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Sources and fate of amino sugars in coastal Peruvian sediments

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Abstract

Amino sugars are involved in the marine carbon and nitrogen cycles and comprise a geochemically significant fraction of marine organic material (OM). However, information on abundance and distribution of these compounds in marine sediments is scarce. Three sediment cores (<50 cm) from the coastal region off Peru were investigated for concentrations of glucosamine (GlcN), galactosamine (GalN), mannosamine (ManN), and muramic acid (Mur). The sum of the four amino sugars accounted for 1.0–2.4% of organic carbon and 1.9–3.8% of nitrogen in the sediments. At the shallowest (102 m) and the deepest site (1278 m), carbon-normalized concentrations decreased down-core, suggesting preferential degradation of amino sugars compared to bulk sedimentary OM. At the site from the center of the oxygen minimum zone (238 m), amino sugar concentrations were high throughout the core, pointing to enhanced preservation of amino sugars under anoxic conditions. GlcN (44–56 mol%) and GalN (33–42 mol%) were the dominant amino sugars in all investigated samples, while ManN (6–14 mol%) and Mur (1–4 mol%) were significantly less abundant. Mur was predominantly associated with cell wall remains rather than with living bacteria, since bacterial abundances estimated based on Mur concentrations were up to 500 times higher than cell counts reported for sediments from this area. GlcN/GalN-ratios (1.1–1.7) indicated that chitin, a polymer of GlcN, was not a major contributor to the amino sugar pool of the investigated sediments. Furthermore, GlcN/Mur-ratios (13–68) are inconsistent with a predominant contribution of intact peptidoglycan, which exhibits a 1:1-ratio. The present study includes a compilation of previously published information on distribution and abundance of amino sugars in the marine environment. Both concentrations and ratios observed in the Peruvian sediments fall in the range of values reported for OM in water column and sediments from different oceanic regions and water depths. Although specific sources for the majority of sedimentary amino sugars remain unidentified, there are indications for a major prokaryotic origin. As suggested in previous studies, the uniform amino sugar compositions of altered marine OM and particularly the close association of GlcN and GalN, which is similar to the ratio observed in living bacteria, are consistent with a transformation of planktonic into bacterial OM.

1. Introduction

Amino sugars represent an important compound class in living and dead marine organic material (OM). They are widely distributed as building blocks of abundant biopolymers, particularly glucosamine (GlcN) in chitin, a structural polymer in many marine invertebrates, fungi, and algae (Gooday, 1990), and GlcN and muramic acid (Mur) in peptidoglycan, a major constituent of bacterial cell walls (Madigan et al., 2000). Amino sugars are derivatives of monosaccharides with one hydroxy-group substituted by an amino-group, which is mostly acetylated in biopolymers. As nitrogen-containing organic compounds, amino sugars are involved in both the marine carbon and nitrogen cycles.

Most studies on amino sugars (also known as hexosamines) in the marine realm have been limited to the analysis of GlcN and galactosamine (GalN) (Ittekkot et al., 1984a,b; Müller et al., 1986; Haake et al., 1993; Gupta et al., 1997; Dauwe and Middelburg, 1998; Jennerjahn and Ittekkot, 1999; Jennerjahn et al., 1999; Gupta and Kawahata, 2000). Ratios of GlcN and GalN have been used to identify OM sources, with high values being characteristic of high abundances of chitin-rich zooplankton

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(e.g., Müller et al., 1986; Gupta and Kawahata, 2000). Amino sugars were found to be, on average, more resistant to degradation than amino acids (Baas et al., 1995; Nagata et al., 2003), probably due to their association with structural polymers. THAA/THHA-ratios [(total hydrolysable amino acids)/(total hydrolysable hexosamines)] have successfully been used as indicators of OM freshness, with higher values indicating fresh material and lower values more degraded material (e.g., Gupta and Kawahata, 2000).

Recently, additional data have become available on abundance and distribution of mannosamine (ManN) and Mur in marine OM, but this information is mostly limited to particulate (POM) and dissolved OM (DOM) in the water column (Kaiser and Benner, 2000; Benner and Kaiser, 2003). Since peptidoglycan is the only known source of Mur, relatively low Mur concentrations in marine DOM suggest that peptidoglycan remnants are minor constituents of this pool. In contrast, the abundance of GlcN and GalN and surprisingly constant and low GlcN/GalN-ratios (typically <3) indicate a major prokaryotic source of marine DOM.

In soil science, amino sugars are routinely used to characterize microbial community structures, namely to estimate relative contributions of fungi and bacteria (e.g. Kandeler et al., 2000; Amelung, 2001; Glaser et al., 2004). Amino sugars are stabilized in soils and persist after the death of cells; they therefore provide an indicator for dead rather than for living microbial biomass (Glaser et al., 2004). Historically, there have been attempts to establish Mur analysis for estimating bacterial abundances in marine POM and sediments (e.g., King and White, 1977; Moriarty, 1977; Mimura and Romano, 1985). Some of these studies revealed a good correspondence of cell number estimates based on Mur concentrations and actual bacterial counts from cell staining (e.g., Mimura and Romano, 1985). However, using Mur concentrations to derive bacterial numbers is based on the assumption that peptidoglycan of dead cells is rapidly degraded; a prerequisite that conflicts with results of recent studies on peptidoglycan degradation in aquatic systems (e.g., Jørgensen et al., 2003; Nagata et al., 2003).

Sediments from the coastal upwelling region off Peru are deposited under oxygen-deficient to anoxic conditions. Based on studies in this region, Parkes et al. (1993) proposed that bacterial necromass, i.e., dead bacterial biomass, may account for the accumulation of recalcitrant OM in high productivity areas. The sediments investigated in this study are characterized by high organic carbon concentrations, a dominance of marine OM originating from the highly productive overlying water masses, and high rates of bacterial remineralization, which also indicate high abundances of active sedimentary bacteria (Fossing, 1990; Niggemann, 2005). For the purpose of this study, we have chosen sediments that represent different depositional conditions with respect to water depth, bottom water oxygen concentration, and physical hydrographical impact (Reinhardt et al., 2002; Böning et al., 2004). Sediment accumulation rates are typically high in the investigated region (>0.1 cm $year^{-1}$; Reimers and Suess, 1983), and thus the sediments provide a high resolution record of OM input and OM degradation.

The aim of this study is (1) to broaden the data base on abundance and distribution of amino sugars in marine sediments, (2) to evaluate the potential of amino sugars to trace sources and diagenetic changes of marine OM, and (3) to relate Mur and peptidoglycan concentrations in sediments to bacterial bio- and/or necromass.

2. Material and methods

2.1. Sampling

Sampling was carried out during RV Sonne cruise 147 in June 2000 (Kudrass, 2000). The sampling area and the positions of the investigated sites are shown in Fig. 1. At the time of sampling, the oxygen minimum zone in the water column (<0.5 ml O_2 L^{-1}) extended from 50 to 650 m and the sediment at 29MC and 71MC was covered by oxygen-depleted bottom water. A detailed description of the sampling area and the geochemistry of individual sites are given in Böning et al. (2004) and Niggemann (2005). These studies showed that 29MC represents a typical shallow, near-coastal site in coastal upwelling regions, with a dominance of fresh OM, high bacterial sulfate reduction rates, and high biomass of the sulfur bacteria *Thioploca*. Site 71MC is characteristic of mud-wave field sediments that exhibit high organic carbon concentrations dominated by refractory OM. Although sulfate reduction rates were low at this site, high *Thioploca* biomass was observed. Site 81MC was chosen as a deep sea reference, with low organic carbon concentrations and dominance of altered OM. Sulfate reduction rates were low at this site and *Thioploca* sheets were absent.

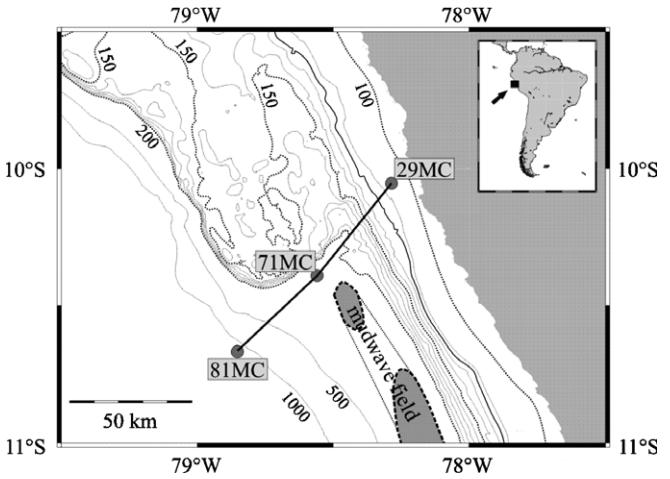

Fig. 1. Map of the investigated area with bathymetry (adopted from Reinhardt et al., 2002) and location of sampling sites 29MC (102 m water depth; 10°03.28S, 78°17.10W), 71MC (238 m; 10°23.42S, 78°33.51W), and 81MC (1278 m; 10°40.04S, 78°51.15W).

Sediment samples were retrieved using a multi-corer to recover an undisturbed surface. Sediment recoveries were 40 cm at 29MC, 48 cm at 71MC, and 18 cm at 81MC. The sediment cores were sliced in 1-cm intervals in the upper 6 cm and in 2-cm intervals below 6 cm. Samples were transferred to clean glass vials and frozen at −25 °C immediately after sampling. The sediment samples were freeze-dried and homogenized by grinding in an agate mortar.

2.2. Analyses

Total carbon (TC) and total nitrogen (TN) concentrations were determined on freeze-dried samples by combustion/gas chromatography (Carlo Erba NA-1500 CNS analyzer) with a precision of ±0.7% for N and ±0.6% for C, respectively. Total inorganic carbon (TIC) was measured on a CM 5012 CO_2 Coulometer (UIC) after acidification with phosphoric acid (3 M). The precision for TIC was ±0.4%. Total organic carbon (TOC) was calculated as the difference of TC and TIC. The C/N-ratio was calculated as the molar ratio of TOC and TN.

Amino sugars (GlcN, GalN, ManN, and Mur) were determined following the procedure of Zhang and Amelung (1996). According to the nitrogen concentration of the sample, 50–250 mg of freeze-dried sediment was hydrolyzed with 10 ml of 6 N HCl for 8 h at 105 °C. In our laboratory, these hydrolysis conditions have been shown to release maximum yields of amino sugars, confirming previous results of Zhang and Amelung (1996). The hydrolysate was neutralized with 1.5 N KOH and desalted by dilution in methanol. Conversion of amino sugars to aldononitrile acetate derivatives was carried out according to the method of Guerrant and Moss (1984). Gas chromatographic analysis was performed on a Hewlett–Packard (HP) 5890 Series II instrument equipped with a flame ionization detector and a HP5 column (50 m length, 0.32 mm ID, and 0.17 μm film thickness). Carrier gas was helium. The oven temperature program was set to an initial temperature of 120 °C (held for 1 min), heating rates were 10 °C min^{-1} to 250 °C (held for 2.5 min) and 20 °C min^{-1} to 270 °C (held for 2 min). For quantification, the ratio of amino sugar peak and internal standard (myo-inositol) peak in the sample were compared to peak area ratios of standard samples with known concentrations. Reported recoveries of amino sugars for the applied analysis procedure are >90% for GlcN, GalN, and ManN, and >80% for Mur (Zhang and Amelung, 1996). Average mean deviations for duplicates in this study were 6, 7, 16, and 27% for GlcN, GalN, ManN, and Mur, respectively.

3. Results

3.1. Total amino sugar concentrations

On a sediment dry weight (dw) basis, total amino sugar concentrations (sum of GlcN, GalN, ManN, and Mur) were strongly correlated with the TOC ($r^2 = 0.98$, $n = 34$) and the TN ($r^2 = 0.98$, $n = 34$) concentrations of the respective samples. In detail, amino sugar concentrations were highest at 71MC, where TOC concentrations were significantly higher ($p < 0.001$) than at the other sites (Table 1). Lowest amino sugar concentrations were found at 81MC and in the deeper part of 29MC, coinciding with comparably low TOC concentrations of 2.7–3.8 and 1.0–2.1% dw, respectively. In order to highlight possible minor differences in the relative lability of individual amino sugars, data are presented as TOC- and TN-normalized amino sugar concentrations.

In all investigated samples, the four amino sugars together made up a similar fraction of TOC (1.0–2.4%) and TN (1.9–3.8%), regardless of water depth of the sampling site and observed differences in the degradation state of the sedimentary OM (Niggemann, 2005; Fig. 2). At 29MC and 81MC the percentages were highest near the sediment surface and decreased with increasing sediment depth, from 2.4% to 1.3% TOC and 3.2% to 1.9% TN at 29MC, and from 2.0% to 1.3% TOC and 3.1% to 2.0% TN at 81MC, respectively. At 71MC the percentages remained relatively constant down-core, 1.9 ± 0.1% TOC and 3.3 ± 0.2% TN.

3.2. Individual amino sugars

GlcN was the most abundant amino sugar in all investigated samples (Table 1), making up 44–56 mol% of the analyzed amino sugars, followed by GalN accounting for 33–42 mol%. ManN and Mur were minor contributors, making up 6–14 and 1–4 mol%, respectively. Down-core and inter-core variability in concentration of every amino sugar partly reflected differences in TOC concentrations. In general, TOC-normalized concentrations of GlcN and GalN were higher at 71MC and 29MC than at 81MC (Table 1). At 29MC and 81MC they decreased with increasing sediment depth, whereas 71MC revealed no down-core trend. TOC-normalized concentrations of ManN were on average lower at 29MC and 81MC compared to 71MC. At 29MC and 81MC, ManN concentrations decreased in the upper part of the sediment and remained rather constant in the deeper part of the sediment. At 71MC, concentrations of ManN were generally less variable, without a distinct down-core trend. For Mur lowest and comparably constant concentrations were found at 81MC, whereas Mur concentrations at 29MC and 71MC were higher and more scattered.

3.3. Amino sugar ratios

Molar ratios of glucosamine and galactosamine (GlcN/GalN) covered a narrow range (1.1–1.7), with an average value of 1.4 ± 0.1 for all investigated samples (Fig. 3). Inter-core variations were small, average ratios for the different sites were 1.3 ± 0.2 at 29MC, 1.4 ± 0.1 at 71MC, and 1.5 ± 0.1 at 81MC. At all sites, highest GlcN/GalN ratios occurred in the uppermost cm (1.7 at 29MC, 1.6 at

Table 1
TOC concentrations, C/N-ratios (molar TOC/TN), total amino sugar concentrations (sum of individual amino sugars), and TOC-normalized concentrations of glucosamine (GlcN), galactosamine (GalN), mannosamine (ManN), and muramic acid (Mur) in all investigated sediment samples

Site, depth (cm)	TOC (% dw)	C/N molar	Total amino sugars (μmol gdw^{-1})	GlcN (μmol gTOC^{-1})	GalN (μmol gTOC^{-1})	ManN (μmol gTOC^{-1})	Mur (μmol gTOC^{-1})
29MC, 0–1	4.8	8.1	15.8	180	108	35	5
29MC, 2–3	6.1	8.9	15.2	136	91	17	7
29MC, 4–5	6.4	9.2	18.0	141	117	18	3
29MC, 6–8	6.1	9.0	12.9	92	88	24	6
29MC, 10–12	5.1	9.6	13.6	135	101	21	9
29MC, 14–16	6.0	9.9	15.7	134	109	15	2
29MC, 18–20	4.8	9.6	11.5	125	92	16	5
29MC, 22–24	5.3	9.2	12.7	127	93	17	5
29MC, 26–28	2.1	9.2	4.9	112	91	18	6
29MC, 30–32	2.1	9.6	4.2	101	82	19	6
29MC, 34–36	2.0	9.1	3.7	89	75	17	4
29MC, 38–40	1.0	8.3	1.9	96	69	16	4
71MC, 0–1	14.3	10.2	41.4	156	100	29	4
71MC, 1–2	15.0	10.2	37.3	128	85	31	5
71MC, 2–3	16.4	11.0	42.8	135	90	30	5
71MC, 4–5	15.1	11.0	42.6	150	107	24	2
71MC, 6–8	16.8	10.8	43.2	135	91	27	5
71MC, 10–12	17.2	10.8	40.9	121	81	28	8
71MC, 14–16	16.9	11.0	39.6	119	85	23	8
71MC, 18–20	10.7	9.9	27.2	124	93	36	4
71MC, 22–24	14.3	10.5	35.0	127	83	25	10
71MC, 26–28	12.8	10.9	33.7	137	95	28	4
71MC, 30–32	12.7	11.0	30.1	118	88	27	3
71MC, 34–36	14.8	11.1	37.4	121	97	30	3
71MC, 38–40	12.3	9.9	29.1	115	88	30	3
71MC, 42–44	10.2	9.0	27.8	129	102	36	5
71MC, 46–48	13.7	10.0	38.8	153	106	22	3
81MC, 0–1	3.3	9.1	9.3	157	95	23	2
81MC, 1–2	3.4	10.3	7.2	110	72	28	5
81MC, 2–3	2.6	8.4	5.6	116	74	24	5
81MC, 4–5	2.2	9.1	5.2	134	89	13	4
81MC, 6–8	3.8	11.5	5.2	70	48	15	3
81MC, 10–12	3.0	10.5	4.3	79	55	9	3
81MC, 14–16	2.7	9.0	4.9	94	65	19	4

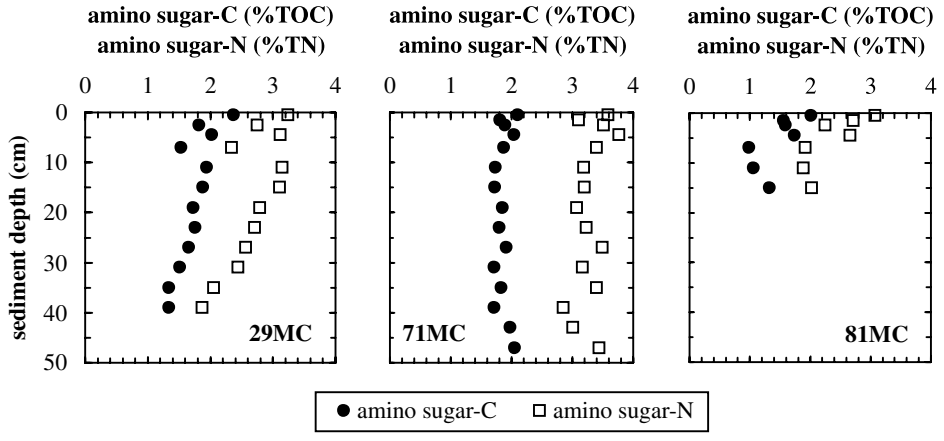

Fig. 2. Depth profiles of amino sugar carbon as percent of total organic carbon and of amino sugar nitrogen as percent of total nitrogen at 29MC, 71MC, and 81MC.

71MC and 81MC) and in general, GlcN/GalN ratios were higher near the sediment surface than deeper in the cores. A continuous down-core decrease was only observed at 81MC.

The molar ratios of glucosamine and mannosamine (GlcN/ManN, data not shown) ranged from 3.5 to 10.0. They showed strong scatter in the upper part of all sediment cores and distinct decrease deeper in the cores at sites

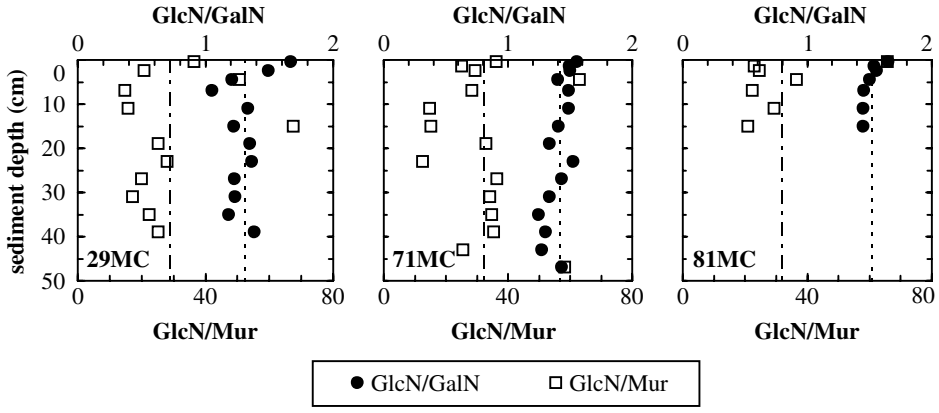

Fig. 3. Molar ratios of glucosamine to galactosamine (GlcN/GalN) and glucosamine to muramic acid (GlcN/Mur) versus sediment depth at 29MC, 71MC, and 81MC. Dotted lines give average GlcN/GalN-ratios; broken lines give average GlcN/Mur-ratios at the respective sites.

29MC and 71MC. In general, GlcN/ManN ratios were higher at 29MC (6.6 ± 1.5) and 81MC (6.2 ± 2.2) than at 71MC (4.7 ± 1.0). The molar ratios of glucosamine and muramic acid (GlcN/Mur) fell in the range 13–68 and showed strong scatter throughout the cores (Fig. 3). Part of this high variability can be explained by the rather low analytical precision related to Mur analysis.

4. Discussion

4.1. Contribution of amino sugars to sedimentary organic carbon and nitrogen

The fractions of TOC and TN that are made up by amino sugar carbon and nitrogen in the sediments off Peru fall within the range of values previously reported for sediments from different oceanic regions, and various water and sediment depths (Table 2). Most published amino sugar studies were limited to the analysis of GlcN and GalN. However, the concentrations of these two compounds provide a good estimate for the total amino sugar concentration since Mur and ManN together contribute a maximum of 16% to the total amino sugar pool of sediments (this study; Liebezeit, 1993) and marine POM (Benner and Kaiser, 2003).

The down-core decrease of amino sugar carbon and amino sugar nitrogen contributions at 29MC and 81MC (Fig. 2) suggest a preferential degradation of amino sugars compared to bulk sedimentary OM during diagenesis. In general, down-core decreasing concentrations might also be interpreted as representing changes in input over time. However, down-core profiles of other sediment parameters, like chlorin and lipid concentrations and bulk organic carbon isotopic compositions, show no indications for major compositional changes of the OM that accumulated in the investigated sediments (Niggemann, unpublished results). Therefore, we assume that the amino sugar content of the OM reaching the sediments was constant over the time span sampled. Consequently, down-core decreasing amino sugar yields at 29MC and 81MC are interpreted as the result of OM degradation. An increasing degradation state with sediment depth at these two sites is also indicated by increasing C/N-ratios (Table 1) and increasing Chlorin Indices (Niggemann, unpublished results), the latter providing a measure for the freshness of sedimentary chlorins (Schubert et al., 2005). The finding that more degraded OM is impoverished in amino sugars is in accord with observations of Liebezeit (1993) who reported that in a 12-m long core from the Bransfield Strait, turbidite

Table 2
Amino sugar carbon (in % TOC) and amino sugar nitrogen (in % TN) concentrations and GlcN/GalN-ratios reported for sediments from different oceanic regions and water depths, in comparison to results of this study

Location	Water depth (m)	Sediment depth (cm)	Amino sugar-C (% TOC)	Amino sugar-N (% TN)	GlcN/GalN	Reference
North Sea	3–270	0–15	1.1–2.3 (1.7)[a]	1.3–4.2 (2.7)[a]	0.3–16.3 (3.6)[a]	Dauwe and Middelburg (1998)
Antarctic Ocean	2983	0–35	0.4–1.4	n.a.[b]	1.2 ± 0.3[c]	Liebezeit (1993)
Antarctic Ocean	1951	0–38	0.8–1.2	n.a.[b]	1.2 ± 0.2[c]	Liebezeit (1993)
Antarctic Ocean	1956	0–1150	0.5–1.5	n.a.[b]	1.2 ± 0.2[c]	Liebezeit (1993)
Bay of Bengal	3290	Surface	0.8	1.2	1.2	Gupta et al. (1997)
Brazil margin	940–1280	0.0–0.5	2.1–3.2 (2.6)[a]	3.9	1.1–1.3 (1.2)[a]	Jennerjahn and Ittekkot (1999)
Peru margin	102–1278	0–47	1.0–2.4 (1.7)[a]	1.5–3.9 (2.9)[a]	1.1–1.7 (1.4)[a]	This study

[a] Values in parentheses give average values.
[b] n.a., not available.
[c] Mean ± SD.

sequences, typically dominated by reworked material, exhibited lower amino sugar concentrations (amino sugar-C: 0.5–1.1% of TOC) than sediments derived from pelagic sedimentation.

At 71MC relatively constant amino sugar concentrations throughout the core (Fig. 2) are consistent with a dominance of reworked, homogenized material. At this site, strong bottom currents cause intense mixing by suspension and redeposition of the mudwave sediment (Reinhardt et al., 2002). Several sediment parameters, e.g., increased C/N-ratios (Table 1) and low TOC-normalized concentrations of labile compounds like fatty acids and chlorins (Niggemann, 2005), indicate that the OM accumulating at 71MC is mostly in an advanced state of degradation. From what we showed above, accumulation of such refractory OM should be reflected in reduced amino sugar concentrations. However, the contributions of amino sugar carbon and amino sugar nitrogen to TOC and TN at the sediment surface are similar at all three sites (Fig. 2). The constant down-core profiles suggest that at 71MC, located in the center of the water column oxygen minimum zone, both bulk TOC (Table 1) and amino sugars are mostly inaccessible to microbial degradation, consistent with the low organic carbon mineralization rates observed at this site (Niggemann, 2005). OM that accumulates at 71MC—both from pelagic sedimentation and laterally imported resuspended material—is in contact to oxygen only during the short transit from the euphotic zone to the upper boundary of the oxygen minimum zone. An enhanced preservation of OM due to limited oxygen exposure time is in agreement with earlier studies of Hartnett et al. (1998) and Hedges et al. (1999).

4.2. Amino sugars as source and quality indicators

In the coastal upwelling region off Peru, primary production rates are high year-round (e.g., Zuta and Guillén, 1970), supplying a constantly high rain of fresh OM that is dominated by phytoplankton detritus. The contributions of amino sugar carbon and amino sugar nitrogen to TOC and TN in the investigated sediments off Peru are in the range of values reported for marine POM (Fig. 4). In general, freshly produced OM is characterized by low amino sugar concentrations, e.g., amino sugar carbon and nitrogen account for 0.1–0.5% of TOC and 0.1–0.6% of TN in phototrophic algae, and for 0.3–1.2% of TOC and 0.3–0.9% of TN in natural populations of heterotrophic bacteria (Benner and Kaiser, 2003). Higher concentrations of amino sugars in marine POM are mostly due to a contribution of chitin-rich material derived from zooplankton. High surface water productivity leads to an increase of phytoplankton biomass relative to zooplankton biomass and is therefore reflected in lower contributions of amino sugar carbon and amino sugar nitrogen to TOC and TN of bulk POM (Müller et al., 1986).

The amino sugar composition provides evidence that chitin was not a major contributor to the sedimentary amino sugar pool off Peru. Chitin is a polymer of GlcN and high chitin concentrations are reflected in high GlcN/GalN-ratios (up to >20), as reported for zooplankton-rich POM (Müller et al., 1986; Gupta et al., 1997; Gupta and Kawahata, 2000). The ratios observed in the sediments off Peru (1.1–1.7) are similar to those reported for small-size (0.1–60 μm), zooplankton-poor POM (Benner and Kaiser, 2003), and fall within the range of values previously observed in sediments (Table 2). Slightly lower GlcN/

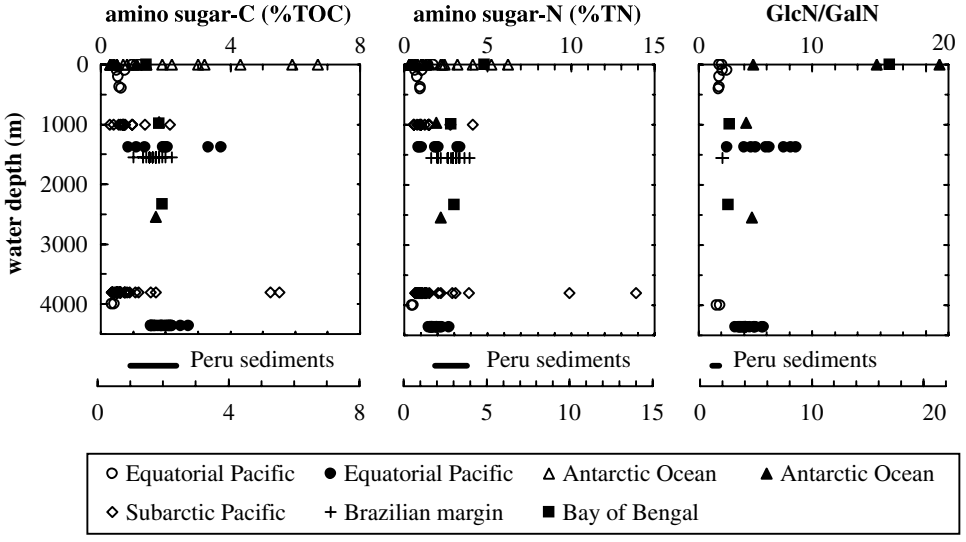

Fig. 4. Amino sugar carbon as percent of total organic carbon, amino sugar nitrogen as percent of total nitrogen, and GlcN/GalN-ratios reported for particulate organic matter (POM) from different oceanic regions and water depths plotted versus water depth. Equatorial Pacific (open circles: Benner and Kaiser, 2003; closed circles: Gupta and Kawahata, 2000), Antarctic Ocean (Müller et al., 1986; open triangles: 75–150 μm POM, closed triangles: >150 μm POM), Subarctic Pacific (Haake et al., 1993), Brazilian margin (Jennerjahn et al., 1999), Bay of Bengal (Gupta et al., 1997). Data ranges for Peruvian sediments (this study) are plotted for comparison.

GalN-ratios prevail in sediments from greater water depth (Liebezeit, 1993; Gupta et al., 1997; Jennerjahn et al., 1999), whereas ratios >10 were found in shallow coastal waters (<5 m water depth; Dauwe and Middelburg, 1998). Decreasing GlcN/GalN-ratios with increasing water depth reflect the rapid degradation of chitin in the water column. Chitin is relatively resistant to decay when complexed with protein in invertebrate cuticles (Baas et al., 1995), but once this protective coating is lost, the polysaccharide is easily broken down by enzymatic hydrolysis (Gooday, 1990). However, it is unlikely that chitinaceous material is preferentially degraded over biopolymers containing GalN. Consequently, decreasing GlcN/GalN-ratios indicate that during OM degradation the contribution of another amino sugar source with lower GlcN/GalN-ratio gradually increases. In other words, the amino sugar signature of chitin (high GlcN/GalN) may gradually be replaced by that of bacteria (GlcN/GalN $<\sim 3$; Benner and Kaiser, 2003). This transformation of planktonic into bacterial biomass might also explain the slight down-core decrease of GlcN/GalN-ratios in the sediments (Fig. 3).

The proposed scenario is supported by decreasing GlcN/ManN-ratios observed deeper in the sediment at 29MC and 71MC. As for GalN, a preferential preservation of ManN over GlcN is unlikely. The very low ManN concentrations found in natural samples suggest that ManN is not selectively preserved and the strong down-core decrease of ManN concentrations in the upper part at 29MC and 81MC is consistent with a rapid decomposition of ManN. ManN is common in bacterial products (Kenne and Lindburg, 1983) and widely distributed in membrane glycolipids as a building block of sialic acids. Reported GlcN/ManN-ratios are 2–46 for bacteria and 8–18 for algae, respectively (Benner and Kaiser, 2003; Glaser et al., 2004). The ratios observed in the investigated sediments (5.7 ± 1.7, $n = 34$) provide further evidence that during OM degradation bacterial biomass becomes dominant over algae material.

4.3. Bacterial contribution to living and dead sedimentary OM

Based on the concentrations of Mur, which occurs in a 1:1-ratio with GlcN in peptidoglycan, intact units of this bacterial cell wall polymer accounted for 4.0 ± 1.6 mol% of the total amino sugar pool and for 3.9 ± 1.6% of total GlcN. Since peptidoglycan is the only known source for Mur, this amino sugar is a specific biomarker for bacterial cell wall material. For sediment bacteria Moriarty (1977) suggested a Mur concentration of 60 nmol mgC^{-1} assuming a predominance of gram-negative bacteria, a value similar to Mur concentrations reported for cultivated soil bacteria (61 ± 25 nmol mgC^{-1}; Glaser et al., 2004). Using an average carbon content for pelagic coastal marine bacteria of 30.2 fg $cell^{-1}$ (Fukuda et al., 1998), we calculate an average bacterial Mur concentration of 1.8 amol $cell^{-1}$. This value is very close to Mur concentrations of cultivated sediment bacteria (1.9–2.1 amol $cell^{-1}$, Mimura and Romano, 1985). If all analyzed Mur was associated with intact bacterial cells, the observed Mur concentrations would reflect bacterial abundances of $0.02–0.79 \times 10^{12}$ cells gdw^{-1}, which equals $0.04–1.34 \times 10^{12}$ cells cm^{-3} wet sediment (with a dry weight/wet volume ratio of 1.7). These numbers are up to 500 times higher than counts of living bacteria in surface sediments off Peru ($\sim 3 \times 10^{9}$ cells cm^{-3}; Parkes et al., 1993), indicating that most Mur was not associated with living bacteria, but with cell wall remains. Bacterial abundance estimates based on the non-protein amino acid D-Ala, which is also associated with peptidoglycan, showed similar discrepancies between estimated and counted numbers (Pedersen et al., 2001; Grutters et al., 2002). Obviously, peptidoglycan persists in the sediments after the death of the cells. Hence, Mur concentrations in sediments are an indicator for bacterial necromass rather than for living bacterial biomass. Bacterial necromass has been suggested as a main component of refractory OM in sediments (Lee, 1992; Parkes et al., 1993), and there is growing evidence that cell wall remains make up a significant fraction of sedimentary OM (Pedersen et al., 2001; Grutters et al., 2002).

Considering the cell number estimates based on Mur concentrations and assuming the unlikely case that all bacterial carbon was preserved after the death of cells (30.2 fg $cell^{-1}$; Fukuda et al., 1998), bacterial carbon accounts for at most 3–17% of sedimentary TOC. These maximum estimates are much lower than bacterial biomass contributions to the carbon pool of decomposing phytoplankton (Harvey and Macko, 1997) and vascular plant tissue (Tremblay and Benner, 2006). Furthermore, these estimates are inconsistent with the presumed transformation of plankton OM into bacterial OM, suggested by the low and relatively constant GlcN/GalN and GlcN/ManN-ratios. Hence, although Mur is predominantly associated with dead bacterial material, it appears to be an indicator for rather fresh necromass. This is consistent with previous studies indicating that even though the turnover time of Mur is much longer than that of the living organism (Glaser and Gross, 2005), Mur is more labile than other amino sugars, particularly GlcN (Hicks et al., 1991; Ogawa et al., 2001; Nagata et al., 2003; Benner and Kaiser, 2003; Glaser and Gross, 2005; Tremblay and Benner, 2006).

The diagenetic lability of Mur has consequences for the applicability of the GlcN/Mur-ratio as a source indicator. In living gram-negative bacteria the majority of GlcN is not associated with peptidoglycan, and yields of Mur in natural and cultivated bacterial assemblages are 2–15-fold lower than those of GlcN (Benner and Kaiser, 2003; Glaser et al., 2004). Therefore, one would expect that high GlcN/Mur-ratios indicate living cells, whereas a dominance of dead cells, i.e., empty cell sacks, lowers this ratio towards the 1:1-ratio found in peptidoglycan. However, the opposite has been found in a decomposition study of plant tissue, where GlcN/Mur-ratios were lowest when bacterial activity was maximal and sharply increased when decomposition rates declined (Tremblay and Benner, 2006).

Accordingly, even the lowest GlcN/Mur-ratios observed in this study—minimum GlcN/Mur-ratio was 13—are much higher than the peptidoglycan ratio, indicating that although bacterial cell walls and their remnants may make up an important fraction of sedimentary OM, intact peptidoglycan units are only a minor contributor.

4.4. The remaining mystery of sedimentary amino sugars

So what are the main constituents comprising the sedimentary amino sugars? Obviously, the most prominent amino sugar polymers, chitin and peptidoglycan, cannot explain abundances and distribution of amino sugars in the investigated sediments. Low GlcN/GalN-ratios are inconsistent with chitin being a major contributor and high GlcN/Mur-ratios argue against a predominant role of peptidoglycan. Further, partly due to lack of data, we have no unambiguous explanation for abundance and distribution of ManN. However, ratios of GlcN/GalN and GlcN/Mur indicate that some remnants of bacterial cells are selectively preserved during OM degradation and rapidly imprinted on the composition of sedimentary OM.

In general, the interpretation of amino sugar data would profit from a clearer definition of the analytical window of amino sugar analysis. Hydrolysis conditions are optimized simply to maximize amino sugar yields and reported recoveries are limited to pure substances, i.e., simple biopolymers without association with protective matrices (Zhang and Amelung, 1996; Kaiser and Benner, 2000). We do not know whether the hydrolysis conditions chosen completely hydrolyze all fresh OM and whether they also successfully attack refractory OM. Compound-specific isotope analysis might help to identify different pools and further elucidate the biogeochemistry of amino sugars in sediments. First studies on carbon isotopic composition of amino sugars in soils revealed valuable information on different turnover times of individual amino sugars (Glaser and Gross, 2005).

This study provides further evidence that OM degradation results in a rather homogeneous amino sugar pool. Beside the narrow ranges covered by TOC- and TN-normalized sedimentary amino sugar carbon and amino sugar nitrogen concentrations, the ratio of the dominating amino sugars GlcN and GalN indicates a similar composition of the altered amino sugar pool (Fig. 3). A close association of GlcN and GalN in marine OM was also observed by Benner and Kaiser (2003), who report surprisingly narrow ranges of GlcN/GalN-ratios in POM and UDOM (1–2, average 1.5), and interpret them as a prokaryotic signature. Based on studies of bacterially specific D-amino acids, bacterial remains had previously been suggested to be a major component of refractory DOM in the ocean (Boon et al., 1998; McCarthy et al., 1998). In conclusion, our results support the proposed dominance of bacterially derived amino sugars in altered OM and thereby provide further evidence for a major prokaryotic source of refractory, molecularly mostly uncharacterized OM.

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