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## Tidal Flushing of Ammonium From Intertidal Salt Marsh Sediments: The Relative Importance of Adsorbed Ammonium

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Intertidal sediments are areas of high nutrient processing. During low tides, air exposure of the sediment increases the rate of degradation of organic matter, causing the ammonium concentration in the sediment to increase between tidal inundations (1). At high tide, when the flooding water inundates the lower part of the salt marsh, ammonium is often released from the sediment to the water column by diffusion and convection (1, 2, 3). However, temporary seasonal import of ammonium from the water column to the sediment has also been observed (4).

In the sediment, a dynamic equilibrium exists between ammonium dissolved in the pore water and that adsorbed onto either inorganic particles or organic matter (5). The ratio between dissolved and adsorbed ammonium can be expressed by the unitless equilibrium constant  $K_D$  (6). Since ammonium adsorption to sediment particles and organic matter is a rapid and reversible process (5), not only does pore water ammonium have the potential of being flushed out of the sediment, but the ammonium adsorbed also has the potential of being released to the inundating water, due to a rapid shift in the equilibrium. This study investigates the importance of adsorbed ammonium during tidal flushing.

In the field, tidal flushing of ammonium was studied in late July 2002 in a salt marsh area in the Plum Island Sound, Massachusetts. The study area was dominated by *Spartina alterniflora* and was regularly flooded. Tidal flushing was studied during one tidal cycle in late July at temperatures of 20.9 °C, 22.2 °C, and 23.5 °C for sediment, inundating water, and air, respectively. The amount of ammonium flushed from the sediment was determined as the difference in sediment ammonium concentration before and after inundation. Sediment cores were collected in 6.5-cm diameter acrylic plastic cylinders 1 h before and 1 h after inundation. The cores were sliced in 1-cm sections immediately after sampling. From depths of 1, 2, 3, 5, 7, and 10 cm, subsamples of 3–8 g were collected and placed on ice until further analysis. Total pore water and exchangeable ammonium was extracted from the sediment using 2M KCl (5), and the ammonium concentration was determined by the phenol hypochlorite method (7).

In the laboratory, a  $K$ -value depth profile was measured under comparable conditions. Sediment cores were collected in the same sampling area during high tide when the sediment was inundated. The cores were placed in a lighted growth chamber at 25 °C and

left inundated overnight to equilibrate core temperature. Subsequently, the water column was removed, and the sediment surface was left exposed to air for 12 h, after which the cores were sliced using the same method as in the field. Subsamples were collected for the determination of total ammonium concentration, pore water ammonium concentration, and sediment density. Pore waters were separated from sediments by centrifugation, and the concentration of adsorbed ammonium was determined as the difference between total- and pore-water ammonium. The  $K_D$ -value is determined as

$$K_D = \frac{[\text{NH}_4^+]_{\text{adsorbed}} (\mu\text{mol/g.ww.sed.})}{[\text{NH}_4^+]_{\text{porewater}} (\mu\text{mol/g.ww.sed.})}$$

and measured at the same depths as the ammonium concentration profiles.

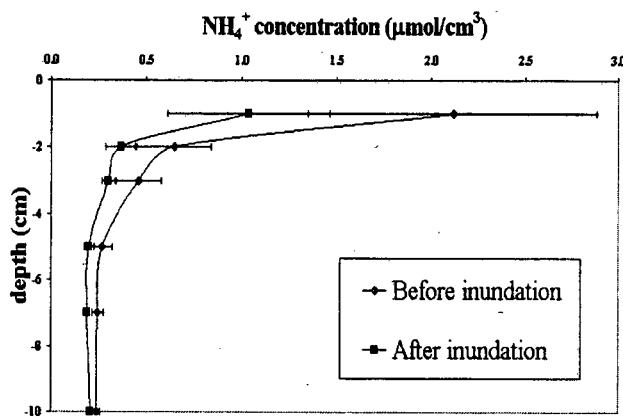
The difference between the total ammonium profiles before and after inundation indicates that a substantial amount of ammonium is released from sediment at this location during inundation at high tides (Fig. 1A). The effect of flushing was greatest in the top 0–1-cm sediment layer, where 50% of the available ammonium was lost. The effect steadily decreased with depth, and at 10-cm depth only 10% of the available ammonium was released (Fig. 1B). In the upper 0–5 cm, more than 50% of the ammonium flushed from each sediment layer originated from the adsorbed pool; in the upper 0–1 cm, this value was as high as 95%. Hence the pool of adsorbed ammonium can account for a significant part of the ammonium released by tidal flushing.

Ammonium adsorbed onto sediment particles and organic matter is by far the largest ammonium pool in the sediment (Fig. 1C). In the upper 0–1-cm sediment layer, this pool can be up to 50 times larger than the pool of ammonium dissolved in the pore water. Farther down in the sediment, from the depths 2 cm to 10 cm, the pool of adsorbed ammonium is still dominant, but is here only about 10 times larger than the dissolved pool.

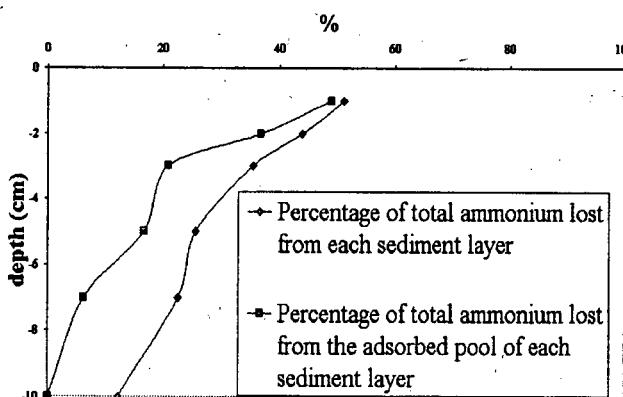
Since the proportion of ammonium released from the sediment exceeds the proportion of ammonium dissolved in the pore water, the flushing of ammonium from the sediment during inundation is not only a result of ammonium being released from the pore water by diffusive and convective forces, but much more a result of a change in the conditions determining the ammonium adsorption

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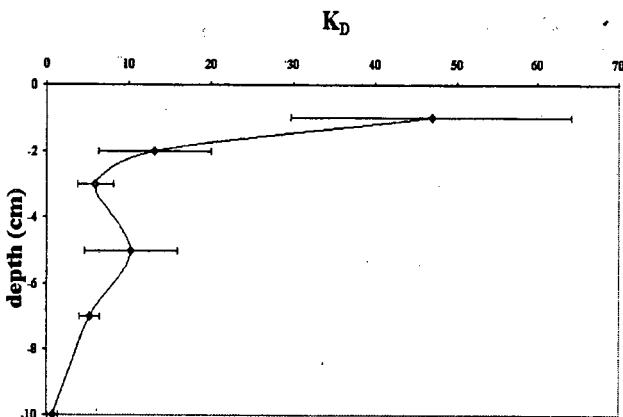
A



B



C



**Figure 1.** (A) Ammonium concentration profiles before and after inundation. (B) Percentage of total ammonium removed from each sediment layer due to tidal flushing, and percentage of total ammonium lost from the adsorbed ammonium pool. (C)  $K_d$  profile after 12 h of air exposure.

equilibrium. Based on the difference in the ammonium concentration in the sediment before and after inundation, the release of ammonium from the sediment over a tidal cycle was calculated to be 18.6 mmol/m<sup>2</sup>. That accounts for as much as 37% of the total ammonium in the upper 10-cm sediment layers, of which 80% originated from the adsorbed ammonium pool. These values are in accordance with other data for ammonium flushing (1, 2), and indicate that studies examining the loss of ammonium in sediments need to consider the adsorbed pools as well as the dissolved pools.

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