

# Short-term pore water ammonium variability coupled to benthic boundary layer dynamics in Alfacs Bay, Spain (Ebro Delta, NW Mediterranean)

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**ABSTRACT:** Pore water ammonium concentration profiles in a temporal series of undisturbed sediments from the inner edge of the estuarine front in Alfacs Bay (Ebro Delta, Spain, NW Mediterranean) were measured. Results show accumulation of ammonium in pore waters in the fall. Changes in pore water ammonium concentrations from September to October fit the constant source solution of Fick's second law of diffusion, so that increasing ammonium could be related to diffusion from a constant source at the sediment-water interface. Environmental conditions for the diffusional transport into the top 10 cm depth of the sediment column are discussed. The coincidence of calm hydrodynamic conditions and high inputs of fresh organic matter to the sediment would allow the development of an interfacial viscous layer with enhanced metabolism. The storage of reactive substances in this layer is proposed as a mechanism that may cause sediments to be enriched with dissolved substances. On the other hand, transition from nonstationary October ammonium profiles to a new stationary state was shown to occur 30 d after the breakdown of the viscous layer. Indeed, these predicted pore water profiles were found at Stn 5 in March of the 2 years sampled. From these results, a model is proposed in which short-term variability of pore water ammonium is related to benthic boundary layer dynamics, nitrification rates and diffusional transport of ammonium in the sediment.

**KEY WORDS:** Ammonium · Pore water · Diffusion · Pulse-sedimentation

## INTRODUCTION

Accretion of particles (mineral and organic) creates an historical record in undisturbed sediments. Moreover, vertical distributions of dissolved compounds in pore water reflect the pe-pH gradients due to bacterial metabolism linked to organic matter breakdown. Thus, vertical gradients of electron acceptors and metabolic end-products in the sediment reflect the distribution of these processes. Equations based on diffusion laws can be used in dealing with the depth distribution of the various reactions and products (Crank 1975, Berner 1980).

In coastal and estuarine areas, concentration profiles of dissolved constituents in interstitial water often differ markedly from steady-state profiles (Lasaga & Holland 1976, Aller 1980) due to seasonal changes in deposition and reactivity. Particularly, accumulation of ammonium in pore water has been found following sedimentation and has been linked to the breakdown

of fresh organic matter (Lerat et al. 1990, Lomstein et al. 1990).

Sediment-water fluxes are greatly influenced by the flow conditions above the sediment (Morse 1974). When water flows over the sediment (e.g. seawater in the salt-wedge estuarine circulation), a benthic boundary layer develops in the lower part of the flow due to the frictional drag between the water and the sediment. Low flow velocities over fine-grained sediments determine the appearance of a thin layer of water, known as the viscous layer, where conditions approach laminar flow and transport is through molecular diffusion. Spatial and temporal changes of flow velocities in the boundary layer (e.g. the development and breakdown of the viscous layer) can lead to changes in the sediment-water fluxes and, hence, can affect the concentrations of dissolved compounds in pore waters.

This paper examines some physical conditions and processes involved in the short-term pore water ammonium variability of surface estuarine sediments.

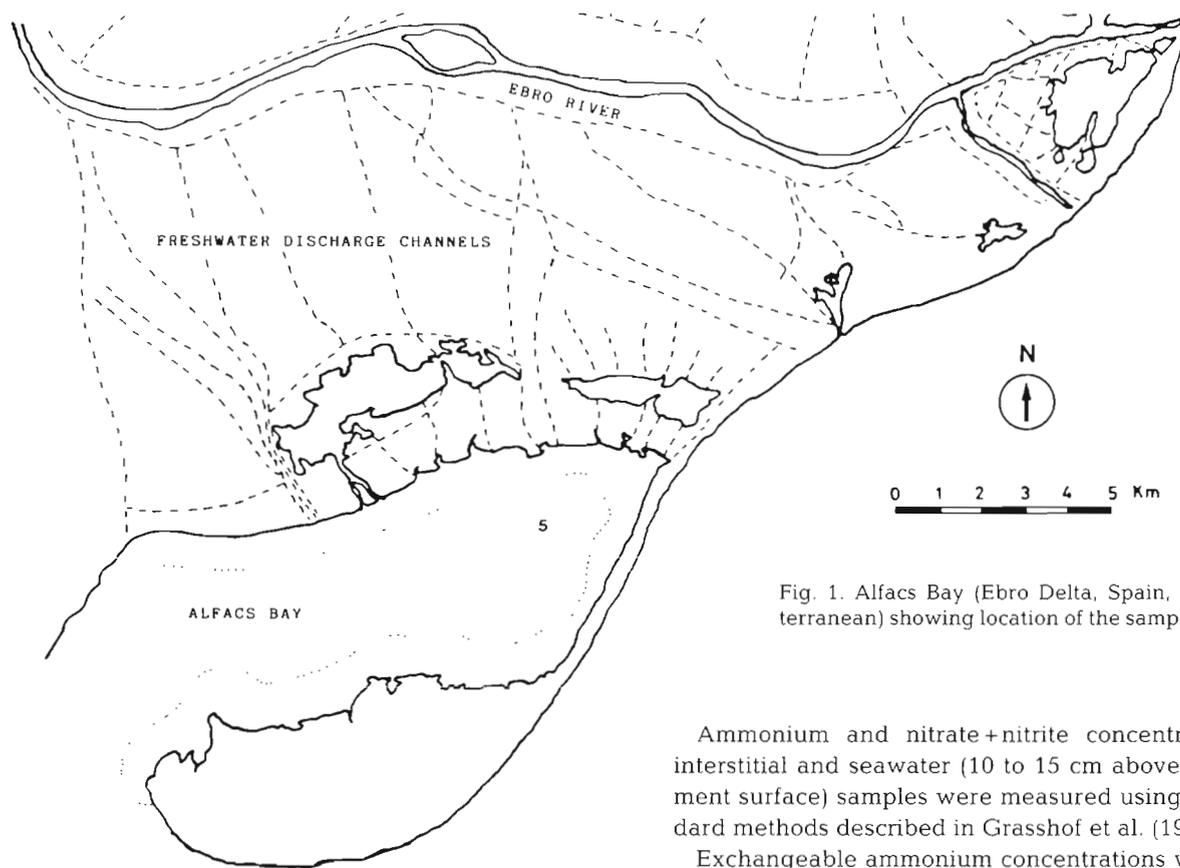


Fig. 1. Alfacs Bay (Ebro Delta, Spain, NW Mediterranean) showing location of the sampling station

## METHODS

Sediments from a 5 m deep station in Alfacs Bay (Ebro Delta, Spain, NW Mediterranean, Stn 5 in Fig. 1) were sampled on 4 occasions from 25 March 1987 to 20 March 1988 as part of a research program on sediment-water nutrient fluxes (Vidal et al. 1989, 1992, Vidal 1994). Alfacs Bay receives freshwater, mainly through discharge channels, from March to October. Inflowing freshwater slides over the more saline water beneath, giving rise to a salt-wedge estuarine circulation. The sampling station was located at the inner salt-wedge estuarine front, in a zone characterized by low current velocities and high sedimentation (Camp 1995).

Sediment cores were collected by hand in rigid plastic tubes 7 cm in diameter and 40 cm long and immediately frozen ( $-20^{\circ}\text{C}$ ). Cores were sawn into 1 to 2 cm lengths and the sediment samples thus obtained were homogenized. Sediment samples were kept in an anaerobic cabinet (Don Whitley Scientific Limited) with a gas mixture (10% hydrogen, 10%  $\text{CO}_2$ , 80% nitrogen) during the pore water extraction procedure. Interstitial waters were extracted by centrifugation [3500 rpm ( $2750 \times g$ ), 15 min] and filtration (Millepore HAWP02500) of the sediment slices.

Ammonium and nitrate+nitrite concentrations in interstitial and seawater (10 to 15 cm above the sediment surface) samples were measured using the standard methods described in Grasshof et al. (1983).

Exchangeable ammonium concentrations were analyzed in wet sediment samples using the extraction with 2 N KCl (Rosenfeld 1979).

Samples for organic carbon determinations, obtained from 2 core replicates taken 30 September 1987, were washed with diluted HCl to eliminate carbonates. Organic carbon and nitrogen were then determined on dry, ground treated and untreated samples, respectively, with a Carlo Erba CNS Analyzer.

Porosity was evaluated from the sediment weight loss at  $105^{\circ}\text{C}$ . Bulk density was then calculated from the dry weight of each sediment slice. Organic matter concentrations were evaluated from the weight loss after ignition at  $450^{\circ}\text{C}$  for 3 h.

## RESULTS AND DISCUSSION

### Sediment characteristics

Porosity, bulk density and loss on ignition in the top 1 cm of sediment were 0.7 and  $0.5 \text{ g dry wt cm}^{-3}$  and 6% of dry weight sediment, respectively.

Organic carbon and nitrogen concentrations ranged from about 2 and  $0.25 \text{ mmol g}^{-1}$  dry wt, respectively, in the superficial sediment to about 1 and  $0.1 \text{ mmol g}^{-1}$  dry wt below 10 cm depth. Organic carbon and nitrogen concentrations in the top 1 cm of sediment did not

show any significant variation between the sampling periods (1.8 to 1.9 and 0.25 to 0.26 mmol g<sup>-1</sup> dry wt, respectively; Vidal 1991).

**Pore water ammonium accumulation**

Pore water ammonium concentrations were at a minimum in March and a maximum in October (Fig. 2). From 30 September to 30 October, 7 mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> accumulated in the upper 10 cm of sediment (from the increases in the dissolved ammonium content calculated from the differences in concentration and the porosity at each depth interval), while 70 mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> were released to the overlying water in the same period (2.3 mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> d<sup>-1</sup>, from bell-jar incubations; Vidal 1991).

Since ammonium concentrations in bottom seawater were low (from 0.3 to 12.2 μM) compared to pore waters, and data on sediment exchangeable ammonium showed no change in this period (Fig. 3), the source of ammonium could be expected to be organic decomposition from: (1) bulk sediment organic matter and/or (2) recently settled organic matter.

Ammonium profiles from September to October (Fig. 2) followed the shape sequence that would be expected if ammonium was diffusing out from a constant source located at the top sediment layer (Duursma & Hoede 1967). Accordingly, a constant source solution to Fick's second law of diffusion based on the error function described by Duursma & Hoede (1967), with minor modifications, was used to account for September to October ammonium accumulation (Eq. 1).

$$C(z,t) = \frac{qz}{2D_{ef}\sqrt{\pi}} \left[ \left( 2 \frac{\sqrt{D_{ef}(t+k)}}{z} \exp\left(-\frac{z^2}{4D_{ef}(t+k)}\right) - \sqrt{\pi} \operatorname{erfc}\left(\frac{z}{2\sqrt{D_{ef}(t+k)}}\right) \right] \quad (1)$$

where C(z,t) is the ammonium concentration (mM) at depth z (cm) and time t (days), q is the constant source (mM d<sup>-1</sup>) at z = 0, D<sub>ef</sub> is the coefficient for effective diffusion in the sediment (cm<sup>2</sup> d<sup>-1</sup>), k is a time interval prior to the onset of the diffusion problem (t = 0, 30 September 1987), x is the ammonium concentration at

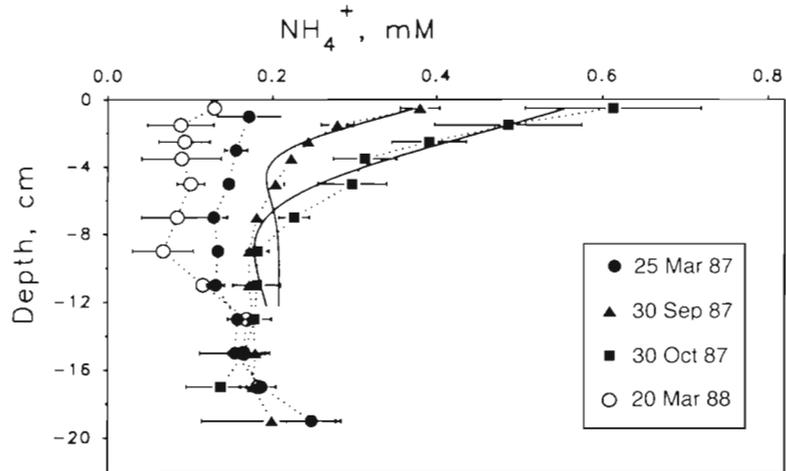


Fig. 2. Pore water ammonium. Horizontal bars are standard errors of 3 core replicates. Solid lines are least squares fitting of the uppermost 10 cm values from September and October profiles to Eq. (1)

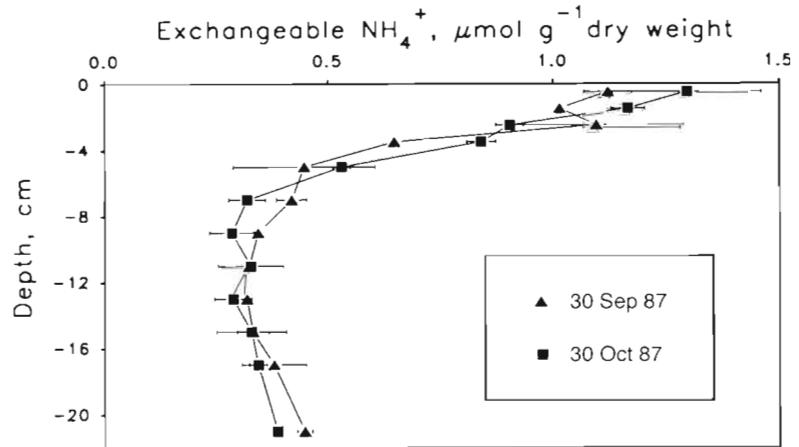


Fig. 3. Exchangeable ammonium. Horizontal bars are standard errors of 3 core replicates

t = -k, equal for all depths, and erfc is the complementary error function.

Least squares fitting of Eq. (1) to the September–October profiles (Fig. 2) gives: q = 0.044 mM d<sup>-1</sup>; D<sub>ef</sub> = 0.174 cm<sup>2</sup> d<sup>-1</sup>; k = 11 d; and x = 0.208 mM, with a 6% average error between observed and equation-estimated ammonium concentration values.

**Parameters included in the diffusion equation**

The value for x obtained from Eq. (1) (0.208 mM) is similar to the values found below 10 cm depth and is somewhat higher than those determined from the surface sediment in March (Fig. 2). The assumption of x being a constant in Eq. (1) implies that the profile is vertical at time -k. There are 2 reasons which justify this assumption. First, the low temporal variability of

ammonium concentrations below 10 cm depth suggests that they reflect equilibrium concentrations not affected by seasonal deposition/decomposition processes, as is the case for the surface sediment. Accordingly, the concentration changes found in the surface layer can be seen in relation to this value of  $x$ . Second, the evolution of pore water ammonium profiles, which shows near uniform concentrations with depth in March, also points to the validity of this assumption.

In contrast to  $x$ , the conformity of the resulting value for  $k$  (11 d) depends on whether September–October conditions can be extrapolated to the past. That is,  $k$  refers to the elapsed time from concentration  $x$  to the resulting September profile, assuming the parameters from Eq. (1) remain valid. The very focus on September and October profiles is due to the short time interval sampled and also to the hydrodynamic stability of the water at this time in Alfacs Bay (see below).

The diffusion coefficient obtained ( $D_{ef} = 2.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) reflects net transport of ammonium through surface sediments (0 to 10 cm) once the influence of tortuosity, adsorption onto particles, and any other factors modifying molecular diffusion are taken into account. This  $D_{ef}$  value compares well with those generally found in marine sediments of similar porosities, which include the effects of adsorption ( $4.0 \pm 0.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $\Phi = 0.64$  to  $0.79$ ; Krom & Berner 1980). The resulting  $D_{ef}$  suggests that fauna activities have little effect on pore water ammonium profiles in fall, since bioturbation would result in a higher  $D_{ef}$  (from  $\sim 10^{-5}$  to  $\sim 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ ; Aller 1982).

The ratio of the amount of ammonium released into the water to that accumulated in the pore waters per 30 d ( $70/7 \text{ mmol m}^{-2}$ ) agrees with the ratio between the diffusion coefficients of ammonium in particle-free water and in the sediment [ $D_0/D_{ef} = (19.8/2.01) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ;  $D_0$  at  $T = 25^\circ\text{C}$ ; Li & Gregory 1974]. This suggests that transport of ammonium from and to the sediment is mainly by molecular diffusion, and that ammonium is transported to the overlying water with a diffusion coefficient near  $D_0$ , thus indicating that the ammonium comes from a very high porosity layer.

Calculations from Fick's first law of diffusion using the diffusion constant in the water of  $1.7 \text{ cm}^2 \text{ d}^{-1}$ , and considering a transport length of 5 mm, give an ammonium flux of  $6.8 \text{ mmol m}^{-2} \text{ d}^{-1}$  for March profiles ( $0.2 \text{ mM NH}_4^+$  in the top 1 cm sediment layer and null concentrations in the overlying water). This flux agrees with that determined from bell-jar incubations in March ( $5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ , the maximum value recorded for Alfacs Bay; Vidal 1991). Similar calculations for October profiles ( $0.6 \text{ mM NH}_4^+$  in the top 1 cm sediment layer) result in an ammonium flux of  $20.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ , while fluxes in bell-jar incubations

were  $2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ . A concentration gradient of about  $70 \mu\text{mol cm}^{-4}$  is required to support this latter value, so that ammonium concentration in the water would have to be about  $0.53 \text{ mM}$  to maintain the sediment surface concentrations against the diffusional gradient to the water. This concentration is likely to occur when a stagnant viscous layer, with conditions of laminar flow and transport through molecular diffusion, remains over the sediment (Morse 1974). Otherwise, eddy diffusion would quickly dissipate the ammonium at the sediment surface. Furthermore, this layer is regarded not merely as a diffusional barrier to the sediment-water exchanges, but also as a layer in which restricted transport, due to the shift from eddy to molecular diffusion, allows for the retention of particulate and dissolved materials. The characteristics of the viscous layer are therefore different from those of the overlying water and the surface sediment. This layer appears as an organic-rich incubation layer, with high metabolism, increasing the concentration of metabolic end products over the sediment. Besides, lower oxygen concentrations have been found 10 cm above the sediment in September and October ( $4.4$  and  $6.6 \text{ mg l}^{-1}$ , respectively) compared to the other samplings (from  $7.5$  to  $8.9 \text{ mg l}^{-1}$ ; Vidal 1991).

The constant source  $q$  ( $0.044 \text{ mM d}^{-1}$ ) refers to the velocity of dissolved ammonium increase at the viscous layer. A constant decomposition rate is assumed in Eq. (1) to maintain the ammonium source  $q$  constant. Zero-order kinetics of decomposition are representative of short time reactions, although there is an overall first-order reaction for longer periods (Berner 1980, Matisoff et al. 1981) (Fig. 4). Conditions for a constant

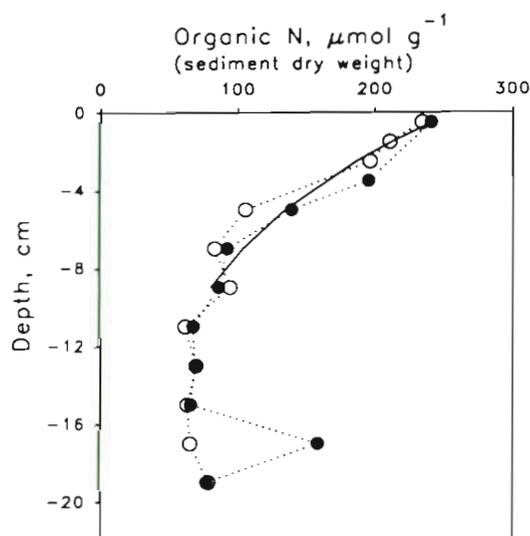


Fig. 4. Sediment organic nitrogen. Solid line shows the least squares fitting to an exponential decay equation:  $N_i = N_0 e^{-kz}$  ( $N_0 = 257.8 \mu\text{mol g}^{-1}$  dry wt and  $k = 0.130 \text{ cm}^{-1}$ ). Data from 2 core replicates (30 September 1987)

source of ammonium at the interface can occur after high frequency sedimentation events, as a consequence of the cumulative series of successive pulse-decay curves, owing to the short time lag between organic deposition and ammonium release from organic breakdown. Hence, ammonium input from the interface to underlying sediment can be coupled to the fast decomposition of recently settled organic matter from estuarine phytoplankton blooms supported by a relatively long period of hydrodynamic stability of the water, as has been stated for other estuaries (Legendre 1990).

Indeed, the development of phytoplankton blooms is frequent in summer and fall in Alfacs Bay (Delgado 1987, unpubl. data). They occur especially in September following the interruption of the freshwater inflows to the Bay for some weeks, before the discharge channels are ultimately closed in November (because of agricultural work in the rice fields which extend over the delta plain; Prat et al. 1988, Camp 1995). Changes in chlorophyll concentrations from 1–3 to 10–25 mg m<sup>-3</sup> have been found in these blooms (Delgado 1987). Sedimentation is probably high and can be supported by the water confinement induced by the cessation of the estuarine circulation in September.

On an areal basis the  $q$  of 0.044 mM d<sup>-1</sup> is equivalent to an amount of 13.2 mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> cm<sup>-1</sup> for the 30 d period (considering a viscous layer of porosity = 1). From this  $q$  value and the integrated figure of ammonium stored in pore waters (7 mmol m<sup>-2</sup>; Fig. 2) a 5 mm depth viscous layer acting as ammonium source site is calculated.

The maintenance of a 5 mm viscous layer over the sediment seems appropriate to the calm hydrodynamic conditions common in the Bay in September. The water enclosure induced by the lack of the estuarine circulation determines an intense evaporation (nearly one-third of the freshwater inputs), which causes temperature decreases of 3 to 5°C, and so a decrease in the ratio of densities between the Bay water and the outside Mediterranean water. Under these conditions, the renewal time of the water in the Bay increases to about 30 d (Camp 1995). Changes in the bottom current velocities from 8–10 to 2–4 cm s<sup>-1</sup> have been found at the mouth of the Bay following the interruption of freshwater inflow (Camp 1995). Therefore, the shear stress at the bottom must be low, especially at the station studied, due to its location at the inner edge of the estuarine front. Thus, the physical environment makes the existence of this viscous layer possible.

Unequal settling velocities of inorganic and organic particles facilitate the persistence of organic matter within the viscous layer, which would have a high organic matter content, a high decomposition rate and

a high ammonium concentration. Retention of part of the ammonium production in this compartment relies on the equilibrium between mass (particulate) inputs, reaction rates for ammonium production and nitrification, and diffusion (dissolved) outputs (Lasaga & Holland 1976).

### Fresh versus bulk organic decomposition

With the 1 mm yr<sup>-1</sup> sedimentation rate assumed in Alfacs Bay, bulk organic nitrogen decomposition in the top 1 mm sediment layer would contribute 7 µmol l<sup>-1</sup> d<sup>-1</sup>. The 1 mm yr<sup>-1</sup> accretion of sediment results from taking into account the particulate inputs to the Bay via discharge channels (0.2 to 0.5 mm yr<sup>-1</sup>; Mu oz 1990), and the average phytoplankton primary production (0.4 mm yr<sup>-1</sup>; Delgado 1987). This 1 mm yr<sup>-1</sup> sediment accretion is consistent with bathymetric records for the last 30 yr in Alfacs Bay and it is of realistic magnitude for estuarine and shelf sediments (references in Aller 1982 and Parsons et al. 1984).

A bulk organic decomposition of 7 µmol l<sup>-1</sup> d<sup>-1</sup> in the surface 1 mm sediment is insufficient to meet both the constant source and the flux to/from surface sediments. In contrast, the settlement of a typical 10 to 25 mg chl *a* m<sup>-3</sup> phytoplankton bloom over a 5 m depth water column would contribute 25 to 60 mmol N m<sup>-2</sup> (using for calculations the ratio of organic C:chl *a* = 40:1; Parsons et al. 1984). The occurrence of 2 sedimentation events in 1 mo is common during summer and fall (Delgado unpubl. data), so that the input of fresh planktonic debris to the sediment would explain both the ammonium accumulated in pore waters (7 mmol m<sup>-2</sup>) and the ammonium released to the water (70 mmol m<sup>-2</sup>).

The transitory development of benthic viscous layer production and accumulation of ammonium can be regarded as a key mechanism in explaining the pore water ammonium increase found in late summer and fall or after the sedimentation of phytoplankton blooms in Alfacs Bay, as well as in other coastal areas (Klump & Martens 1989, Jensen et al. 1990, Lerat et al. 1990). Furthermore, the production of reactive substances in this layer may also explain the behaviour of other elements (Klinkhammer & Palmer 1991), as well as other phenomena linked to the metabolism of bottom communities (Tsunogai & Noriki 1987).

### Nitrification and denitrification

The constant source  $q$  accounts for the net diffusive flux of ammonium into the top 10 cm sediment column, and therefore it does not include the fraction

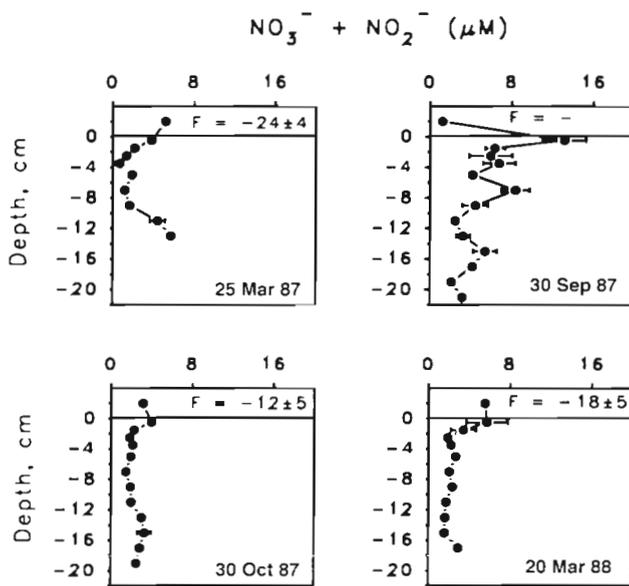


Fig. 5. Pore water nitrate + nitrite. Bottom water concentrations are also depicted. Horizontal bars are standard errors of 3 core replicates.  $F$  refers to nitrate + nitrite fluxes (mean values  $\pm$  SEM, from bell-jar incubations; Vidal 1991).  $F$  was not measured on 30 September 1987

of ammonium lost by nitrification. Nitrate plus nitrite profiles in Fig. 5 suggest nitrification in this sediment. Except for September profiles, pore water nitrate concentrations are low and surface concentrations approach values in the overlying water. In addition, nitrate uptake to the sediment was measured on 3 occasions (data in Fig. 5 obtained from bell-jar incubations; Vidal 1991; unfortunately, we have no data from September). These data point to a process of denitrification coupled to nitrification (Jenkins & Kemp 1984).

To calculate the first-order rate constant for nitrification ( $K_N$ ) and denitrification ( $K_D$ ), pore water ammonium and nitrate profiles, respectively, were modeled according to the equation of Vanderborght & Billen (1975):

$$C = C_0 e^{-(K/D)^{1/2} z} \quad (2)$$

with  $K$  equal to  $K_N$  or  $K_D$  for nitrification and denitrification respectively, and  $D$  equal to  $D_{ef}$  ( $2.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ).

$K_N$  equals  $0.0014 \text{ d}^{-1}$  (September) and  $0.0064 \text{ d}^{-1}$  (October) with a mean of  $0.0047 \text{ d}^{-1}$  computed from the 2 profiles.  $K_D$  equals  $0.0030 \text{ d}^{-1}$  (September) and  $1.83 \text{ d}^{-1}$  (October), averaging  $0.27 \text{ d}^{-1}$  for the 2 profiles. These constant rates indicate a close coupling of denitrification to nitrification, which would explain the low nitrate concentrations and the vertical profiles observed.

### Nonstationary approach for short-term pore water ammonium variability

According to the model proposed for pore water ammonium accumulation, ammonium profiles would return to profiles that resemble those of March after the breakdown of the viscous layer. Indeed, this can occur in late fall or early winter, owing to the strong winds common in the Bay. The breakdown of this layer would cause an instantaneous jump of the ammonium concentrations above the sediment, which would result in changes in the sediment-water fluxes and a gradual adjustment of pore water profiles to the new conditions. The time required to reach a new stationary state can be calculated according to the equation of Vanderborght & Billen (1975), expressed as the sum of the new stationary state and a transient term as follows:

$$C = C_2 e^{-(K_N/D_{ef})^{1/2} z} + 1/2(C_1 - C_2) \left\{ e^{-(K_N/D_{ef})^{1/2} z} \text{erfc} \left[ (k_N t)^{1/2} - z/(4D_{ef} t)^{1/2} \right] - e^{(K_N/D_{ef})^{1/2} z} \text{erfc} \left[ (k_N t)^{1/2} + z/(4D_{ef} t)^{1/2} \right] \right\} \quad (3)$$

with the initial conditions:

$$C(z, 0) = C_1 e^{-(K_N/D_{ef})^{1/2} z}$$

$$C(0, t) = C_1 \quad \text{for } t < 0$$

$$C(0, t) = C_2 \quad \text{for } t > 0$$

Concentration profiles have been computed for increasing times after a jump from  $1.3$  (constant source  $q$  of  $0.044 \text{ mM d}^{-1} \times 30 \text{ d}$ ) to  $0.2 \text{ mM}$  ammonium in the bottom water (Fig. 6). The new stationary state (*sensu* Vanderborght & Billen 1975) is reached 30 d later and the pore water ammonium concentrations approach those observed in March (1987 and 1988; Fig. 2).

### Pore water ammonium coupled to benthic viscous layer dynamics

Diffusive fluxes and sedimentation, in relation to flow conditions at the sediment-water interface, seem to determine the short-term variability of pore water ammonium concentrations of the surface sediment at Stn 5 in Alfacs Bay. The proposed model is compatible with the environmental conditions and its seasonality in the Bay, and with independent measurement of sediment-water fluxes. Nevertheless, the exact quantification and significance of certain processes (e.g. bioturbation) remain to be assessed. Macrofauna and meiofauna were found in this sediment at lower densities than in other zones of the Bay and were mainly dis-

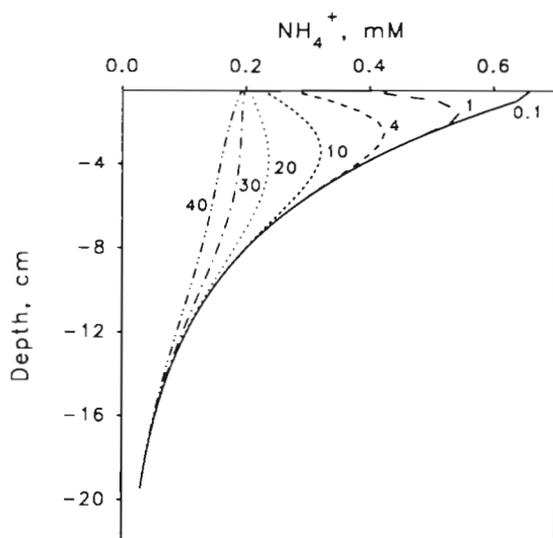


Fig. 6. Vertical profiles of ammonium concentrations in pore water after a jump from 1.3 to 0.2 mM of ammonium in the bottom water. Curves computed for increasing times: 0.1 to 40 d

tributed at the surface (Palac n et al. 1991, 1992), probably because of the high sedimentation and low water current at this site (Camp 1995). Pore water profiles like that of March (Fig. 2) are frequently attributed to fauna irrigation, though, as shown in Fig. 6, they can be also obtained by diffusion and nitrification. The influence of benthic organisms on the metabolism and transport in the sediment depends on the species composition, population densities and depth distribution, so that sediment stabilization or destabilization, aggregates production with a loose attachment to the underlying bed (like a fluff layer) or sediment irrigation can occur (Eckman et al. 1981, Luckenbach 1986, Andersen & Kristensen 1991, Krager & Woodin 1993).

The series of ammonium profiles in Fig. 2 are like those typically found in experimental solutions after the migration of particles (molecules) from a point source (Berg 1983, Richardson & McSween 1989), whereas the series in Fig. 6 are typical of the reverse diffusional transport (out of the solution). Diffusion gives a realistic general explanation to both series. Both Figs. 2 and 6 show the hysteretical nature of the process of filling and emptying of surface sediments with ammonium through diffusive transport.

## CONCLUSIONS

In summary, our data suggest that the match between calm hydrodynamic conditions and high frequency inputs of fresh organic matter reaching the sediment surface allows the development of a viscous layer over the sediment with enhanced metabolism.

Metabolic processes feed this natural organic-rich incubation layer with dissolved substances and lead to steep concentration gradients with the contiguous compartments. Downward diffusional flux of ammonium replenishes pore waters before the burial of particulate materials. Both the magnitude and pattern of temporal changes in pore water profiles reveal the environmental conditions required for this replenishment. Diffusion and nitrification coupled to denitrification would return to a March-like profile after the breakdown of the viscous layer. In accordance, a model is proposed in which short-term (month) pore water ammonium variability is related to benthic boundary layer dynamics.

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## LITERATURE CITED

- Aller, R. C. (1980). Diagenesis near the sediment-water interface of Long Island Sound: I. Decomposition and nutrient element geochemistry (S, N, P). *Adv. Geophys.* 22: 235-348
- Aller, R. C. (1982). The effects of macrobenthos on chemical properties of marine sediment and overlying water. In: McCall, P. L., Tevesz, M. J. S. (eds.) *Animal-sediment relations*. Plenum, New York, p. 53-102
- Andersen, F. O., Kristensen, E. (1991). Effects of burrowing macrofauna on organic matter decomposition in coastal marine sediments. *Symp. zool. Soc. Lond.* 63: 69-88
- Berg, H. C. (1983). *Random walks in biology*. Princeton University Press, Princeton
- Berner, R. A. (1980). *Early diagenesis: a theoretical approach*. Princeton University Press, Princeton
- Camp, J. (1995). *Ecology and dynamics of an estuarine Mediterranean bay (Alfacs Bay)*. Ph.D. dissertation Univ. of Barcelona
- Crank, J. (1975). *The mathematics of diffusion*. Oxford University Press, Oxford
- Delgado, M. (1987). *Fitoplancton de las bah as del Delta del Ebro*. *Invest. Pesq.* 51: 517-548
- Duursma, E. K., Hoede, C. (1967). Theoretical, experimental and field studies concerning molecular diffusion of radioisotopes in sediments and suspended solid particles of the sea. Part A. Theories and mathematical calculations. *Neth. J. Sea Res.* 3: 423-457
- Eckman, J. E., Nowell, A. R., Jumars, P. A. (1981). Sediment destabilization by animal tubes. *J. mar. Res.* 39: 361-374
- Grasshoff, K., Ehrhardt, M., Kremling, K. (1983). *Methods of seawater analysis*. Verlag Chemie, Weinheim
- 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., Lomstein, E., Sorensen, J. (1990). Benthic  $\text{NH}_4^+$  and  $\text{NO}_3^-$  flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. *Mar. Ecol. Prog. Ser.* 61: 87-96
- Klinkhammer, G. P., Palmer, M. R. (1991). Uranium in the oceans: where it goes and why?. *Geochim. Cosmochim. Acta* 55: 1799-1806

- Klump, J. V., Martens, C. S. (1989). The seasonality of nutrient regeneration in an organic rich coastal sediment: kinetic modeling of changing pore-water nutrient and sulfate distribution. *Limnol. Oceanogr.* 34: 559–577
- Krager, C. D., Woodin, S. A. (1993). Spatial persistence and sediment disturbance of an arenicolid polychaete. *Limnol. Oceanogr.* 38: 509–520
- Krom, M. D., Berner, R. A. (1980). The diffusion coefficients of sulfate, ammonium and phosphate ions in anoxic marine sediments. *Limnol. Oceanogr.* 25: 327–337
- Lasaga, A. C., Holland, H. D. (1976). Mathematical aspects of non-steady-state diagenesis. *Geochim. Cosmochim. Acta* 40: 257–266
- Legendre, L. (1990). The significance of microalgal blooms for fisheries and for the export of particulate organic carbon in oceans. *J. Plankton Res.* 12: 681–699
- Lerat, Y., Lasserre, P., Le Corre, P. (1990). Seasonal changes in pore water concentrations of nutrients and their diffusive fluxes at the sediment-water interface. *J. exp. mar. Biol. Ecol.* 135: 135–160
- Li, Y. H., Gregory, S. (1974). Diffusion of ions seawater and in deep sea sediments. *Geochim. Cosmochim. Acta* 38: 703–714
- Lomstein, E., Jensen, M. H., Sorensen, J. (1990). Intracellular  $\text{NH}_4^+$  and  $\text{NO}_3^-$  pools associated with deposited phytoplankton in a marine sediment (Aarhus Bight, Denmark). *Mar. Ecol. Prog. Ser.* 61: 97–105
- Luckenbach, M. W. (1986). Sediment stability around animal tubes: the roles of hydrodynamic processes and biotic activity. *Limnol. Oceanogr.* 31: 779–787
- Matisoff, G., Fisher, J. B., McCall, P. L. (1981). Kinetics of nutrient and metal release from decomposing lake sediments. *Geochim. Cosmochim. Acta* 45: 2333–2347
- Morse, J. W. (1974). Calculation of diffusive fluxes across the sediment-water interface. *J. geophys. Res.* 79: 5045–5048
- Muñoz, I. (1990). Limnology in the river and drainage channels of the Ebro Delta: physical and chemical factors, phytoplankton and benthic macroinvertebrates. Ph.D. dissertation, Univ. of Barcelona
- Palacín, C., Gili, J. M., Martín, D. (1992). Evidence for coincidence of meiofauna spatial heterogeneity with eutrophication processes in a shallow-water Mediterranean bay. *Estuar. coast. Shelf Sci.* 35: 1–16
- Palacín, C., Martín, D., Gili, J. M. (1991). Features of spatial distribution of benthic infauna in a mediterranean shallow-water bay. *Mar. Biol.* 110: 315–321
- Parsons, T. R., Takahashi, M., Hargrave, B. (1984). Biological oceanographic processes. Pergamon, Oxford
- Prat, N., Muñoz, I., Camp, J., Comin, F. A., Lucena, J. R., Romero, J., Vidal, M. (1988). Seasonal changes in particulate organic carbon and nitrogen in the river and drainage channels of the Ebro Delta (NE Spain). *Verh. int. Verein. Limnol.* 23: 1344–1349
- Richardson, S. M., McSween, H. Y. (1989). *Geochemistry. Pathways and processes.* Prentice Hall, Englewood Cliffs, NJ
- Rosenfeld, J. K. (1979). Ammonium adsorption in nearshore anoxic sediments. *Limnol. Oceanogr.* 24: 356–364
- Tsunogai, S., Noriki, S. (1987). Organic matter fluxes and the sites of oxygen consumption in deep water. *Deep Sea Res.* 34: 755–767
- Vanderborght, J. P., Billen, G. (1975). Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. *Limnol. Oceanogr.* 20: 953–961
- Vidal, M. (1991). Studies on nutrient dynamics in estuarine systems: nutrient and oxygen sediment-water fluxes. Ph.D. dissertation, Univ. of Barcelona
- Vidal, M. (1994). Phosphate dynamics tied to sediment disturbances in Alfacs Bay (NW Mediterranean). *Mar. Ecol. Prog. Ser.* 110: 211–221
- Vidal, M., Morguí, J. A., Latasa, M., Romero, J., Camp, J. (1992). Factors controlling spatial variability in ammonium release within an estuarine bay (Alfacs Bay, Ebro Delta, NW Mediterranean). *Hydrobiologia* 235/236: 519–525
- Vidal, M., Romero, J., Camp, J. (1989). Sediment-water nutrient fluxes: preliminary results of *in situ* measurements in Alfaques Bay, Ebro River Delta. In: Ros, J. D. (ed.) *Topics in marine biology.* Scientia mar. 53: 505–511

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