



# Amino acid composition and $\delta^{15}\text{N}$ of suspended matter in the Arabian Sea: implications for organic matter sources and degradation

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**Abstract.** Sedimentation in the ocean is fed by large aggregates produced in the surface mixed layer that sink rapidly through the water column. These particles sampled by sediment traps have often been proposed to interact by disaggregation and scavenging with a pool of fine suspended matter with very slow sinking velocities and thus a long residence time. We investigated the amino acid (AA) composition and stable nitrogen isotopic ratios of suspended matter (SPM) sampled during the late SW monsoon season in the Arabian Sea and compared them to those of sinking particles to understand organic matter degradation/modification during passage through the water column. We found that AA composition of mixed layer suspended matter corresponds more to fresh plankton and their aggregates, whereas AA composition of SPM in the sub-thermocline water column deviated progressively from mixed layer composition. We conclude that suspended matter in deep waters and in the mixed layers of oligotrophic stations is dominated by fine material that has a long residence time and organic matter that is resistant to degradation. SPM in areas of high primary productivity is essentially derived from fresh plankton and thus has a strong imprint of the subsurface nitrate source, whereas SPM at oligotrophic stations and at subthermocline depths appears to exchange amino acids and nitrogen isotopes with the dissolved organic carbon (DOC) pool influencing also the  $\delta^{15}\text{N}$  values.

## 1 Introduction

Most planktonic organisms and the mineral particles transported into the deep ocean are very small and have very low sinking velocities, so that oceanic sedimentation depends mainly on the formation and settling of large particles (Degen and Ittekkot, 1987; McCave, 1984). These are, generally, formed in surface water involving biological processes. Fecal pellets are a minor proportion of sinking particles (Pilkal and Honjo, 1987), whereas macroscopic aggregates of organic and inorganic matter, the so called marine snow, are the major means of transport of material to the sediments (Aldredge and Silver, 1988). Contrary to the large sinking particles small suspended particles with low sinking velocities remain suspended for months to years if not scavenged by the rare sinking particles (McCave, 1984). Whereas sediment traps, deployed over days or weeks in the water column, are suitable to sample sinking aggregates, filtration of conventional water samples collects the fine grained SPM which does not sink (Silver et al., 1998). There is evidence that in-situ filtration systems sample both fine and large particles so that their composition is intermediate between that of material intercepted by sediment traps and that obtained by filtration of water samples (Abramson et al., 2011; Bishop et al., 1985).

Total organic matter concentrations as well as labile constituents of organic matter in sinking particles intercepted by sediment traps decrease with increasing water depth (Haake et al., 1993a; Haake et al., 1992; Lee et al., 2000). This

suggests that degradation proceeds on large aggregates while sinking in the water column despite their rapid sinking speeds of  $10\text{--}150\text{ m d}^{-1}$  (McDonnell and Buesseler, 2010). Studies of organic constituents such as pigments, AAs, and fatty acids suggest that organic matter in SPM is less degraded than that of sinking particles (Abramson et al., 2011; Lee et al., 1983; Rontani et al., 2011; Wakeham and Canuel, 1988). This is somewhat counterintuitive, as the much longer residence time of fine particles in the water column would imply stronger degradation of organic matter (Degens and Ittekkot, 1987; McCave, 1984). Based on these observations, models of particle aggregation and disaggregation with differential settling of labile and refractory matter have been formulated (Abramson et al., 2011; Lee et al., 1983; Wakeham and Canuel, 1988) with a central concept of photo-oxidation of lipids to radicals in SPM of surface waters that makes them resistant towards biotic degradation (Rontani et al., 2011).

AAs are frequently used to characterise and quantify the degradation state of organic matter. Indicators are AA concentrations, especially their contributions to organic carbon (AA-C %) or nitrogen (AA-N %; Cowie and Hedges, 1994), as well as specific changes in AA monomer distributions. Ratios of individual AAs such as Asp/ $\beta$ -Ala and Glu/ $\gamma$ -Aba (Cowie and Hedges, 1994; Ittekkot et al., 1984b; Lee and Cronin, 1984), or the more complex Reactivity Index (RI; Jennerjahn and Ittekkot, 1997) and Degradation Index (DI; Dauwe and Middelburg, 1998; Dauwe et al., 1999) have been established to classify organic matter degradation (Ingalls et al., 2003; Möbius et al., 2010; Pantoja et al., 2004; Unger et al., 2005). These biogeochemical indicators of organic matter quality were essentially developed for marine sinking particles and sediments. They are of limited use in other sample sets and materials, such as marine SPM and samples from fresh and brackish waters, so that individual and adapted indices (usually derived from statistical analyses of compositional data by principal components analysis PCA) must be developed to differentiate states of degradation (Abramson et al., 2011; Gaye et al., 2007; Goutx et al., 2007; Menzel et al., 2013; Sheridan et al., 2002).

To contribute to the understanding of oceanic particle dynamics and organic matter degradation we collected particulate matter from the Arabian Sea by filtration of large volumes of water (i) from conventional samplers and (ii) by in situ pumps and analysed the particles for AA composition and stable nitrogen isotopic ratios ( $\delta^{15}\text{N}_{\text{PN}}$ ). These data are compared to data from long-term trap investigations in the Arabian Sea (Gaye-Haake et al., 2005; Haake et al., 1992; 1996; Rixen et al., 2009; Schäfer and Ittekkot, 1993, 1995). Nutrient data and  $\delta^{15}\text{N}$  values of nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$ ) are available from some of the sampling sites (Gaye et al., 2013; Rixen et al., 2013) and permit an evaluation of  $\delta^{15}\text{N}_{\text{PN}}$  in relation to the dissolved nitrate source. This serves to test whether SPM influences and contributes to the  $\delta^{15}\text{N}$  signal exported from the mixed layer into the deep ocean.

## 2 Material and methods

### 2.1 Study area

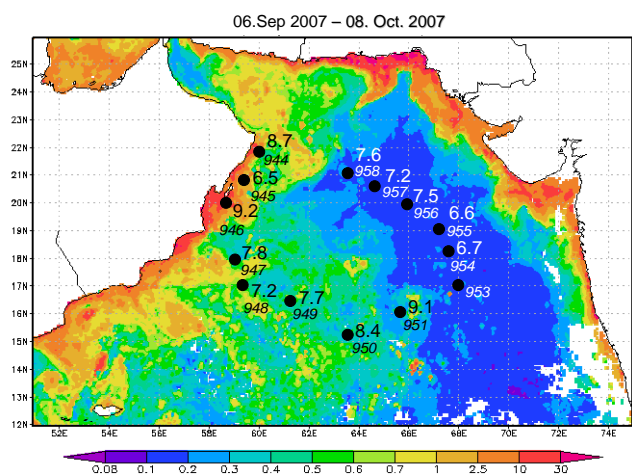
The Arabian Sea is highly productive due to monsoon-driven upwelling of thermocline nutrients along the western margins off Oman and Somalia (Fischer et al., 1996; Wiggert et al., 2005; Woodward et al., 1999). It also hosts one of the world's major oxygen deficient zones (ODZ) situated between 100 m and about 1200 m water depth. There, about one third of the global oceanic nitrogen loss occurs (Gruber, 2008; Gruber and Sarmiento, 1997) mostly due to heterotrophic denitrification (Bulow et al., 2010; Ward et al., 2009). This process has a strong isotopic effect of  $20\text{--}30\text{ ‰}$  (Altabet et al., 1999a; Brandes et al., 1998; Cline and Kaplan, 1975), so that  $\delta^{15}\text{N}_{\text{NO}_3}$  values in the upper ODZ of the Arabian Sea are high and reach up to  $>20\text{ ‰}$  (Yoshinari et al., 1997). Upwelling off Oman occurs during the SW monsoon from June to September, when Ekman pumping brings water from 150 m water depth to the surface (Morrison et al., 1998).  $^{15}\text{N}$  enriched nitrate from the top of the ODZ then reaches the euphotic zone and is further converted into particulate matter by primary producers.

Strongest denitrification is not encountered in the most productive region off Oman but in the northeastern Arabian Sea as reflected in maximum nitrite accumulation in the oxygen-deficient water column interval (Naqvi, 1987, 1991; Yoshinari et al., 1997). This spatial decoupling of the productivity and denitrification maxima is related to the circulation in the basin. The oxygenated Indian Central Water (ICW) enters the Arabian Sea from the southwest (SW) and becomes oxygen and nitrate depleted on its way to the east (Böning and Bard, 2009; Morrison, 1997; Morrison et al., 1998). Local source of mid-water re-oxygenation are the Persian Gulf Water and the Red Sea Water in the western Arabian Sea (Mantoura et al., 1993; Prasad et al., 2001), and a seasonal (SW-monsoonal) undercurrent from the Bay of Bengal flowing north along the Indian margin (Naqvi et al., 2006).

Sediment trap studies in offshore areas and at the Pakistan margin (Gaye-Haake et al., 2005; Schäfer and Ittekkot, 1993) reveal that  $\delta^{15}\text{N}$  of sinking particles sampled in bimonthly to monthly resolution range from  $5$  to  $9\text{ ‰}$  with inter-annual averages ranging from  $5.7\text{--}8.2\text{ ‰}$  (Supplement 1). Early diagenetic processes and diagenetic enrichment at the sediment water interface prior to burial further increases the  $\delta^{15}\text{N}$  of surface sediments to values  $>12\text{ ‰}$  in the central Arabian Sea (Gaye-Haake et al., 2005; Möbius et al., 2011).

#### 2.1.1 Sampling and data source

Water samples were taken at 14 stations with a Seabird SBE 32 Water Sampler equipped with 10 L PVC sample bottles during cruise R/V Meteor 74/1b (Fig. 1). Between 3 L and 45 L of water were filtered on pre-combusted ( $450\text{ }^\circ\text{C}$  overnight) and pre-weighed Whatman GF/F glass fibre filters



**Fig. 1.** Sampling locations in the Arabian Sea. Location numbers are in italic letters, large font indicates  $\delta^{15}\text{N}_{\text{PN}}$ . Colours indicate chl *a* concentrations in  $\text{mg m}^{-3}$  from satellite observations between 6 September and 8 October 2007, available from [http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance\\_id=ocean\\_8day](http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=ocean_8day).

(47 mm diameter) at water depths between 0 m (surface) and 450 m. At five stations in-situ pumps (McLane WTS LV) were used which filtered between 200 L and 950 L water on pre-combusted (450 °C overnight) Whatman GF/F filters (142 mm diameter). Samples were dried at 40 °C for two days and the dry weight of 47 mm filters was used to determine total suspended matter concentrations (SPM) in  $\text{mg L}^{-1}$ . Samples from in-situ pumps were only used for  $\delta^{15}\text{N}$  analyses as filters were not pre-weighed.

The discussion of AAs is based on SPM results shown in Table 1 and AA data of plankton and sediment trap samples taken from Gaye-Haake et al. (2005) and Schäfer and Ittekkot, (1993). Bulk composition of these trap samples is shown in Supplement 1. AA spectra in Mol % of all samples used in this study are shown in Supplement 2. The discussion of nitrate assimilation and  $\delta^{15}\text{N}_{\text{PN}}$  is based on data from SPM of water samplers and in situ pumps and the available data of nitrate concentrations from Rixen et al. (2013) and  $\delta^{15}\text{N}_{\text{NO}_3}$  from Gaye et al. (2013) shown in Table 1.

## 2.2 Analyses

Total carbon and nitrogen were measured by a Carlo Erba Nitrogen Analyser 1500 (Milan, Italy). Particulate organic carbon (POC) was determined after three acid treatments of samples to remove carbonate. Precision of this method is 0.05 % for carbon and 0.005 % for nitrogen. Organic matter (OM) was calculated by multiplying the organic carbon content with 1.8 (Müller et al., 1986). Carbonate carbon is the difference between total and organic carbon. Ratios of  $^{15}\text{N}/^{14}\text{N}$  of particulate nitrogen ( $\delta^{15}\text{N}_{\text{PN}}$ ) were determined using a Delta Plus XP isotope ratio mass spectrometer connected with a ConFlo-III interface after high-temperature

flash combustion in a Thermo Finnigan Flash EA 1112 at 1050 °C. Isotope ratios are reported in ‰ using the delta-notation

$$\delta^{15}\text{N}_{\text{sample}} = \left( \left( \frac{^{15}\text{N}/^{14}\text{N}}{\text{sample}} \right) / \left( \frac{^{15}\text{N}/^{14}\text{N}}{\text{reference}} \right) - 1 \right) \times 1000$$

Pure tank  $\text{N}_2$  calibrated against the reference standards IAEA-N1 (ammonium sulfate,  $\delta^{15}\text{N} = +0.4$  ‰) and IAEA-N2 (ammonium sulfate,  $\delta^{15}\text{N} = +20.3$  ‰) of the International Atomic Energy Agency was used as a working standard.  $\delta^{15}\text{N}$  is given as the per mil deviation from the N-isotope composition of atmospheric  $\text{N}_2$ . Duplicate measurements of samples differ by less than 0.15 ‰. The laboratory's long-term  $2\sigma$  standard deviation for IAEA-N1 standard is 0.09 ‰.

Nutrient concentrations in filtered water samples were determined by a Skalar Autoanalyser and  $\delta^{15}\text{N}_{\text{NO}_3}$  were determined using the “denitrifier method” (Casciotti et al., 2002; Sigman et al., 2001); data are taken from Rixen et al. (2013) and Gaye et al. (2013).

Total hydrolysable AAs and hexosamines (HA) were analysed with a Biochrom 30 Amino Acid Analyser after hydrolysis of ca. 1–2 mg for suspended particulate matter (collected on GF/F filters) with 6 N HCl for 22 h at 110 °C under a pure argon atmosphere. A particle free aliquot was three times evaporated to dryness in order to remove the unreacted HCl; the residue was taken up in an acidic buffer (pH: 2.2). After injection and subsequent separation with a cation exchange resin, the individual AA monomers were post-column derivatized with o-phthaldialdehyde in the presence of 2-mercaptoethanol and detected with a Merck Hitachi L-2480 fluorescence detector. Duplicate analysis of a standard solution according to this method results in a relative error of 0.1 to 1.3 % for the concentrations of individual AA monomers and 0.2 to 3.0 % for individual AA monomers of SPM samples. Molar percentages of individual monomers are used to calculate the RI and the DI. The RI is a ratio of the labile AAs Tyr and Phe divided by the sum of the non-protein AAs  $\beta$ -Ala and  $\gamma$ -Aba (Jennerjahn and Ittekkot, 1997). The DI assesses the diagenetic alteration of a sample by comparing it to a set of 28 samples of different degradational states and environments compiled by Dauwe und Middelburg (1998) and Dauwe et al. (1999). Molar percentages of 14 individual AAs are standardized by the mean and standard deviation of the 28 samples dataset. The DI then integrates the AAs weighed by the factor coefficients for the first axis of the principal component analyses (PCA) of Dauwe et al. (1999) according to the formula:

$$\text{DI} = \sum_i \left[ \frac{\text{var}_i - \text{AVGvar}_i}{\text{STDvar}_i} \right] \cdot \text{fac.coef.}_i \quad (1)$$

where  $\text{var}_i$  is the original mole percentage of each  $\text{AA}_i$ ,  $\text{AVGvar}_i$  and  $\text{STDvar}_i$  are the mean and standard deviations, respectively, and  $\text{fac.coef.}_i$  is the factor coefficient of the first



Table 1. Continued

Station No.	Depth [m]	$\text{NO}_3^-$ [ $\mu\text{mol}$ ]	$\delta^{15}\text{N}_{\text{NO}_3}$ [‰]	$\delta^{15}\text{N}_{\text{PN}}$ [‰]	SPM [ $\text{mg L}^{-1}$ ]	POC [ $\mu\text{g L}^{-1}$ ]	POC [%]	OM [%]	N [%]	C/N	Car-bonate [%]	AA + HA [ $\mu\text{g L}^{-1}$ ]	AA + HA [ $\text{mg g}^{-1}$ sed.]	ASP/ $\beta$ -ALA	GLU/ $\gamma$ -ABA	RI	DI	AA-C [%]	AA-N [%]
956	0			7.48	0.33	72.4	22.1	39.8	3.64	7.1	1.8	56.8	173.3	165.8	112.0	30.4	1.01	33.6	66.2
	25			7.30	0.42	75.1	17.9	32.2	2.64	7.9	0.0	67.4	160.5	155.1	186.0	41.2	1.13	39.0	84.0
	50				0.45	92.8	20.7	37.3	3.13	7.7		79.1	176.4	109.7	159.6	31.7	0.98	36.6	63.4
	100			9.43	0.20	36.1	17.7	31.9	3.29	6.3	3.7	39.1	191.6	150.4	209.4	40.2	0.97	45.9	86.2
	300			8.85	0.26	40.6	15.7	28.3	3.85	4.8	8.2	36.2	140.5	358.6	139.5	39.9	0.96	37.9	60.0
957	0	0.18		7.23	0.28	64.4	22.8	41.1	3.85	6.9	4.1	50.3	178.4	46.8	116.0	18.0	1.03	33.7	63.6
	5	0.16																	
	10	0.17		5.71*															
	15	0.17																	
	25	2.46																	
	50	18.50		5.01*															
	75	22.06	8.11																
	200	16.98		9.41*															
958	0			7.55	0.24	52.2	21.9	39.4	4.02	6.4	2.4	52.7	221.2	113.2	113.9	30.9	1.10	43.9	75.5
	25			7.43	0.27	62.9	23.2	41.8	4.04	6.7	3.9	54.1	199.9	159.1	141.9	38.9	0.97	37.1	68.3
	40			7.25	0.31	64.6	20.9	37.6	4.17	5.8		60.9	197.0	168.2	129.8	39.7	1.02	41.0	64.6
	100			8.75	0.23	33.8	14.6	26.3	2.74	6.2	3.7	33.3	144.2	134.9	124.4	30.5	0.99	42.0	73.7
	300			8.70	0.21	36.6	17.7	31.8	3.36	6.1	6.4	32.0	154.6	178.0	103.7	29.8	0.98	37.1	64.9

axis of the PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation of the 14 AAs with respect to an assumed average molar composition. Higher (lower) values of RI and DI indicate less (more) degradation.

### 3 Results

#### 3.1 SPM, POC, and nitrogen

SPM concentrations between  $1.3\text{--}8.2\text{ mg L}^{-1}$  in Arabian Sea surface waters were encountered at the western stations off Oman (#944–#947) (Fig. 2a). POC concentrations were elevated ( $205\text{--}860\text{ }\mu\text{g L}^{-1}$ ) in the surface mixed layer of these stations, and also along the southern transect (#948–953; Fig. 2b), and both SPM and POC concentrations decreased with depth at these stations (Fig. 2a, b, Table 1).  $\text{SPM} \leq 0.5\text{ mg L}^{-1}$  and  $\text{POC} \leq 100\text{ }\mu\text{g L}^{-1}$  occurred along the northern transect (#954–958) in surface waters and below 100 m at all locations (Table 1).

C/N ratios of SPM on filters are between 5 and 10 with no apparent depth trend. Organic carbon weight percentages vary between 3 and 27 % (Table 1). Lowest percentages were observed in the samples from the western Arabian. Some of these stations have considerably elevated POC concentrations in surface SPM. Samples of the northern transect and most deep samples have POC percentages between 15 and 25 % with no apparent depth related trend. Carbonate percentages are relatively low with values between 0 and 12.6 %.

#### 3.2 $\delta^{15}\text{N}$ ratios of particulate nitrogen

$\delta^{15}\text{N}_{\text{PN}}$  show no clear trend with depth and reveal the largest difference between stations in surface waters < 100 m depth with values of 4.5 to 9.3 ‰ (Fig. 3).  $\delta^{15}\text{N}_{\text{PN}}$  values are between 8.5 and 9.6 ‰ at 100–150 m depth and between 6.9 and 9.4 ‰ at  $\geq 200$  m water depth, respectively (Fig. 3; Table 1). The  $\delta^{15}\text{N}_{\text{PN}}$  of samples from deep-sea pumps are

slightly depleted compared to SPM from water samplers in samples at 15–50 m. The observed differences are quite small and may as well be due to spatial variations in  $\delta^{15}\text{N}_{\text{PN}}$  of the Arabian Sea rather than to the two different techniques.

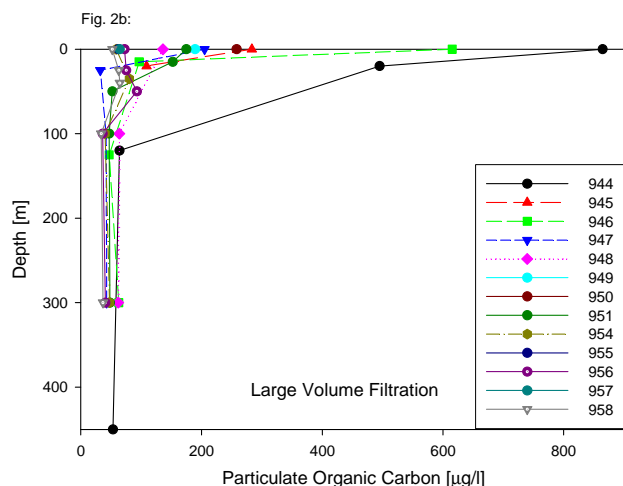
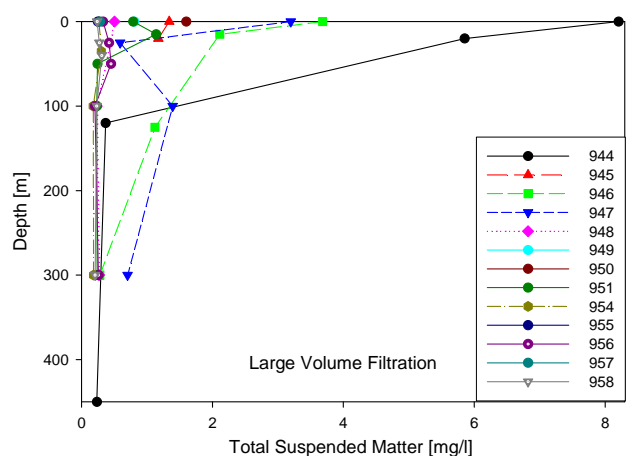
#### 3.3 Amino acids

In the Arabian Sea total hydrolysable AA concentrations are significantly correlated with POC concentrations ( $R^2 = 0.64$ ;  $n = 40$ ) and with N concentrations ( $R^2 = 0.82$ ;  $n = 40$ ). AA and HA concentrations are between 28 and  $297\text{ mg g}^{-1}$  of dry SPM and comprise 20–60 AA-C % and 50–100 AA-N %, respectively. The non-protein AAs are present only in trace amounts so that Asp/ $\beta$ -Ala and Glu/ $\gamma$ -Aba ratios are  $> 100$  in most samples. The DI values are around 1 and the RI values are between 9 and 55, respectively (Table 1). Similar to POC, AA concentrations, AA-C % and AA-N % have no depth trend at stations #951–958.

### 4 Discussion

#### 4.1 SPM concentrations and composition

High SPM and organic carbon concentrations with maxima at stations #944 and #946 were observed in the western Arabian Sea where upwelling was still active in late September 2007 (Fig. 2a and b). The negative correlation between sea surface temperature (SST) and POC concentrations in surface waters ( $R^2 = -0.81$ ,  $n = 14$ ) suggests a close relationship between upwelling related primary productivity and surface water POC concentrations. SPM concentrations are also negatively correlated with SST, but the correlation is less significant. The reason is, probably, a dilution caused by the dust input from the Arabian Peninsula which is very high during the SW monsoon (Ramaswamy et al., 1991). SPM concentrations drop immediately below the thermocline to values below  $0.5\text{ mg L}^{-1}$  equivalent to those in surface water

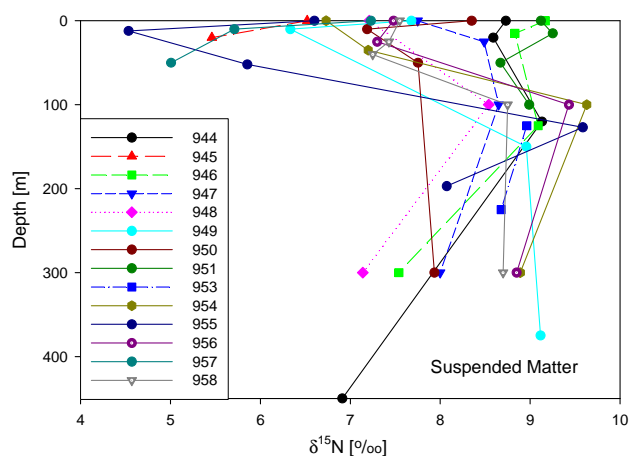


**Fig. 2.** Total suspended matter concentrations (a) and particulate organic carbon concentrations (b) in vertical profiles from the Arabian Sea. Station numbers are indicated in Fig. 1.

along the northern oligotrophic transect. Concentrations below  $0.5 \text{ mg L}^{-1}$  thus represent the standing stock of subthermocline SPM in the Arabian Sea. Elevated SPM concentrations in the surface mixed layer are evidently due to seasonally or locally enhanced productivity, when fresh biomass adds to the standing stock. Minima of SPM and POC concentrations are  $\sim 0.2 \text{ mg L}^{-1}$  and  $\sim 40 \text{ µg L}^{-1}$ , respectively. The mass of POC extrapolated over a water column of 3000–4000 m is between  $120\text{--}160 \text{ g C m}^{-2}$ . Annual average export production of the Arabian Sea is  $\sim 90 \text{ g C m}^{-2} \text{ a}^{-1}$  (Rixen et al., 2005) and the available estimate of the mean residence time water in the ODZ is about  $11 \pm 4 \text{ yr}$  (Olson et al., 1993). The exchange between sinking and suspended POC may, thus, be quite limited.

#### 4.2 Source of organic matter as indicated by amino acid spectra

AA composition of SPM deviates from Arabian Sea plankton, sinking particles and surface sediments. Whereas sink-



**Fig. 3.** Vertical profiles of  $\delta^{15}\text{N}_{\text{NP}}$  in large volume filtration samples from conventional water samplers and in situ pumps.

ing particles (intercepted by sediment traps) and sediments have patterns dominated by Gly > Asp > Glu > Ala (Haake et al., 1992), SPM is dominated by Gly > Glu > Asp > Ser. SPM samples have lower Mol-% non-protein AA ( $\beta$ -Ala and  $\gamma$ -Aba) and considerably higher AA-C % and AA-N % than sinking particles and sediments (Haake et al., 1996), which would suggest that organic matter in SPM is less degraded. Also, commonly used indicators such as Asp/ $\beta$ -Ala and Glu/ $\gamma$ -Aba ratios, and the DI and RI reveal no trend with depth, which would imply that the SPM pool below the surface mixed layer is entirely homogeneous (Table 1; see methods for explanation). But these indicators were developed to trace mineralization and organic matter degradation of sinking particles and sediments (Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Dauwe et al., 1999; Ittekkot et al., 1984a, b; Jennerjahn and Ittekkot, 1997; Lee, 1988), and are likely unsuitable or too coarse to track changes in SPM. To recognise compositional differentiation of SPM, we carried out a PCA of AA Mol-% for the SPM sample set. The highest positive factor loadings were contributed by the AAs Asp, Thr, Ala, Val, Ile, Leu and Phe of which most are abundant in fresh plankton (Gaye et al., 2007; Ingalls et al., 2006; Lee, 1988). The AAs with negative factor loadings (Ser, Glu, Gly and Arg) are some of those considered as typical for carbonaceous and siliceous frustules (Cowie and Hedges, 1992; Hecky et al., 1973), but have so far not been encountered to group in amino acid PCAs (Gaye et al., 2007; Ingalls et al., 2006) (Table 2). This factor thus distinguishes samples based on the presence or absence of fresh plankton. In consequence the scores of individual samples have a clear trend with depth from high scores in shallower samples to low scores in deep samples. Moreover, samples from the mixed layers and the sub-thermocline of high production sites have higher F1 scores than those from less productive sites (Table 2). The basic trend is an enrichment of Glu, Gly and Ser in deep SPM and in low-productivity surface waters, whereas

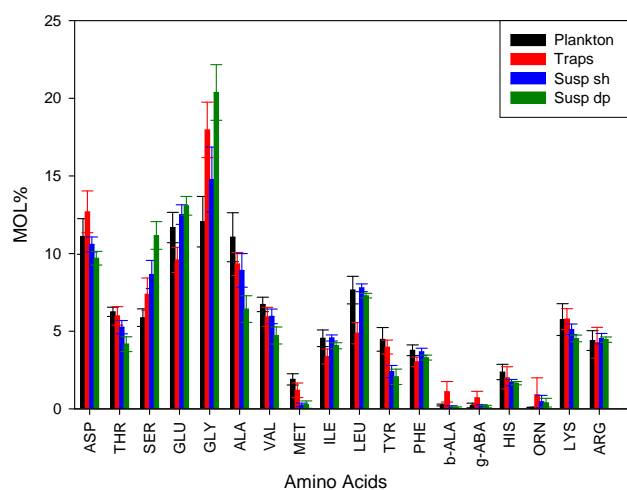
**Table 2.** Factor loadings of individual AAs of a PCA carried out with all analysed amino AAs in Mol % of all SPM samples and a PCA of Mol % of all AAs carried out of SPM, plankton and trap samples (data in Supplement 2). Factor scores of individual SPM samples of the two PCAs sorted by the factor scores of the first factor (F1) of the PCA of SPM only. The sorting is very similar to that of the factor F2 of the PCA which includes SPM, plankton and trap samples (see text for explanation).

Amino Acid	PCA SPM	PCA SPM + Plankton + Traps			PCA SPM	PCA SPM + Plankton + Traps	
	F1 Loading	F1 Loading	F2 Loading		F1 Score	F1 Score	F2 Score
Asp	0.098	0.091	0.002	944-S	1.77	-0.321	1.998
Thr	0.107	0.087	0.125	946-S	1.44	-0.132	1.283
Ser	-0.100	-0.084	-0.129	944-20 m	1.40	-0.238	1.612
Glu	-0.080	-0.099	0.024	950-S	1.34	-0.413	1.594
Gly	-0.107	-0.021	0.231	945-20 m	1.33	-0.118	1.263
Ala	0.105	0.068	0.175	951-15 m	1.06	-0.335	1.331
Val	0.106	0.057	0.195	949-S	0.95	-0.723	1.343
Met	0.014	0.086	0.011	951-S	0.91	-0.299	1.245
Ile	0.102	-0.07	0.170	945-S	0.86	-0.426	1.225
Leu	0.070	-0.089	0.117	946-15 m	0.82	-0.469	1.235
Tyr	0.032	0.092	-0.004	944-120 m	0.74	-0.444	0.566
Phe	0.097	-0.052	0.188	948-S	0.74	-0.434	0.763
$\beta$ -Ala	0.048	0.094	-0.069	958-40 m	0.62	-0.575	0.943
$\gamma$ -Aba	0.045	0.089	-0.059	958-S	0.56	-0.615	0.749
His	0.018	0.084	-0.044	954-S	0.53	-0.686	0.738
Orn	0.031	0.028	-0.029	954-35 m	0.50	-0.424	0.675
Lys	0.069	0.08	0.008	953-S	0.38	-0.833	0.800
Arg	-0.023	-0.029	0.005	957-S	0.31	-0.762	0.384
				956-25 m	0.25	-0.882	0.606
				955-S	0.19	-0.773	0.394
				946-125 m	0.13	-0.743	0.244
				958-25 m	-0.05	-0.848	0.176
				951-50 m	-0.11	-0.834	0.100
				956-50 m	-0.15	-0.920	-0.017
				948-300 m	-0.48	-0.969	-0.347
				946-300 m	-0.53	-0.976	-0.565
				956-S	-0.54	-1.075	-0.370
				944-450 m	-0.55	-0.875	-0.640
				947-100 m	-1.00	-1.178	-0.921
				958-100 m	-1.03	-1.198	-0.999
				956-300 m	-1.15	-1.276	-1.089
				954-100 m	-1.20	-1.033	-1.228
				951-300 m	-1.26	-1.107	-1.541
				951-100 m	-1.39	-1.356	-1.248
				958-300 m	-1.40	-1.230	-1.418
				954-300 m	-1.40	-1.261	-1.489
				956-100 m	-1.46	-1.330	-1.393
				948-100 m	-1.48	-1.375	-1.309
				947-300 m	-1.63	-1.401	-1.561

mixed-layer SPM in productive areas resembles fresh plankton (Fig. 4; Supplement 2).

The depth-related change in AA composition of SPM found in this PCA is different from that observed in sinking particles. Bacterial degradation of sinking fresh plankton and attached bacteria of similar AA composition (Cowie and Hedges, 1992) progresses with depth and shifts the amino acid composition to typical degradation products of proteino-

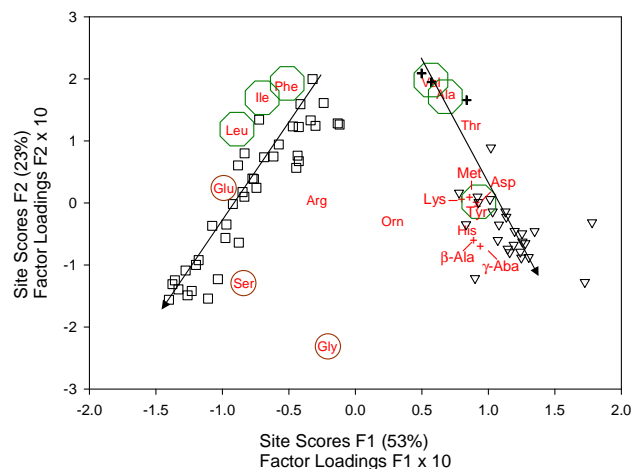
genic AAs, such as the non-protein AAs  $\beta$ -Ala,  $\gamma$ -Aba and Orn (Cowie and Hedges, 1994; Lee and Cronin, 1982; 1984). SPM from the euphotic zone in our sample set is similar to sinking particles caught at 1000–3000 m depth, whereas SPM in samples from depths  $\geq 100$  m is different (Fig. 4; data from Haake et al., 1992; 1996; Supplement 2). Results of a second PCA of all SPM AA spectra from this dataset, average values for sediment trap deployment periods between



**Fig. 4.** AA distribution in Mol % averaged for plankton, suspended matter from the mixed layer (Susp sh), deeper waters (Susp dp) and sediment trap samples (from Haake et al., 1992, 1996).

1986 and 1990, and plankton samples from the Arabian Sea corroborate that SPM on the one hand and plankton/sinking materials on the other hand are compositionally different (Fig. 5). The first factor (53 % of the total variance) has positive loadings of Val, Ala, Thr, Lys, Met, Tyr, Asp, His,  $\beta$ -Ala and  $\gamma$ -Aba, and negative factor loadings of Ser, Glu, Ile and Leu. Scores of individual samples on this factor clearly separate SPM (negative scores) from plankton and trap samples (positive scores). The second factor (23 % of the total variance) reveals modifications related to water depth. High scores mark trap and SPM samples from shallow depths, and low scores SPM samples from sub-thermocline depths and deeper traps. Negative scores of trap samples are related to the enrichment of degradation products Orn and the non-protein AAs, as well as His and Gly. Negative scores of deep SPM are mainly due to the negative loadings of Ser and Gly. The second factor produces a similar order of SPM samples in the expanded dataset including sinking matter and fresh plankton, as the factor analyses carried out using SPM only (Table 2). The results of the second PCA illustrate the difference between sinking and suspended particles and show that AA spectra of SPM and sinking particles depart from plankton and further diverge with depth.

Diverging AA composition of SPM and sinking particles may be related to the difference in source and bulk composition. SPM from the euphotic zone contains aggregated coccolithophorids and diatoms, which are also present in sediment trap samples (H. Schulz, personal communication 2012). SPM from the surface layer thus is probably a mixture of fresh plankton, biogenic aggregates and fine non- or very slow-sinking mineral matter. Admixture of plankton-derived organic matter is obviously correlated to primary productivity.



**Fig. 5.** Results of the PCA carried out on AA spectra (Mol %) of SPM, plankton and trap samples from the Arabian Sea. Symbols indicate the Site scores of individual plankton (crosses), SPM (boxes), and trap samples (triangles). Factor loadings of individual AAs multiplied by 10 are indicated by red AA abbreviations. AAs typical of fresh plankton are marked with a hexagon, AAs enriched with depth on SPM are circled and arrows indicate increasing sampling depths.

It has often been found that AAs enriched in cell walls as well as in tests of carbonaceous and siliceous frustules are more resistant to degradation and become enriched during organic matter degradation (Lomstein et al., 2006). Gly, Thr, and Ser are present in diatom cell walls and siliceous tests (Cowie and Hedges, 1992; Hecky et al., 1973) and Asp and Glu are enriched in foraminiferal tests and are, moreover, preferably adsorbed to carbonates (Carter, 1978; Carter and Mitterer, 1978; Cowie and Hedges, 1992). Selective enrichment in shell matrices could be an important mechanism on sinking particles, because frustules of carbonate (30–70 %) and biogenic opal (10–50 %) dominate bulk composition in all samples (Haake et al., 1993b; Lee et al., 1998). Only Asp is enriched on sinking particles suggesting that degradation of fresh plankton is still predominant over selective preservation of cell wall constituents and adsorbed AAs. On the other hand, Glu, Ser and Gly enrichment in SPM cannot be attributed to preservation of frustules, because their content is rather low in SPM. For example, carbonate contributes only 0–6 % to total SPM in most samples. So, even if the contribution of biogenic opal to total SPM at the upwelling stations is higher than that of biogenic carbonate, we assume that biogenic frustules rarely exceed 10 % of total SPM. Total organic matter percentages are between 5.40–49 % with an average of 32 %; and we assume that lithogenic matter contributes more than 50 % to SPM.

These observations lead to the conclusion that AAs adsorbed to or part of biogenic frustules cannot progressively dominate the AA spectra of SPM. We postulate that instead selective sorption of AAs to lithogenic mineral surfaces may



be an important process influencing SPM AA composition (Carter, 1978; Hedges and Hare, 1987). Sorption of dissolved organic matter to mineral surfaces of different origin has been investigated in detail (Arnarson and Keil, 2005; 2007; Keil et al., 1994; Mayer, 1999). However, the degradability of organic matter appears to be more important for its preservation than the sorption process itself, and degradation can proceed on organic matter adsorbed to mineral surfaces (Satterberg et al., 2003; Taylor, 1995). The high concentrations of organic matter in SPM may not be explained by sorption of dissolved moieties to mineral surfaces only, but may indicate that dissolved organic matter is transferred into the particulate organic matter pool by aggregation (Chin et al., 1998). Studies by McCarthy et al. (2004) and McCarthy et al. (1997) found relatively undegraded dissolved organic nitrogen of an autotrophic origin in the deep ocean which may have been protected from degradation by a gel-matrix structure (Chin et al., 1998).

Sinking particles, on the other hand, are sites of bacterial decomposition of plankton-derived organic matter and accumulate degradation products such as non-protein AAs (Alldredge et al., 1986; Alldredge and Silver, 1988; Lee and Cronin, 1982; Silver et al., 1998). Larger particles escape faster from the euphotic zone due to the “ballast-effect” of biogenic frustules and rapidly transport labile organic matter to the deep sea and to the sediments (Klaas and Archer, 2002; Salter et al., 2010). Due to their fast escape from the photic zone they contain less free radicals that are assumed to prevent microbial degradation (Rontani et al., 2011).

### 4.3 Nitrate assimilation and $\delta^{15}\text{N}_{\text{PN}}$

Arabian Sea subsurface waters have  $\delta^{15}\text{N}_{\text{NO}_3}$  values between 7–8 ‰ (Gaye et al., 2013). This enrichment relative to deep ocean nitrate ( $\delta^{15}\text{N}_{\text{NO}_3} = 4.8$  ‰; Sigman et al., 2000) may be related to upward mixing and diffusion of isotopically enriched nitrate from the upper ODZ, or to recycling of the  $^{15}\text{N}$ -enriched particulate organic matter from upwelling areas where nitrate from the ODZ can reach the surface waters.

Assimilation of nitrate in surface waters follows the “Rayleigh closed system” model, if the substrate is not replenished. In this case the  $\delta^{15}\text{N}_{\text{NO}_3}$  of the nitrate substrate can be calculated according to (Mariotti et al., 1981):

$$\delta^{15}\text{N}_{\text{substrate}} = \delta^{15}\text{N}_{\text{initial.substrate}} -^{15}\varepsilon \{\ln(f)\}. \quad (2)$$

Values for  $f$  (the fraction of nitrate + nitrite remaining) are calculated according to

$$f = ([\text{NO}_3] + [\text{NO}_2]) / ([\text{NO}_3] + [\text{NO}_{3\text{def}}]) \quad (3)$$

where  $\text{NO}_{3\text{def}}$  is the nitrate deficit calculated from the stoichiometric relationship established from Arabian Sea JGOFS data that accounts for a preformed nitrate deficit (Codispoti et al., 2001)

$$\text{NO}_{3\text{def}} = \left( 14.89 \times \left( [\text{PO}_4^{3-}] - 0.28 \right) - \left( [\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+] \right) \right) \times 0.86 \quad (4)$$

The isotopic effect of assimilation can be obtained from the slope of the linear regression of  $\ln(f)$  against the  $\delta^{15}\text{N}_{\text{NO}_3.\text{substrate}}$ . This regression carried out for all  $\delta^{15}\text{N}_{\text{NO}_3}$  from depths  $\leq 100$  m results in  $\varepsilon_{15} = 4.1$  ‰ with a correlation coefficient of  $R^2 = 0.89$  ( $n = 16$ ). The calculated isotopic effect is slightly lower than the isotopic effect of  $\varepsilon_{15} \sim 5.0$  ‰ commonly assumed for assimilation (Sigman et al., 1999; Wada, 1980). Subsurface  $\delta^{15}\text{N}_{\text{NO}_3}$  is about 8 ‰ ( $= \delta^{15}\text{N}_{\text{initial.substrate}}$ ).

Organic matter produced by assimilation should be depleted in  $^{15}\text{N}$  relative to the substrate following the calculation of the instantaneous product

$$\delta^{15}\text{N}_{\text{inst.product}} = \delta^{15}\text{N}_{\text{substrate}} -^{15}\varepsilon. \quad (5)$$

The accumulated product should have a  $\delta^{15}\text{N}$  according to

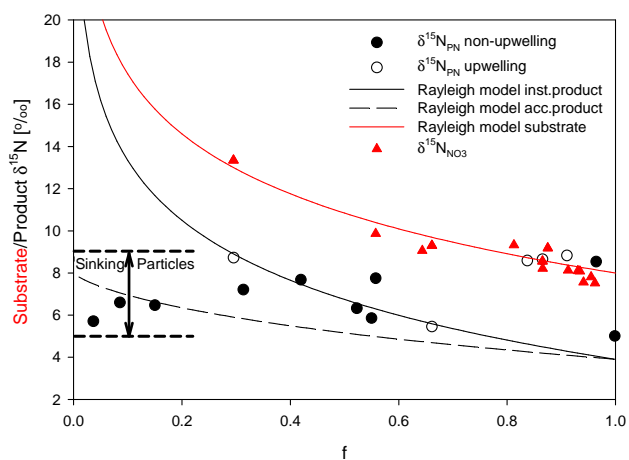
$$\delta^{15}\text{N}_{\text{acc.product}} = \delta^{15}\text{N}_{\text{initial.substrate}} +^{15}\varepsilon \{f/(1-f)\} \ln(f). \quad (6)$$

We would expect the  $\delta^{15}\text{N}_{\text{PN}}$  to be in the range of the instantaneous product rather than the accumulated product because we know from sediment trap studies that productivity signals from surface water are transferred into the deep ocean (1000–3000 m) with a delay of only two weeks (Haake et al., 1996; Rixen et al., 2000).

While  $\delta^{15}\text{N}_{\text{NO}_3}$  in the mixed layer can be explained by Rayleigh fractionation during assimilation, many of the measured  $\delta^{15}\text{N}_{\text{PN}}$  do not plot close to the  $\delta^{15}\text{N}_{\text{inst.product}}$  of Rayleigh fractionation (Fig. 6). Samples from the nitrate-depleted oligotrophic stations (lowest  $f$ ) are lower than the expected  $\delta^{15}\text{N}_{\text{inst.product}}$ . Samples with  $\delta^{15}\text{N}_{\text{PN}}$  above the  $\delta^{15}\text{N}_{\text{inst.product}}$  are from the upwelling areas and from depths in the lower euphotic zone.

There are several explanations feasible for the deviation of  $\delta^{15}\text{N}_{\text{PN}}$  from the calculated  $\delta^{15}\text{N}_{\text{inst.product}}$ . Under the oligotrophic late- to post-monsoon conditions along the northern transect and at the eastern locations the isotopic effect of assimilation may be smaller than  $^{15}\varepsilon = 4$  ‰ due to nutrient limitation. Uptake of regenerated ammonium may also be significant and reduce the  $\delta^{15}\text{N}_{\text{PN}}$  (Waser et al., 1998). The value for  $\delta^{15}\text{N}_{\text{initial.substrate}}$  is possibly higher at the near coastal stations as upwelling from 150 m depth would entrain water with a  $\delta^{15}\text{N}_{\text{NO}_3} \sim 11$  ‰. Also, most of the assimilation may have taken place at shallower depths where the  $f$  ratio is lower.

Although some of the expected patterns such as high  $\delta^{15}\text{N}_{\text{PN}}$  at upwelling stations are found,  $\delta^{15}\text{N}_{\text{PN}}$  cannot be explained by Rayleigh assimilation, whereas the  $\delta^{15}\text{N}_{\text{NO}_3}$  and also the  $\delta^{15}\text{N}$  of sinking particles fit the Rayleigh model (Fig. 6). As described in earlier studies, processes such as aggregation, disaggregation, consumption as well as vertical mixing complicate the interpretation of  $\delta^{15}\text{N}$  from SPM



**Fig. 6.** Lines indicate results of the Rayleigh closed system model using the isotopic effect  $\varepsilon = 4.1$  ‰ calculated for the samples of this study.  $\delta^{15}\text{N}_{\text{PN}}$  (dots) and  $\delta^{15}\text{N}_{\text{NO}_3}$  substrate (red triangles) are measured in the Arabian Sea surface mixed layer are indicated. Values are given in Table 1;  $f$  was calculated according to Eq. (3). The range of  $\delta^{15}\text{N}$  of sediment trap samples is indicated by arrows (data in Supplement 1).

(Altabet, 1988; Altabet, 1989; Voss et al., 1996). In addition to possible reasons for a deviation of individual samples described above, we believe that an important contribution to the observed deviation of the  $\delta^{15}\text{N}_{\text{PN}}$  from the Rayleigh model is the fact that SPM contains not only fresh plankton and aggregates, but also fine material with a very long residence time in the ocean. We know little about source and decomposition of the organic matter in SPM. As SPM from the euphotic zone contains fresh plankton and aggregates it includes the signal of the nitrogen source of plankton, especially when productivity is high.

Our highest  $\delta^{15}\text{N}_{\text{PN}}$  from the two stations of active upwelling during the sampling in September 2007 (late SW-monsoon) are elevated compared to the non-upwelling stations. A study from the spring intermonsoon period in May 1995 revealed the influence of seasonal nitrogen fixation reducing  $\delta^{15}\text{N}_{\text{PN}}$  to 4 ‰ in surface waters around  $10^\circ\text{N}$  in the central Arabian Sea (Montoya and Voss, 2006). In contrast, deep  $\delta^{15}\text{N}_{\text{PN}}$  as well as  $\delta^{15}\text{N}_{\text{PN}}$  sampled under oligotrophic conditions appear to be dominated by organic matter attached to fine, probably, very slowly sinking mineral particles. This organic matter is AA rich with 30–50 % of POC and 50–85 % of total nitrogen contributed by AAs. We hypothesize that due to the long residence time of fine particles in the ocean and their possible exchange with the more homogeneous dissolved organic matter pool the regional differences in  $\delta^{15}\text{N}_{\text{PN}}$  of deep SPM must be much smaller than that in surface SPM, sinking particles and underlying sediments. The differences observed between  $\delta^{15}\text{N}_{\text{PN}}$  in the surface mixed layer and the sub-thermocline depths may be due to this dif-

ference in organic matter source (Altabet, 1988; 1989; Altabet et al., 1999b; Montoya and Voss, 2006; Voss et al., 1996).

#### 4.4 Preservation of the $\delta^{15}\text{N}$ signal of the nitrogen source in sediments

Our snapshot of surface SPM from the late SW-monsoonal upwelling off Oman produced  $\delta^{15}\text{N}_{\text{PN}}$  values of 8.7 and 9.2 ‰ under active upwelling conditions derived from a  $\delta^{15}\text{N}_{\text{NO}_3}$  source of  $\sim 11$  ‰. This difference is due to the isotopic effect of assimilation and confirms that nutrients are not completely utilised in the upwelling areas, but are advected into the central Arabian Sea (Naqvi, 2008). Surface sediments from stations #944 and #945 had  $\delta^{15}\text{N}$  values of 9.4 and 8.8 ‰, respectively, which is remarkably close to the observed  $\delta^{15}\text{N}_{\text{PN}}$  in surface waters. This is in line with the assumption that slope sediments from the ODZ preserve the primary  $\delta^{15}\text{N}$  signal of the N source without a diagenetic enrichment (Altabet et al., 1999b; Möbius et al., 2011) and are thus very good sedimentary archives for the reconstruction of the upwelling and denitrification history. However, in contrast to the core denitrification zone in the northern and northeastern Arabian Sea where  $\delta^{15}\text{N}_{\text{NO}_3}$  values at 150 m are enriched to  $> 20$  ‰ (Gaye et al., 2013), the western Arabian Sea subsurface and upper ODZ waters are ventilated by oxygen rich ICW as well as branches of the Persian Gulf and Red Sea waters (Morrison, 1997; Prasad et al., 2001). This inflow leads to locally depleted  $\delta^{15}\text{N}_{\text{NO}_3}$  values at the depths of upwelling source waters, probably due to nitrite reoxidation (Gaye et al., 2013).

## 5 Conclusions

SPM and sinking particles in deep waters of the Arabian Sea differ in their bulk and AA composition. Sinking particles are plankton-derived and exhibit progressive degradation by becoming depleted in plankton constituents and accumulating products of bacterial degradation with increasing water depth. Surface SPM is basically a mixture of plankton-derived organic matter and organic matter with a typical SPM AA spectrum.

The observed progressive change of SPM AA spectra with depth in our set of samples from the surface to a maximum depth of 450 m could be due to, both, a decreasing dilution with plankton derived organic matter or a progressive enrichment of the AA characteristic of SPM. We suspect that the enrichment of Gly, Ser and Glu is not due to a preferential preservation of organic matter in cell-walls or frustules but rather to sorption or coagulation and attachment of dissolved organic matter to fine particles. The divergence of AA spectra of SPM and sinking particles with water depth further suggests that the exchange between the two particle classes is rather insignificant. This is also corroborated by the relatively small amount of organic carbon in SPM in the Arabian

Sea which is in the same order of magnitude as the total export production of one or two years.

These findings have important implications for  $\delta^{15}\text{N}_{\text{PN}}$  measurements of SPM. Surface SPM from stations with active upwelling has a  $\delta^{15}\text{N}_{\text{PN}}$  signal of 8.7–9.2‰ derived from nitrate with  $\delta^{15}\text{N}_{\text{NO}_3} \sim 11\text{‰}$  from about 150 m water depth. A similar  $\delta^{15}\text{N}$  signal is typical for sediments from the slope of the Oman upwelling area, so that we can assume to find ideal sites for a reconstruction of the upwelling and denitrification history. However,  $\delta^{15}\text{N}_{\text{PN}}$  of SPM from oligotrophic sites and deeper waters do, most probably, not correspond with the nitrogen source, but are dominated by exchange processes with dissolved AAs. We suggest that exchange with the dissolved pool could be an important process modulating organic matter on SPM. This suggested mechanism needs more detailed investigations and its role in the global cycling of elements and their documentation in sediment records needs to be assessed.

**Supplementary material related to this article is available online at <http://www.biogeosciences.net/10/7689/2013/bg-10-7689-2013-supplement.zip>.**

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