

Aliphatic amines in Chesapeake Bay sediments

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Abstract

Aliphatic amines were determined in sediments and sediment pore waters from several contrasting sites in Chesapeake Bay. The aliphatic amines diethylamine, sec-butylamine, n-propylamine, and i-propylamine were detected in a limited number of pore-water samples at concentrations generally less than $\sim 0.6 \mu\text{M}$. The occurrence of these amines showed no obvious correlation to other sediment geochemical parameters. Whole sediment (HF/HCl-extractable) aliphatic amines were less than $\sim 0.8 \text{ nmol/gdw}$. Isoamylamine and 2-methylbutylamine were the only amines that could be detected and quantified in sediment extracts, although diethylamine was below our detection limit in selected samples. When compared to other measured nitrogen pools in the sediments, these observations suggested that aliphatic amines may not represent a significant fraction of the nitrogen that is remineralized in these sediments, although more detailed concentration and rate studies are needed to verify their role in sediment nitrogen cycling. These aliphatic amines also did not appear to represent a major component of the uncharacterized nitrogen in these sediments.

1. Introduction

The study of nitrogen cycling in the marine environment is an area of active research (see Carpenter and Capone, 1983; Blackburn and Sørensen, 1988). Two important aspects of this problem have been the characterization of organic nitrogen compounds found in sediments, and the determination of the specific organic nitrogen compounds involved in sedimentary nitrogen regeneration. While a range of organic nitrogen compounds have been identified in marine sediments (Lee and Olson, 1984; Patience et

al., 1992), a significant fraction of the sedimentary nitrogen remains uncharacterized. Furthermore, with the exception of amino acids (Henrichs and Farrington, 1987; Burdige and Martens, 1988; Cowie and Hedges, 1992), very little is quantitatively known about the early diagenetic processes affecting specific organic nitrogen compounds.

Aliphatic amines represent a class of organic nitrogen compounds that play important roles in some aspects of aquatic nitrogen cycling. They appear to be ubiquitous in marine organisms, where many are used in osmoregulation (Yancey et al., 1982; Wang and Lee, 1995a). Amines such as trimethylamine (TMA), dimethylamine (DMA) and methylamine (MA) have been identified in marine sediments and sediment pore waters, and several processes/sources

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have been suggested to explain their occurrence (Lee and Olson, 1984; Glob and Sørensen, 1987; King, 1988; Lee, 1988; Wang and Lee, 1990, 1993; Yang et al., 1993). Both biotic and abiotic processes are thought to be important, and the geochemistry of these amines is strongly affected by their reactions with sediment particles (Wang and Lee, 1990, 1993, 1995b). Amines may be adsorbed to organic and/or inorganic surfaces in a sediment (these are also referred to as exchangeable amines), and may also be more permanently “fixed” within the lattices of clay minerals in the sediments. Lee and Olson (1984) observed that exchangeable (extracted by LiCl) and fixed (extracted by HCl) DMA and TMA account for less than 0.5% of the total nitrogen in Buzzards Bay sediments and < 0.1% of the total nitrogen in sediments from the eastern tropical North Pacific (ETNP). However, Lee (1988) later observed that HF extraction of these same ETNP sediments recover up to an order of magnitude greater concentrations of MA, DMA and TMA.

Beyond studies of smaller aliphatic amines, little work has been carried out on the biogeochemistry of other amines. Scully et al. (1988) identified five volatile aliphatic amines (i-butylamine, 2-methylbutylamine, i-amylamine, pyrrolidine, and piperidine) in primary municipal wastewater effluent, and their concentrations were comparable to those of the less polar amino acids. Yang et al. (1993) observed several aliphatic amines in coastal and estuarine seawater and sediment pore waters, including n-propylamine, isopropylamine, diethylamine, n-butylamine and pyridine. Scully et al. (1988) suggested that the amines they observed in wastewaters originated from the biochemical decarboxylation of naturally occurring amino acids, catalyzed by an enzyme like pyridoxamine 5'-phosphate (Metzler, 1977). In contrast, the results of Christensen and Blackburn (1980) and Burdige (1991b) suggest that dissolved free amino acids may not be important sources of aliphatic amines in anoxic sediments.

To further characterize the organic nitrogen compounds found in marine sediments and to further examine the processes affecting aliphatic amines in sediments, we have determined aliphatic amines in sediments from several contrasting sites in Chesapeake Bay. The results of these studies are discussed in this paper.

2. Methods

2.1. Study sites

Studies were carried out at four sites in Chesapeake Bay (see map in Burdige and Homstead, 1994). Sites M (38°34'N, 76°26'W) and CB (38°56'N, 76°23'W) are in the mesohaline portion of the Bay (bottom-water salinities [PSS] of ~10–20) where seasonal anoxia (or low oxygen) generally occurs during the summer months (Smith et al., 1992). Site S (37°16'N, 76°8'W) is in the southern Bay (bottom-water salinities of ~20–30), where the bottom waters are well oxygenated year-round. Site N (39°20'N, 76°11'W) is in the northern Bay where bottom-water salinities range from < 0.1 to 10. The water depth at site CB is approximately 30 m, 12 m at site M, and 10 m at sites S and N.

The sediments at sites CB and M are fine grained, highly porous (ϕ -values range from ~0.95 to 0.85 in the upper 20 cm) and organic-rich (>3% organic carbon). Total nitrogen in the sediments ranges from ~0.5–1% (Burdige, unpubl. data). The low C/N ratio of the surface sediments in this portion of the Bay (4.5–9) suggests a predominantly marine and estuarine phytoplankton source for the organic matter in these sediments. Sulfate reduction (and to a lesser extent methanogenesis) dominates carbon metabolism in the sediments of this portion of the Bay (Marvin and Capone, 1992; Roden et al., 1995). The sediments in this portion of the Bay only contain macrofauna seasonally, when the upper few centimeters of sediments are colonized by small polychaetes and bivalves in the spring (Kemp et al., 1990). These organisms disappear from the sediments in the summer with the onset of anoxic or low-oxygen conditions in the bottom waters.

Site S, the southern Bay site, is heavily bioturbated, primarily by tube-dwelling and burrowing organisms (Schaffner, 1990). The site has integrated annual rates of sulfate reduction and measured ΣCO_2 benthic fluxes that are roughly half those of the mid-Bay region (Marvin and Capone, 1992; Burdige and Homstead, 1994). The sediments at site S are coarser grained, have lower organic carbon (~0.5%) and total nitrogen (~0.05%) contents, and are less porous (ϕ -values range from 0.5 to 0.6 in the upper

20 cm) than those at sites CB and M. The sediments at site N are clay-dominated and iron-rich, contain ~ 2–4% organic carbon, ~ 0.2% total nitrogen, and have sediment porosities ranging from 0.75 to 0.85 (Burdige, unpubl. data). Organic matter in these sediments appears to be largely refractory and terrestrially-derived (J. Cornwell, pers. commun., 1994). The sediments at site N contain a diverse community of mixed polychaetes and bivalves, including abundant *Rangia* clams (W. Boynton, pers. commun., 1994). Additional data on the geochemistry of these sites are discussed below and elsewhere (site CB: Burdige, 1991b; San Diego-McGlone, 1991; Sholkovitz et al., 1992; sites M, N and S: Burdige, 1991a, 1993; Burdige and Homstead, 1994; Roden et al., 1995).

2.2. Sample collection

Sediment cores were collected by box core and sub-cored for sediment analyses. All sub-cores were stored at in-situ temperatures until processed (within 12 h of collection). Sub-cores for pore-water analyses were sectioned and pore waters extracted using sediment squeezers (Reeburgh, 1967; Burdige and Martens, 1990) operated at low pressures (20–40 psi = ~ 1.5–3 atm). Pore waters were processed on-board ship as described previously (Burdige and Martens, 1990; Burdige and Homstead, 1994). Sediment “squeezer cakes” were saved (frozen at –20°C) for later analysis. Samples for methane analyses were collected as described previously (Reeburgh, 1980; Alperin et al., 1992).

Pore-water samples (minimum of 50 ml) for the analyses of dissolved aliphatic amines were only collected from site CB sediments, and were filtered on-board ship through a 0.45 µm filter into polyethylene bottles and acidified with two drops of concentrated sulfuric acid. These bottles were refrigerated on-board ship until they were returned to Norfolk where they were frozen in a –80°C freezer until analyzed. In contrast, aliphatic amines in sites S, M, and N sediments were determined using whole sediment samples. Sediment sub-cores were sectioned on-board ship as discussed above and whole wet sediment sections were stored frozen in plastic bags until extracted and analyzed in the lab (see below).

2.3. Dissolved and solid phase analyses

Sulfate was determined turbidimetrically (Tabatabai, 1974; Burdige, 1991a) while ammonium was determined by a modified version of the phenol-hypochlorite method (Gieskes et al., 1991). ΣCO_2 was determined by infrared detection using a modified Oceanography International Total Carbon Analyzer (Burdige, 1991a). Methane was determined by gas chromatography and flame ionization detection using a headspace technique (Alperin and Reeburgh, 1984), after thawing the frozen, basified sediment samples. Amino acids were determined by an HPLC technique using pre-column OPA derivatization (Burdige and Martens, 1988, 1990). Particulate nutrient analyses (C and N) were performed by high-temperature combustion using a Carlo Erba NCS elemental analyzer (Verardo et al., 1990). Aliphatic amines were determined as discussed below.

2.4. Determination of aliphatic amines

The extraction method used for the combined measurement of exchangeable and fixed amines in the sediments was based on the method of Wang and Lee (1990). The frozen sediment was first thawed and centrifuged to remove pore water, and 0.68 ml of a 10^{-4} M sec-butylamine solution was added as an internal standard to a 32 g portion of the remaining homogenized sediment. This was mixed with 150 ml of 5 N HF/1 N HCl in a Nalgene beaker, and stirred for 24 h. The extracted sediment was then removed by centrifugation, and the acid extract neutralized with sodium hydroxide while immersed in an ice bath. Any solid precipitates formed were removed by centrifugation and 110 ml of the supernatant was then used for purge-and-trap concentration of the amines.

The purge-and-trap method used to remove aliphatic amines from sediment extracts/pore waters was similar to that described by Scully et al. (1988), except that a 110 ml sample of sediment extract or a 50 ml pore-water sample was used. Approximately 35 g KCl and 1.6 g KOH were added to a sediment extract sample, which was then purged at 300 ml/min for 2.25 h with ultra high-purity helium gas (approximately 16 g of KCl and 0.7 g KOH was used for the pore-water samples). Amines purged

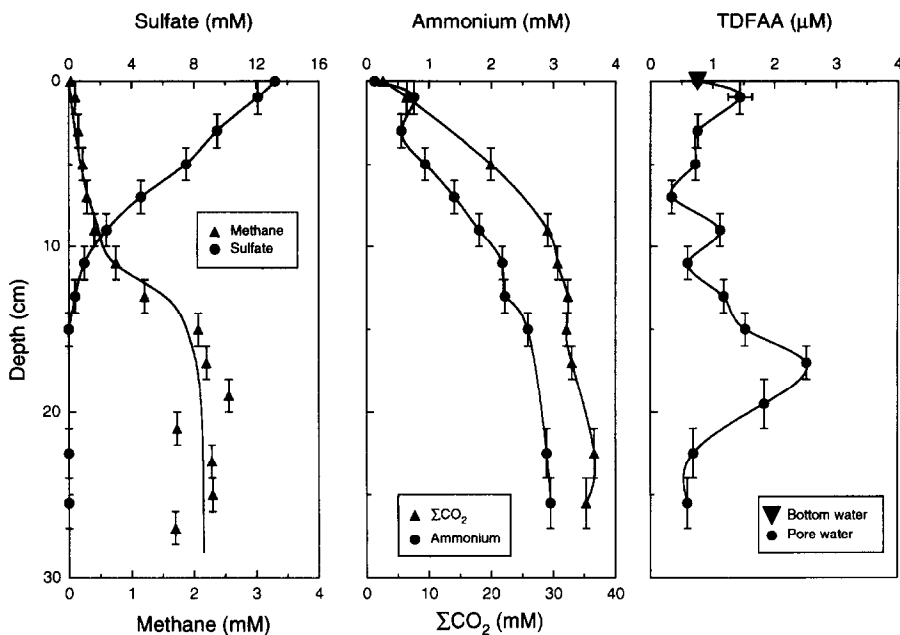


Fig. 1. Pore-water concentrations of: sulfate, methane, ammonium, ΣCO_2 and total dissolved free amino acids (TDFAA), all vs. depth, in core CB-41 collected at site CB on 6/21/88.

from the sample were trapped on cartridges containing copper chloride coated on acid-washed Chromosorb W (60/80 mesh). The recovered amines were concentrated into 1 ml of benzene, and derivatized with 1 μl heptafluorobutyric anhydride (instead

of 10 μl as per Scully et al., 1988) and 20 μl of 0.05 M trimethylamine in benzene.

Derivatized samples were analyzed by gas chromatography with electron capture detection or by GC/MS using both electron impact ionization (EI)

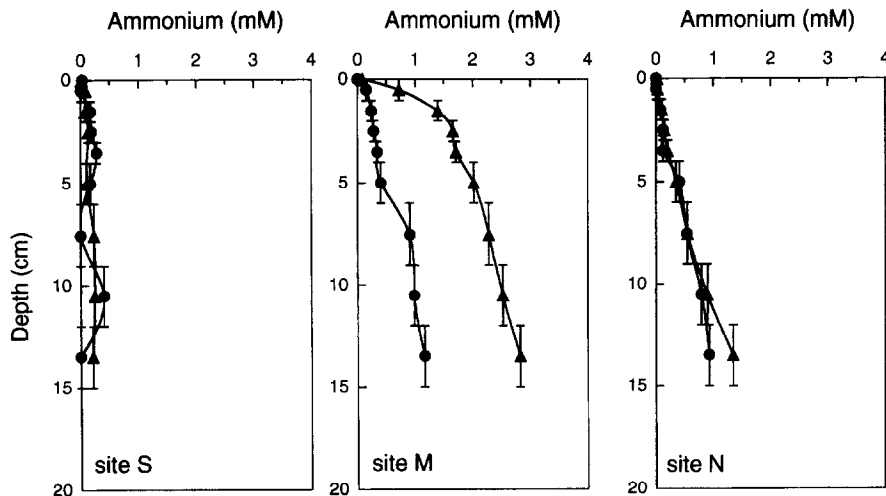


Fig. 2. Pore-water ammonium concentrations vs. depth in cores collected at sites M, N and S in March (●) and July (▲) 1992.

and methane chemical ionization (CI) to confirm molecular weight determinations. Both chromatographs were equipped with DB-5 columns (J&W Scientific). After an initial column temperature of 55°C for 10 min, the temperature was increased at 10°C/min to 150°C. Unknowns were identified by comparing their retention times and their EI and CI mass spectra with those of standards. Amines were quantified by both GC/ECD and GC/MS analysis.

The aliphatic amines we examined in this study included: i-propylamine, n-propylamine, sec-butylamine, diethylamine, i-butylamine, n-butylamine, 2-methylbutylamine, i-amylamine, pyrrolidine, piperidine, n-hexylamine, 1-methylheptylamine. Other amines with similar volatilities (i.e. with less than nine carbon atoms per molecule) could also be detected, but no chromatographic peaks other than those reported here were detected above background levels. For analytical and chromatographic reasons the procedures described here were unable to quantify the smaller amines trimethylamine (TMA), dimethylamine (DMA) and methylamine (MA).

3. Results

Inorganic and total dissolved free amino acid (TDFAA) pore-water profiles at site CB (Fig. 1) were similar to those observed in other anoxic sediments such as Cape Lookout Bight (Martens and Klump, 1984; Burdige and Martens, 1990), and other portions of the meso-haline Chesapeake Bay, including site M (Matisoff et al., 1975; Burdige, 1991b; Burdige and Homstead, 1994; also see Fig. 2). As in other anoxic marine sediments (Henrichs and Farrington, 1987; Burdige and Martens, 1990) glutamic acid, β -aminoglutaric acid, alanine, glycine and serine were the major amino acids found in the TDFAA pool of site CB sediments (data not shown). The concentration of total hydrolyzable amino acids in site CB surface sediments (109–140 $\mu\text{mol/gdw}$) and the THAA/TN molar ratio (0.25–0.44) were comparable to those observed in other coastal marine sediments (Henrichs and Farrington, 1987; Burdige and Martens, 1988; Cowie and Hedges, 1992). Aspartic acid, glutamic acid, alanine, glycine, serine, alanine, and valine were again the predominant hydrolyzable amino acids (data not shown).

Table 1
Dissolved aliphatic amines in site CB sediment pore waters

Depth (cm)	I-PA	n-PA	sec-BA	di-EA	Pip
CB-41 (6/88)^a					
0–10 *	N				
10–15	d	0.07	0.05	0.30	nd
15–20	N				
20–25	d	d	d	0.33	nd
CB-12-1 (2/89)^b					
0–5	N				
5–10	nd	nd	nd	0.62	d
10–20 *	N				

All concentrations are μM . Symbols: I-PA = i-propylamine; n-PA = n-propylamine; sec-BA = sec-butylamine; di-EA = diethylamine; Pip = piperidine. N = no amines were detected in this sample; N/A = sample not analyzed; nd = not detected; d = detected by GC/ECD but not confirmed by GC/MS.

* = analyzed as two individual 5 cm sediment sections.

^a In a companion core collected on this date (CB-42), piperidine was detected by GC/ECD but could not be confirmed by GC/MS in pore waters from the 0–5 and 10–15 cm sections.

^b In a companion core collected on this date (CB-12-2), no amines were detected in the pore waters of the upper 20 cm of sediment.

Site S sediments show virtually no sulfate and ΣCO_2 pore-water gradients (Burdige and Homstead, 1994), and ammonium gradients that were almost an order of magnitude smaller than those seen in site M and CB sediments (Fig. 2). The lack of significant pore-water gradients at site S does not result from substantially lower rates of biogeochemical processes in these sediments, but rather appears to occur due to bioturbation (macrofaunal bioirrigation and/or sediment mixing) of these sediments (see section 2.1. above and Burdige and Homstead, 1994, for further details). Finally, the sediments at site N showed evidence of ammonium and ΣCO_2 production due to sulfate reduction and other organic matter remineralization processes (e.g. manganese and iron reduction; Burdige, 1993; also see Fig. 2).

3.1. Pore-water aliphatic amines

Pore-water aliphatic amines were determined in cores collected at site CB in June 1988 and February 1989 (Table 1). In the vast majority of the samples collected on these two sampling dates none of the aliphatic amines that could be detected by our proce-

dures were found in the pore waters. In pore-water samples that did contain amines, only five amines were detected and/or quantified. One secondary amine, diethylamine, was found in a total of three pore-water samples from cores collected on both

sampling dates. The concentration of diethylamine ranged from 0.3 to 0.6 μM . In one of these samples (CB-41, 10–15 cm), two other amines (sec-butylamine and n-propylamine) were also observed at lower concentrations (0.05 and 0.07 μM , respectively).

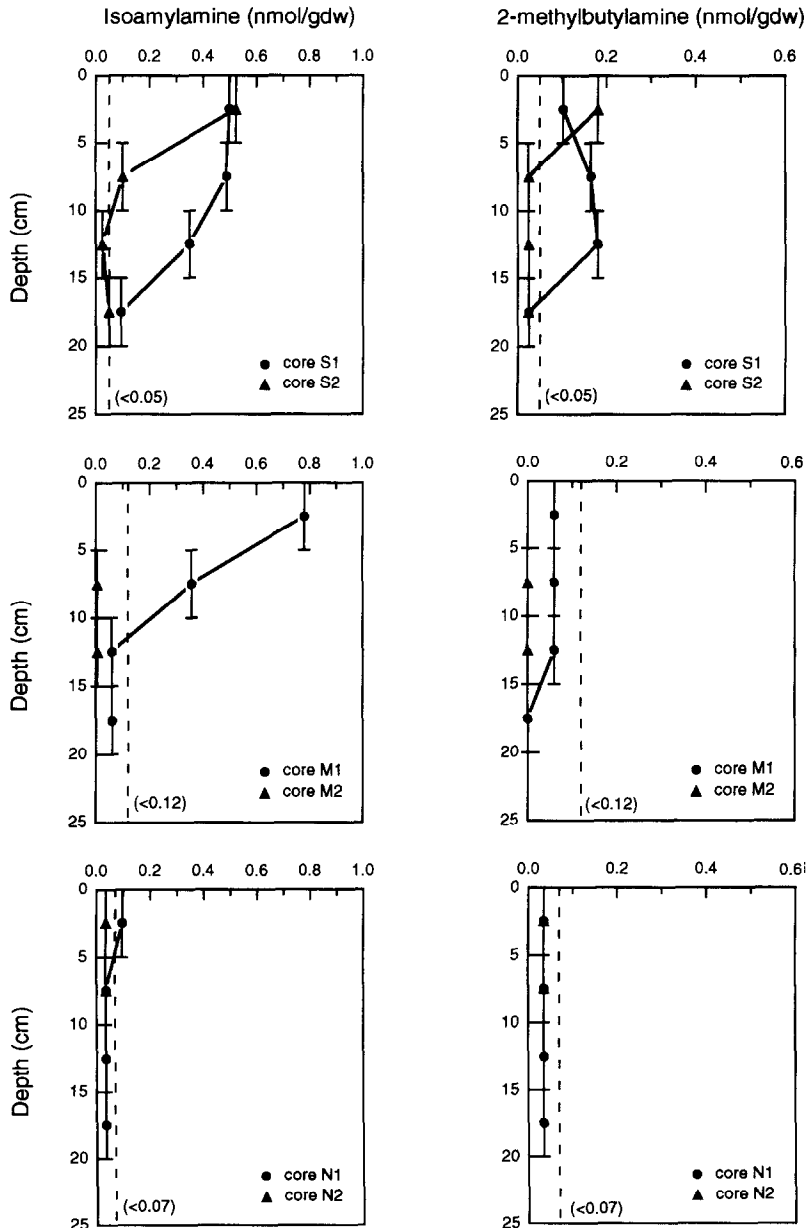


Fig. 3. Whole sediment concentrations of isoamylamine and 2-methylbutylamine vs. depth in cores collected at sites M, N and S in May 1993. The vertical dashed lines and the values in parentheses indicate the detection limits for each set of analyses, based on the analytical detection limits and the specific amounts of sediment extracted.

These two amines, along with *i*-propylamine and piperidine, were also detected in several samples by electron capture detection but could not be confirmed by GC/MS analysis.

3.2. Sedimentary aliphatic amines

Sediments from sites S, M and N were analyzed for aliphatic amines in cores collected during May, 1993 (Fig. 3). Aliphatic amines were also determined in sediments collected at site S in July and September 1993. Of the amines that could be detected by our procedures, only three amines were detected and/or quantified. Isoamylamine (I-AA) and 2-methylbutylamine (2-MBA) were observed in sediments from all three sites in May 1993. In contrast, these two amines, along with diethylamine were either below detection or not detected in cores collected at site S in July and September 1993 (data not shown). Depth-integration of the May 1993 data indicated that the amounts of I-AA, 2-MBA and total amines were highest in the southern Bay sediments and lowest in the northern Bay sediments (Table 2).

In general, I-AA concentrations were higher than those of 2-MBA in sediments collected in May 1993 (Fig. 3), and the highest concentration of I-AA was observed in the surficial sediments at site M. However, the depth distributions of these amines also

Table 2
Depth-integrated aliphatic amine concentrations in sites S, M and N sediments (May 1993)

		I-AA	2-MBA	Total amines
Site S	Core S1	120	38	158
	Core S2	53	15	68
	Average			113
Site M	Core M1 ^a	20	< 6	~ 20–26
Site N	Core N1	< 12	< 11	< 23
	Core N2	< 6	< 6	< 12
	Average			< ~ 17

All depth-integrated amounts are 10^{-6} mg N/cm², and were determined using the data in Fig. 3, and the average porosities and dry sediment densities for the sediments at the three sites (Burdige and Homstead, 1994; unpubl. data).

Symbols: I-AA = isoamylamine; 2-MBA = 2-methylbutylamine.

^a Integrated concentrations were not calculated for core M2 due to the lack of aliphatic amine concentration data for the 0–5 cm section (see Fig. 3).

Table 3
Depth-integrated total nitrogen and aliphatic amine concentrations in sites S, M and N sediments (May 1993)

	TN (mg N/cm ²)	TAA (10^{-6} mg N/cm ²)	TAA/TN (%)
Site S	7	113	0.002%
Site M	25	~ 20–26	~ 10^{-6} %
Site N	17	< ~ 17	< 10^{-6} %

Symbols: TN = depth-integrated total nitrogen; TAA = depth-integrated total sedimentary aliphatic amines. TAA is from Table 2, while TN was calculated as discussed in Table 2 using unpublished total nitrogen data for the three sites.

suggested that amines were more “evenly” dispersed in the upper 20 cm of site S sediments. The high concentration of I-AA in the surface sediments of core M1 decreased rapidly with depth, and I-AA was below detection at depths greater than 10 cm. Unfortunately, a comparison of this observation with core M2 is not possible since the 0–5 cm section of this core was lost during sampling. In site M sediments 2-MBA was either not detected or below the detection limit in both cores. Finally, with the exception of I-AA in the 0–5 cm section in core N1, both amines were below detection in site N sediments (Fig. 3).

4. Discussion

The concentrations of pore-water aliphatic amines in site CB sediments (Table 1) are similar to the generally < 1 μ M concentrations of MA, DMA and TMA observed in other marine and estuarine sediments (Sørensen, 1987; King, 1988; Wang and Lee, 1990; Yang et al., 1993), and are comparable to the pore-water concentrations of ethylamine, *n*-propylamine, diethylamine, and pyridine reported by Yang et al. (1993). The concentrations of sedimentary amines observed here (Table 3) are similar to, or up to two orders of magnitude smaller, than the concentrations of MMA, TMA, and DMA observed in other sediments (see references above and Lee, 1988).

Previous studies of the geochemistry of these smaller amines have shown that they are strongly adsorbed to sediment surfaces, and that adsorption/desorption reactions play a significant

role in affecting the geochemistry of these compounds (Wang and Lee, 1990, 1993). The low to non-detectable dissolved aliphatic amine concentrations observed in site CB sediments are consistent with this observation, although the lack of combined pore-water and solid phase analyses of the same sediment samples precludes a more quantitative discussion of these phenomena using our data. The observed pore-water dissolved aliphatic amine concentrations at site CB also showed no obvious correlation to other geochemical parameters of these sediments, and will not be discussed further.

4.1. Sources of aliphatic amines in marine sediments

Aliphatic amines are found in many plants, animals and bacteria [see references in Scully et al. (1988) and Wang and Lee (1995a)], although of all the amines observed here (see Table 1 and Fig. 3) the biological source of diethylamine has not been described. The amines I-AA and 2-MBA can also be produced by the biological decarboxylation of the amino acids leucine and isoleucine (List and Hetzel, 1960; Metzler, 1977), and such decarboxylation reactions have been proposed to explain the occurrence of these (and other) aliphatic amines in wastewater (Scully et al., 1988). While leucine and isoleucine are found in marine sediments and sediment pore waters (Henrichs et al., 1984; Henrichs and Farrington, 1987; Burdige and Martens, 1988, 1990; Cowie and Hedges, 1992), previous radiotracer studies with other amino acids (alanine and glutamic acid) could not detect the occurrence of such decarboxylation processes during the remineralization of these amino acids in anoxic estuarine, tidal flat and coastal sediments (Christensen and Blackburn, 1980; Burdige, 1991b).

A comparison of site M and S depth profiles of aliphatic amines in May 1993 (Fig. 3 and Table 2) indicated not only lower total concentrations of amines in site M sediments, but also a much more rapid attenuation with depth in their concentrations. This suggested that benthic macrofauna and/or processes associated with bioturbated sediments could be responsible for these distributions. Such a suggestion is consistent with previous studies of TMA cycling in Danish coastal sediments (Glob and Sørensen, 1987; Sørensen, 1987). At the same time, the

high concentrations of amines in cores collected at site S in May, 1993, and the lack of detectable amines in cores collected at this site in July and September, 1993 may result from a high degree of spatial heterogeneity at the site. Temporal differences in either the abundances of source organisms and/or rates of amine production and consumption may also play a role.

Site N sediments contain very low levels of amines (Fig. 3), yet also contain benthic macrofauna (see discussion above). Differences in the type and abundance of macrofauna in these sediments (and in the aliphatic amines associated with these organisms) may play a role in explaining these observations. Furthermore, differences in the sources of organic matter to site N sediments (e.g. nitrogen-poor terrestrial organic matter versus more nitrogen-rich marine and estuarine phytodetritus) may also affect the distribution of aliphatic amines in these sediments. Further studies will be required to examine all of these suggestions.

4.2. The importance of aliphatic amines in sediment nitrogen regeneration

When the results in Fig. 3 are compared to typical hydrolyzable amino acid and total nitrogen concentrations in coastal sediments (THAAs \approx 10–100 $\mu\text{mol/gdw}$; TN \approx 0.05–1% = 35–700 $\mu\text{mol/gdw}$; see Results section and references cited above), they indicate that these aliphatic amines are a minor component of the nitrogen found in these sediments (also see Table 3). If we use these data to calculate aliphatic amine “budgets” for these sediments, this suggests that aliphatic amine remineralization accounts for less than \sim 1% of the total nitrogen remineralization in these sediments [see Martens and Klump (1984) and Burdige and Martens (1988) for a discussion of how these budgets are calculated]. This calculation assumes that aliphatic amines are input to these sediments as a part of the organic material sinking out of the water column (as is generally assumed for the vast majority of the particulate nitrogen and hydrolyzable amino acids found in sediments), and that changes with depth in aliphatic amine concentrations result from their remineralization to inorganic nutrients (e.g. ammonium and CO_2). In-situ production (and rapid turnover) of these sedi-

mentary amines could, however, makes these compounds more important in the dynamics of nitrogen cycling in these sediments (e.g. Wang and Lee, 1995b). More detailed seasonal concentration and turnover studies are needed, however, to examine this suggestion.

4.3. The importance of aliphatic amines in comprising the uncharacterized sedimentary nitrogen

A comparison of depth-integrated amounts of total nitrogen and total aliphatic amines in these sediments indicated that these amines represent much less than 1% of the total sedimentary nitrogen (Table 3). In addition, the possible temporal trends in amine concentrations in site S sediments (see Results section above) further suggested that amines are not significant organic nitrogen compounds in Chesapeake Bay sediments. Since the analytical procedures used in our study should have extracted the maximum amounts of sedimentary amines, these observations suggested that these aliphatic amines are not likely a significant component of the uncharacterized nitrogen in estuarine and coastal sediments. An examination of the data in Wang and Lee (1990) for sedimentary concentrations of MA and DMA in several nearshore sediments suggests that MA and DMA also represent less than ~10% of the sedimentary nitrogen in the environments they studied.

The low amine concentrations observed in our study are somewhat surprising given the fact that aliphatic amines are produced by a wide range of marine and estuarine organisms. To account for the low sedimentary concentrations we observed, either these aliphatic amines represent a relatively small fraction of the total organic nitrogen in these organisms, or the turnover rates of these amines (in either the water column or in the sediments) are very rapid. Additional studies will be required to examine these suggestions.

Further studies are also required to verify whether aliphatic amines are a significant component of the nitrogen in deep-sea sediments, where both total nitrogen and hydrolyzable amino acids are found at much lower concentrations than those in estuarine and coastal sediments (e.g. Whelan and Emeis, 1992). Differences in the sources and reactivity (e.g. Wang and Lee, 1995b) of aliphatic amines and amino acids

in open ocean marine environments could possibly increase the importance of aliphatic amines in deep-sea sediments (Lee, 1988).

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References

- Alperin, M.J. and Reeburgh, W.S., 1984. Geochemical observations supporting anaerobic methane oxidation. In: R.L. Crawford and R.S. Hanson (Editors), *Microbial Growth on C-1 Compounds*. ASM, Cleveland, OH, pp. 282–289.
- Alperin, M.J., Reeburgh, W.S. and Devol, A.H., 1992. Organic carbon remineralization and preservation in sediments of Skan Bay, Alaska. In: J.K. Whelan and J.W. Farrington (Editors), *Productivity, Accumulation, and Preservation of Organic Matter in Recent and Ancient Sediments*. Columbia Univ. Press, New York, NY, pp. 99–122.
- Blackburn, T.H. and Sørensen, J. (Editors), 1988. *Nitrogen Cycling in Coastal Marine Environments*. Wiley, New York, NY.
- Burdige, D.J., 1991a. The kinetics of organic matter mineralization in anoxic marine sediments. *J. Mar. Res.*, 49: 727–761.
- Burdige, D.J., 1991b. Microbial processes affecting alanine and glutamic acid in anoxic marine sediments. *FEMS Microbiol. Ecol.*, 85: 211–231.
- Burdige, D.J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. *Earth Sci. Rev.*, 35: 249–284.
- Burdige, D.J. and Homstead, J., 1994. Fluxes of dissolved organic carbon from Chesapeake Bay sediments. *Geochim. Cosmochim. Acta*, 58: 3407–3424.
- Burdige, D.J. and Martens, C.S., 1988. Biogeochemical cycling in an organic-rich marine basin -10. The role of amino acids in sedimentary carbon and nitrogen cycling. *Geochim. Cosmochim. Acta*, 52: 1571–1584.
- Burdige, D.J. and Martens, C.S., 1990. Biogeochemical cycling in an organic-rich marine basin -11. The sedimentary cycling of dissolved free amino acids. *Geochim. Cosmochim. Acta*, 54: 3033–3052.
- Carpenter, E.J. and Capone, D.G. (Editors), 1983. *Nitrogen in the Marine Environment*. Academic, New York, NY.
- Christensen, D. and Blackburn, T.H., 1980. Turnover of tracer (¹⁴C, ³H labelled) alanine in inshore marine sediments. *Mar. Biol.*, 58: 97–103.

- Cowie, G.L. and Hedges, J.I., 1992. Sources and reactivities of amino acids in a coastal marine environment. *Limnol. Oceanogr.*, 37: 703–724.
- Gieskes, J.M., Gamo, T. and Brumsack, H., 1991. Chemical methods for interstitial water analysis aboard JOIDES RESOLUTION. *Ocean Drill. Progr. Tech. Note*, 15.
- Glob, E. and Sørensen, J., 1987. Determination of dissolved and exchangeable trimethylamine pool in sediments. *J. Microbiol. Methods*, 6: 347–355.
- Henrichs, S.M. and Farrington, J.W., 1987. Early diagenesis of amino acids and organic matter in two coastal marine sediments. *Geochim. Cosmochim. Acta*, 51: 1–15.
- Henrichs, S.M., Farrington, J.W. and Lee, C., 1984. Peru upwelling region sediments near 15°S. 2. Dissolved free and total hydrolyzable amino acids. *Limnol. Oceanogr.*, 29: 20–34.
- Kemp, W.M., Sampou, P., Mayer, M., Henricksen, K. and Boynton, W.R., 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. *Limnol. Oceanogr.*, 35: 1545–1563.
- King, G.M., 1988. Distribution and metabolism of quaternary amines in marine sediments. In: T.H. Blackburn and J. Sørensen (Editors), *Nitrogen Cycling in Coastal Marine Environments*. Wiley, New York, NY, pp. 143–172.
- Lee, C., 1988. Amino acid and amine biogeochemistry in marine particulate material and sediments. In: T.H. Blackburn and J. Sørensen (Editors), *Nitrogen Cycling in Coastal Marine Environments*. Wiley, New York, NY, pp. 125–141.
- Lee, C. and Olson, B.L., 1984. Dissolved, exchangeable and bound aliphatic amines in marine sediments: initial results. *Org. Geochem.*, 6: 259–263.
- List, P.H. and Hetzel, H., 1960. Basic constituents of fungi. VIII. Biogenic amines and amino acids in *Coprinus micaceus*. *Planta Med.*, 8: 105–112.
- Martens, C.S. and Klump, J.V., 1984. Biogeochemical cycling in an organic-rich marine basin -4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. *Geochim. Cosmochim. Acta*, 48: 1987–2004.
- Marvin, M.C. and Capone, D.G., 1992. Benthic microbial metabolism along the Chesapeake estuarine transect. 1992 ASLO Aquat. Sci. Meet., Santa Fe, NM (abstr.).
- Matisoff, G., Bricker III, O.P., Holdren, G.R. Jr. and Kaerk, P., 1975. Spatial and temporal variations in the interstitial water chemistry of Chesapeake Bay sediments. In: T.M. Church (Editor), *Marine Chemistry in the Coastal Environment*. Am. Chem. Soc. Symp. Ser., 18, pp. 343–363.
- Metzler, D.E., 1977. *Biochemistry: The Chemical Reactions of Living Cells*. Academic, New York, NY.
- Patience, R.L., Baxby, M., Bartle, K.D., Perry, D.L., Reiss, G.W. and Rowland, S.J., 1992. The functionality of organic nitrogen in some recent sediments from the Peru upwelling region. *Org. Geochem.*, 18: 161–169.
- Reeburgh, W.S., 1967. An improved interstitial water sampler. *Limnol. Oceanogr.*, 12: 163–165.
- Reeburgh, W.S., 1980. Anaerobic methane oxidation: rate depth distributions in Skan Bay sediments. *Earth Planet. Sci. Lett.*, 47: 345–352.
- Roden, E.E., Tuttle, J.H., Boynton, W.R. and Kemp, W.M., 1995. Carbon cycling in mesohaline Chesapeake Bay sediments 1. POC deposition rates and mineralization pathways. *J. Mar. Res.*, in press.
- San Diego-McGlone, M.L., 1991. *Estuarine Redox Processes in Chesapeake Bay*. Ph.D. dissertation. Old Dominion Univ., Norfolk, VA.
- Schaffner, L.C., 1990. Small-scale organism distributions and patterns of species diversity: evidence for positive interactions in an estuarine benthic community. *Mar. Ecol. Prog. Ser.*, 61: 107–117.
- Scully, F.E. Jr., Johnson, J.D., Howell, G.D., Penn, H.H. and Mazina, K., 1988. Small molecular weight organic amino nitrogen compounds in treated municipal wastewater. *Environ. Sci. Technol.*, 22: 1186–1190.
- Sholkovitz, E.R., Shaw, T.J. and Schneider, D.L., 1992. The geochemistry of rare earth elements in the seasonally anoxic water column and sediments of Chesapeake Bay. *Geochim. Cosmochim. Acta*, 56: 3389–3402.
- Smith, D.E., Leffler, M. and Mackiernan, G., 1992. *Oxygen Dynamics in the Chesapeake Bay, A Synthesis of Recent Research*. Maryland Sea Grant Coll., MD.
- Sørensen, J., 1987. Influence of benthic fauna on trimethylamine concentrations in coastal marine sediments. *Mar. Ecol. Prog. Ser.*, 39: 15–21.
- Tabatabai, M.A., 1974. A rapid method for determination of sulfate in water samples. *Environ. Lett.*, 7: 237–243.
- Verardo, D.J., Froelich, P.N. and McIntyre, A., 1990. Determination of organic carbon and nitrogen in marine sediments using a Carlo Erba NA-1500 analyzer. *Deep-Sea Res.*, 37: 157–165.
- Wang, X.-C. and Lee, C., 1990. The distribution and adsorption behavior of aliphatic amines in marine and lacustrine sediments. *Geochim. Cosmochim. Acta*, 54: 2759–2774.
- Wang, X.-C. and Lee, C., 1993. Adsorption and desorption of aliphatic amines, amino acids and acetate by clay minerals in marine sediments. *Mar. Chem.*, 44: 1–23.
- Wang, X.-C. and Lee, C., 1995a. Sources and distribution of aliphatic amines in salt marsh sediments. *Org. Geochem.*, 22: 1005–1021.
- Wang, X.-C. and Lee, C., 1995b. Decomposition of aliphatic amines and amino acids in anoxic salt marsh sediments. *Geochim. Cosmochim. Acta*, 59: 1787–1797.
- Whelan, J.K. and Emeis, K.-C., 1992. Sedimentation and preservation of amino compounds and carbohydrates in marine sediments. In: J.K. Whelan and J.W. Farrington (Editors), *Productivity, Accumulation, and Preservation of Organic Matter in Recent and Ancient Sediments*. Columbia Univ. Press, New York, NY, pp. 176–200.
- Yancey, P.H., Clark, M.E., Hand, S.C., Bowler, R.D. and Somero, G.N., 1982. Living with water stress: evolution of osmolyte systems. *Science*, 217: 1214–1222.
- Yang, X.-H., Lee, C. and Scranton, M.I., 1993. Determination of nanomolar concentrations of individual dissolved low molecular weight amines and organic acids in seawater. *Anal. Chem.*, 65: 572–576.