

Organic Nitrogen Release from Resuspended Sediments in the Thames Estuary



Mekibib DAWIT¹, D. Michael REVITT¹ and Mark F. FITZSIMONS²

¹ Urban Pollution Research Centre, Middlesex University, Bounds Green Road, LONDON N11 2NQ, UK

² Petroleum and Organic Geochemistry Group, Dept. of Environmental Sciences, University of Plymouth, PLYMOUTH PL4 8AA, UK



ABSTRACT

Concentrations of the methylamines (MAs) were determined in surface sediments from the outer Thames Estuary, UK. Extraction of MAs from the sediment solid phase was carried out using a widely used single-volume extraction with 2 M KCl (20 mL per g dry sediment) and compared with a multi-volume extraction (3 x 20 mL followed by 3 x 40 mL). The multi-volume technique recovered much higher amounts of MAs, with the single-volume step rarely recovering more than 50 % of the multi-volume total.

Experiments were carried out in which sediment samples were resuspended in overlying water in order to measure the rate of MA release from the sediments. This occurred rapidly and maximum concentrations were usually measured after 2 h, with desorption from the solid phase accounting for most of the MAs released into solution. The measured concentrations at the end of the experiment were greater than those recovered through single-volume and, in some cases, multi-volume extraction, suggesting that single-volume extraction can seriously underestimate the bioavailable MAs in sediments. SPM concentrations, which were measured through a tidal cycle at one site, increased as high tide approached and showed that the sediment concentrations used in the resuspension experiments were reasonably close to those measured in the field.

The results of this study show that the mobility and bioavailability of ON in estuarine sediments may not be accounted for using single-volume extraction, while factors such as resuspension must be evaluated in macro-tidal systems.

1. INTRODUCTION

Estuarine sediments play an important role in nitrogen (N) cycling. In general, sediments are considered as sinks for organic nitrogen (ON) and sources of NH_4^+ , which can diffuse across the sediment-water interface¹.

Reactions at particle surfaces strongly influence the distributions and concentrations of the ON fraction in sediments. For example, amino acids and amines can undergo ionic bonding with negatively-charged surface exchange sites on particles due to the protonation of their amino groups at seawater pH (7-8), which decreases their bioavailability^{2,3}. This 'exchangeable' fraction is usually determined through a single extraction of dry sediment with a concentrated ionic solution, at a solid to solution ratio of 1:10 or 1:20. The fraction not extracted is then considered as 'fixed' within the particle⁴. However, the existence of sediment NH_4^+ pools with different exchange capacities has been reported⁵, the more tightly bound of which was released through multi-volume extraction with KCl. The release of tightly-bound NH_4^+ during resuspension of sediments in overlying water has also been observed⁶. Little is known regarding the behaviour of ON under these conditions, however, despite the fact that particulate N is almost entirely organic.

Estuarine bacteria usually prefer to utilise dissolved free amino acids and ammonium over other nitrogen sources, such as nitrate, urea and DNA^{7,8}. Indeed, in the nitrate-rich Thames Estuary (UK), amino acids were found to be the preferred nitrogen substrate⁹. Thus, an understanding of the conditions under which ON can be released from sediments is necessary for the accurate determination of N fluxes to the water column and management of activities such as dredging, which involve the resuspension of estuarine sediment.

In this study, we investigated the abundance of a group of ON compounds, the methylamines [(CH_2NH_2), (CH_3) $_2\text{NH}$, (CH_3) $_3\text{N}$], in surface sediments collected from the Thames Estuary. Their concentration in the solid phase was determined by using single- and multi-volume extractions of sediment with KCl. These results were then compared with the concentrations measured when wet sediment was resuspended in overlying water from each site. The implications for the bioavailability of ON in estuarine sediments is discussed.

2. MATERIALS AND METHODS

2.1 Sample collection

Sampling was carried out in the outer Thames Estuary on 20 November 2001. Sediment cores (TE1-TE4) and overlying water were collected along a transect extending from Southend to upper Benfleet Creek (Fig. 1). Sediment cores were collected using acid-washed PVC coring tubes (150 x 70 mm), and placed in a cool box (-10 °C) for transport back to the laboratory, where a section of surface sediment (0-5 mm) was removed for analysis. The individual sections were centrifuged (3000 rpm, 5 min) and the supernatant passed through a 0.45 μm filter into acid washed glass vials. MAs were determined in the pore-water and sediments by microdiffusion and analysis by GC-NPD⁹.

2.2 Extraction of MAs from sediment

For single-volume extraction, a sample of wet sediment (1 g) was centrifuged (3000 rpm, 1 h) to remove the pore-water. A solution of KCl (20 mL, 2 M), spiked with NaN_3 (0.1 % w/v, which was used as a biocide), was then added and the resulting slurry shaken (150 rpm, 25 °C, 24 h). After centrifugation, the supernatant was removed, filtered, and the filtrate analysed for MAs as stated in 2.1. For multi-volume extraction, the sediment was extracted with five additional volumes of KCl (2 x 20 mL then 3 x 40 mL) and the filtered supernatant analysed as detailed in 2.1.

2.3 Resuspension experiments

Wet sediment samples (1 g) were mixed with overlying water (1 L, spiked with 0.1 % w/v NaN_3) in an acid-washed nalgene bottle. The bottles were agitated on a mechanical shaker (48 h, 25 °C) and the mixture sub-sampled (10 mL) at various intervals. Sub-samples were filtered and the MA concentration in the filtrate determined according to 2.1. All experiments were carried out in duplicate.

2.4 Measurement of SPM

Concentrations of suspended particulate material (SPM) were measured in samples taken through part of a tidal cycle at sampling point TE3 on 21 March 2002. Water samples (0.5 L) were collected at hourly intervals and filtered through pre-weighed 0.45 μm filters that had been dried to constant weight. The filters were then dried at 105 °C and weighed to determine the SPM concentration.

(0-5 mm)	ϕ	% MA extracted		
		MMA	DMA	TMA
TE1	0.4	40 56	39 59	44 60
TE2	0.4	48 52	43 54	48 53
TE3	0.6	41 33	43 36	34 44
TE4	0.7	43 26	38 28	60 29

Table 1. Table showing the percentage of MAs released after a single volume extraction (20 mL, 2 M KCl) relative to the total amount obtained after the multi-volume extraction. Data in red are the percentage MAs released after a single volume extraction (20 mL, 2 M KCl) relative to the amount recovered from the resuspension experiments.

3. RESULTS

3.1 Sediment extraction

Multi-volume extraction was more efficient at releasing exchangeable MAs from the solid phase (Table 1). In only one case was > 50 % the final MA concentration obtained after single-volume extraction (TMA, TE4), though a second extraction yielded typically 70-90 % of the final MA concentration (e.g. Fig. 2). All samples showed the same pattern of release.

3.2 MA release through resuspension

Release of MAs from resuspended sediments was rapid in all samples, with up to 99 % of the final concentration released after 30 min and maximum concentrations typically observed after 2 h. The release pattern for sample TE3 is shown in Fig. 3. This was the only sample in which the dissolved concentration of the MAs decreased after 2 h. Release from resuspended sediments accounted for a higher MA concentration than single-volume sediment extraction in all cases and was greater than that obtained through multi-volume extraction for TE3 and TE4 (Table 1).

3.3 SPM concentrations

SPM concentrations increased from an initial concentrations of 53 mg/L at low tide to 256 mg/L when the final water sample was taken approximately 1 hour after high tide (Fig. 4)

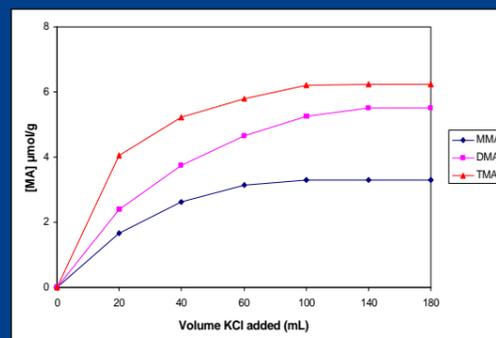


Fig. 2. Cumulative extracted MAs from Core TE4 (0-5 mm)

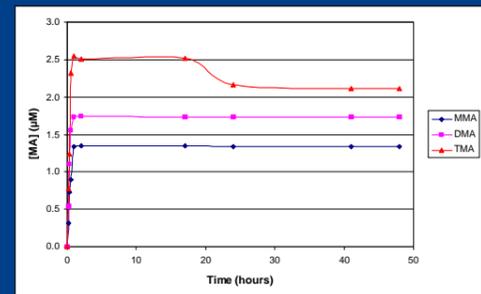


Fig. 3. Release of MAs during resuspension of sediment from site TE3

4. DISCUSSION

Multi-volume extraction of sediments with KCl released considerably more of the MAs into solution than a single-volume extraction. It has been suggested that NH_4^+ pools with differing exchange capacity can exist within the same sample⁵. However, as a base which is capable of undergoing hydrogen bonding with water molecules, it may be more likely that equilibrium is reached between the solid and liquid phase during each extraction. MAs are highly soluble in natural waters due to protonation and hydrogen bonding. Their sediment adsorption coefficients are usually much higher than for NH_4^+ and can be explained in terms of the successive replacement of hydrogen atoms with methyl groups, resulting in less hydrogen bonding (i.e. $K_{\text{TMA}} > K_{\text{DMA}} > K_{\text{MMA}}$)⁹. However, the extent of adsorption did not appear to restrict their release from the sediments, which occurred in the same proportion as their relative abundances in the solid phase. Thus, TMA, which was more abundant than MMA and DMA in the solid phase, was also released in greatest amount into solution during resuspension.

MA release through resuspension was considerably greater than could be recovered by single-volume extraction. The MAs released into the overlying water during the resuspension experiments were predominantly desorbed from the solid phase, with pore-water release accounting for only a small percentage of the final concentration. Sediment samples with highest porosity showed greatest release of MAs from the solid phase, which even exceeded the amount recovered through multi-volume extraction in most cases (Table 1). It is, perhaps, not surprising that MAs are more easily released under such a high water to solid ratio, where exchange with seawater cations and hydrogen bonding with water molecules is likely to shift the adsorption equilibrium towards the dissolved phase.

SPM levels at site TE3 increased noticeably as high tide approached (Fig. 4). Since the TE3 sediment sample had a porosity of 0.6, these results confirmed that the solid to water ratio used in the resuspension mixtures was a reasonable reflection of SPM levels in the creek water.

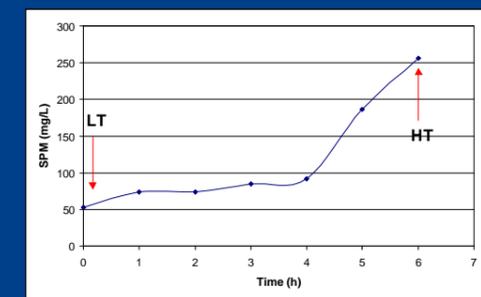


Fig. 4. SPM concentrations measured at sampling site TE3 on 21/3/02

Our results suggest that, as for NH_4^+ , single-volume extraction of MAs at a 20:1 ratio of solution to sediment can considerably underestimate the exchangeable MA pool in sediments. During sediment resuspension, release of MAs into the overlying water occurred predominantly through desorption, with pore-water contribution only a minor fraction of the total flux. Although these concentrations were much lower than observed for NH_4^+ , the fact that ON substrates are preferred by bacteria in the outer Thames Estuary⁹ may mean that sediment release of amino acids and MAs is disproportionately important. Further work will include a study of the behaviour of amino acids and bulk ON during sediment resuspension.

Dredging of estuarine sediments releases bound NH_4^+ into the water column⁶. The results of this study suggest that some of the ON fraction may be similarly desorbed. Thus, an assessment of the impact of dredging processes on water quality must include the mobility of the ON fraction if accurate fluxes are to be determined.

5. ACKNOWLEDGEMENTS

We are grateful to the Environment Agency (Thames Region) and Middlesex University for financial support

6. REFERENCES

- Rocha C. 1998. *Limnology & Oceanography* 43: 823-831
- Henrichs S.M. & Sugai. 1993. *Geochimica et Cosmochimica Acta* 57: 823-835
- Wang X.C. & Lee C. 1993. *Marine Chemistry* 44: 1-23
- Wang X.C. & Lee C. 1990. *Geochimica et Cosmochimica Acta* 54: 2759-2774
- Laima M.J.C. 1992. *Marine Ecology Progress Series* 82: 75-84
- Morin J. & Morse J.W. 1999. *Marine Chemistry* 65: 97-110
- Jørgensen N.O.G. et al. 1999. *Aquatic Microbial Ecology* 18: 247-261
- Middleburg J.J. & Nieuwenhuize. 2000. *Marine Ecology Progress Series* 203: 13-21
- Fitzsimons M.F. et al. 2001. *Environmental & Experimental Botany* 46: 225-236

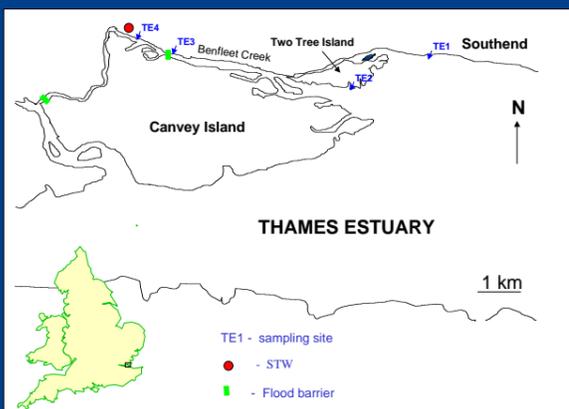


Fig. 1. Map showing the section of the outer Thames Estuary from which sediment and water samples were collected