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What can we learn from amino acids about oceanic organic matter cycling and degradation?

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Abstract

Amino acids (AA) mainly bound in proteins are major constituents of living biomass and non-living organic material in the oceanic particulate and dissolved organic matter pool. Uptake and cycling by heterotrophic organisms lead to characteristic changes in AA composition so that AA based biogeochemical indicators are often used to elucidate processes of organic matter cycling and degradation. We analyzed particulate AA in a large sample set collected in various oceanic regions covering sinking and suspended particles in the water column, sediment samples as well as dissolved AA from water column and pore water samples. The aim of this study was to test and improve the use of AA derived biogeochemical indicators as proxies for organic matter sources and degradation, and to better understand particle dynamics and interaction between the dissolved and particulate organic matter pools. A principal component analysis (PCA) of all data delineates diverging AA compositions of sinking and suspended particles with increasing water depth. A new sinking particle and sediment degradation indicator (SDI) allows a fine-tuned classification of sinking particles and sediments with respect to the intensity of degradation, which is associated with changes of bulk $\delta^{15}N$ ratios. This new indicator furthermore is sensitive to sedimentary redox conditions and can be used to detect past anoxic early diagenesis. A second indicator emerges from the AA spectra of suspended particulate matter (SPM) in the epipelagic and that of the meso- and bathypelagic ocean and is a residence time indicator (RTI). The characteristic changes in AA patterns from shallow to deep SPM are recapitulated in the AA spectra of the dissolved organic matter (DOM) pool, so that deep SPM is more similar to DOM than to any of the other organic matter pools. This implies that there is equilibration between finely dispersed SPM and DOM in the deep sea, which may be driven by microbial activity combined with annealing and fragmentation of gels. As these processes strongly depend on physico-chemical conditions in the deep ocean, changes in quality and degradability of DOM may strongly affect the relatively large pool of suspended and dissolved AA in the ocean that amounts to 15 Pg amino acid carbon (AAC) and 89±29 Pg AAC, respectively.

1 Introduction

Amino acids are ubiquitous in living organisms and comprise a major share of characterized organic matter in the particulate and dissolved pool in the ocean (Lee, 1988; Wakeham et al., 1984; Zhang et al., 2016; Davis et al., 2009; Lee et al., 2004). AA comprise more than 80 % of total organic carbon in fresh autochthonous plankton while allochthonous organic matter from continental runoff and atmospheric deposition has lower AA contents (Degens and Ittekkot, 1983; Degens and Ittekkot, 1985). Most of the primary productivity occurs in the sunlit surface layer of the ocean and most of the allochthonous material is also transported into surface waters. Thus, organic matter concentrations including their major biogenic constituents generally, have a surface maximum and decrease with depth (Peters et al., 2018; Gaye et al., 2013; Wakeham and Lee, 1993). The main mechanism behind this depth dependent distribution is that most of the organic matter is recycled in surface waters while only a small proportion of surface particles leaves the surface waters by gravitational settling in the form of macroaggregates or fecal pellets. Particles comprising organic matter, shells, frustules of organisms and mineral matter sink at speeds of 200 m day^{-1} on average and constitute the export from the surface mixed layer or euphotic zone into the deep ocean, where part of it can ultimately reach the sediments (Alldredge and Silver, 1988; Alldredge, 1998; Pilskaln and Honjo, 1987; Fowler and Knauer, 1986; Karl et al., 1988; Rixen et al., 2019b). Sinking particles are caught by moored or floating sediment traps while SPM is sampled by filtration or ultrafiltration of water from water samplers or by pump systems (Yamaguchi and McCarthy, 2018). SPM is too small to sink and therefore – like DOM – predominantly enters deep water by subduction of surface waters (Resplandy et al., 2019; Boyd et al., 2019) and is transported passively following the route of ocean water along the ocean conveyer belt (Silver et al., 1998; Mccave, 1984). It has thus been surmised that the long residence time of SPM in the water column should result in a more degraded state compared with organic matter of sinking particles (Mccave, 1984; Degens and Ittekkot, 1984). Studies of pigments, AA and fatty acids, however, do not find such a systematic difference between the two types of particles and even indicate that SPM can be less degraded than sinking particles (Abramson et al., 2011; Rontani et al., 2011; Wakeham and Canuel, 1988). In two studies of AA composition in the Benguela Upwelling System and in the Arabian Sea it was shown that the degradation pathways of SPM and sinking particles differ as their AA compositions diverge with depth (Gaye et al., 2013; Nagel et al., 2009). These studies suggested that there is only little interaction between suspended and sinking particle pools below the euphotic zone. Due to its long residence time in the ocean, SPM appears to interact with DOM

(Gaye et al., 2013) and therefore carries different AA signatures related to genesis and history of organic matter cycling in its specific water mass (Nagel et al., 2016). Whereas information on the composition of sediment trap samples has been compiled in comprehensive studies (Honjo et al., 2008; Rixen et al., 2017; Wilson et al., 2012; Rixen et al., 2019a), similar compilations of the profuse literature on suspended matter are yet missing.

On the way to the deep sea the flux of sinking particles is reduced by disaggregation and organic matter degradation. Suess (1980) empirically derived the first power function for organic carbon decay based on sediment trap data. Subsequently, a large number of similar functions where calculated for various oceanic areas based on trap experiments (Rixen et al., 2017; Rixen et al., 2002; Armstrong et al., 2002; Martin et al., 1987). Early work on AA had produced similar decay functions combining data from Atlantic and Pacific trap experiments (Lee and Cronin, 1982, 1984). As AA decay faster than bulk organic carbon (Haake et al., 1993b; Haake et al., 1992; Haake et al., 1996; Lee et al., 2004; Wakeham and Lee, 1989; Whelan and Emeis, 1992), they are often considered as "labile" constituents of bulk organic matter. This is supposedly due to their preferential uptake as a nitrogen (N) source for further synthesis of AA or as a source of essential AA for heterotrophs (Ittekkot and Arain, 1986; Ittekkot et al., 1986). This has been questioned, as a large proportion of the oceanic organic N pool is comprised of AA that are not bioavailable (Aluwihare et al., 2005). In addition to the quantification of AA decay, degradation state of organic matter (proteins) can be assessed by characteristic changes in AA monomer composition which, furthermore, have the potential to elucidate sources of organic matter and degradation processes (Ittekkot et al., 1984a; Ittekkot et al., 1984b; Dauwe and Middelburg, 1998; Dauwe et al., 1999; Jennerjahn and Ittekkot, 1997).

DOM is defined by the pore size of the filters it passes through which is 0.2-0.7 µm (Carlson and Hansell, 2015) and thus includes some picoplankton cells and all viruses (Aristegui et al., 2009). DOM in surface water is partly labile and can originate from the exudates and lysis of organisms, passive diffusion, or "overflow" out of phytoplankton and bacteria; grazers can excrete or egest DOM, it can furthermore be leached from their fecal pellets or released by sloppy zooplankton feeding and is thus primarily released and also taken up in the surface ocean (Carlson and Hansell, 2015). Moreover, terrestrially derived DOM is transported into surface waters by rivers and via the atmosphere (Benner et al., 2005). Deep DOM has a different source than simply transport of surface DOM by intermediate and deep water formation and mixing, as deep DOM is refractory in nature and has been heterotrophically altered by cycling and degradation processes (Yamaguchi and Mccarthy, 2018). The possible source of deep DOM may be the release from sinking or suspended particles associated with microbial degradation on particles and in the ambiance of particles by processes such as solubilizing organic matter by ectohydrolase (Cho and Azam, 1988; Ciais et al., 2014; Aristegui et al., 2009). DOM can also be released from sediment pore water into overlying waters (Lahajnar et al., 2005). Stable isotope ratios of nitrogen ($\delta^{15}N$) in ultrafiltered DOM (UDOM) showed no systematic change with depth and suggested a common microbial source or viral lysis (Mccarthy et al., 2007).

Studies combining nuclear magnetic resonance (NMR) spectroscopy with AA hydrolysis of different intensity identified amide-N and amine-N as the dominant form of organic N in DOM (Mccarthy et al., 1997; Aluwihare et al., 2005). Between 45 and 86 % of dissolved organic nitrogen (DON) were found to be bound in proteins but only a small part could be converted into AA by acid hydrolysis (Aluwihare et al., 2005). Differences of hydrolysis conditions can explain the large range of AA contribution to dissolved organic carbon found in different experiments. Mild acid hydrolysis of AA resulted in amino acid carbon contributions to total dissolved carbon (AAC/C) between 0.4 and 4 % with a reduction from 1-4 % AAC/C % in surface waters to 0.4-0.8 % in waters >1.000 m (Guo et al., 2018; Davis and Benner, 2005). Moreover, this reduction was associated with a progressive AA degradation (Kim et al., 2017; Davis and Benner, 2005). Stronger acid hydrolysis resulted in AAC/C of 5-10 % (Ittekkot, 1981; Keil and Kirchman, 1999; Mccarthy et al., 1997).

Understanding and quantifying AA degradation is required to estimate the diagenetic imprint on $\delta^{15}N$ ratios of particulate matter. N-isotope ratios are reported in ‰ using the delta notation and the $^{15}N/^{14}N$ of air N_2 as the reference standard:

$$\delta^{15}N_{\text{sample}} = ((^{15}N/^{14}N)_{\text{sample}} / (^{15}N/^{14}N)_{\text{reference standard}} - 1) * 1000 \quad (1)$$

$\delta^{15}N$ ratios track major shifts between N pools and are commonly used to reconstruct the N cycle from sedimentary archives (Galbraith et al., 2013). Amino acid nitrogen (AAN) comprises 80-100 % of N in fresh organic matter and is the precursor of most of the N buried in sediments and ultimately stored in the form of ammonium, adsorbed to clay minerals (Boyd, 2001; Waples and Sloan, 1980; Müller, 1977). Considerable AA degradation already occurs in the water column and progresses during organic matter burial in the sediments so that the impact of diagenetic processes on $\delta^{15}N$ has to be accounted for (Möbius et al., 2010; Möbius et al., 2011; Niggemann et al., 2018; Carr et al., 2016). Ammonification leads to a diagenetic increase of $\delta^{15}N$ values by up to 6.5 ‰ in deep sea sediments while there is little effect during organic matter burial in shelf and slope sediments due to the higher sedimentation rates and sub- to anoxic diagenetic conditions (Tesdal et al., 2013; Robinson et al., 2012; Möbius, 2013; Gaye-Haake et al., 2005). Such $\delta^{15}N$ increases were shown to correlate with AA derived degradation indicators so that the primary $\delta^{15}N$ signal from the water column can be reconstructed (Gaye-Haake et al., 2005; Gaye et al., 2009; Möbius et al., 2011).

In the following synoptic compilation of AA data, we will examine the differences in AA spectra of a large data set that combines dissolved and particulate AA from plankton, suspended and sinking material, and sediments from different oceanic regions, as well as from riverine to brackish-marine conditions. Focusing on processes in the water column the data serve to (i) test existing AA based biogeochemical indicators of organic matter sources and degradation, (ii) better understand transformation and degradation processes of organic matter in aquatic environments reflected by AA composition in sinking and suspended particles and total dissolved AA (TDAA), (iii) investigate the impact of such processes on the $\delta^{15}N$ values and (iv) identify open questions which may be pursued with the help of AA analyses in the future.

2 Amino acid derived biogeochemical indicators of organic matter origin and degradation

Amino acid concentrations and the contribution of AA carbon (AAC) and AAN as percentages of total organic carbon (AAC/C %) or total N (AAN/N %) are used to determine the degradation state of organic matter in the marine realm as both decrease with increasing organic matter degradation (Wakeham and Lee, 1993; Cowie and Hedges, 1994). AAN/N % >50 % are characteristic of fresh organic matter in the freshwater and marine realm (Menzel et al., 2015; Haake et al., 1992; Haake et al., 1993b). AA contribute >60 % to total organic carbon (AAC/C %) in fresh plankton and suspended matter in surface waters whereas AAC/C % drop to values <20 % in sinking particles and suspended matter from subsurface water (Wakeham and Lee, 1993). AAC/C % values are often below 10 % in freshwater environments and indicate the enhanced input of land plants enriched in carbohydrates and lignin rather than enhanced organic matter degradation (Menzel et al., 2015).

Ratios of individual AA such as Asp/β-alanine (β-Ala) and Glu/γ-aminobutyric acid (γ-Aba) (Cowie and Hedges, 1994; Ittekkot et al., 1984a; Lee and Cronin, 1984), or the Reactivity Index (RI) (Jennerjahn and Ittekkot, 1997) and the Degradation Index (DI) (Dauwe et al., 1999; Dauwe and Middelburg, 1998) have often been used to scale organic matter degradation (Niggemann et al., 2018; Unger et al., 2005; Ingalls et al., 2006; Ingalls et al., 2004; Pantoja et al., 2004; Möbius et al., 2010). After acid hydrolysis we can neither distinguish between Asp and asparagine (Asn) nor between Glu and glutamine (Gln) so that our Asp measurements comprise Asp+Asn and our Glu comprise Glu+Gln. Asn, Gln and Glu are the primary products of N assimilation and all other AA are synthesized from them (Loick-Wilde et al., 2018; Riccardi et al., 1989; Hildebrandt et al., 2015). Asp and Glu are the major AA in bacteria, vascular plant tissue, phytoplankton, zooplankton and fungi (Cowie and Hedges, 1992). High relative contents of Asp and Glu, therefore, indicate fresh organic matter and the ratios of Asp/β-Ala and Glu/γ-Aba are high in fresh organic matter as β-Ala and γ-Aba are degradation products of Asp and Glu, respectively (Lee and Cronin, 1984). β-Ala and γ-Aba also become relatively enriched during organic matter degradation as these non-protein AA are not taken up by heterotrophic organisms (Ittekkot et al., 1984b). Although Asp/β-Ala and Glu/γ-Aba are often used in concert to study degradation processes, they are likely to deviate as Glu accumulates in plant material while Asp accumulates in degraded sediments (Möbius et al., 2011).

The relative accumulation of the non-protein AA is also expressed by the RI which is the ratio of the very labile aromatic AA Tyr and Phe and the non-protein AA β-Ala and γ-Aba. The RI is a useful indicator of organic matter quality and is, generally, between 0 (very degraded) and 15 (very fresh) (Jennerjahn and Ittekkot, 1997). It is applicable not only in studies of sinking and suspended matter in marine and brackish environments (Unger et al., 2005; Gaye et al., 2007) but also as a proxy for degradation state in the sediment column (Möbius et al., 2011). The enrichment of Asp and Glu in sediments is related to their enrichment in carbonate shells (Ittekkot et al., 1984a) and to adsorption of primarily acidic AA onto carbonate minerals (King and Hare, 1972), whereas basic AA primarily adsorb onto silicate minerals (Hedges and Hare, 1987; Keil et al., 1994; King, 1975).

The DI, the integral of 14 protein AA, assesses the diagenetic alteration of a sample by comparing it to a set of 28 sediment samples of different degradation states and environments. Molar percentages of individual AA are standardised by the mean and standard deviations of the 28-sample data set. The DI then integrates the result of this standardized values weighed by the factor coefficients for the first axis of the PCA of Dauwe et al. (1999) according to the formula:

$$\mathrm{DI} = \sum_i \left[\frac{\mathrm{var}_i - \mathrm{AVGvar}_i}{\mathrm{STDvar}_i} \right] \cdot \mathrm{fac.coef.}_i \qquad (2)$$

where var_i is the original mole percentage of each AA_i, $AVGvar_i$ and $STDvar_i$ are the mean and standard deviations, respectively, and $fac.coef._i$ is the factor coefficient of the first axis of the PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation of AA with respect to an assumed average molar composition. The DI ranges approximately from -2 to +3 where negative values indicate more and positive values less degradation than the average.

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 were 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). Such indices are usually derived from a principal component analyses (PCA) of Mol% AA. Menzel et al. (2015) used data from a suite of lake samples from different climate regimes in India for a PCA and suggested to use the factor coefficients of the AA to calculate a lake sample degradation index (LI). Gaye et al. (2007) calculated a new degradation index for sediment traps from the Kara Sea whereas Unger et al. (2005) used the established DI and RI to classify sediment and suspended water samples from the river endmembers Ob and Yenisei into the brackish-marine Kara Sea. The DI was even applied to trace dissolved AA degradation (Davis and Benner, 2005; Guo et al., 2018), although the DI is originally based on marine sediments only (Dauwe et al., 1999). An indicator of oxic vs. anoxic organic matter degradation in the water column and in sediments was proposed by Menzel et al. (2015) for lake samples. Based on work by Cowie et al. (1995) on marine sediments the ox/anox indicator is the quotient of AA preserved under oxic diagenetic conditions to those preserved in anoxic water or sediments and is thus higher in oxic than in anoxic sediments:

$$ox/anox = \frac{\text{Asp} + \text{Glu} + \beta\text{-Ala} + \gamma\text{-Aba} + \text{Lys}}{\text{Ser} + \text{Met} + \text{Ile} + \text{Leu} + \text{Tyr} + \text{Phe}} \qquad (3)$$

with Lys being lysine and Ser being serine. Ox/anox ratios <1.0 indicate anoxic and ratios >1.5 oxic diagenesis (Menzel et al., 2015).

The stability of AA vs. hexosamines (HA) has been discussed since the early research on AA and HA in natural material. Fresh plankton was observed to have AA/HA ratios of 13-25 (Degens and Mopper, 1975) which is a mixed signal of phytoplankton with an AA/HA ratio of >80 and zooplankton with a ratio of ~9 due to chitinaceous skeletons of many zooplankters (Mayzaud and Martin, 1975). Low AA/HA are also observed in cell walls of fungi and bacteria.

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As the building blocks of chitin, HA were assumed to be more resistant to degradation than bulk AA (Muller et al., 1986). This is, however, challenged by studies of enzyme activities which were observed to respond to substrate availability so that the activity of chitobiase and chitinase as high as that of glucosidase (Boetius et al., 2000a; Boetius and Lochte, 1994; Boetius et al., 2000b; Smith et al., 1992) suggesting intense degradation also of chitin. Glucosamine (Gluam) is the main constituent of chitin and while Galactosamine (Galam) is relatively enriched in bacterial cell walls (Walla et al., 1984; Kandler, 1979). The Gluam/Galam ratio has, therefore, been used to distinguish bacterial material from zooplankton rich material (Haake et al., 1993b; Benner and Kaiser, 2003; Niggemann and Schubert, 2006). Gluam/Galam ratios > 4 were found in sinking particles (Haake et al., 1993b; Haake et al., 1992; Lahajnar et al., 2007), ratios of < 3 usually indicate relatively high contribution of microbial OM and values between 1 and 2 are characteristic of sediments and indicate an enrichment of microbial biomass (Benner and Kaiser, 2003).

3. Materials and Methods

3.1 Sampling

A total of 1425 samples were taken in different oceanic areas and water depths and include 218 sediment trap samples, 489 sediment samples, 608 SPM samples and 110 water and pore water samples (Fig. 1). Five additional plankton samples were taken in the Arabian Sea and from the Namibian upwelling area by plankton tows between 0-100 m and between 100-700 m water depths. Sea water was filtered through Whatman GF/F filters and dried at 40°C in order to obtain SPM samples. An aliquot of the filtrate was stored deep frozen for AA analyses. Sediment trap samples were wet sieved on board and comprise the <1mm fraction filtered with polycarbonate nuclepore filters of 0.45 µm pore size and dried at 40°C. Sediment samples from multicores, box grabs, box cores, or gravity cores were taken by spatula or syringes from cold stored cores and were freeze dried before analyses. Surface samples represent either the upper 0.5 cm or 1 cm of a sediment core. Pore-water samples were taken by rhizons and stored frozen before analyses (see methods in Paul et al., 2018). 18 water samples taken off Namibia were separated into two size classes by ultrafiltration (Brockmeyer and Spitzy, 2013). The size classes 50 kDa-0.7 µm and 1 kDa-0.7 µm were used for AA analyses.

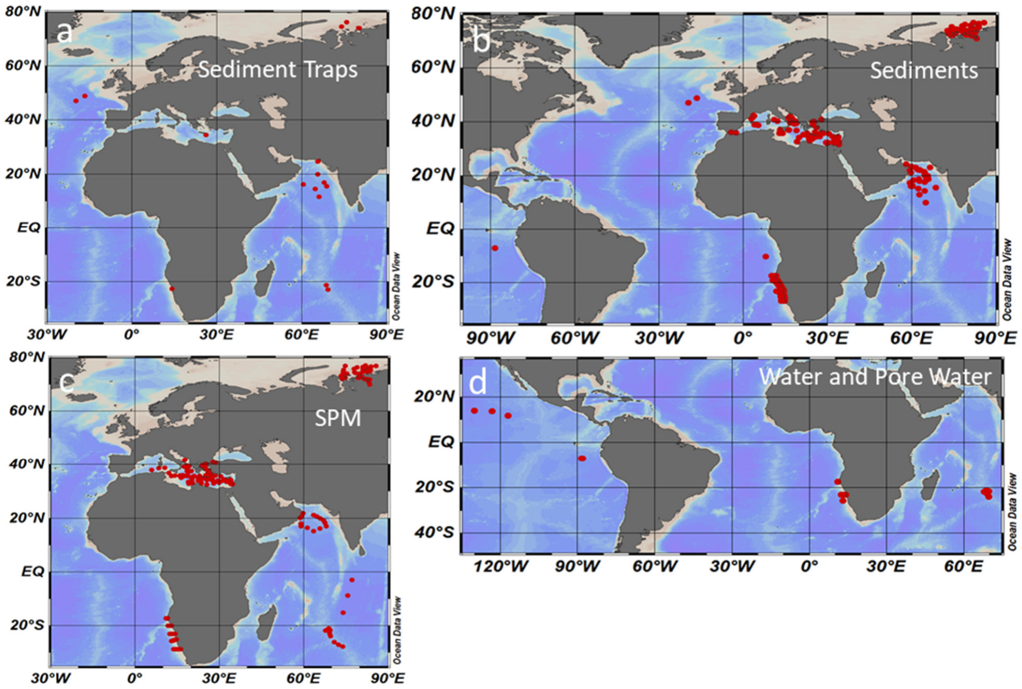

Figure 1: Stations of sediment trap deployments (a), sediments (b), SPM (c) and water and pore sampling (d).

3.2 Analytical methods

Total carbon and N were measured with a Carlo Erba Nitrogen Analyser 1500 (Milan, Italy) or a EURO EA3000 elemental analyzer. Particulate organic carbon (POC) was measured after treatment of weighed samples with 1N HCl to remove carbonate. The precision of this method is 0.05% for carbon and 0.005% for N. Carbonate carbon was calculated by subtracting organic carbon from total carbon. Ratios of $^{15}N/^{14}N$ of particulate N were determined using a Thermo Finnigan MAT 252 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. Part of the samples were measured with an Elementar IsoPrime 100 isotope ratio mass spectrometer after high temperature combustion in an Elementar CHNOS Vario isotope elemental analyser at 950 °C. Pure tank N_2 calibrated against the reference standards IAEA-N1 (ammonium sulfate, $\delta^{15}N = +0.4$ ‰ versus air N_2) and IAEAN2 (ammonium sulfate, $d^{15}N = +20.3$ ‰) of the International Atomic Energy Agency was used as a working standard. Duplicate measurements of samples differ by less than 0.15 ‰. The laboratory's long-term standard deviation for IAEA-N1 standard is 0.09 ‰.

Dissolved organic carbon (DOC) concentrations [mg/L] were determined via a high temperature combustion method (POC-V$_{CSH}$ Analyzer, Shimadzu). Sampled water was filtered through pre-combusted Whatman GFF filters and inorganic carbon was removed by 2 M HCl prior to injection into the combustion tube where organic carbon is oxidized to CO_2 at 680 °C with a platinum catalyst. A 5-point calibration from 0.5 to 5 mg DOC/L was used. The error of measurement is less than 2 % (Brockmeyer and Spitzy, 2013).

Total dissolved AA, particulate AA and hexosamines (HA) of selected samples were analyzed with a Biochrom 30 Amino Acid Analyzer. Acid hydrolysis with 6N HCl for 22 h at 110°C under a pure argon atmosphere was carried out on ca. 3 ml of filtrate of water samples, on 1-2 mg of suspended matter collected on GF/F filters, on 1-2 mg of sediment trap samples, or on 1-50 mg of freeze dried surface sediments. A particle free aliquot was evaporated three times 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 water or particulate matter samples. Due to acid hydrolysis, Asp and Asn are both measured as Asp and Glu and Gln are both measured as Glu. The other AA measured are Thr, Ser, Gly, Ala, valine (Val), Met, Ile, Leu, Tyr, Phe, β-Ala, γ-Aba, histidine (His), ornithine (Orn), Lys and arginine (Arg). The measured HA are Gluam and Galam.

3.3 Statistical analyses

To investigate the differences of AA composition and to recognize the interaction and pathways of degradation between the different pools we carried out a PCA of AA monomer contributions in Mol %. Met was excluded as it is below detection limit in many samples. The PCA was carried out using the program SPSS Statistics 22. PCAs have often been used to analyze large databases (Xue et al., 2011) in order to trace organic matter degradation, group and categorize samples and develop indices such as the DI of Dauwe et al. (1999) using summary statistics

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(see equation 1). A PCA is an orthogonal transformation of a set of variables into a new set of uncorrelated variables called principal components. New axes are chosen in order to explain as much as possible of the variance within the data set on a few main axes of highest correlation. The first component explains most of the variance within the data set, consecutively followed by the remaining components in the order of their decreasing capacity to explain the variance within the data set. The selection of the most relevant components can be done by selecting those with eigenvalues (the variances of the principal components) >1. Alternatively, the kink method can be applied selecting those components from a plot of eigenvalues (scree plot), which describe a steep slope of declining variance followed by a "kink" after which the principal components add only small amounts to the variance. The factor loadings of the variables (in this case the individual amino acids) are their projections on the new axis. The factor score of each data set from a sampling location is obtained by multiplying the standardized data with the factor loadings (also called factor coefficients). A high (low) factor score shows that a sample has high (low) concentrations of the variables with high factor loadings. A plot of factor loadings of the variables compared with a plot of the factor scores of samples helps to visualize the relation of the samples to the variables and thus to identify the processes behind the results of the PCA.

4 Results

4.1 Organic carbon, nitrogen and amino acid content

The POC (N) content is 35.9 % (5.9%) in plankton and 1.65-46.4 % (0.21-10.14 %) in sediment trap samples. In sediments, POC (N) contents drop to 0.10-13.5 % (0.02-1.72 %). SPM has POC (N) contents of 0.94-45.4 % (0.09-12.08 %). DOC content in water samples is between 0.5-1.1 mg L^{-1} and DOC in pore water samples is between 3.9-29 mg L^{-1}.

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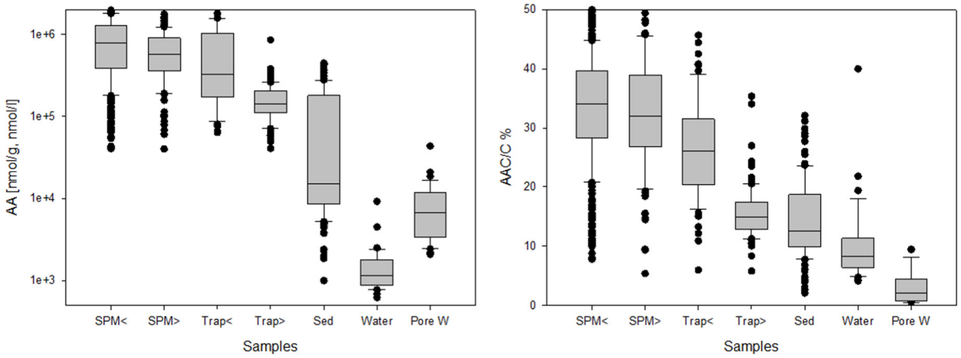

Figure 2: Box and Whisker plots of AA content in nmol g^{-1} or nmol L^{-1} (a) and of AAC/C % (b) in SPM from water depths <200m (SPM<) and >200m (SPM>), in sediment traps at water depth <200m (Trap<) and >200 m (Trap>), in sediments (Sed), in water samples (Water) and in pore water samples (Pore W). Boxes comprise the upper and lower quartile and lines indicate median; whiskers delineate the 10 and 90 percentile; outliers are marked by dots.

AA contents are grouped into SPM and trap samples taken at water depths <200m (shallow) and >200m (deep) (Fig. 2, Table 1). AA contents are highest in SPM samples and shallow sediment traps (<200m water depth) with values between 40-4307 µmol g^{-1} (Fig. 2) and averages of 662-908 µmol g^{-1} (Table 1). AA contents are lower in traps from water depth >200m with an average of 164 µmol g^{-1}. Sediments have lowest AA contents of all particulate matter samples with an average of 50 µmol g^{-1} (Table 1). TDAA concentrations are between 0.6-44 µmol L^{-1} and AA contents are lower in water than in pore water samples with averages of 3.2 and 8.8 µmol L^{-1}, respectively.

The AAC/C is between 5.4-66 % in SPM and traps samples and the AAN/N (not shown) is between 3.7-100 %. The overall pattern found for AAC/C (Fig. 2b) is similar to the pattern of AA contents (Fig. 2a) but there is more overlap of AAC/C between the different groups. Sediments have AAC/C between 2.7-50 % and AAN/N between 3-78 % (not shown). The contribution of AAC to DOC (AAC/C) in water samples is between 4-40 % and in pore water samples between 0.5-9 %.

AA contents of sinking and suspended particles decrease with water depth and the most significant decrease occurs in the upper ocean (Fig. 3a). The decay constant of AA of sinking particles is twice as high as the decay constant of AA of SPM (Fig. 3 a, b). Kara Sea samples were excluded from these calculations as their AA contents are low due to the strong dilution by material from rivers and resuspended sediments in this near-shore environment. It is also notable that AAC/C and AAN/N (not shown) significantly decrease between shallow and deep traps and from deep traps to sediments while AAC/C of SPM show little decrease between shallow and deep samples (Fig. 2b).

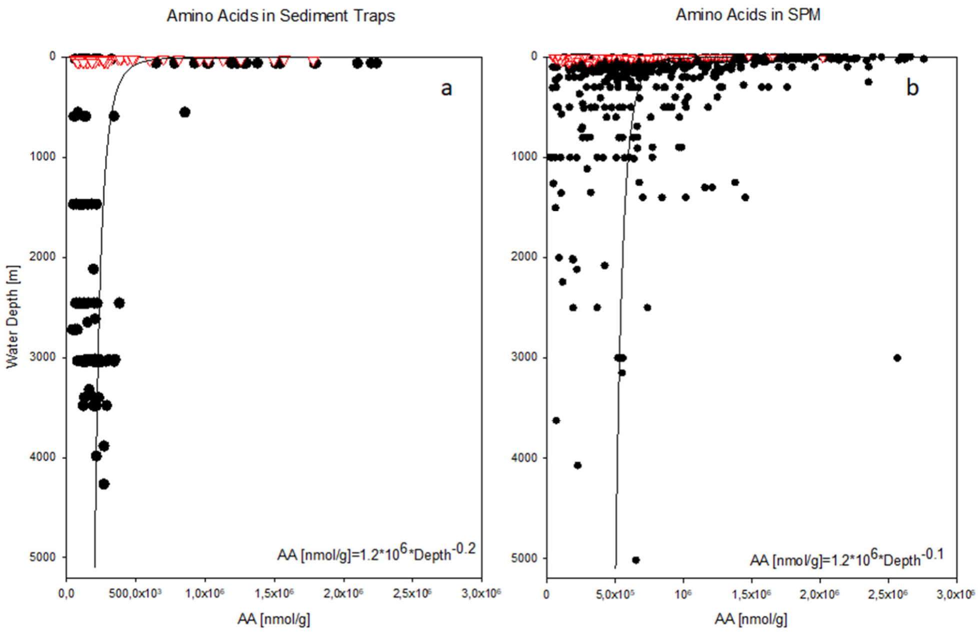

Figure 3: AA contents in nmol g^{-1} in sediment traps (a) and SPM (b). Red triangles mark samples from the Kara Sea, black dots are samples from the other trap and SPM locations shown in Figure 1. The decay functions are calculated from samples excluding Kara Sea samples.

4.2 Amino acid composition

Dominant AA in plankton samples are Glu, Gly, Val and Asp. Sinking particles and sediments have increasing Mol% of Gly, Asp, β-Ala, γ-Aba and Orn contents while the Mol% of Glu, Ala, Val, Met, Ile, Leu, Tyr and Phe decrease (Fig. 4a). The AA enriched from plankton via SPM to water and pore water samples are Ser, Gly, β-Ala, γ-Aba, Orn and His while all other AA decrease (Fig. 4b). Amino acid spectra in water and pore water samples are very similar (Fig. 4c).

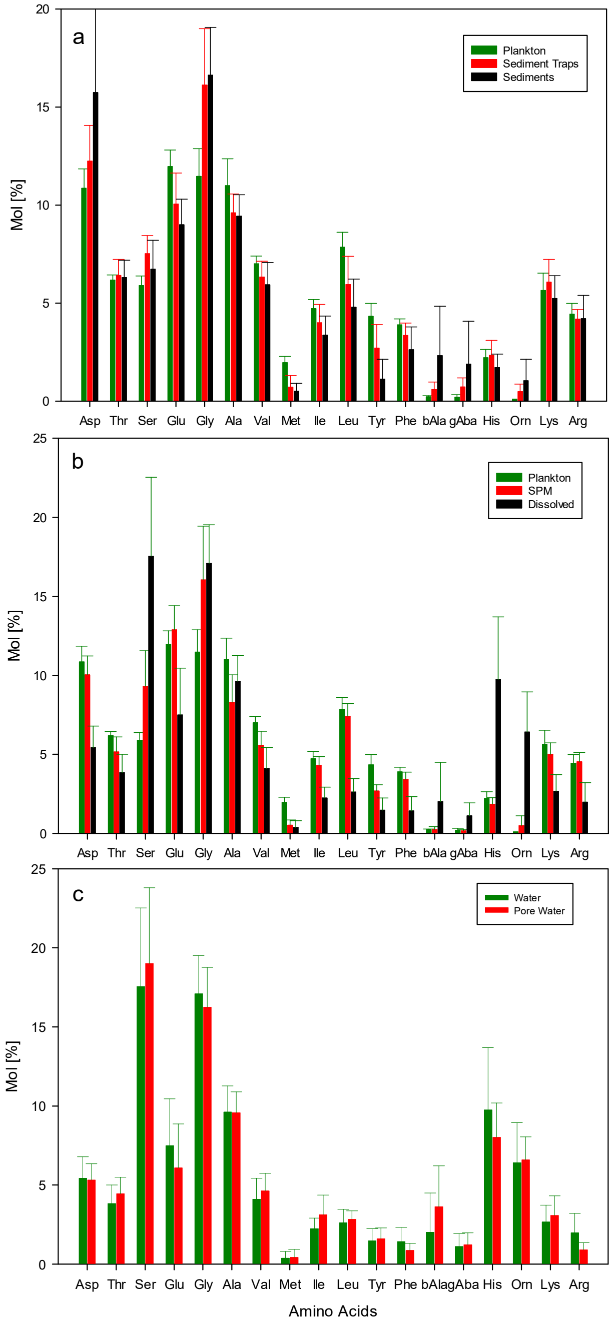

Figure 4: Average concentrations of individual AA (Mol%) and 1 σ standard deviation (vertical bars) in plankton, sediment trap and sediment samples (a), in plankton, SPM and water samples (b) and in water samples (green) and in pore water (red) (c).

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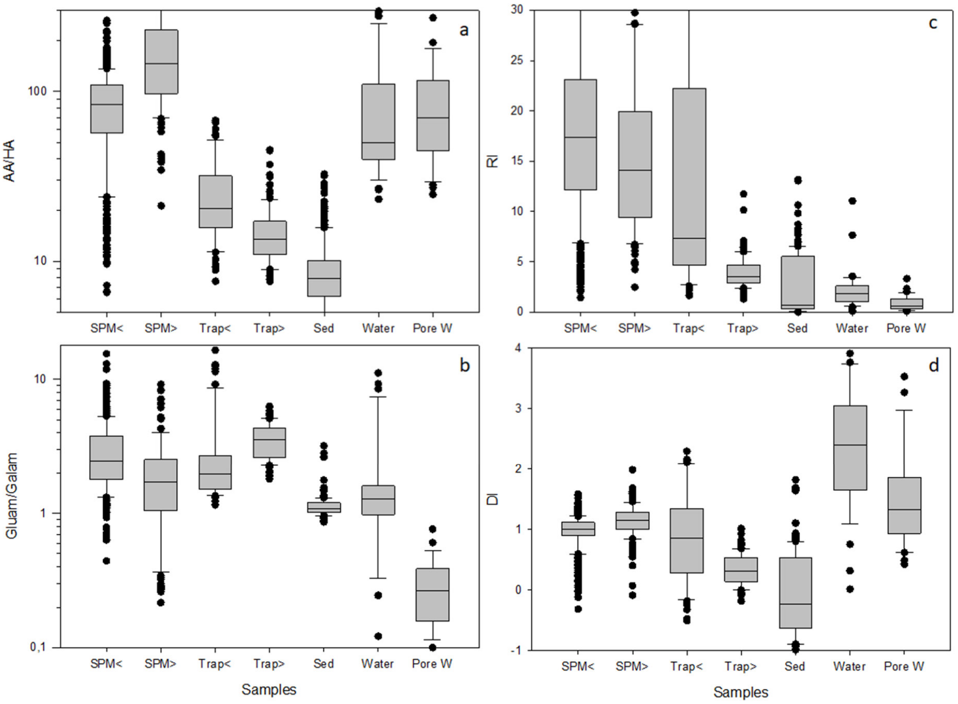


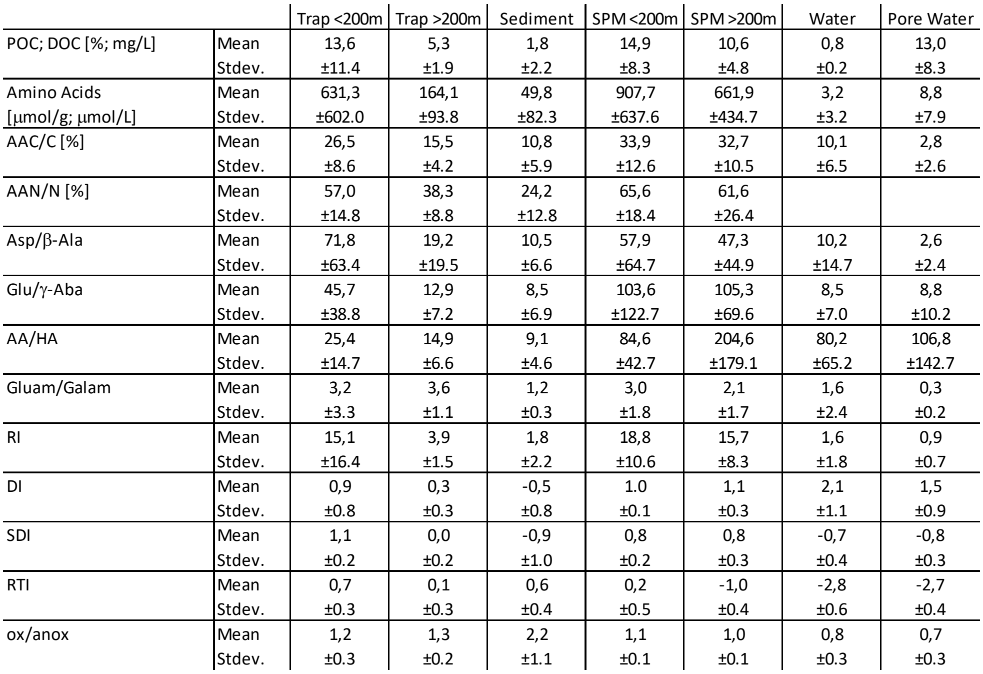
Figure 5: Box and Whisker plot of AA/HA ratios (a) and Gluam/Galam ratios (b), RI (c) and DI (d) in SPM from water depths <200m (SPM<) and >200m (SPM>), in sediment traps at water depth <200m (Trap<) and >200 m (Trap>), in sediments (Sed), in water samples (Water) and in pore water samples (Pore W). Outliers are marked by dots. Note logarithmic scales of AA/HA (a) and Gluam/Galam (b).

The biogeochemical indicator AA/HA is higher in SPM than in sediment trap samples with averages of 103 in shallow and 105 in deep SPM while Gluam/Galam ratios slightly decrease with depth (Fig. 5a, b; Table 1). The AA/HA decrease from shallow via deep traps to sediments with averages of 25.4, 14.9 and 9.1, respectively, while the Gluam/Galam is in a similar range in deep traps compared to shallow traps but is lower in sediments than in traps (Fig. 5a, b; Table 1). The RI (Fig. 5c; Table 1) shows the same pattern as the ratios of Asp/β-Ala and the Glu/γ-Aba (Table 1) has high values in SPM and shallow traps (averages of 15.1-18.8) and no significant trend between shallow and deep SPM samples. The RI decreases from shallow to deep traps and further to the sediments. Water samples have similar values as sediment samples with average RI of 1.8 and 1.6, respectively, and pore waters have an even lower average RI of 0.9. Similar to the RI the DI is not significantly different in shallow and deep SPM samples

(Fig. 5d; Table 1) while it decreases from shallow sediment traps via deep traps to sediments. In contrast to the RI where water samples have lowest values the highest DI values are found in water and pore water samples.

In summary, common biogeochemical indicators of organic matter degradation (RI, Asp/β-Ala, Glu/γ-Aba) drop and thus imply increasing degradation between shallow and deep sediment traps and between deep traps and sediments, while these indicators reveal little or no degradation with depth in SPM (Fig. 5; Table 1). The enhanced DI values, furthermore, imply that water and SPM samples are less degraded than deep trap and sediment samples and that dissolved AA in water samples are least degraded.

Table 1: Mean values and standard deviation (Stdev.) of POC [%], DOC [mg/L], amino acid (AA) content [µmol/g or µmol/L], AAC/C%, AAN/N%, ratios of Asp/β-Ala, Glu/γ-Aba, AA/HA and Gluam/Galam, the RI, DI, SDI*, RTI* and ox/anox ratio summarized in traps at <200m and >200m water depth, sediments, SPM <200m and >200m water depth, water samples and pore water samples. *definition of these indicators in part 5.2 below.



		Trap <200m	Trap >200m	Sediment	SPM <200m	SPM >200m	Water	Pore Water
POC; DOC [%; mg/L]	Mean	13,6	5,3	1,8	14,9	10,6	0,8	13,0
	Stdev.	±11.4	±1.9	±2.2	±8.3	±4.8	±0.2	±8.3
Amino Acids [µmol/g; µmol/L]	Mean	631,3	164,1	49,8	907,7	661,9	3,2	8,8
	Stdev.	±602.0	±93.8	±82.3	±637.6	±434.7	±3.2	±7.9
AAC/C [%]	Mean	26,5	15,5	10,8	33,9	32,7	10,1	2,8
	Stdev.	±8.6	±4.2	±5.9	±12.6	±10.5	±6.5	±2.6
AAN/N [%]	Mean	57,0	38,3	24,2	65,6	61,6		
	Stdev.	±14.8	±8.8	±12.8	±18.4	±26.4		
Asp/β-Ala	Mean	71,8	19,2	10,5	57,9	47,3	10,2	2,6
	Stdev.	±63.4	±19.5	±6.6	±64.7	±44.9	±14.7	±2.4
Glu/γ-Aba	Mean	45,7	12,9	8,5	103,6	105,3	8,5	8,8
	Stdev.	±38.8	±7.2	±6.9	±122.7	±69.6	±7.0	±10.2
AA/HA	Mean	25,4	14,9	9,1	84,6	204,6	80,2	106,8
	Stdev.	±14.7	±6.6	±4.6	±42.7	±179.1	±65.2	±142.7
Gluam/Galam	Mean	3,2	3,6	1,2	3,0	2,1	1,6	0,3
	Stdev.	±3.3	±1.1	±0.3	±1.8	±1.7	±2.4	±0.2
RI	Mean	15,1	3,9	1,8	18,8	15,7	1,6	0,9
	Stdev.	±16.4	±1.5	±2.2	±10.6	±8.3	±1.8	±0.7
DI	Mean	0,9	0,3	-0,5	1.0	1,1	2,1	1,5
	Stdev.	±0.8	±0.3	±0.8	±0.1	±0.3	±1.1	±0.9
SDI	Mean	1,1	0,0	-0,9	0,8	0,8	-0,7	-0,8
	Stdev.	±0.2	±0.2	±1.0	±0.2	±0.3	±0.4	±0.3
RTI	Mean	0,7	0,1	0,6	0,2	-1,0	-2,8	-2,7
	Stdev.	±0.3	±0.3	±0.4	±0.5	±0.4	±0.6	±0.4
ox/anox	Mean	1,2	1,3	2,2	1,1	1,0	0,8	0,7
	Stdev.	±0.3	±0.2	±1.1	±0.1	±0.1	±0.3	±0.3

5 Discussion

5.1 Changes during organic matter degradation

Our summary of AA data from various locations in the world ocean corroborates earlier findings that the AA spectra of plankton and sinking particles are similar in surface waters while degradation of organic matter by zooplankton and microbes imparts characteristic changes to AA spectra with increasing water depth (Lee, 1988). The AA spectra track the successive degradation of organic matter during sedimentation from the plankton source via sinking particles, their incorporation into sediments and their further degradation after burial. The most characteristic changes along this sedimentation pathway are the relative enrichments (in Mol%) of Gly, Asp and the non-protein AA β-Ala, γ-Aba and Orn and the relative decrease of AA produced by fresh plankton such as Glu, Ala, Val, Met, Ile, Leu, Tyr and Phe (Fig. 4a). These changes are depicted by the common biogeochemical indicators: the ratios of proteinaceous AA vs. non-protein AA (RI and Glu/γ-Aba) decrease along this pathway. Asp/β-Ala ratios also decrease because β-Ala becomes relatively more enriched than Asp. The DI, originally derived from sediment samples of different degradation states (Dauwe et al., 1999; Dauwe and Middelburg, 1998), decreases from positive values in fresh plankton and most sinking particles to negative values in sediments as it integrates the products of Asp and Gly multiplied with negative factors, and the products of Glu, Met, Ile, Leu, Tyr and Phe multiplied with positive factors (Dauwe et al., 1999).

In contrast, the AA in SPM evolve along a different path than the sedimentation pathway (Gaye et al., 2013). Shares of Ser, Gly, ß-Ala, γ-Aba, His and Orn increasewith water depth, whereas almost all other AA become relatively depleted (Fig. 4b). These trends in AA spectra of SPM are also seen in the DOM phase of sea water and lead to maxima of Ser, Gly and His (Figs. 4b, c). The striking difference in AA distribution of SPM (Fig. 4) on the one hand and sinking particles and sediments on the other hand suggest that there is little exchange between the two types of particles in the ocean. Sinking particles build up sediments and the degradation pathways evident in the water column - namely the accumulation of degradation products and acidic AA often absorbed to carbonates - continue in the sediments. SPM, however, follows a different pathway that is not captured by the common AA based biogeochemical indicators of organic matter degradation (Table 1; Fig. 5) so that novel biogeochemical indicators are required to characterize their AA changes.

5.2 Results of a PCA: two new biogeochemical indicators

A PCA of individual AA (Mol %, Fig. 6a) of all samples compiled in this study results in two factors which explain 59 % of the total variance within the data set. The first factor delineates the well-known changes along the degradation pathway from plankton via sinking particles to sediments. Phe, Ile, Leu, Glu and Tyr (enriched in fresh plankton) have the highest F1 loadings while Asp, ß-Ala and γ-Aba (accumulating during degradation) have the lowest negative F1 loadings. Highest F2 loadings are found for Asp, Thr, Lys and Val while Gly, Orn, His and Ser have the most negative F2 loadings. Factor scores of the individual samples (Fig. 6b) plot in a triangular shape with plankton and fresh organic matter from surface waters at the apex with highest F1 and F2 scores. The diverging sides of the triangle mark particles and sediments decreasing in F1 scores on one side and SPM with decreasing F2 scores on the other side (Fig. 6b). Similar trends were observed in earlier studies based on local data sets (Nagel et al., 2016; Gaye et al., 2013). That samples from greatly different environments reveal the same divergence between sinking particles and SPM with only little overlap (Fig. 4) suggest a general mechanism operating globally. Most of the overlap encompasses SPM samples from the Kara Sea which were sampled at water depths below 100 m. The Kara Sea is characterized by sediment resuspension related to strong riverine input in combination with sea ice dynamics so that many of the Kara Sea SPM samples are mixed with resuspended sediments (Gaye et al., 2007; Unger et al., 2005). TDAA analyzed in water and pore water form a cluster with significantly different AA composition from particulate matter, but instead recapitulating the enrichments of Orn, His, Ser and Gly observed in SPM (Fig. 6b).

The precise separation of the degradation pathway of sinking particles and sediments from SPM and DOM by the PCA suggests that we can use the first factor (F1) to calculate a new sinking particle and sediment degradation index (SDI)

$$SDI = \sum_i \left(\frac{var_i - AVG.var_i}{STD.var_i}\right) \times Loadings\,.F1_i \qquad (4)$$

where var_i is the original mole percentage of each AA_i, $AVGvar_i$ and $STDvar_i$ are the mean and standard deviations, respectively, and $Loading.F1_i$ is the factor loading of the first axis (F1) of the PCA of the individual amino $acid_i$ shown in Table 2. The second factor (F2) - normalized in the same way with the averages and standard deviations of the same PCA - can be used as an indicator of changes in the AA composition of SPM depending on its residence time in the ocean (see discussion below) and is therefore named residence time index (RTI)

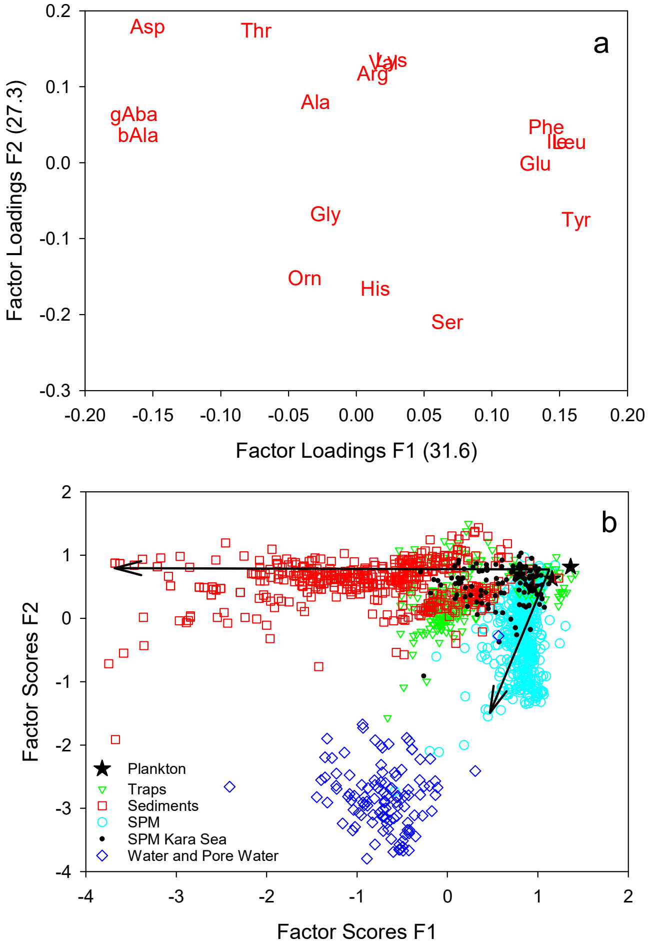


Figure 6: Results of a PCA of AA (Mol%) of all samples of this study with factor loadings of amino acids for the first and second factor (a) and factor scores of samples (b). Arrows indicate progressive deviation in composition from the plankton source, essentially with increasing water and sediment depths.

$$RTI = \sum_i \left(\frac{var_i - AVG.var_i}{STD.var_i}\right) \times Loadings\,.\,F2_i \qquad (5)$$

and is calculated in the same way as the SDI but the factor loadings of the second axis (F2) of the PCA of the individual amino acid$_i$ (Table 2) is inserted for the term *Loadings.F2$_i$*. Most of the F1 loadings resemble those of the DI of Dauwe et al. (1999) (Table 2) and the SDI and DI thus are significantly correlated.

A close look at the results in Fig. 6 (see also Figure S1) shows that the new indicator SDI allows a separation of trap samples from <200 m water depth from those from greater depths. At an SDI value of 0.5, lower values indicate stronger degradation in the deep samples. Likewise, SPM from >200 m depths has lower RTI than most of the samples from shallower depths. Deep trap samples and deep SPM samples form two clearly separated clusters with different SDI and RTI (see Figure S1 for further details).

Table 2: Factor loadings of F1 and F2 for calculating the SDI and RTI, respectively, average [Mol%] and standard deviations (Std. Dev.) of AA of samples used for the PCA shown in Figure 5 in comparison with the factor loadings (named factor coefficients) of the DI published by Dauwe et al (1999) and their averages [Mol%] and standard deviations used for the DI based on 28 sediment samples.

Amino Acid	Loadings F1 SDI	Average [Mol%]	Std. Dev.	Loadings F2 RTI	DI	DI Average [Mol%]	DI Std. Dev.
Ser	0.067	8.7	3.6	-0.210	0.015	7.2	1.9
His	0.014	2.4	2.3	-0.166	0.158	1.0	0.8
Orn	-0.038	1.2	1.9	-0.152	-	-	-
Tyr	0.162	1.9	1.1	-0.075	0.178	2.1	1.2
Gly	-0.023	16.2	2.8	-0.068	-0.099	17.6	3.8
Glu	0.132	10.5	2.5	-0.001	0.065	10.0	2.3
Leu	0.157	5.9	1.9	0.027	0.169	6.6	1.5
Ile	0.148	3.8	1.0	0.028	0.139	4.5	0.8
β–Ala	-0.161	1.3	2.0	0.036	-	-	-
Phe	0.140	2.9	1.0	0.047	0.134	3.2	1.2
γ–Aba	-0.164	1.0	1.6	0.064	-	-	-
Ala	-0.030	9.1	1.5	0.080	-0.043	11.8	0.8
Arg	0.012	4.2	1.1	0.117	-0.115	6.1	2.3
Val	0.020	5.7	1.1	0.132	-0.044	7.6	1.1
Lys	0.026	5.1	1.2	0.135	-	-	-
Thr	-0.074	5.7	1.2	0.174	-0.129	7.1	1.5
Asp	-0.154	12.2	4.3	0.179	-0.102	13.4	2.7

5.2.1 The SDI as an indicator of degradation and oxic vs. anoxic diagenetic conditions of sinking particles and sediments

In order to test the performance of our new degradation indices and to find out if individual AA can be used in place of the SDI and RTI, we separated SPM samples from sinking particles and sediments and correlated the common biogeochemical indicators and individual AA (Mol %) of SPM with the RTI of individual samples while we correlated the same variables of sinking particles and sediments with the SDI (Table 3). We assume that correlations with Pearson

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correlation coefficients R>0.50 can be considered as "strong correlations" (Cohen, 1988). The SDI correlates moderately to strongly with the common degradation indicators and the best positive correlation is found between SDI and the DI (Table 3). The strong correlation among the degradation indicators with POC contents indicates that this common and often measured variable is a good indicator of relative organic matter quality in sinking particles and sediments and all other degradation indices (except the SDI and DI) do not perform better than POC concentrations (see correlation coefficients in Table 3). The DI and the SDI, which are to some extent interchangeable, allow a fine tuning of degradation intensities. The negative correlation of the ox/anox ratio with the SDI is preconditioned, as it is the quotient of AA enriched by degradation to those enriched in fresh plankton. It should be noted that this negative correlation is even better than the positive correlation of the DI and the SDI. A close look at the SDI and ox/anox shows that sediment samples from the regions with bottom water anoxia (Namibian shelf < 200 m depths; Arabian Sea slope at 775 m) have lower ox/anox ratios and distinctly higher SDI values compared with samples from similar depths and oxygenated bottom water (e.g. Mediterranean Sea, Kara Sea, Eastern Pacific). The SDI and the ox/anox show a linear correlation coefficient of R=-0.92 but the relationship is actually logarithmic (Fig. 7a). The SDI better depicts the spectral changes in samples deposited under anoxic diagenetic conditions such as those from the Namibian shelf (Nagel et al., 2016) and the Arabian Sea mid-water oxygen minimum zone (Suthhof et al., 2001) while the ox/anox ratio better resolves variations in samples of strong oxic degradation so that the SDI is in fact better suited to determine the threshold of anoxic vs. oxic diagenesis. In anoxic sediments the SDI is close to the SDI in sediment traps so that we surmise that anoxic diagenetic conditions preserve the primary SDI signal from the water column (Fig. 7b). The SDI can thus be used to distinguish anoxic from oxic diagenetic conditions in sediment cores. The SDI performs better than the ox/anox indicator as it better resolves low values corresponding to low oxygen concentrations, and also better than the DI as the latter less significantly correlates with the ox/anox indicator (Figure S2). The good significant correlation of the SDI and POC (Table 3; R=0.57), furthermore, implies that anoxic conditions favor the accumulation of POC or vice versa. It has been debated whether sub- to anoxic diagenetic conditions enhance preservation as experiments showed similar degradation rates at oxic and anoxic diagenetic conditions (Henrichs and Reeburgh, 1987). There is, however, ample evidence that POC contents are enhanced in anoxic sediments so that the reduced proto- and metazoan grazing of bacteria by other organisms may be responsible for the observed enhanced preservation (Lee, 1992).

Table 3: Pearson correlation coefficients of the SDI, RI, DI, Asp/β-Ala and Glu/γ-Aba with selected AA*, the RTI, AAC/C, AAN/N, AA ratios and degradation indices, water depth (Depth), POC and TN contents (%) and AA content (nmol/g) in sediment trap and sediment samples (column 2-6). Pearson correlation coefficients of the RTI, RI, DI, Asp/β-Ala and Glu/γ-Aba with selected AA, the SDI, AAC/C, AAN/N, AA ratios and degradation indices, water depth (Depth), POC and TN contents (%) and AA content (nmol/g) in SPM samples (column 8-12).

* Only AA with a correlation coefficient R≥0.50 with at least one of the indicators are shown.

1	2	3	4	5	6	7	8	9	10	11	12
Traps and Sediments	SDI	RI	DI	Asp/β-Ala	Glu/γ-Aba	SPM	RTI	RI	DI	Asp/β-Ala	Glu/γ-Aba
Asp	***-0.68***	-0.30	***-0.83***	-0.25	-0.32	Asp	***0.81***	0.00	***-0.61***	0.13	-0.17
Thr	0.12	-0.25	-0.25	0.03	0.07	Thr	***0.86***	-0.02	***-0.57***	0.06	-0.16
Ser	0.32	0.03	0.16	0.09	0.16	Ser	***-0.91***	-0.15	0.08	-0.11	-0.01
Gly	-0.21	-0.32	-0.45	-0.31	-0.31	Gly	***-0.90***	-0.17	0.12	-0.11	0.04
Ala	0.46	0.07	0.17	0.03	0.11	Ala	***0.91***	0.09	-0.43	0.11	-0.09
Val	***0.67***	0.31	0.48	0.29	0.31	Val	***0.88***	0.07	-0.26	0.08	-0.09
Ile	***0.87***	0.48	***0.76***	***0.52***	***0.55***	Ile	***0.68***	0.34	0.26	0.26	0.02
Leu	***0.88***	0.49	***0.76***	***0.52***	***0.56***	Leu	***0.65***	0.47	0.28	0.35	0.11
Tyr	***0.72***	0.39	***0.76***	0.34	0.32	Tyr	-0.14	0.27	***0.66***	0.02	0.23
Phe	***0.89***	0.38	***0.79***	0.40	0.44	Phe	***0.78***	0.37	0.04	0.29	0.06
β-Ala	***-0.85***	-0.27	-0.44	-0.32	-0.35	β-Ala	-0.08	***-0.66***	-0.19	***-0.52***	-0.12
γ-Aba	***-0.79***	-0.25	-0.37	-0.28	-0.35	γ-Aba	0.24	***-0.53***	***-0.65***	-0.20	-0.40
Lys	***0.56***	0.14	0.43	0.15	0.15	Lys	***0.71***	0.05	-0.20	0.03	-0.06
SDI		0.45	***0.82***	0.46	0.51	SDI	0.07	0.49	***0.83***	0.23	0.28
RTI	0.04	-0.01	-0.26	0.03	-0.05	RTI		0.10	-0.34	0.12	-0.08
AAC/C%	***0.56***	***0.51***	***0.53***	***0.56***	***0.56***	AAC/C%	-0.08	0.14	0.22	0.06	0.09
AAN/N%	***0.55***	0.40	0.49	0.47	0.47	AAN/N%	-0.05	0.06	0.03	-0.06	0.08
AA/HA	***0.54***	***0.58***	***0.54***	***0.73***	***0.75***	AA/HA	***-0.57***	0.11	0.32	-0.01	0.16
Gluam/Galam	0.36	*0.43*	0.44	0.40	0.35	Gluam/Galam	0.27	0.43	0.16	0.28	0.08
Asp/β-Ala	0.46	***0.93***	***0.57***		***0.85***	Asp/β-Ala	0.12	***0.74***	0.10		0.07
Glu/γ-Aba	***0.51***	***0.93***	***0.56***	***0.85***		Glu/γ-Aba	-0.08	0.37	0.24	0.07	
RI	0.45		0.49	***0.93***	***0.93***	RI	0.10		0.33	***0.74***	0.37
DI	***0.82***	0.49		***0.51***	***0.56***	DI	-0.34	0.33		0.10	0.24
ox/anox	***-0.91***	-0.30	***-0.71***	-0.31	-0.37	ox/anox	***0.67***	-0.19	***-0.50***	-0.10	-0.09
Depth	***-0.67***	-0.28	***-0.54***	-0.28	-0.37	Depth	***-0.55***	-0.12	0.23	-0.11	0.04
POC	***0.57***	***0.79***	***0.67***	***0.77***	***0.76***	POC	0.27	0.30	0.13	0.25	-0.03
N	0.45	0.46	***0.50***	0.39	0.39	N	0.29	0.30	0.13	0.24	-0.01
AA	***0.51***	***0.84***	***0.60***	***0.79***	***0.76***	AA	0.17	0.28	0.15	0.20	0.01

The core SO90-111 KL from the oxygen minimum on the Pakistan margin was used to reconstruct changes in oxygenation during the last 60 ka BP based e.g. on $\delta^{15}N$ values of total N (Suthhof et al., 2001). The $\delta^{15}N$ values fluctuated between enhanced values in warm phases due to denitrification in the mid-water oxygen minimum and lower values in cold phases when the oxygen minimum zone was weaker or absent (Suthhof et al., 2001). The SDI very precisely tracks these changes (Fig. 7c) and in accordance with the threshold discernable in Fig. 7b we propose that the divide between oxic and anoxic diagenetic conditions is at SDI values between 0 and -0,2 with SDI<-0.2 indicating oxic and SDI >0 indicating oxic diagenetic conditions (Fig. 7a, b). The work of (Carr et al., 2016) - relying on the DI - suggests that signals of changes in redox conditions can be preserved even down to 200 m core depth.

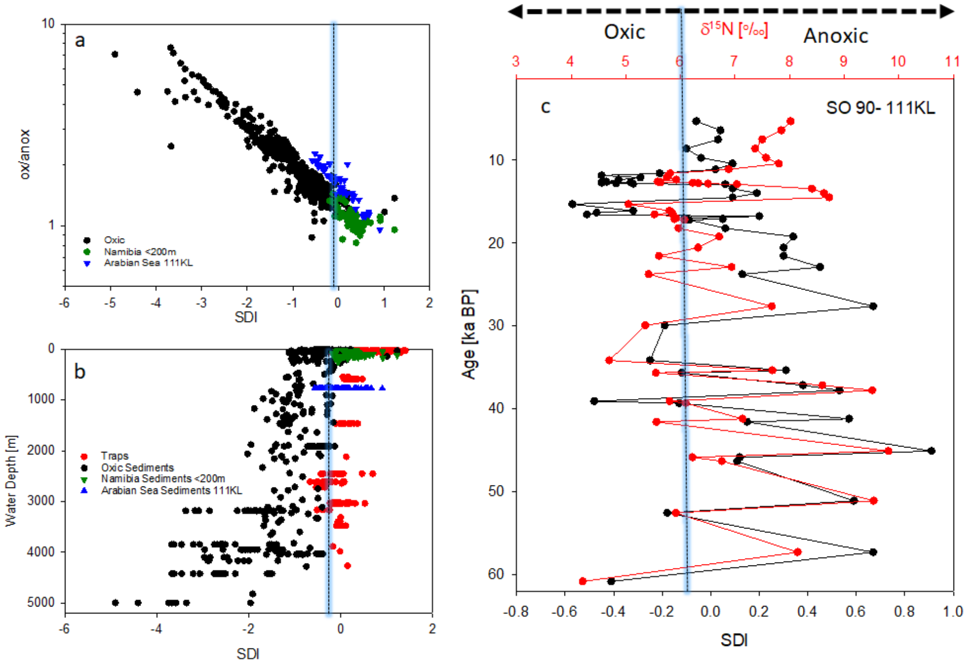

Figure 7: SDI indicator plotted against the log(ox/anox ratio) for oxic sediments (black) and suboxic to anoxic sediments from Namibia (green) and the Arabian Sea (blue) (a). SDI plotted with water depth (in m) of sediment trap deployment (red) and of sediment sampling (see color code of a) (b). SDI and the $\delta^{15}N$ of total N with sediment depth in sediment core SO90-111 KL correlated with an R^2=0.48 (c); the blue bar marks the threshold of the SDI delimiting oxic and anoxic diagenetic conditions at an SDI value of about -0.1.

4.2.2 The RTI as an indicator of suspended matter residence time

Changes in SPM are depicted by changes in RTI factor loadings (Fig. 5b) which are basically due to the relative depletion of Phe, Ile, Leu, Glu and Tyr dominant in fresh plankton and the enrichments of Gly, Ser, Orn and Lys. Both, Ser and Gly (Mol %) are strongly linearly anticorrelated with the RTI (R=-0.91 and -0.90) showing that they can be used instead of the RTI to determine the SPM residence time in the water column. The anticorrelation of the RTI with water depth (Table 3) is due to the RTI decrease in the upper 200 m only, while it remains constant below this depth (Fig. 8).

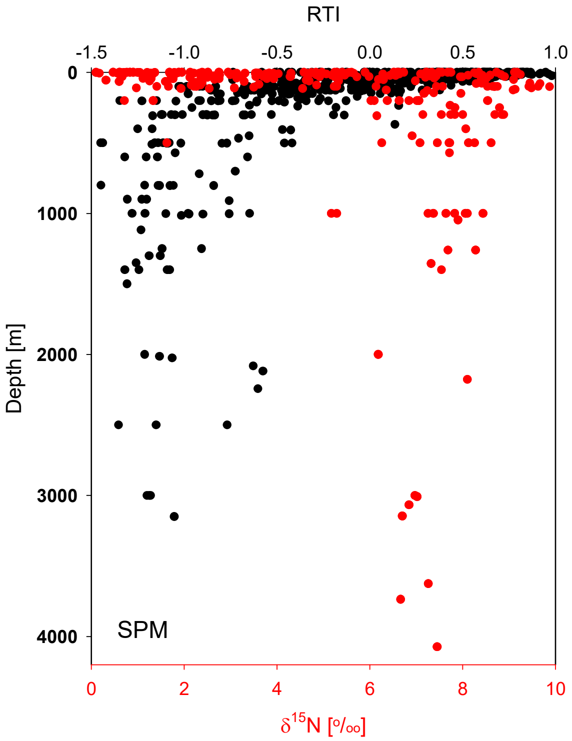

Figure 8: The RTI (black dots) and the $\delta^{15}N$ values (red dots) of SPM with water depths [m].

Below 200 m SPM becomes distinctly decoupled from sinking aggregates. SPM sampled in the upper ocean mixed layer and euphotic zone includes fresh plankton whereas below the surface mixed layer this fresh material is limited to the rare large sinking aggregates and the chance that SPM interacts with sinking particles decreases with water depth due to the scarcity of both (Mccave, 1984). The observed constant AA composition below 200 m water depth suggests that SPM is largely refractory and the AA are barely accessible to further microbial degradation or uptake. The age of the water masses in the upper ocean mixed layer is less than 100 years while deeper waters have ages of several 100 years to maxima of 1600 years in the deep Indian and Pacific Oceans (England, 1995; Gebbie and Huybers, 2012). Solubilization of particulate matter by exoenzymes and the subsequent uptake in dissolved form (Carlson and Hansell, 2015; Aristegui et al., 2009) leads to an almost complete turnover of originally diverse surface derived organic matter. It is thus feasible that bacterial biomass comprises a large amount of organic matter in compartments of long residence times. However, fresh bacteria and fungi have quite similar AA composition as plankton (Cowie and Hedges, 1992) while SPM AA composition is fundamentally different. The high AA/HA ratios associated with relatively high Gluam/Galam ratios both not having a clear trend with water depth also suggest that the contribution of bacterial biomass to SPM is small and does not increase with water depth (Table 1; Fig. 5a, b). The observed changes in SPM are thus more likely related to adsorption processes and macromolecule formation of material not digestible to deep sea organisms and resistant to their enzymes. DOM was shown to become adsorbed to mineral surfaces (Keil and Kirchman, 1993; Keil and Kirchman, 1994; Keil et al., 1994; Arnarson and Keil, 2005, 2007). However, degradation of adsorbed AA proceeds on particles (Satterberg et al., 2003; Taylor, 1995). Thus, the constant AA composition in SPM at depths >200 m may indicate that SPM is in equilibrium with the TDAA which likewise show no depth dependent changes in AA composition (Figure S3). Feasible candidate processes to explain the homogeneity are AA scavenging by SPM or formation of gels (3D networks = biopolymers) which can anneal to larger sizes so that part of the dissolved AA can be passed from the dissolved to the particulate organic carbon pool (Druffel and Williams, 1990; Orellana and Leck, 2015). This process is, however, reversible so that there is probably an exchange between the gel and particulate matter phase as well as between gels of different sizes and complexities depending on pH, temperature, the presence of ligands, pollutants or UV radiation (Orellana and Leck, 2015). Generally, hydrophobic AA (Ala, Val, Met, Ile, Leu, Phe, Pro, Trp) and aromatic AA (His, Tyr) are more likely to form gels and aggregates (Orellana and Leck, 2015). Our results indicate that an equilibrium may be attained between the dissolved phase and SPM after a relatively short time so that the AA composition of SPM is constant below 200 m water depth. If there is no further significant scavenging of SPM by sinking particles and no degradation of AA on SPM, their abundance could increase due to further adsorption of DOM. However, large zooplankters may be able to utilize the SPM pool (Koppelmann et al., 2009; Gloeckler et al., 2018; Hannides et al., 2013) and further studies are required to elucidate the fate of SPM in the ocean.

5.3 Composition of total dissolved amino acids in sea water and pore water

The uniform TDAA distribution with depth shows that most of the respiration is taking place in shallow waters as is the case also for DOC (Reinthaler et al., 2006). After this instantaneous utilization of AA by bacteria there are only small changes in the TDAA spectra (Figure S3) and Ser, Gly and His uniformly become the major TDAA in sea water and pore water. It is possible that the selective accumulation of these AA in the dissolved phase is due to their excretion or their association with exoenzymes. Ser is present in N-acyl homoserine lactone (AHLs) which is a class of bacterially produced signaling molecules involved in bacterial quorum sensing; these compounds serve to regulate growth by changing gene expressions, for example, in order to influence population density or phenotype (Parsek et al., 1999; Klein et al., 2009). His changes from its protonated to deprotonated form at a pH of 6 and is therefore often present at the active sites of enzymes. Ser and Gly may simply remain dissolved in sea water as they are hydrophilic. Once mixed into the deeper ocean the scarcity of bacteria or the incorporation of AA into gels could be the reason for their recalcitrance. However, we do not assume that a considerable part of the TDAA belong to dissolved free AA. Because the differences between the samples from different regions are much smaller than the difference between the molecular weight fractions and sea water vs. pore-water (Figure S3), we surmise that the formation and transformation processes of DOC are very uniform in the ocean. This assumption is based on limited data so that these results are rather preliminary. We also do not have enough spatial coverage of SPM and TDAA data in the deep ocean to detect AA utilization by organisms or sorption and desorption processes. Both these organic matter pools are large (see below), so that such investigations are important to estimate the possible role of these pools in oceanic carbon sequestration and the reactions to global change (Ridgewell and Arndt, 2015).

5.4 δ^{15}N values in sinking and suspended matter and evidence for nitrogen sources and transformation processes

The δ^{15}N values in sediments can preserve information on N sources throughout the geological history (Sun et al., 2019; Gaye et al., 2018; Kienast et al., 2008). However, δ^{15}N values may be modulated by organic matter cycling and diagenetic processes which are replicated and thus traceable in the AA composition not least because AA are the main identifiable contributors to N. The increase of δ^{15}N values by about 2 ‰ on average during organic matter burial and early diagenesis in the upper sediments (Robinson et al., 2012; Tesdal et al., 2013) is corroborated by a parallel shift in AA based degradation indicators (Gaye-Haake et al., 2005; Möbius et al., 2010). In contrast to sediments, there are no clear depth related trends in δ^{15}N values of sinking particles in the water column of the epi- to mesopelagic ocean (Gaye-Haake et al., 2005; Yang et al., 2017; Altabet, 2006). AA based biogeochemical indicators revealed degradation with depth at specific trap sites (Haake et al., 1993a) and δ^{15}N analyses of individual amino acids showed that degradation is proceeding on sinking particles (Mccarthy et al., 2007) with δ^{15}N changes of “trophic” AA while δ^{15}N of “source”AA remained constant (McCarthy et al., 2006).

However, degradation of sinking particles is much smaller than degradation at the sediment water interface and in our large data set that integrates many different areas of study the small to moderate changes in AA degradation are obviously obliterated, as neither AA contents (Fig. 3), nor the SDI (Fig. 7), the AAC/C % (Figure S4) nor AAN/N % (not shown) reveal any significant trends in sinking particles in the deep ocean.

AA composition of SPM as expressed in the RTI is constant and SPM is rather recalcitrant at water depths >200 m. Paralleling this, the δ^{15}N values of SPM are about 6-8 ‰ on average in all our studies carried out (Fig. 8). In previous studies δ^{15}N values of SPM where reported to increase from ≤5 ‰ in surface waters to values between 6-8 ‰ below 200 m water depth which was attributed to organic matter degradation on SPM (Yang et al., 2017; Altabet et al., 1991; Hannides et al., 2013; Emeis et al., 2010). However, SPM samples from the Arabian Sea upwelling area show decreasing δ^{15}N values from an average of 8.6 ‰ at water depth above to 7.4 ‰ at depths below 200 m (Gaye et al., 2013). It is thus reasonable that SPM has a constant δ^{15}N value in the mesopelagic and bathypelagic ocean. This is an additional indicator of a common process determining the AA composition and their δ^{15}N values of SPM and probably also of DOM sampled below water depths of 200 m (equivalent to an age of ≥100 years; (England, 1995; Gebbie and Huybers, 2012).

5.5 Abundance of amino acids in the ocean

Based on POC, TN and AA fluxes and the area of the open ocean and shallow seas (Costello et al., 2010) we can estimate annual downward fluxes (Table S5). Average POC flux of compilations of trap fluxes were between 1.65 g m^{-2} a^{-1} (Wilson et al., 2012) and 2.74 g m^{-2} a^{-1} (Rixen et al., 2019a) while our subset of trap samples from the open ocean (>2000 m water depth) averages to 3.06 g m^{-2} a^{-1}. For open ocean traps this results in total fluxes of 0.51-0.94 PgC a^{-1}. Our average flux estimates for TN are 0.13 PgN a^{-1} and for AAC are 0.15 PgAA a^{-1}. The flux rates over the shelves and slopes bear, however, large uncertainty because productivity is by several orders of magnitude higher than in offshore areas and spatially variable. Our first estimate, simply based on an average of our fluxes caught in traps deployed in areas of water depth < 2000 m arrives at POC fluxes of 5.4 PgC a^{-1}, TN fluxes of 0.9 PgN a^{-1} and AAC fluxes of 1.36 Pg AAC a^{-1}. Thus 85-90 % of fluxes occur in near shore environments corroborating that 95 % or the total marine organic carbon is buried in these environments (Hedges and Keil, 1995). The total sinking fluxes in the proximal plus distal ocean add up to 6.3 PgC a^{-1}, 1.0 PgN a^{-1} and, respectively, 1.51 Pg AAC a^{-1} (see Table S5 for further details).

The largest organic carbon pool in the ocean is DOC with an inventory of 632±32 PgC (Carlson and Hansell, 2015; Hansell et al., 2009) and the largest N pool is DON with 77±23 PgN (Gruber, 2008; Bronk, 2002). Dissolved AA are thus the largest AA pool in the ocean even if AA comprise only a minor amount of DOC. We have only few measurements of AA concentrations, which range between 0.1-0.2 mg/L with an average of 0.16 mg/L in all water samples excluding bottom water. Based on these data we can estimate that AA comprise about 200±70 Pg which would contribute about 35±11 Pg AAN and about 89±29 Pg AAC to the oceanic DON and, respectively, DOC pools. Accordingly, AAC contributes about 14 % to DOC while AAN contributes 45 % to total oceanic DON. This is in the low range of an estimate of 45-86 % AAN based on NMR spectroscopy with acid hydrolysis recovering about half of this AAN pool (Aluwihare et al., 2005).

The constant contents and composition of TDAA throughout the ocean indicates that it belongs to the recalcitrant or refractory pool of DOC; this pool is hardly removed in the deep sea and may only be degraded by photochemical reactions as it is returned into surface waters in the course of ocean circulation (Legendre et al., 2015). Our TDAA data reveal no depth dependent trend but our data coverage is not sufficient to detect any spatial variation. The distribution of DOC is, however, well known with its maximum in surface water with 40-80 µmol C kg^{-1} and depletion in deep water with DOC concentrations from >50 µmol C kg^{-1} in the North Atlantic to 39 µmol C kg^{-1} in the North Pacific deep water (Carlson and Hansell, 2015; Hansell et al., 2009). Due to our limited number of measurements we may have missed spatial variations which could elucidate TDAA sources and cycling processes in the ocean as is the case for DOC. Respiration of DOC may be an important removal process in shallower waters (Reinthaler et al., 2006) while a large proportion of the DOC reduction on its way to the Pacific on the deep conveyer belt could be related to adsorption to POC, partly via gel formation (Druffel and Williams, 1990).

TDAA may be among the constituents of DOC, which interact with SPM as both are transported with their specific water masses by the ocean conveyer belt. Interaction with SPM is suggested by the relative similarity in AA composition of TDAA and SPM. Moreover, SPM carries the second largest pool of POC and AA in the ocean which has not been accounted for in carbon budgets and which role in oceanic biogeochemical cycling has received little attention. The total abundance of POC, TN and AA in SPM can be calculated using average concentrations (Tab. 1) in the ocean volume between 0-200 m and between 200 m and the sea floor (Costello et al., 2010). These calculations show that there are 443 Pg of total suspended matter in the ocean of which organic carbon comprises 48 PgC, amino acids 35 PgAA and, total nitrogen 6 PgN. The relative similarity of AA spectra in SPM and TDAA suggests interaction between the two pools at shallower depths and the build-up of an equilibrium, so that both pools remain constant in concentrations and composition with depths. Like DOC, which was suggested to be recalcitrant in the deep sea (Hansell and Carlson, 2013), SPM may only be affected by degradation and repackaging into aggregates as it is reintroduced into surface water by ocean circulation. Several studies, however, suggest that SPM may be an important food source for deep living zooplankton (Koppelmann et al., 2009; Hannides et al., 2013; Gloeckler et al., 2018). If there are no removal processes in the deep ocean, we would expect SPM and their organic constituents to be exported from the Atlantic via the deep ocean circulation and to accumulate in the Pacific.

6 Conclusions

The PCA of a set of 1425 samples consisting of sinking particle, SPM, sediment and water samples produced two factors which separate AA in sinking particles and sediments on the one hand from SPM and DOM on the other hand. As the PCA produced two branches diverging with water and, respectively, sediment depth, strong interactions between the sinking and suspended particles pools can be excluded.

The relative degradation of sinking particles and sediments, dominated by Gly, Asp, Glu and Ala, can be tracked by a new degradation indicator named SDI derived from the first factor of the PCA and correlated with the often-used degradation index DI. Except the SDI and the DI all other biogeochemical indicators are not better than POC concentrations for a relative classification of organic matter degradation. The SDI is, moreover, capable to separate oxic and anoxic diagenetic conditions at an SDI between 0 to -0.2 (with values <-0.2 indicating oxic and values >0 indicating anoxic diagenetic conditions). Application of the SDI furthermore, shows that the diagenetic signal from the water column is preserved in sediments deposited under anoxic conditions. The correlation of the SDI with POC shows that anoxic diagenesis enhances POC accumulation in sediments compared to oxic diagenesis.

A novel biogeochemical indicator derived from the second factor of the PCA named RTI depicts the transformation of SPM enriched in plankton derived AA in the epipelagic ocean to a constant composition in the meso- and bathypelagic ocean. The deep SPM is probably the residue of microbial processing and is not utilizable by enzymes under the present oceanic conditions. This constant composition of SPM is corroborated by a constant δ^{15}N value below 200 m irrespective of the area of study.

DOM has constant AA composition throughout the water column, dominated by Ser, Gly, His, Ala and Orn, pursuing the same accumulation AA pathway as found in deep SPM. Comparison with literature data shows that the amount of AA released, depends on the intensity of hydrolysis and that about 50 % of the amide linkages detectable by NMR spectroscopy cannot be hydrolyzed. Similar to SPM the proteins are not utilizable by microorganisms. Protein-like dissolved material was determined to be on average 2670 years old (Loh et al., 2004), showing that these refractory molecules are cycled for several times before they can be removed by as yet unknown processes.

Based on our AA data we have calculated the total oceanic AA inventory and found that TDAA are the largest oceanic AA pool with a total amount of 200±70 PgAA and AA comprise 14 % of the oceanic DOC and 45 % of oceanic DON.

The pool transported with SPM is 35 PgAA. SPM, furthermore, carries 48 PgC and 6 PgN not accounted for in global carbon and nitrogen budgets. At present it is not known how the oceanic DOM and SPM-particulate organic matter pool is formed and how this rather recalcitrant organic matter can be removed from its abient water mass. It is feasible that these organic matter pools have fluctuated in the past due to change in oceanic physicochemical conditions (Ridgwell and Arndt, 2015). It is intriguing to understand how the accumulation or reduction of this carbon and nitrogen pools has interacted with climate and environmental changes in the geological history but it is vital to understand the response to ongoing and future climate change.

Data Availability

Excerpts of the data were used in previous publications (i) from the Kara Sea in Gaye et al. (2007) Nagel et al. (2005) and Unger et al. (2009), (ii) from the northern Indian Ocean in Gaye et al. (2013), Gaye-Haake et al. (2005), Möbius et al. (2011) and Suthhof et al. (2001), (iii) from the Mediterranean Sea in Möbius (2013) and Möbius et al. (2010), (iv) from the Namibian upwelling in Nagel et al. (2016) and (v) from the Pacific in Paul et al. (2018). The entire data set will be made available in PANGAEA. Data from the Pacific are available at: https://doi.pangaea.de/10.1594/PANGAEA.885391, https://doi.pangaea.de/10.1594/PANGAEA.881804, https://doi.pangaea.de/10.1594/PANGAEA.881813.

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Author Contribution

BG, NL, TR and KE designed the study and led the projects in which samples were taken and analyzed. NL developed and refined the AA analyses. NL, NH and SP contributed and analyzed samples from the southern Indian Ocean and the Pacific. BG wrote the manuscript with contributions of all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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