05$   | $2.4 \pm 0.4$ | $6.0 \pm 2.5$  |
| 1–2            | $0.148 \pm 0.04$   | $1.3 \pm 0.3$ | $2.6 \pm 0.6$  |
| 2–3            | $0.074 \pm 0.02$   | $4.8 \pm 1.2$ | $8.5 \pm 2.1$  |
| 3–4            | $0.121 \pm 0.01$   | $3.7 \pm 0.4$ | $6.7 \pm 0.7$  |
| 4–5            | $0.171 \pm 0.03$   | $3.4 \pm 0.6$ | $3.9 \pm 2.6$  |

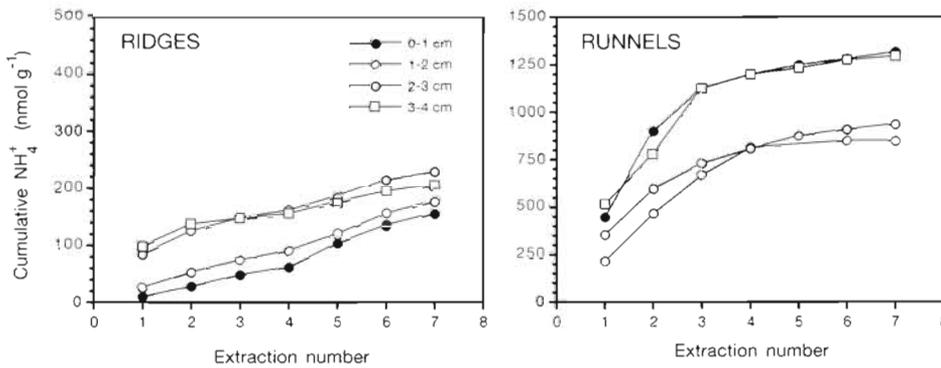


Fig. 4. Cumulative  $\text{NH}_4^+$  content plotted against number of KCl extractions. The 4–5 cm stratum was omitted to avoid overlapping lines

increasing porewater  $\text{NH}_4^+$  concentrations. We extend this explanation to complex  $\text{K}^+$  effects and possibly to ion-pairing processes affecting  $\text{NH}_4^+$  exchange.

Ridges and runnels are both silt type sediments with similar low contents of C (1.1 and 1.3%) and N (0.2 and 0.2%) and similar grain sizes, but differing in  $\text{CaCO}_3$

content (Table 1). In ridges, grain size fractions ( $<50 \mu\text{m}$ ) did not significantly correlate with  $\text{EDA}_{\text{rec}}$  ( $r^2 = 0.55$ ,  $p > 0.05$ ) but were inversely correlated with TAA ( $r^2 = 0.77$ ,  $p < 0.05$ ).  $\text{CaCO}_3$  did not significantly correlate with  $\text{EDA}_{\text{rec}}$  ( $r^2 = 0.50$ ,  $p > 0.05$ ) or with TAA ( $r^2 = 0.56$ ,  $p > 0.05$ ). In runnels, grain size fractions ( $<50 \mu\text{m}$ ) did not correlate significantly with TAA ( $r^2 = 0.66$ ,  $p > 0.05$ ) or with  $\text{EDA}_{\text{rec}}$  ( $r^2 = 0.62$ ,  $p > 0.05$ ). The same was the case for  $\text{CaCO}_3$  and organic N. These differences suggest that adsorbed  $\text{NH}_4^+$  has a different source in these structures and that organic N plays a minor role in the dynamic behaviour of adsorbed  $\text{NH}_4^+$  pools.

Bioturbation effects may also account for a higher  $\text{NH}_4^+$  yield in runnels compared to ridges. Indeed, in the 0–5 cm strata, *Hydrobia* sp. averaged 35 ind.  $\text{cm}^{-2}$  in runnels but only 2 ind.  $\text{cm}^{-2}$  in ridges, and accounted for over 90% of total fauna present in the cores. They eat benthic diatoms, so their higher populations in runnels may reflect higher sediment activity in that zone (Laima et al. unpubl.). They can thus enhance  $\text{NH}_4^+$  regeneration and alter  $\text{NH}_4^+$  concentrations in sediment pore water by means of excretion including fecal pellets and bioturbation (Jönsson et al. 1993).

In summary, these results clearly highlight the following points:

(1) Preliminary experiments involving analysis of the reconstituted pool in 1-step extractions of ridge and runnel sediments showed that it is important to check whether current extraction techniques correctly assess the adsorbed  $\text{NH}_4^+$  pool. These data are in agreement with earlier observations that the KCl technique, when applied to coastal muddy sediments, should be used with caution (Laima 1994).

(2) Ridges and runnels are sedimentary structures placed side by side in the mudflat. They exhibit enormous differences with respect to  $\text{NH}_4^+$  extraction efficiency, adsorption to their particulate phases, and relationships with sediment parameters. Results clearly show that runnel bedforms contain high, multiple pools of adsorbed  $\text{NH}_4^+$ . The turnover rate of these adsorbed pools, their influence on diffusive  $\text{NH}_4^+$

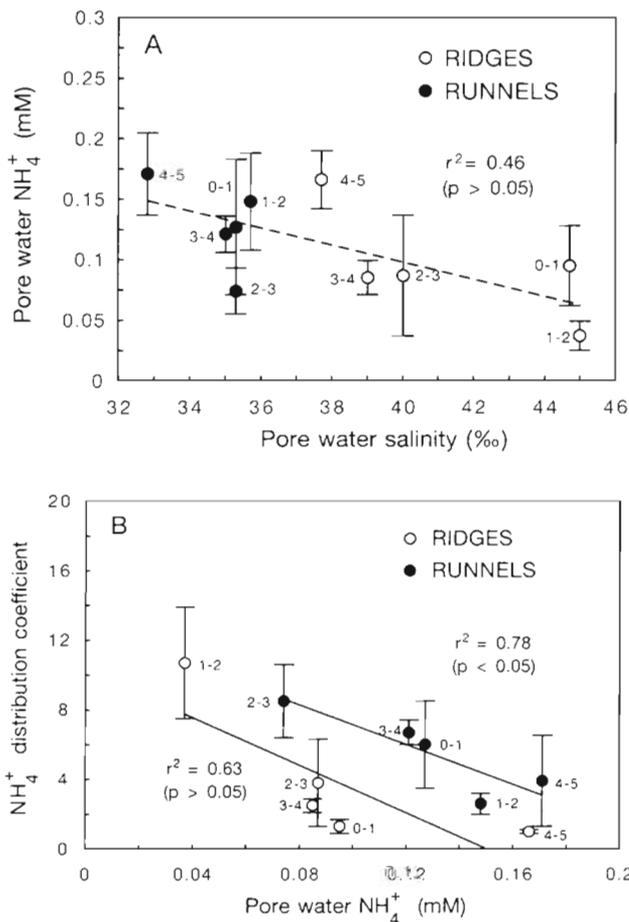


Fig. 5. (A) Relationship between porewater salinity and porewater  $\text{NH}_4^+$  concentrations ( $n = 3$ ) in ridges (o) and runnels (●). Regression analysis was performed using pooled data from ridges and runnels. (B) Relationship between average ( $n = 3$ ) porewater  $\text{NH}_4^+$  concentration and  $K_D$  values obtained from using KCl in multiple extractions

fluxes at the sediment-water interface, and possible influence on the N cycle, are unknown. Therefore, they should be the subject of further research.

(3) Spatial heterogeneity is an important issue when nutrient budgets are calculated for a particular environment. This study was restricted to the effect of 2 sedimentary structures on the spatial distribution of  $\text{NH}_4^+$  pools. As other complex sedimentary forms are present in the bay, distribution patterns of  $\text{NH}_4^+$  pools may be even more complex.

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