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Fluff deposition on intertidal sediments: effects on benthic biota, ammonium fluxes and nitrification rates

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Abstract. The effects of fluff deposit on benthic biota, NH_4^+ fluxes and nitrification was studied in the laboratory using waterlogged and reflooded intertidal sediments from Marennes-Oléron Bay, France. The fluff deposit was enriched in NH_4^+ compared to underlying sediments, and promoted changes of the sediment pH, E_h, C:N ratio, C:chl *a* ratio and the NH_4^+ efflux to overlying water. Statistical analysis showed that pore water NH_4^+ concentrations were strongly influenced by interactions between fluff, drying, depth and bioturbation. The fluff deposit resulted in anoxia in the top sediments and moved the nitrification zone to surface layers in fluff. However, the NH_4^+ enrichment in fluff did not significantly change actual nitrification rates (range 0–1 mmol m^{-2} d^{-1}) or potential nitrification rates (range 3–11 mmol NO_3^- m^{-2} d^{-1}).

Introduction

Fluff material found at the bottom of some estuaries and coastlines is a near-bottom mobile suspension generally containing a high concentration of bacteria and clay particles, and its importance in the management of estuarine environments is recognised (Huelsemann 1982). The rheological properties of this cohesive material are very complex and there have been many different models for predicting the mutual effects of currents and waves on its behaviour (Mehta and Wartel 1991; Ali et al. 1992). This material can be the center of fermentation processes and anaerobic hydrolysis, and when particles are suspended in the water column, the organic products formed can enter the aerobic metabolic cycle, thus contributing to a decrease of dissolved oxygen concentrations (Maurice 1993). In intertidal mudflats, alternation in sedimentation and resuspension events can produce oxic/anoxic oscillations, which can vary with the tidal cycle (Abril et al. 1999). Knowledge of geochemical processes is therefore important for the understanding of the role of these sediments as temporary sources and sinks of organic matter.

It is recognized that the hydrodynamics of intertidal flats results from the combination of several forcings, mainly the tidal currents, the waves and the associated

winds, and drainage (Le Hir et al. 2000). Semi-diurnal tidal cycles induce constant variations of conditions in the top sediment layers, mainly due to inundation, temperature fluctuations and light exposure. The way floodwater spreads over these areas is complex, and mixing associated with this inundation has impacts on the sediment-pore water equilibrium of some chemical species and on the turnover of nutrients (Laima et al. 1999).

Sources of ammonium in coastal sediments include decay of phytoplankton and microphytobenthos (Yamada et al. 1987), decomposition of litter material derived from salt marsh plants, excretion by benthic organisms (Lomstein et al. 1989), and molecular diffusion of NH_4^+ from deeper sediment layers with high ammonium production (Berner 1980). The transformation and transport of ammonium in these environments is complex, being influenced by morphological, physical, chemical and biological factors. In the sediment, ammonium can be nitrified to nitrite and subsequently to nitrate or it can be consumed by benthic biota. Through diffusion and biologically mediated transport, NH_4^+ can migrate to other parts of the sediment or it can be released to overlying water (Blackburn and Henriksen 1983; Klump and Martens 1987). Part of the NH_4^+ produced is sorbed onto the sediment particles by ion exchange reactions or organic ligants and therefore is not directly available for the processes mentioned above. It has also been shown that short-term variations of sediment temperature during the emersion period strongly affect the turnover of NH_4^+ (Vouvé et al. 2000) and that emersion can depress the nitrification (Laima et al. 2002).

In this study we try to answer the following question: does fluff accumulation in intertidal sediments induce changes of biogeochemical processes in the surface sediments? We carried out controlled incubation experiments using intact waterlogged sediments as well as samples that have been exposed to air influence for 3 days before reflooding with natural seawater. Parameters measured were concentrations of dissolved NH_4^+ and NO_3^- + NO_2^-, net fluxes to overlying water, actual and potential nitrification rates, macrofauna species diversity and biomass, E_h, pH, organic C, total N and chl *a* concentrations

Sampling and methods

Study area

Marennes-Oléron bay is located in the middle of the southwest coast of France and extends over about 180 km^2 between Oléron Island and the mainland (Figure 1). It includes large intertidal mudflats covering about 60% of the whole surface at low spring tides. These mudflats are a major source of primary production to the ecosystem and support high microphytobenthic biomasses (Guarini et al. 1998). Exchanges of water and suspended sediments between land and sea are affected through a drainage system of channels, which sometimes exhibit a dendritic system similar to river drainage systems (Verger 1968). In addition, some mudflats show a

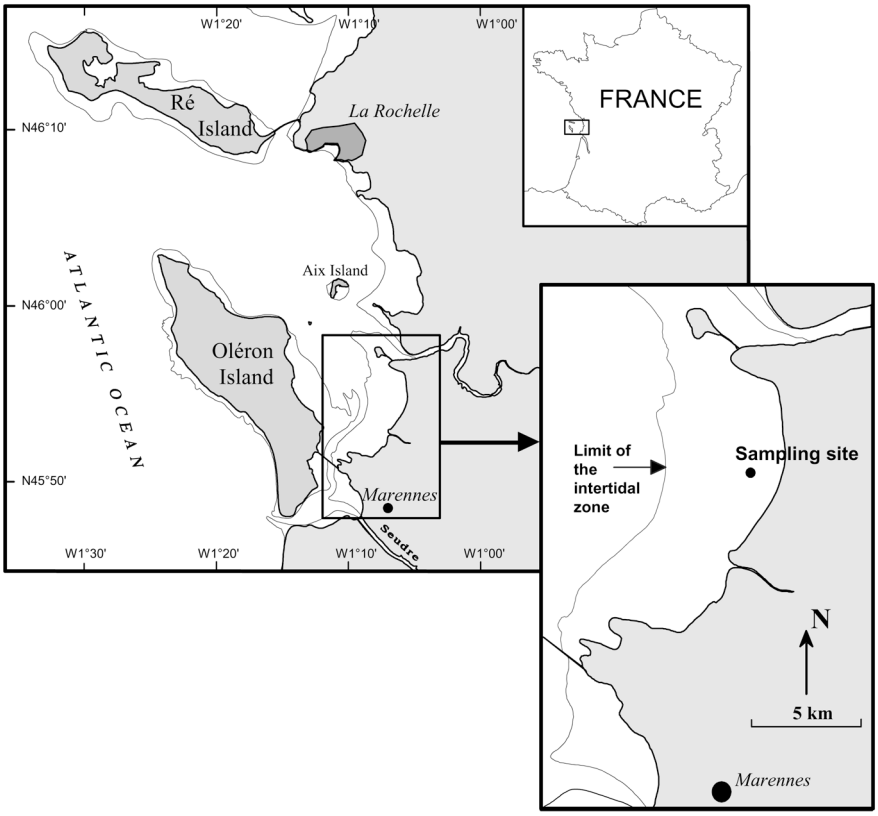

Figure 1. Location of the sampling site in the intertidal Brouage mudflat in the Bay of Marennes-Oléron, SW France. The intertidal zone limit or the bathymetric level corresponding to the largest possible low tide, is indicated on the graph to the right.

secondary hydrographic system overlapping the first one and are composed of successive parallel concave structures, the runnels, and convex structures, the ridges. Both drainage systems are well represented in the study area, Montportail-Brouage mudflat, which is the largest flat on the eastern side of the bay (Germaneau and Sauriau 1996). The area of parallel ridges and runnels, stretching over the main part of the mudflat, is crossed in the lower half of the flat by large dendritic channels (Gouleau et al. 2000).

This double system is affected by time variations of erosion and sedimentation events. For instance, up to 20 cm of fluff can be deposited within a single tidal cycle, covering any morphological structure (Figure 2a). On the other hand, exceptional storms can resuspend runnel deposits and erode ridges (Figure 2b). The fluff is found at all "low" sites, such as creeks and channels, in the mudflat. In the eastern mudflat of Marennes-Oléron, the fluff is found essentially in all runnels. Its thickness is about 1–2 cm. The fluff material may overlap the ridges forming a film

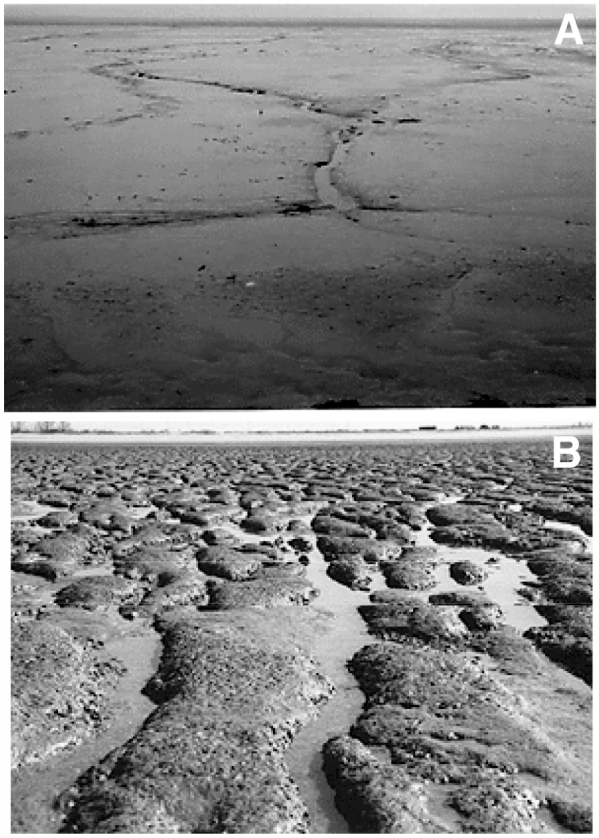

Figure 2. Photo of the Brouage mudflat, SW France.; A. Sediment covered by a thin fluff layer (W % > 200%). Run-off creeks are seen over the entire area.; B. The same area without fluff coverage. The fluff had been transported away after a storm event, leaving rigid criss-cross structures (W % < 100 %) and open water channels between them.

of some millimeters thick. It can also accumulate at the high mudflat, in some cases forming a 10 cm thick layer close to the grassy shore. In the runnels, the fluff is overlain by a thin water layer (2–5 cm) and is never exposed to air. In contrast, the thin fluff layer present on the ridges, is exposed, during emersion, to capillary ascension-evaporation phenomena, promoting a rapid variation of water content (40% loss of the initial value during 4 hours of emersion) and a rise of salinity in the interstitial water, which can double during hot summer months (Gouleau 1979).

Sediment sampling

Sampling took place in the upper part of the mudflat (Figure 1) where sediments are frequently exposed to air. Fluff material was sampled on 23 June 1999 (neap tide period, tidal range 5.0 m) at high tide, sieved through a 1-mm mesh and ho-

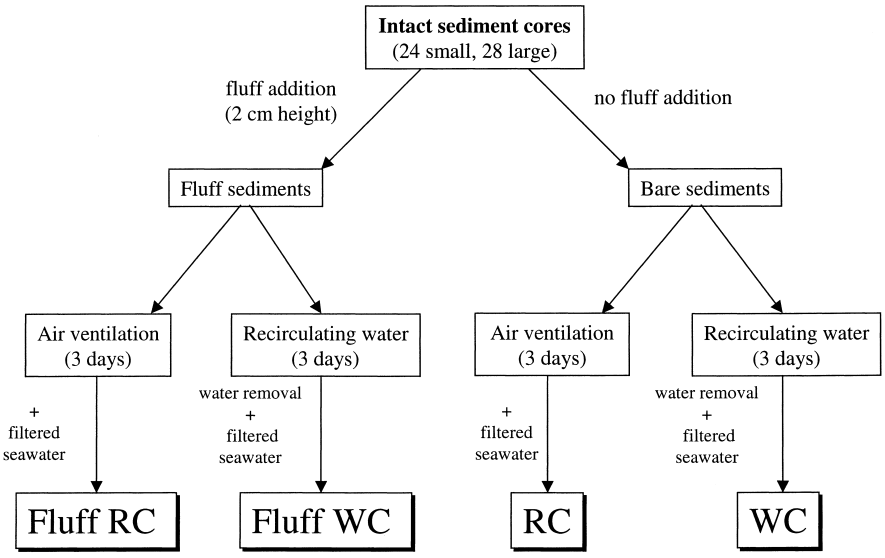

Figure 3. Schema resuming the preparation of start cores used in this study.

mogenized. Sediments were sampled on 24 June 1999, during the emersion period. A set of 24 small cores (5.4 cm i.d., 20 cm long) and a set of 28 larger cores (7.5 cm i.d., 15 cm long) were taken side-by-side, covering about 6 m^2 of homogenous mudflat area. To obtain representative seawater samples of relatively long residence times (ca 4 hours), bottom seawater used in the incubation assays was sampled during the previous high tide.

Preparation of start cores and sediment processing

A 2 cm layer of fluff was added to half of the cores (12 small cores and 14 large cores). Half of the fluff amended cores and half of the control cores were air-dried under fan ventilation for 3 days at *in situ* temperature (25 °C), under natural light-dark cycles. The length of ventilation corresponds to an extreme emersion period known to occur in the upper parts of bay mudflats and tidal marshes during neap tides. The remaining half of fluff and control cores were kept for 3 days in a recirculating water-filled incubator held at *in situ* conditions of temperature and oxygen, and under natural light-dark cycles. An air-pumping system ensured the maintenance of oxygen conditions in the incubator water, and therefore no stirring was applied to surface water of individual cores. Using a constant water-sediment height ratio, overlying water from individual cores was replaced by *in situ* filtered seawater (cellulose acetate filters, 0.45 μm of pore size) containing 20 μM NO_3^- + NO_2^- and 7 μM NH_4^+. These are called fluff-waterlogged cores (fluff WC) and control waterlogged cores (WC). Similarly, filtered seawater was added to desiccation cores. These are called fluff-reflooded cores (fluff RC) and control reflooded cores (RC). Figure 3 resumes the procedure used to prepare the start cores.

Water overlying larger cores (6 WC + 6 fluff WC + 6 RC + 6 fluff RC) was carefully drained off. The pH was measured using a pH meter (Knick Portamess 651-2, USA) and the E_h using a saturated calomel electrode (Ingold 406 M6-S7) as reference and a Pt- electrode (4800 M5). Immediately after drainage, WC and RC series (no added fluff) were cut into 0/– 0.5, – 0.5/– 1, – 1/– 2, – 2/– 3, – 3/– 4 and –4/– 6 cm slices. Fluff series were cut into 2/1.5, 1.5/1, 1/0, 0/– 0.5, – 0.5/– 1, – 1/– 2 cm slices, the first 3 slices contain the added fluff and the deeper slices the top 2 cm of sediments. Slices from 2 corresponding cores were pooled, to obtain 3 replicates for each system. A portion of pooled sediment (series A) was purged in N_2 and centrifuged (3000 × *g*, 10 min at 0 °C) in gas-tight containers. Pore water was filtered through GF/F filters (0.7 μm pore size) and frozen at – 20 °C until solute analysis. Part of the remaining portion (series B) was used for measurements of organic particular carbon, total nitrogen, chl *a*, proteins and porosity.

Macrofaunal abundance was estimated by sieving pooled sediment slices of the larger cores through 0.5-mm mesh screens, preserving with 4% buffered formalin and staining with Rose Bengal for subsequent sorting. Specimens in each sample were identified and counted. Dry biomasses were assessed by weighing after decalcification (0.1 N HCl) and drying at 60 °C for at least 48 h.

Nitrification assays

Sediment O_2 consumption was measured by time series of O_2 samples and the procedure described by Sloth et al. (1992) was used to calculate the percent O_2 in the core headspace (24%) to equilibrate with the measured O_2 consumption. As nitrification inhibitor we used acetylene, which is a standard practice in coastal sediments (Sloth et al. 1992; Lohse et al. 1993; Caffrey and Miller 1995; Laima et al. 1999). Prior to incubations, acetylene was bubbled through seawater after trapping with 0.1 M phosphoric acid to remove any contamination by NH_4^+. Assays were carried out using sixteen small cores (4 WC + 4 fluff WC + 4 RC + 4 fluff RC) in the dark at *in situ* temperature (25 °C). Cores were stoppered and the headspace was filled with a mixture of 24% O_2 + 76% air using 60-ml syringes. At 0, 3.7, 5.7, 6.7, 8.5 and 10 hours after the start water samples were gently pushed out by injecting more of the gas mixture. Samples were immediately analysed for NH_4^+. At hour 10, acetylene-saturated water (2% vol:vol) was added to the water phase of twelve cores (3 WC + 3 RC + 3 fluff WC + 3 fluff RC). One core from each series was left without acetylene to check for steady flux conditions. The water phase (1–2 ml) was further sampled at 0.8, 1.8, 3.7, 12.2, 16.3, 19.6, 22.5 and 34.6 hours after acetylene addition and analysed for NH_4^+. The acetylene blockage technique has the statistical advantage over other methods in that the same core serves for measuring NH_4^+ fluxes before and after inhibition, so the flux variability among cores does not interfere with the measured rates. For each individual core, the NH_4^+ build-up in the overlying water was fit through regression lines both before and after acetylene addition and the actual nitrification rate was calculated by subtracting the NH_4^+ flux after inhibition from the flux obtained before inhibition, at steady-state flux conditions. Some individual cores gave lower slopes after inhibition as

against prior to inhibition, and data obtained from such cores were not included in calculations of actual nitrification rates.

Potential nitrification was determined using the pooled sediment samples (series B) from which a portion was also used for pore water extraction. Duplicate samples (ca 1 cm^3) from each layer were wet-sieved (1.5 mm mesh) to remove large detritus and macrofauna and the sieved sediment was shaken in 100 ml incubation flasks with 50 ml of filtered seawater from the sampling site and enriched with 1 mM NH_4Cl. A control set was prepared without NH_4^+ enrichment. The slurries were shaken aerobically (Henriksen et al. 1981; Mayer et al. 1995; Joye and Hollibaugh 1995) in the dark at the *in situ* temperature of 25 °C. Five water samples per core were taken during a 24-hour period, filtered through sterilized GF/F filters and stored at −20 °C until analysis of NO_3^-. From a linear increase of NO_3^- concentration with time, the slope of the regression line gives the potential nitrification rate, which is proportional to the number of nitrifying bacteria (Henriksen et al. 1981). Growth of nitrifiers during these incubations was insignificant due to the relatively long generation time (several days) of these organisms (Kaplan 1983).

Chemical analyses

Water contents of sediments and fresh fluff were measured as weight loss after drying at 60 °C. The C-N composition of organic matter was measured using a CHN Carlo Erba 1500 Auto analyser and the method of Hedges and Stern (1984). Chl *a* was measured using the Lorenzen's method (Lorenzen 1966). Ammonium was determined by the salicylate method (Laima 1992). Nitrate and nitrite were measured using the Strickland and Parsons (1972), slightly modified for a Skalar Auto analyser (detection limit = 0.05 μM). Salinity was measured using a microprocessor conductivity meter LF 320 WTW and a standard conductivity cell Tetracom 325. Proteins were hydrolysed by 5.8 N HCl during 24 hours at 105 °C, and then neutralized by 1.9 N NaOH. The released dissolved free amino acids (DFAA) were then determined by pre-column fluorescence derivatization with o-phthaldialdehyde using reverse-phase liquid chromatography (Lindroth and Mopper 1979). The continuous flux analysis system Kontron was used, as based on the method of Delmas et al. (1990). Fluorescence detection was performed with excitation at 340 nm and emission at 450 nm.

Statistical analyses

The design resulting from the four combinations of treatments (ventilation versus waterlogged and deposition of fluff versus control) can basically fit a fully crossed two-factor ANOVA with replications. This model was used to test significant differences in nitrification rates and NH_4^+ fluxes because data were assessed by differences in regression slopes and gave only one observation per core. Random assignment of cores to treatments insured independence of the observations (Sokal and Rohlf 1981). On the other hand, tests of differences between cores in depth profiles of salinity, E_h, pH, protein and nitrogen compounds, that were repeatedly measured

within each core, do not fit the same design because data from depth profiles within a core would be spatially correlated. An appropriate design that included the two previous factors and a within-core factor "depth levels" is a partially hierarchical design that is more complex than a simple split-plot design (von Ende 1993). Consequently, the third factor is nested within the factors "ventilation treatment" and "deposition of fluff treatment", and the core effect is declared in the analysis as a random effect. As a result "ventilation treatment", "fluff treatment" and their interaction were tested over the core effect, and the other terms over the error term. Since both univariate and multivariate analysis of variance can handle partially hierarchical designs (see von Ende (1993)), results from ANOVA and MANOVA (in which each depth level is a variable) were successively used in order to obtain a more acute test of any differences occurring between depth levels amongst treatments.

All analyses were performed with the MINITAB package release 10.2, using the ANOVA procedure in the case of balanced designs and the GLM procedure in the case of unbalanced designs. Homoscedasticity was tested prior each analysis using the Bartlett's test. Since this test is sensitive to non-normal distributions (Underwood 1981), we used small α value (ca 1%) as recommended by Scherrer (1984, p. 389). Otherwise, the $\log_{10}$ transformation was used to counterbalance variance heterogeneity. Other assumptions about residuals (normal distribution, independence, mean = 0) were graphically tested after each analysis.

Results and discussion

Macrofauna assemblages

At least 13 species were found: the oligochaete *Tubificoides benedeni* (Udekem), the polychaetes *Aphelochaeta* (*Tharyx*) *marioni* (de Saint-Joseph), *Hediste* (*Nereis*) *diversicolor* (O. F. Müller, 1776), *Nephtys hombergii* Savigny, *Pseudopolydora antennata* (Claparède), *Pygospio elegans* Claparède and *Streblospio shrubsolii* (Buchanan), the gastropods *Hydrobia ulvae* (Montagu), *Retusa truncatula* (Bruguière), the bivalves *Abra tenuis* (Montagu), *Macoma balthica* (Linnaeus) and *Scrobicularia plana* (da Costa) and the crustacean *Idotea neglecta* G.O. Sars. Dominant species in abundances were *Tubificoides benedeni, Pygospio elegans, Abra tenuis* and *Hydrobia ulvae*. However, *Abra tenuis*, *Macoma balthica* and *Tubificoides benedeni* were dominant in biomass. The macrofauna species assemblage characterizes an unstable habitat from the upper parts of the mudflat submitted to diffuse freshwater inputs and frequent erosion/deposition events (Germaneau and Sauriau 1996; Gouleau et al. 2000).

More than 95% of macrofauna abundances and biomasses were recorded within the top 3 cm layer of WC and RC (Figure 4). The observed vertical distribution of species is consistent with that reported by Gal'tsova (1982); Reise (1985); Zwarts and Wanink (1989) for oligochaetes, polychaetes and bivalves, respectively. Since

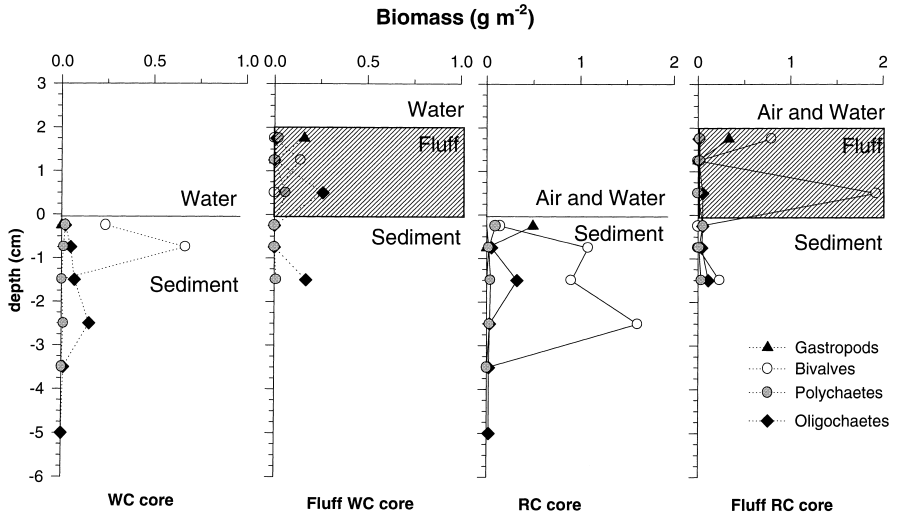

Figure 4. Distribution of major biomass assemblages in waterlogged and reflooded systems with and without added fluff.

the burying depth of surface deposit-feeding bivalves depends on their shell size (Zwarts and Wanink 1989), this result was expected for *Macoma balthica* and *Scrobicularia plana* whose shell size ranged from 5 to 12 mm. Consequently, their burying depths were less than 3 cm (Figure 4).

Occurrence of macrofauna species within the fluff layer, which was initially free-free, showed that all species were capable of migrating into added fluff layers within the 3-d period: all gastropods migrated to the fluff-water interface and most of bivalves and annelids migrated into the subsurface fluff layers. There were no significant differences in the proportion of migrating gastropods and bivalves between fluff WC and fluff RC systems (Figure 4). However, migration rates were higher (ca. + 15%) for oligochaetes and polychaetes in fluff WC than in fluff RC. This may have been due to the negative influence of desiccation and high temperature on vertical migration of annelids as reported by Dye (1978); Gal'tsova (1982) from field studies. As shown in Figure 4, upwards migration of species to the fluff deposit can strongly increase the mixing of underlying top sediment layers, in addition to their natural feeding activities that enhance vertical biodiffusivity (Rhoads 1974; Wheatcroft et al. 1990). Tubificidae annelids such as *Tubificoides sp.* are known to be conveyor-belt or head-down deposit feeders with their posterior end at or above the sediment-water interface. On the other hand, Cirratulidae and Spionidae annelids such as *Aphelochaeta* (*Tharyx*) *sp.* and *Pygospio sp.* are reverse conveyor-belt in that they feed at the surface and egest biodeposits at depth. Finally, although bivalves such as *Macoma balthica* and *Scrobicularia plana* are surface deposit-feeders and facultative suspension feeders, they can also gather their food from deeper parts of the sedimentary column.

Sedimentary organic matter

The C:chl *a* ratio is an indicator of the relative contribution of phytoplankton or/and microphytobenthos to sedimentary organic matter, thus reflecting its photosynthetic activity (Parsons 1975). Whereas the C:chl *a* ratio of about 40 is characteristic for living benthic diatoms and a C:chl *a* ratio of about 500 has been measured in surface sediments with high photosynthetic activity (de Jonge 1980). A generally observed increase of this ratio with sediment depth reflects a more detritic origin of organic matter in deeper sediment layers (Maksymowska (1998) and literature cited therein) and was also found in studied sediments (Table 1). Measured C:chl *a* in the top horizons (about 750 in bare sediments and about 550 in fluff systems) denote the presence of high microphytobenthic biomass. A 3-fold increase of the C:chl *a* ratio was registered in the fluff sediments as compared to bare sediments (ANOVA $p < 0.001$). This suggests that the fluff deposit stimulated the decay of surface microphytobenthos following the blockage of light penetration in the sediment. Simultaneously, we observed a 3-fold decrease of C:chl *a* ratio in the fluff surface during the 3-d period (Table 1 – difference between fresh fluff and uppermost layers of fluff RC and fluff WC systems). In both fluff RC and fluff WC the exposure of fluff to light favoured the development of microphytobenthic biomass, which in turn influenced the decrease of the C:N ratio and the increase of protein concentration in fluff (Table 1).

The C:N ratio of organic matter being mineralised is one parameter that regulates the availability of NH_4^+ to nitrification and diffusion from sediments (Fenchel et al. 1998). The C:N ratio of organic matter is strongly influenced by both origin and mineralization rate of this organic matter (Borodovski 1965; Prahl et al. 1980; Roman 1980). The pre-incubation period (3 days of drying or immersion) resulted in higher organic matter mineralization in fluff systems compared to bare sediments. This is supported by the higher sediment C:N ratio as influenced by fluff (ANOVA $p = 0.006$) the effect being greatest in the 0/– 1 cm layer (MANOVA, $p \leqslant 0.033$ in the 0/– 1 cm layer and $p > 0.05$ below – 1 cm) and by the decrease of protein concentrations in surface sediments (ANOVA $p = 0.017$), mostly in the top 0/– 0.5 cm (MANOVA $p < 0.004$ in the 0/– 0.5 cm layer and $p > 0.05$ below – 0.5 cm) (Table 1). Furthermore, N mineralization (0/– 2 cm) during the pre-incubation period is higher in waterlogged compared to reflooded systems, as indicated by the increased C:N ratios in the later (ANOVA $p < 0.001$). This might indicate comparatively higher NH_4^+ losses from waterlogged systems than those actually measured during the nitrification assays (Table 2).

For all systems, the C:N and C:chl *a* ratios of surface layers indicate the presence of labile, easily degradable organic matter (Table 1). This can result into high NH_4^+ production that might be assimilated by benthic microorganisms. In fact, the strong increase of chl *a* concentration on top of the fluff RC during 3 days of incubation (9.6 μg g^{-1} in fresh fluff compared to 21.5 ± 0.5 μg g^{-1} in surface layer of fluff RC – Table 1) suggests that some pore water NH_4^+ was taken up by microalgae. When sediments are directly exposed to air, benthic algae can only assimilate nutrients derived from pore water constituents. However, higher chl *a* con-

Table 1. June 1999. Some properties of fresh fluff, reflooded and waterlogged sediment systems (3-day incubation- see text) and systems after addition of 2 cm of fluff to the top sediment (3-day incubation- see text). Mean values ± SD are shown (n = 3). ND- not determined. The sediment-fluff boundary is marked with a borderline and the sediment surface was set to zero.

Layer		Org C μg mg^{-1}	Tot N μg mg^{-1}	Protein mg g^{-1}	Chl *a* μg g^{-1}	C:N ratio	C:chl *a* ratio
Fresh fluff		14.1	1.7	2	9.6	8.1	1469
Fluff	1.5/2 cm	13.7 ± 0.5	1.9 ± 0.1	2.5 ± 0.2	27.2 ± 2.2	7.3 ± 0.1	505 ± 30
WC	1/1.5 cm	12.0 ± 0.2	1.6 ± 0.0	2.1 ± 0.1	9.6 ± 0.7	7.5 ± 0.1	1247 ± 77
	0/1 cm	11.7 ± 0.4	1.5 ± 0.0	2.5 ± 0.4	7.1 ± 1.5	7.5 ± 0.0	1701 ± 358
	0/– 0.5 cm	9.8 ± 0.4	1.2 ± 0.1	1.7 ± 0.2	5.4 ± 1.0	7.8 ± 0.2	1834 ± 233
	– 0.5 /– 1 cm	9.6 ± 0.7	1.2 ± 0.1	1.7 ± 0.3	4.3 ± 0.2	7.8 ± 0.1	2202 ± 206
	– 1/– 2 cm	7.5 ± 0.8	1.0 ± 0.1	ND	2.9 ± 0.2	7.8 ± 0.0	2534 ± 99
Fluff	1.5/2 cm	12.7 ± 0.1	1.9 ± 0.0	2.4 ± 0.2	21.5 ±0.5	6.8 ± 0.1	591 ± 19
RC	1/1.5 cm	12.3 ± 0.9	1.6 ± 0.0	2.1 ± 0.1	6.1 ± 1.3	7.4 ± 0.5	2068 ± 387
	0/1 cm	11.7 ± 0.3	1.6 ± 0.0	1.9 ± 0.0	6.9 ± 0.3	7.1 ± 0.2	1675 ± 105
	0/– 0.5 cm	9.8 ± 1.1	1.3 ± 0.1	1.7 ± 0.0	4.0 ± 0.9	7.4 ± 0.1	2578 ± 940
	– 0.5/– 1 cm	9.0 ± 1.2	1.2 ± 0.1	1.6 ± 0.2	3.7 ± 0.2	7.4 ± 0.1	2388 ± 171
	– 1/– 2 cm	7.1 ± 0.9	0.9 ± 0.1	ND	2.5 ± 0.3	7.5 ± 0.3	2856 ± 335
WC	0/– 0.5 cm	11.7 ± 0.4	1.6 ± 0.1	2.2 ± 0.3	15.8 ± 0.5	7.1 ± 0.1	742 ± 6
	– 0.5/– 1 cm	9.9 ± 2.2	1.3 ± 0.3	2.0 ± 0.6	6.5 ± 1.0	7.7 ± 0.1	1513 ± 124
	– 1/– 2 cm	9.1 ± 1.2	1.2 ± 0.2	ND	4.4 ± 0.9	7.7 ± 0.1	2109 ± 134
RC	0/– 0.5 cm	11.2 ± 0.1	1.6 ± 0.0	2.0 ± 0.1	14.5 ± 1.7	7.0 ± 0.1	781 ± 105
	– 0.5/– 1 cm	9.4 ± 0.7	1.3 ± 0.1	1.7 ± 0.1	6.2 ± 0.4	7.1 ± 0.1	1530 ± 149
	– 1/– 2 cm	5.9 ± 3.2	0.8 ± 0.4	ND	2.9 ± 0.5	7.2 ± 0.1	1928 ± 901

Table 2. Net ammonium fluxes, calculated diffusive fluxes at the sediment-water interface or fluff-sediment interface, actual nitrification in WC (n = 3), fluff WC (n = 2), RC (n = 3) and fluff RC (n = 3) and potential nitrification in bare sediment systems (0/– 0.5 cm) and in fluff systems (1.5/2 cm) (n = 2). Oxygen consumption was measured in one core from each system before and after acetylene addition to overlying water. All rates are expressed as mmol m^{-2} d^{-1}. ND- not determined.

Sediment System	Net NH_4^+ efflux	Calculated NH_4^+ efflux[a]	Nitrif. rate (Actual)	Nitrif. rate (Potential)	O_2 flux into sediment[b]
WC	1.368 ± 0.57	0.387 ± 0.23	0.092 ± 0.62	8.339 ± 2.55	5.3 ± 2.5
fluff	1.826 ± 0.45	0.887 ± 0.17	0.368 ± 0.03	10.927 ± 12.45	5.7 ± ND
WC		0.012 ± 0.04			
RC	0.693 ± 0.38	– 0.047 ± 0.04	0.517 ± 0.48	11.462 ± 2.37	6.7 ± 1.4
fluff	1.674 ± 0.55	0.324 ± 0.03	1.108 ± 0.63	3.030 ± 6.84	7.0 ± 2.5
RC		0.058 ± 0.04			

[a] using Fick's first law and the Archie relation (Berner 1980):Flux = $- D \Phi^3 (C')_{z=0}$ where D = diffusion coefficient in sea water (Li and Gregory 1974) corrected for salinity and temperature, Φ = porosity of the uppermost depth interval in sediment or the uppermost interval in fluff systems, C' = concentration gradient with depth and z = depth in the core.; [b] Core incubation method in the dark.

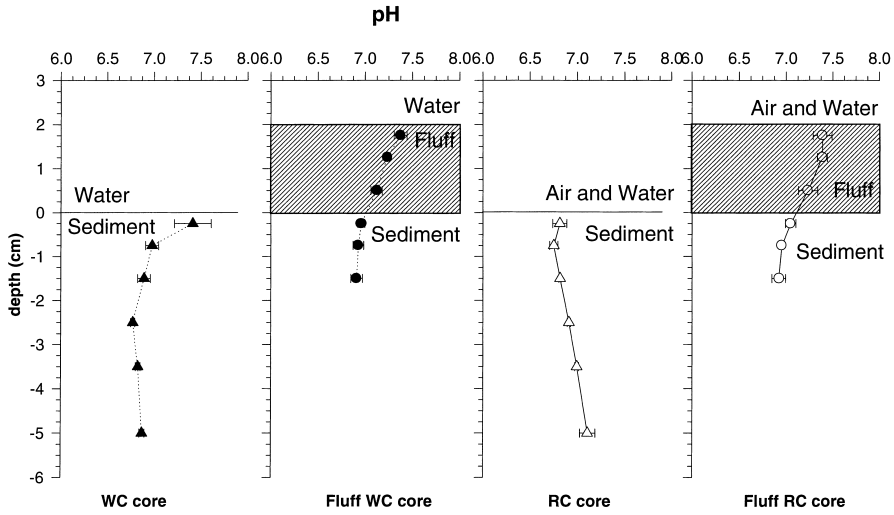

Figure 5. Depth pH profiles in waterlogged and reflooded systems with and without fluff deposits. Means and SDs are shown (n = 3). The fluff pH was slightly more alkaline than the surface of bare sediments.

centrations and lower C:chl *a* ratio in surface layer of fluff WC compared to fluff RC could be due to absence of dessication and photo-inhibition in former.

pH and E_h gradients

ANOVA showed that the sediment pH was influenced by drying and depth ($p < 0.001$) but not by the fluff deposit ($p = 0.88$). Specifically, drying influenced the pH

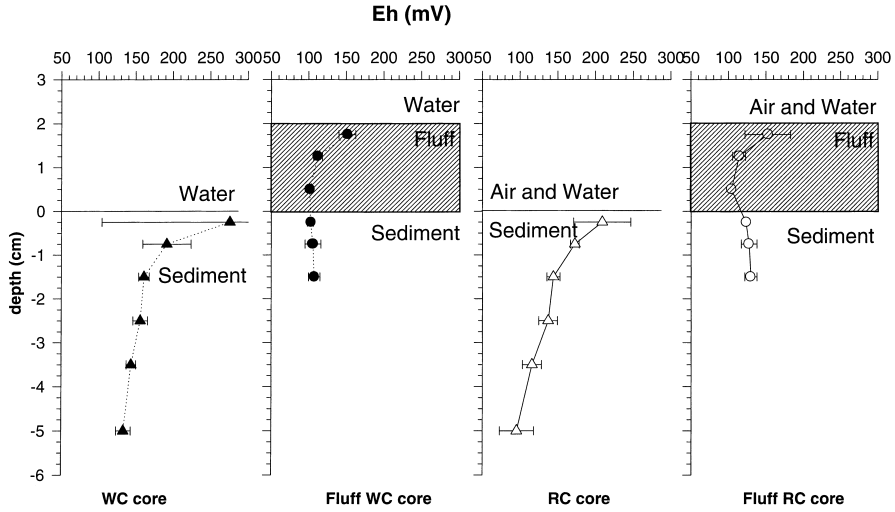

Figure 6. Depth E_h profiles in waterlogged and reflooded systems with and without fluff deposits. Means and SDs are shown (n = 3). Note the general fall of E_h in fluff systems and the absence of E_h gradients at the sediment-fluff boundary. Very steep E_h gradients in the fluff layer indicate rapid O_2 consumption rates.

in the 0/− 1 cm layer (MANOVA $p < 0.002$) and also significantly changed pH depth profiles through the interactions drying *x* fluff ($p = 0.002$) and drying *x* fluff *x* depth ($p = 0.004$). In the presence of molecular oxygen, the decomposition of organic matter can be expressed as:

$$(CH_2)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 \rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 106H_2O$$

The products of organic matter mineralization lead to 6 times more acid production that alkaline ones, so that calcareous matter buffers the pH as long as $CaCO_3$ is available. The surface pH in RC was lower than in the respective waterlogged controls (Figure 5). This pH fall must reflect changes of the CO_2–$CaCO_3$ buffering system, because CO_2 produced by O_2 consumption will lower the pH and may dissolve carbonates and metal hydroxides.

The sediment E_h decreases with depth as a result of bacterial degradation of organic matter. Sediments were reducing in June, since all E_h potentials with the exception of two were below + 200 mV, the point which Mortimer (1942) suggests as a barrier between oxidizing and reducing conditions. The general effect of the fluff deposit was the blockage of the O_2 diffusion to the underlying sediments, resulting in a fall of E_h (ANOVA, $p = 0.006$). After a brief incubation period (3 days) E_h gradients were observed within the fluff deposit but not in the sediment-fluff boundary region (Figure 6). This is explained by bioturbation caused by upward macrofauna migration in sediments.

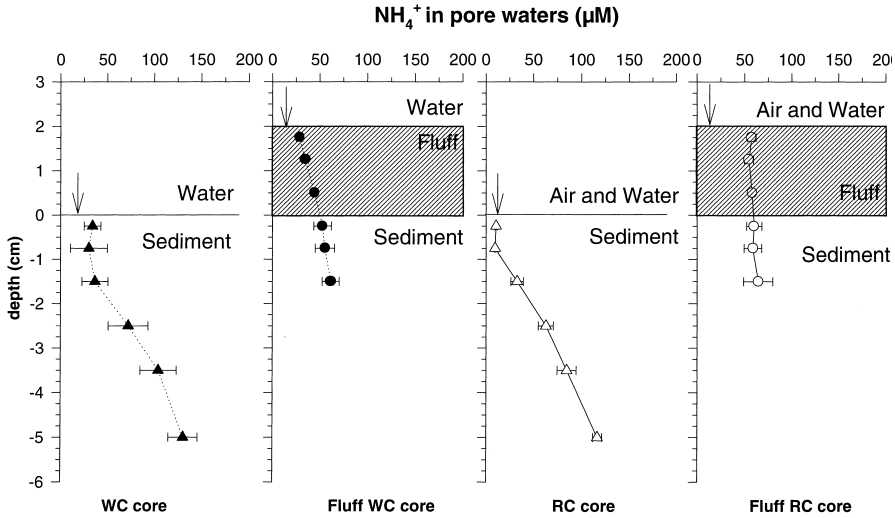

Figure 7. Depth pore water NH_4^+ profiles in waterlogged and reflooded systems with and without fluff deposits. Means and SDs are shown for each system (n = 3). Arrows show the bottom water concentration.

Ammonium depth gradients, fluxes and nitrification

Concentrations of pore water NH_4^+ increased progressively with depth (ANOVA, p = 0.012) (Figure 7) whereas drying caused a loss of NH_4^+ in the top layers of the RC system (ANOVA, log NH_4^+ p = 0.002). This might be due to ion-pairing processes that at high salinities can stimulate the release of NH_4^+ to water (Seitzinger et al. 1991; Rysgaard et al. 1999). As expected, depth salinity gradients in RC and fluff RC systems did not compare with either WC or fluff WC where gradients were absent (Figure 8). There was a strong effect of all parameters: depth, fluff and drying alone on the NH_4^+ data as well as from their interaction (ANOVA log NH_4^+ p < 0.01). Fluff addition resulted in a flatten out of NH_4^+ profiles (Figure 7, fluff addition effects on NH_4^+, p < 0.001). Absence of such gradients is likely caused by bioturbation in all investigated layers.

The sediment water net NH_4^+ fluxes before acetylene inhibition increased with time and ranged between 0.69 and 1.82 mmol m^{-2} d^{-1} (Table 2). Compared to bare sediments, the fluff deposit significantly increased the NH_4^+ release to water by 33% in fluff WC and by 22% in fluff RC (2-way ANOVA, p = 0.009). This might result from higher N concentrations in fluff compared to surface sediments (1.9 ± 0.1 μg mg^{-1} in fluff WC and fluff RC and 1.6 ± 0.1 μg mg^{-1} in WC and RC, Table 1). Hence, substrate availability was higher in fluff systems than in bare sediments. No effects of drying or resulting interaction fluff *x* drying were found to change the NH_4^+ efflux to water. In general, the measured net fluxes were much greater than the calculated diffusive fluxes and the flux at the sediment-fluff boundary was al-

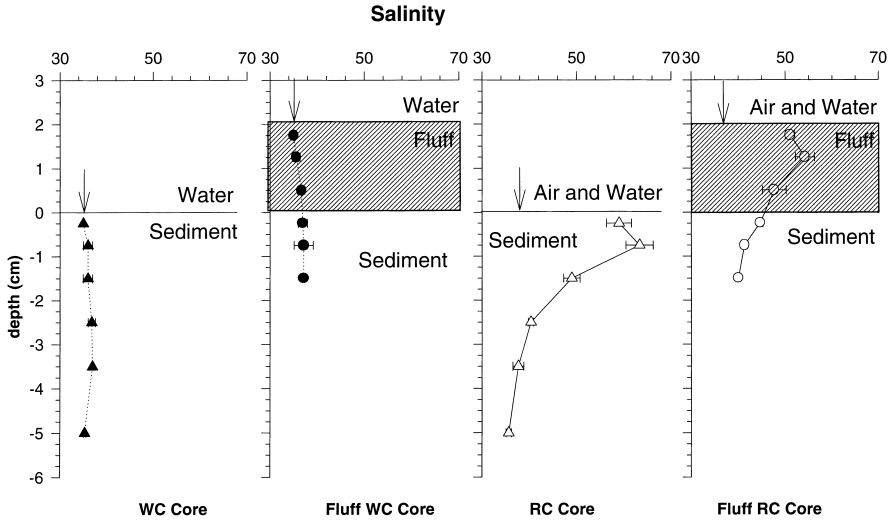

Figure 8. Changes in pore water salinity with depth in waterlogged (n = 3) and reflooded (n = 3) systems with and without fluff addition.

ways lower than the flux at the sediment-water boundary. This is likely caused by bioturbation from upward movement of macrofauna in the cores (Figure 4).

An increase of NH_4^+ availability to nitrifiers is expected during desiccation of sediments, because advective pore water transport to upper strata will occur. Hence, extra NH_4^+ could be available to nitrifying bacteria, particularly in fluff WC systems where NH_4^+ gradients were observed (Figure 7). However, the actual nitrification rate did not change among different systems (ANOVA $p > 0.05$) and fluff and desiccation, alone or combined, did not play a significant role on the nitrification rate (ANOVA $p = 0.099$). Importantly, salinity changes in the pore water (from 32 to > 50 in the top 0/− 0.5 cm) did not affect the actual nitrification in our experimental systems. This suggests a broad salinity tolerance of nitrification, a finding consistent with the observations of MacFarlane and Herbert (1984) in nitrifying bacteria isolated from a Scottish estuary. The variability of nitrification rates was high (up to > 100% in the WC systems) and this denotes high sediment heterogeneity (Table 2). Also, drying and fluff effects had no impact on the distribution and relative population size of nitrifiers, potential nitrification rates were similar for all strata regardless of sediment system (ANOVA $p > 0.05$) (Table 2). Effects of sediment heterogeneity on nitrification should be further investigated with e.g. isotopic methods.

The O_2 uptake rates in dark incubated sediments, which represent the total sediment oxygen consumption, varied between 5.3 and 7.0 mmol m^{-2} d^{-1} (Table 2). Similar rates have been measured in northern Adriatic sediments (Epping and Helder 1997) but are lower compared to other coastal sites (Boynton et al. 1991). The specific role of O_2 on the nitrification is difficult to assess, because these dark O_2 uptake rates include both heterotrophic consumption and nitrification. Also, het-

erotrophic bacteria have a much higher affinity than nitrifiers for O_2 at low O_2 concentrations ($K_m < 1$ μM O_2) and hence likely to out compete nitrifying bacteria.

In summary, our results indicate that fluff deposits which can be present during daily emersion-immersion cycles of intertidal mudflats, have impacts on the distribution of benthic biota, pH, E_h and ammonium distribution. Effects on nitrification should be further investigated with isotopic methods. Very short NH_4^+ turnover times (fraction of an hour, during the productive period), increasing primary productivity have been reported (Suttle et al. 1990), and it is well known that phytoplankton often benefit from external inputs of the limiting nutrient (Malone et al. 1988). However, the time scale of the coupling between production and regeneration in mudflats is not clear. Fluff deposits can be regarded as an important source of mobilizing NH_4^+ to the surface sediment, and, if light is available, the photosynthetic biomass could take advantage of this *stimulus* by consuming the additional input of this nutrient, thus increasing biomass production.

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