

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

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13

14 **Abstract**

15 Amino acids (AA) mainly bound in proteins are major constituents of living biomass and non-
16 living organic material in the oceanic particulate and dissolved organic matter pool. Uptake and
17 cycling by heterotrophic organisms lead to characteristic changes in AA composition so that
18 AA based biogeochemical indicators are often used to elucidate processes of organic matter
19 cycling and degradation. We analyzed particulate AA in a large sample set collected in various
20 oceanic regions covering sinking and suspended particles in the water column, sediment
21 samples as well as dissolved AA from water column and pore water samples. The aim of this
22 study was to test and improve the use of AA derived biogeochemical indicators as proxies for
23 organic matter sources and degradation, and to better understand particle dynamics and
24 interaction between the dissolved and particulate organic matter pools. A principal component
25 analysis (PCA) of all data delineates diverging AA compositions of sinking and suspended
26 particles with increasing water depth. A new sinking particle and sediment degradation
27 indicator (SDI) allows a fine-tuned classification of sinking particles and sediments with respect
28 to the intensity of degradation, which is associated with changes of bulk $\delta^{15}\text{N}$ ratios. This new
29 indicator furthermore is sensitive to sedimentary redox conditions and can be used to detect
30 past anoxic early diagenesis. A second indicator emerges from the AA spectra of suspended

31 particulate matter (SPM) in the epipelagic and that of the meso- and bathypelagic ocean and is
32 a residence time indicator (RTI). The characteristic changes in AA patterns from shallow to
33 deep SPM are recapitulated in the AA spectra of the dissolved organic matter (DOM) pool, so
34 that deep SPM is more similar to DOM than to any of the other organic matter pools. This
35 implies that there is equilibration between finely dispersed SPM and DOM in the deep sea,
36 which may be driven by microbial activity combined with annealing and fragmentation of gels.
37 As these processes strongly depend on physico-chemical conditions in the deep ocean, changes
38 in quality and degradability of DOM may strongly affect the relatively large pool of suspended
39 and dissolved AA in the ocean that amounts to 15 Pg amino acid carbon (AAC) and 89 ± 29 Pg
40 AAC, respectively.

41 **1 Introduction**

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

74 pools below the euphotic zone. Due to its long residence time in the ocean, SPM appears to
75 interact with DOM (Gaye et al., 2013b) and therefore carries different AA signatures related to
76 genesis and history of organic matter cycling in its specific water mass (Nagel et al., 2016).
77 Whereas information on the composition of sediment trap samples has been compiled in
78 comprehensive studies (Honjo et al., 2008; Wilson et al., 2012; Rixen et al., 2019a, b), similar
79 compilations of the profuse literature on suspended matter are yet missing.

80 On the way to the deep sea the flux of sinking particles is reduced by disaggregation and organic
81 matter degradation. Suess (1980) empirically derived the first power function for organic
82 carbon decay based on sediment trap data. Subsequently, a large number of similar functions
83 were calculated for various oceanic areas based on trap experiments (Rixen et al., 2019b;
84 Rixen et al., 2002; Armstrong et al., 2002; Martin et al., 1987). Early work on AA had produced
85 similar decay functions combining data from Atlantic and Pacific trap experiments (Lee and
86 Cronin, 1982, 1984). As AA decay faster than bulk organic carbon (Haake et al., 1993b; Haake
87 et al., 1992; Haake et al., 1996; Lee et al., 2004; Wakeham and Lee, 1989; Whelan and Emeis,
88 1992), they are often considered as “labile” constituents of bulk organic matter. This is
89 supposedly due to their preferential uptake as a nitrogen (N) source for further synthesis of AA
90 or as a source of essential AA for heterotrophs (Ittekkot and Arain, 1986; Ittekkot et al., 1986).
91 This has been questioned, as a large proportion of the oceanic organic N pool is comprised of
92 AA that are not bioavailable (Aluwihare et al., 2005). In addition to the quantification of AA
93 decay, degradation state of organic matter (proteins) can be assessed by characteristic changes
94 in AA monomer composition which, furthermore, have the potential to elucidate sources of
95 organic matter and degradation processes (Ittekkot et al., 1984a; Ittekkot et al., 1984b; Dauwe
96 and Middelburg, 1998; Dauwe et al., 1999; Jennerjahn and Ittekkot, 1997).

97 Ratios of individual amino acids such as the Reactivity Index (RI) (Jennerjahn and Ittekkot,
98 1997) or the Degradation Index (DI) normalizing AA data to the results of a principal
99 component analyses (PCA) (Dauwe et al., 1999; Dauwe and Middelburg, 1998) have often been
100 used to scale organic matter degradation (Niggemann et al., 2018; Unger et al., 2005; Ingalls et
101 al., 2006; Ingalls et al., 2004; Pantoja et al., 2004; Möbius et al., 2010). These biogeochemical
102 indicators of organic matter quality were essentially developed for marine sinking particles and
103 sediments. Although based on marine sediments only (Dauwe et al., 1999) the DI was applied
104 for example to SPM samples from the brackish environment (Unger et al. 2005) or even to trace
105 dissolved AA degradation (Davis and Benner, 2005; Guo et al., 2018). Other work used
106 individual and adapted indices to differentiate the states of degradation in SPM or DOM

107 samples and samples from lakes, groundwater and rivers (Abramson et al., 2011; Gaye et al.,
108 2007; Goutx et al., 2007; Kaiser and Benner, 2009; Menzel et al., 2013; Peter et al. 2012;
109 Sheridan et al., 2002).

110 Understanding and quantifying AA degradation is required to estimate the diagenetic imprint
111 on $\delta^{15}\text{N}$ ratios of particulate matter. This is important as $\delta^{15}\text{N}$ ratios track major shifts between
112 N pools and are commonly used to reconstruct the N cycle from sedimentary archives
113 (Galbraith et al., 2013). Amino acid nitrogen (AAN) comprises 80-100 % of N in fresh organic
114 matter and is the precursor of most of the N buried in sediments and ultimately stored in the
115 form of ammonium, adsorbed to clay minerals (Boyd, 2001; Waples and Sloan, 1980; Müller,
116 1977). Considerable AA degradation already occurs in the water column and progresses during
117 organic matter burial in the sediments so that the impact of diagenetic processes on $\delta^{15}\text{N}$ has to
118 be accounted for (Möbius et al., 2010; Möbius et al., 2011; Niggemann et al., 2018; Carr et al.,
119 2016). Ammonification leads to a diagenetic increase of $\delta^{15}\text{N}$ values by up to 6.5 ‰ in deep
120 sea sediments while there is little effect during organic matter burial in shelf and slope
121 sediments due to the higher sedimentation rates and sub- to anoxic diagenetic conditions
122 (Tesdal et al., 2013; Robinson et al., 2012; Möbius, 2013; Gaye-Haake et al., 2005). Such $\delta^{15}\text{N}$
123 increases were shown to correlate with AA derived degradation indicators so that the primary
124 $\delta^{15}\text{N}$ signal from the water column can be reconstructed (Gaye-Haake et al., 2005; Gaye et al.,
125 2009; Möbius et al., 2011).

126 DOM comprising the largest oceanic organic matter pool is defined by the pore size of the
127 filters it passes through which is 0.2-0.7 μm (Carlson and Hansell, 2015) and thus includes
128 some picoplankton cells and all viruses (Aristegui et al., 2009). DOM in surface water is partly
129 labile and can originate from the exudates and lysis of organisms, passive diffusion, or
130 “overflow” out of phytoplankton and bacteria; grazers can excrete or egest DOM, it can
131 furthermore be leached from their fecal pellets or released by sloppy zooplankton feeding and
132 is thus primarily released and also taken up in the surface ocean (Carlson and Hansell, 2015).
133 Moreover, terrestrially derived DOM is transported into surface waters by rivers and via the
134 atmosphere (Benner et al., 2005). Deep DOM has a different source than simply transport of
135 surface DOM by intermediate and deep water formation and mixing, as deep DOM is refractory
136 in nature and has been heterotrophically altered by cycling and degradation processes
137 (Yamaguchi and McCarthy, 2018) discernible e.g. from their composition of dissolved AA
138 (Kaiser and Benner, 2009; McCarthy et al., 2004). The possible source of deep DOM may be

139 the release from sinking or suspended particles associated with microbial degradation on
140 particles and in the ambiance of particles by processes such as solubilizing organic matter by
141 ectohydrolase (Cho and Azam, 1988; Ciais et al., 2014; Aristegui et al., 2009). DOM can also
142 be released from sediment pore water into overlying waters (Lahajnar et al., 2005). Stable
143 isotope ratios of nitrogen ($\delta^{15}\text{N}$) in ultrafiltered DOM (UDOM) showed no systematic change
144 with depth and suggested a common microbial source or viral lysis (McCarthy et al., 2007).

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

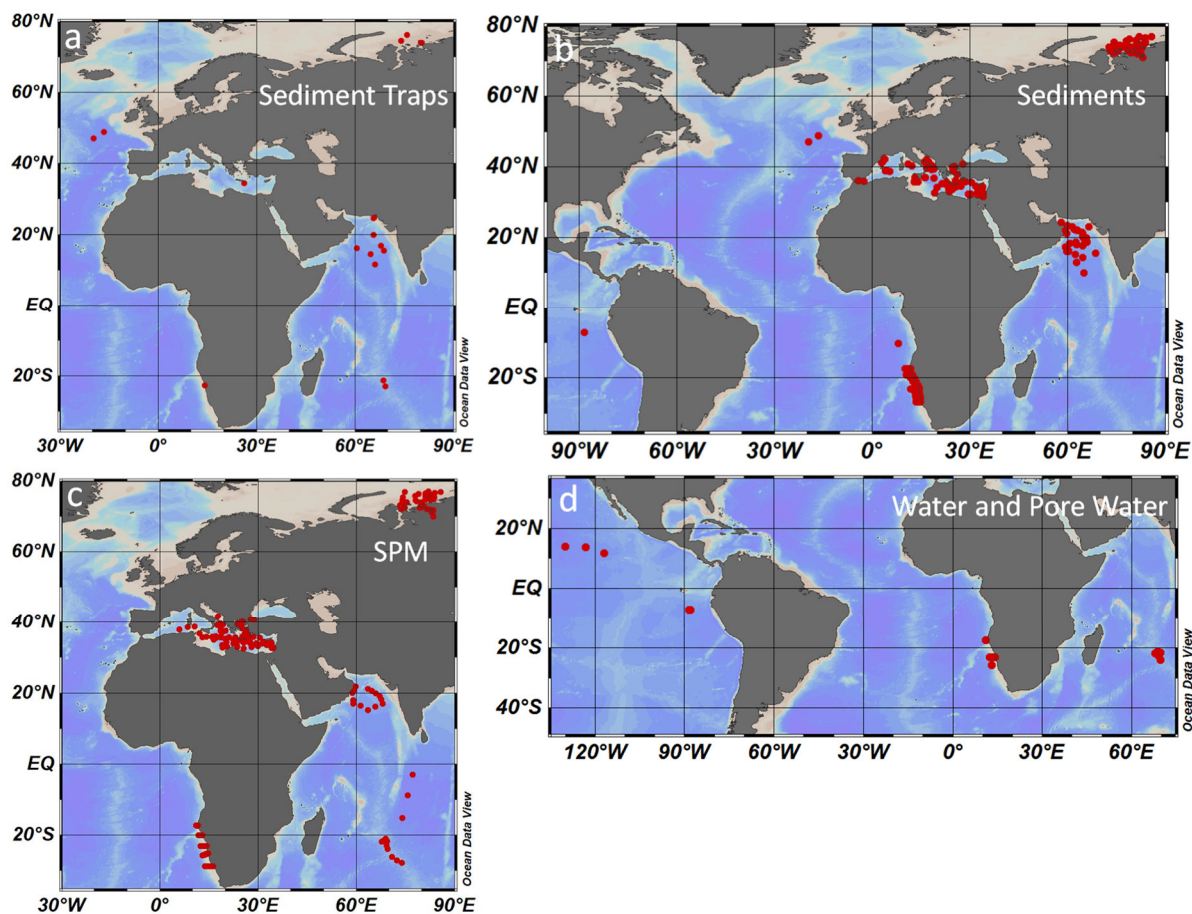
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155 **2. Materials and Methods**

156 **2.1 Sampling**

157 A total of 1425 samples were taken for AA analyses in different oceanic areas and water depths
158 between 1993 and 2017 and include 218 sediment trap samples, 489 sediment samples, 608
159 SPM samples and 110 water and pore water samples (Fig. 1a-d). Five additional plankton
160 samples were taken in the Arabian Sea and from the Namibian upwelling area by plankton tows
161 between 0-100 m and between 100-700 m water depths. In the Kara Sea - a shallow shelf sea
162 strongly impacted by water and suspended matter discharge from the rivers Ob and Yenisei -
163 sediment traps, surface sediments, and suspended matter were sampled (Gaye et al., 2007;
164 Gaye-Haake et al., 2003; Nagel et al., 2009; Unger et al., 2005). In the deep Mediterranean Sea
165 sediment traps and surface sediments were sampled (Möbius et al., 2010). SPM from the
166 Mediterranean Sea was only analyzed for $\delta^{15}\text{N}$ values (Emeis et al., 2010). Sediment trap as
167 well as surface sediment, SPM and water samples were taken along cross shelf transects off
168 Namibia (Nagel et al., 2013; Nagel et al., 2016). Sediment trap samples and short sediment
169 cores were taken at two stations in the northeastern Atlantic (Lahajnar et al., 2005; Turnewitsch

170 et al., 2017; Turnewitsch et al., 2015). In the Arabian Sea sediment trap, SPM, and surface
171 sediment samples were taken in the deep ocean and on the continental slope including a core
172 within the oxygen minimum zone at water depths of 775m (Gaye et al., 2013b; Gaye et al.,
173 2013a; Rixen et al., 2014; Gaye-Haake et al., 2005; Suthhof et al., 2001; Suthhof et al., 2000).
174 In the Indian Ocean Subtropical Gyre sediment trap, SPM and water samples were taken
175 (Harms et al., 2019; Harms et al., 2021) and samples from the equatorial North Pacific and
176 eastern South Pacific comprise bottom water, pore water and sediment core samples (Paul et
177 al., 2018).



178
179 Figure 1: Stations of sediment trap deployments (a), sediment (b), SPM (c) water and pore water
180 sampling (d).

181
182 Sea water was filtered through glass fiber filters (Whatman GF/F) with a nominal pore size of
183 0.7 μm and filters were dried at 40°C in order to obtain SPM samples. At some stations water
184 samples were taken by deep freezing an aliquot of the filtrate for TDAA analyses. In addition,
185 18 water samples taken off Namibia were separated into two size classes by ultrafiltration
186 (Brockmeyer and Spitzzy, 2013). The size classes 50 kDa-0.7 μm and 1 kDa-0.7 μm were used

187 for TDAA analyses. Sediment trap samples were wet sieved on board and comprise the <1mm
188 fraction, filtered with polycarbonate nuclepore filters of 0.45 µm pore size and dried at 40°C.
189 Sediment samples from multicores, box grabs, box cores, or gravity cores were taken by spatula
190 or syringes from cold stored cores and were freeze dried before analyses. Surface samples
191 represent either the upper 0.5 cm or 1 cm of a sediment core. Pore-water samples were taken
192 by rhizons with a mean pore size of 0.15 µm and stored frozen before analyses (see methods in
193 Paul et al., 2018).

194

195 **2.2 Analytical methods**

196 Total carbon and N were measured with a Carlo Erba Nitrogen Analyser 1500 (Milan, Italy) or
197 a EURO EA3000 elemental analyzer. Particulate organic carbon (POC) was measured after
198 treatment of weighed samples with 1N HCl to remove carbonate. The precision of this method
199 is 0.05% for carbon and 0.005% for N. Carbonate carbon was calculated by subtracting organic
200 carbon from total carbon. Ratios of ¹⁵N/¹⁴N of particulate N were determined using a Thermo
201 Finnigan MAT 252 isotope ratio mass spectrometer connected with a ConFlo-III interface after
202 high-temperature flash combustion in a Thermo Finnigan Flash EA 1112 at 1050°C. Part of the
203 samples were measured with an Elementar IsoPrime 100 isotope ratio mass spectrometer after
204 high temperature combustion in an Elementar CHNOS Vario isotope elemental analyzer at 950
205 °C. Pure tank N₂ calibrated against the reference standards IAEA-N1 (ammonium sulfate,
206 δ¹⁵N= + 0.4 ‰ versus air N₂) and IAEAN2 (ammonium sulfate, δ¹⁵N= + 20.3 ‰) of the
207 International Atomic Energy Agency was used as a working standard. Duplicate measurements
208 of samples differ by less than 0.15 ‰. The laboratory's long-term standard deviation for IAEA-
209 N1 standard is 0.09 ‰. N-isotope ratios are reported in ‰ using the delta notation and the
210 ¹⁵N/¹⁴N of air N₂ as the reference standard:

$$211 \delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference standard}} - 1) * 1000 \quad (1)$$

212 Dissolved organic carbon (DOC) concentrations [mg/L] were determined of water and pore
213 water samples via a high temperature combustion method (POC-V_{CSH} Analyzer, Shimadzu).
214 Inorganic carbon was removed by 2 M HCl prior to injection into the combustion tube where
215 organic carbon is oxidized to CO₂ at 680 °C with a platinum catalyst. A 5-point calibration from
216 0.5 to 5 mg DOC/L was used. The error of measurement is less than 2 % (Brockmeyer and
217 Spitzzy, 2013).

218 TDAA, particulate AA and hexosamines (HA) were analyzed with a Biochrom 30 Amino Acid
219 Analyzer. Acid hydrolysis with 6N HCl for 22 h at 110°C under a pure argon atmosphere was
220 carried out on ca. 3 ml of filtrate of water and pore water samples, on 1-2 mg of suspended
221 matter collected on Whatman GF/F filters, on 1-2 mg of sediment trap samples, or on 1-50 mg
222 of freeze dried surface sediments. A particle free aliquot was evaporated three times to dryness
223 in order to remove the unreacted HCl; the residue was taken up in an acidic buffer (pH 2.2).
224 After injection and subsequent separation with a cation exchange resin, the individual AA
225 monomers were post-column derivatized with o-phthaldialdehyde in the presence of 2-
226 mercaptoethanol and detected with a Merck Hitachi L-2480 fluorescence detector. Duplicate
227 analysis of a standard solution according to this method results in a relative error of 0.1 to 1.3%
228 for the concentrations of individual AA monomers and 0.2 to 3.0% for individual AA
229 monomers of water or particulate matter samples. Due to acid hydrolysis, aspartic acid (ASP)
230 and asparagine (Asn) are both measured as Asp and glutamic acid (Glu) and glutamine (Gln)
231 are both measured as Glu. The other AA measured are threonine (Thr), serine (Ser), glycine
232 (Gly), alanine (Ala), valine (Val), methionine (Met), isoleucine (Ile), leucine (Leu), tyrosine
233 (Tyr), phenylalanine (Phe), β -Alanine (β -Ala), γ -aminobutyric acid (γ -Aba), histidine (His),
234 ornithine (Orn), lysine (Lys) and arginine (Arg). The HA together with AA are glucosamine
235 (Gluam) and galactosamine (Galam) and their total contents were corrected with a factor of 1.4
236 for loss during hydrolysis (Muller et al., 1986).

237

238 **2.3 Amino acid derived biogeochemical indicators of organic matter origin and** 239 **degradation**

240 Amino acid concentrations and the contribution of AA carbon (AAC) and AA nitrogen (AAN)
241 as percentages of total organic carbon (AAC/C %) or total N (AAN/N %) are used to determine
242 the degradation state of organic matter in the marine realm as both decrease with increasing
243 organic matter degradation (Wakeham and Lee, 1993; Cowie and Hedges, 1994). AAN/N %
244 >50 % are characteristic of fresh organic matter in the freshwater and marine realm (Menzel et
245 al., 2015; Haake et al., 1992; Haake et al., 1993b). AA contribute >60 % to total organic carbon
246 (AAC/C %) in fresh plankton and suspended matter in surface waters whereas AAC/C % drop
247 to values <20 % in sinking particles and suspended matter from subsurface water (Wakeham
248 and Lee, 1993). AAC/C % values are often below 10 % in freshwater environments and indicate

249 the enhanced input of land plants enriched in carbohydrates and lignin rather than enhanced
250 organic matter degradation (Menzel et al., 2015).

251 Asn, Gln and Glu are the primary products of N assimilation and all other AA are synthesized
252 from them (Loick-Wilde et al., 2018; Riccardi et al., 1989; Hildebrandt et al., 2015). Asp and
253 Glu are enriched in bacteria, vascular plant tissue, phytoplankton, zooplankton and fungi and
254 their high relative contents of Asp and Glu therefore, indicate fresh organic matter (Cowie and
255 Hedges, 1992). The ratios of Asp/ β -Ala and Glu/ γ -Aba are high in fresh organic matter and
256 drop with organic matter degradation as β -Ala and γ -Aba are degradation products of Asp and
257 Glu, respectively (Lee and Cronin, 1984). β -Ala and γ -Aba also become relatively enriched
258 during organic matter degradation as these non-protein AA are not taken up by heterotrophic
259 organisms (Ittekkot et al., 1984b).

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

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

$$275 \quad DI = \sum_i \left[\frac{\text{var}_i - \text{AVGvar}_i}{\text{STDvar}_i} \right] \cdot \text{fac.coef}_i \quad (2)$$

276 where var_i is the original mole percentage of each AA_i , AVGvar_i and STDvar_i are the mean and
277 standard deviations, respectively, and fac.coef_i is the factor coefficient of the first axis of the
278 PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation of AA with

279 respect to an assumed average molar composition. The DI ranges approximately from -2 to +3
280 where negative values indicate more and positive values less degradation than the average.

281 A specifically designed index for dissolved substances (DOM-DI) calculated in the same way
282 as the DI was based on a PCA of a set of marine DOM samples and resulted in DOM-DI values
283 from 5 in surface waters to -3 in deep waters (Kaiser and Benner, 2009). The values to calculate
284 the marine DOM-DI (averages, standard deviations and factor coefficients of F1) can be found
285 in Peters et al. (2012).

286 An indicator of oxic vs. anoxic organic matter degradation in the water column and in sediments
287 was proposed by Menzel et al. (2015) for lake samples. Based on work by Cowie et al. (1995)
288 on marine sediments the ox/anox indicator is the quotient of AA preserved under oxic
289 diagenetic conditions to those preserved in anoxic water or sediments and is thus higher in oxic
290 than in anoxic sediments:

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

292 ox/anox ratios <1.0 indicate anoxic and ratios >1.5 oxic diagenesis (Menzel et al., 2015).

293 The stability of AA vs. HA has been discussed since the early research on AA and HA in natural
294 material. Fresh plankton was observed to have AA/HA ratios of 13-25 (Degens and Mopper,
295 1975) which is a mixed signal of phytoplankton with an AA/HA ratio of >80 and zooplankton
296 with a ratio of ~9 due to chitinous skeletons of many zooplankters (Mayzaud and Martin,
297 1975). Low AA/HA are also observed in cell walls of fungi and bacteria. As the building blocks
298 of chitin, HA were assumed to be more resistant to degradation than bulk AA (Muller et al.,
299 1986). This is, however, challenged by studies of enzyme activities which were observed to
300 respond to substrate availability so that the activity of chitobiase and chitinase is as high as that
301 of glucosidase (Boetius et al., 2000a; Boetius and Lochte, 1994; Boetius et al., 2000b; Smith et
302 al., 1992) suggesting intense degradation also of chitin. Gluam is the main constituent of chitin
303 and while Galam is relatively enriched in bacterial cell walls (Walla et al., 1984; Kandler,
304 1979). The Gluam/Galam ratio has, therefore, been used to distinguish bacterial material from
305 zooplankton rich material (Haake et al., 1993b; Benner and Kaiser, 2003; Niggemann and
306 Schubert, 2006). Gluam/Galam ratios > 4 were found in sinking particles (Haake et al., 1993b;
307 Haake et al., 1992; Lahajnar et al., 2007), ratios of < 3 usually indicate relatively high

308 contribution of microbial OM and values between 1 and 2 are characteristic of sediments and
309 indicate an enrichment of microbial biomass (Benner and Kaiser, 2003).

310 **2.4 Statistical analyses**

311 To investigate the differences of AA composition and to recognize the interaction and pathways
312 of degradation between the different pools we carried out a PCA of AA monomer contributions
313 in Mol %. Met was excluded as it is below detection limit in many samples. The PCA was
314 carried out using the program SPSS Statistics 22. PCAs have often been used to analyze large
315 databases (Xue et al., 2011) in order to trace organic matter degradation, group and categorize
316 samples and develop indices such as the DI of Dauwe et al. (1999) using summary statistics
317 (see equation 2). A PCA is an orthogonal transformation of a set of variables into a new set of
318 uncorrelated variables called principal components. New axes are chosen in order to explain as
319 much as possible of the variance within the data set on a few main axes of highest correlation.
320 The first component explains most of the variance within the data set, consecutively followed
321 by the remaining components in the order of their decreasing capacity to explain the variance
322 within the data set. The selection of the most relevant components can be done by selecting
323 those with eigenvalues (the variances of the principal components) >1. Alternatively, the kink
324 method can be applied selecting those components from a plot of eigenvalues (scree plot),
325 which describe a steep slope of declining variance followed by a “kink” after which the
326 principal components add only small amounts to the variance. The factor loadings of the
327 variables (in this case the individual amino acids) are their projections on the new axis. The
328 factor score of each data set from a sampling location is obtained by multiplying the
329 standardized data with the factor loadings (also called factor coefficients). A high (low) factor
330 score shows that a sample has high (low) concentrations of the variables with high factor
331 loadings. A plot of factor loadings of the variables compared with a plot of the factor scores of
332 samples helps to visualize the relation of the samples to the variables and thus to identify the
333 processes behind the results of the PCA.

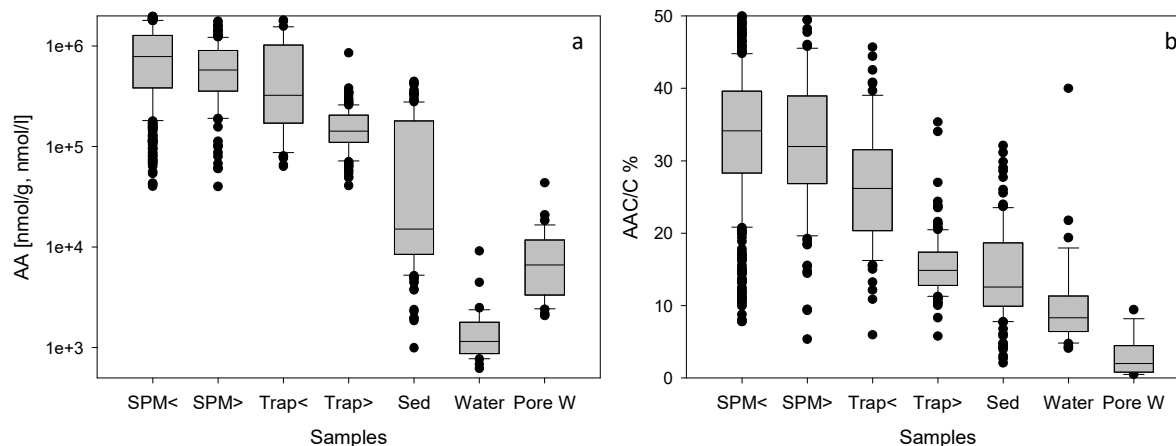
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335 **2 Results**

336 **3.1 Organic carbon, nitrogen and amino acid content**

337 The POC (N) content is 35.9 % (5.9%) in plankton and 1.65-46.4 % (0.21-10.14 %) in sediment
338 trap samples. In sediments, POC (N) contents drop to 0.10-13.5 % (0.02-1.72 %). SPM has

339 POC (N) contents of 0.94-45.4 % (0.09-12.08 %). DOC concentration in water samples is
 340 between 0.5-1.1 mg L⁻¹ and DOC in pore water samples is between 3.9-29 mg L⁻¹.

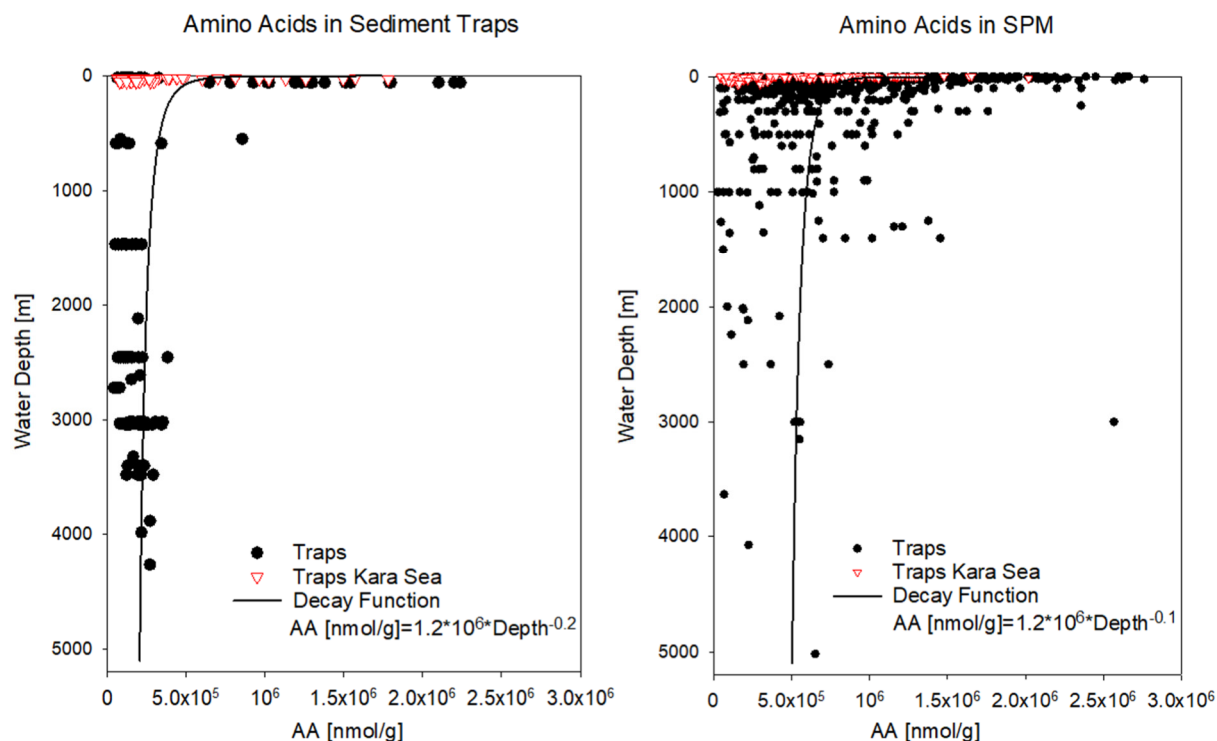


341
 342 Figure 2: Box and Whisker plots of AA concentrations in nmol g⁻¹ or nmol L⁻¹ (a) and of AAC/C
 343 % (b) in SPM from water depths <200m (SPM<) and >200m (SPM>), in sediment traps at
 344 water depth <200m (Trap<) and >200 m (Trap>), in sediments (Sed), in water samples (Water)
 345 and in pore water samples (Pore W). Boxes comprise the upper and lower quartile and lines
 346 indicate median; whiskers delineate the 10 and 90 percentile; outliers are marked by dots; some
 347 outliers above the 90 percentile are cut off in the figure for better perceptibility of trends.

348
 349 AA concentrations are grouped into SPM and trap samples taken at water depths <200m
 350 (shallow) and >200m (deep) (Fig. 2, Table 1). AA concentrations are highest in SPM samples
 351 and shallow sediment traps (<200m water depth) with values between 40-4307 μmol g⁻¹ (Fig.
 352 2) and averages of 662-908 μmol g⁻¹ (Table 1). AA concentrations are lower in traps from water
 353 depth >200m with an average of 164 μmol g⁻¹. Sediments have lowest AA concentrations of all
 354 particulate matter samples with an average of 50 μmol g⁻¹ (Table 1). TDAA concentrations are
 355 between 0.6-44 μmol L⁻¹ and AA concentrations are lower in water than in pore water samples
 356 with averages of 3.2 and 8.8 μmol L⁻¹, respectively. **TDAA concentrations of water samples**
 357 **decrease from the epipelagic (2.5±2.9 μmol L⁻¹) to the meso- and bathypelagic ocean (1.2±0.5**
 358 **μmol L⁻¹) whereas bottom waters have enhanced TDAA concentrations even higher than those**
 359 **in surface waters (6.0±3.4 μmol L⁻¹).**

360 The AAC/C is between 5.4-66 % in SPM and traps samples and the AAN/N (not shown) is
 361 between 3.7-100 %. The overall pattern found for AAC/C (Fig. 2b) is similar to the pattern of
 362 AA concentrations (Fig. 2a) but there is more overlap of AAC/C between the different groups.
 363 Sediments have AAC/C between 2.7-50 % and AAN/N between 3-78 % (not shown). The

364 contribution of AAC to DOC (AAC/C) in water samples is between 4-40 % and in pore water
 365 samples between 0.5-9 %.



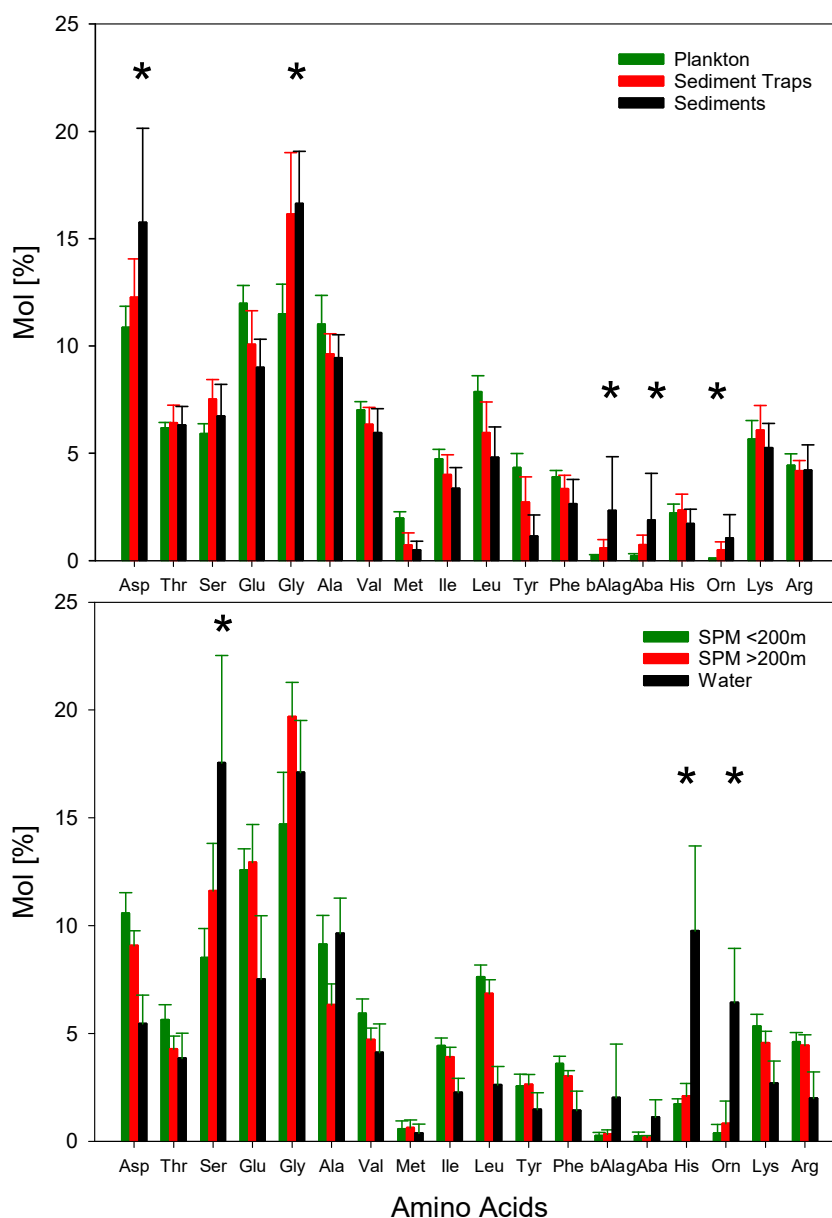
366
 367 Figure 3: AA concentrations in nmol g⁻¹ in sediment traps (a) and SPM (b). Red triangles mark
 368 samples from the Kara Sea, black dots are samples from the other trap and SPM locations shown
 369 in Figure 1. The decay functions are calculated from samples excluding Kara Sea samples.

370
 371 AA concentrations of sinking and suspended particles decrease with water depth and the most
 372 significant decrease occurs in the upper ocean (Fig. 3a). The decay constant of AA of sinking
 373 particles is twice as high as the decay constant of AA of SPM (Fig. 3 a, b). Kara Sea samples
 374 were excluded from these calculations as their AA concentrations are low due to the strong
 375 dilution by material from rivers and resuspended sediments in this near-shore environment (see
 376 3.2 and 4.2). It is also notable that AAC/C and AAN/N (not shown) significantly decrease
 377 between shallow and deep traps and from deep traps to sediments while AAC/C of SPM show
 378 little decrease between shallow and deep samples (Fig. 2b).

379
 380 **3.2 Amino acid composition**

381 While the AA concentrations of sinking particles from traps show a distinct decrease with water
 382 depths the changes in AA composition are lesser so that we averaged all AA spectra irrespective

383 of water depths and area of study to compare them with plankton and sediment samples (Figure
 384 4a). Dominant AA in plankton samples are Glu, Gly, Ala and Asp. Sinking particles and
 385 sediments are also dominated by these AA but in the order of Gly, Asp, Glu and Ala (Fig. 4a).
 386 Mol% Asp, Gly, β -Ala, γ -Aba and Orn increase from plankton via sinking particles to sediments
 387 while Mol% of Glu, Ala, Val, Met, Ile, Leu, Tyr and Phe decrease (Fig. 4a). These trends are
 388 further continued with depths in sediment cores (not shown).
 389

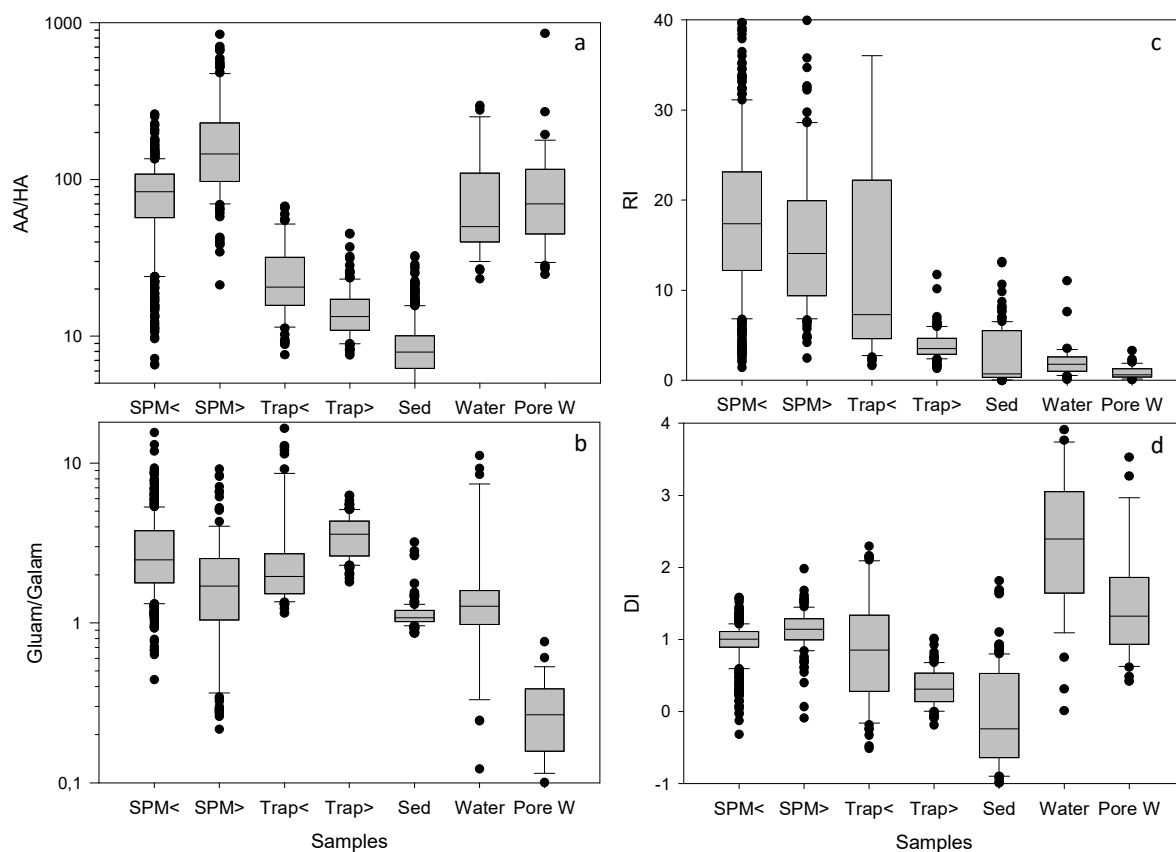


390
 391 Figure 4: Average concentrations of individual AA (Mol%) and 1 σ standard deviation (vertical
 392 bars) in plankton (green), sediment trap (red) and sediment (black) samples (a), in SPM from
 393 water depths <200m (green), >200m (red) and TDAA in water samples (black) (b). Asterisks

394 mark the AA with increasing Mol% from plankton via sediment trap samples to sediments (a)
 395 and from shallow SPM via deep SPM to TDAA of water samples.
 396

397 AA composition of SPM shows a clear trend with water depth with enrichments of Mol% Ser,
 398 Glu, Gly, Orn and His and decreases of almost all other AA from shallow waters (<200 m) to
 399 deep waters (>200m) and decreases are most pronounced for Asp, Thr and Lys (Fig. 4b). These
 400 trends are partly resumed by TDAA in water samples with a further enrichment of Mol% Ser,
 401 Orn and His, while Mol% Glu and Gly slightly decrease in water samples compared with deep
 402 SPM (Fig. 4b). AA spectra of pore waters (not shown) are very similar to water samples.

403



404

405 Figure 5: Box and Whisker plot of AA/HA ratios (a) and Gluam/Galam ratios (b), RI (c) and
 406 DI (d) in SPM from water depths <200m (SPM<) and >200m (SPM>), in sediment traps at
 407 water depth <200m (Trap<) and >200 m (Trap>), in sediments (Sed), in water samples (Water)
 408 and in pore water samples (Pore W). Outliers are marked by dots; some outliers above the 90
 409 percentile are cut off for better perceptibility of trends. Note logarithmic scales of AA/HA (a)
 410 and Gluam/Galam (b).

411

412 Biogeochemical indicators reveal the subtle depth dependent trends in sediment traps and
 413 therefore the biogeochemical indicators were averaged separately for shallow and deep

414 sediment trap and SPM samples (Fig. 5, Table 1). The AA/HA in SPM and water samples -
415 with averages between 80.2 and 204.6 - are higher than in traps and sediments (Fig. 5a, b; Table
416 1). The AA/HA decrease from shallow via deep traps to sediments with averages of 25.4, 14.9
417 and 9.1, respectively. The Gluam/Galam is highest in SPM samples, slightly lower in shallow
418 and deep traps and lower in sediments, water and pore water (Fig. 5a, b; Table 1). The RI (Fig.
419 5c; Table 1) shows the same pattern as the ratios of Asp/ β -Ala and the Glu/ γ -Aba (Table 1),
420 with no clear trend between shallow and deep SPM samples and decreases from shallow to deep
421 traps and further to the sediments. Water samples have similar values as sediment samples with
422 average RI of 1.8 and 1.6, respectively, and pore waters have an even lower average RI of 0.9.
423 Similar to the RI the DI is within the same range in shallow and deep SPM samples and the
424 mean values are very close (Fig. 5d; Table 1) while the DI decreases from shallow sediment
425 traps via deep traps to sediments. In contrast to the RI where water samples have lowest values,
426 the highest DI values are found in water and pore water samples. **The DOM-DI averages of**
427 **2.0 \pm 0.6 and 2.1 \pm 0.7 in water and, respectively, pore water samples are in fact very close to the**
428 **DI averages (Table 1).**

429 In summary, common biogeochemical indicators of organic matter degradation (RI, Asp/ β -Ala,
430 Glu/ γ -Aba) and bacterial OM accumulation (AA/HA, Gluam/Galam) drop and thus imply
431 increasing degradation between shallow and deep sediment traps and between deep traps and
432 sediments, while these indicators reveal little or no degradation with depth in SPM as the
433 patterns of relative enrichment vs. decreases found in SPM and partly also in TDAA of water
434 and pore water samples differ from the degradation pathway depicted by common
435 biogeochemical indicators (Fig. 4, 5; Table 1). The enhanced DI values furthermore, imply that
436 water and SPM samples are less degraded than deep trap and sediment samples and that TDAA
437 in water and pore water samples are least degraded.

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447 Table 1: Mean values and standard deviation (Stdev.) of POC [%], DOC [mg/L], amino acid
 448 (AA) concentrations [$\mu\text{mol/g}$ or $\mu\text{mol/L}$], AAC/C%, AAN/N%, ratios of Asp/ β -Ala, Glu/ γ -
 449 Aba, AA/HA and Gluam/Galam, the RI, DI, SDI*, RTI* and ox/anox ratio summarized in traps
 450 at <200m and >200m water depth, sediments, SPM <200m and >200m water depth, water
 451 samples and pore water samples. *definition of these indicators in part 4.2 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 [$\mu\text{mol/g}$; $\mu\text{mol/L}$]	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

452

453

454 4 Discussion

455 4.1 Changes during organic matter degradation

456 Our summary of AA data from various locations in the world ocean corroborates earlier
 457 findings that degradation of organic matter by zooplankton and microbes imparts characteristic
 458 changes to AA spectra so that the differences in AA composition are much larger between types
 459 of organic matter and from different water and sediment depths than between different oceanic
 460 areas (Lee, 1988). The AA spectra track the successive degradation of organic matter during
 461 sedimentation from the plankton source via sinking particles, their incorporation into sediments

462 and their further degradation after burial. The most characteristic changes along this
463 sedimentation pathway are the relative enrichments (in Mol%) of Gly, Asp and the non-protein
464 AA β -Ala, γ -Aba and Orn and the relative decrease of AA produced by fresh plankton such as
465 Glu, Ala, Val, Met, Ile, Leu, Tyr and Phe (Fig. 4a). These changes are depicted by the common
466 biogeochemical indicators: the ratios of proteinaceous AA vs. non-protein AA (RI and Glu/ γ -
467 Aba) decrease along this pathway. Asp/ β -Ala ratios also decrease because β -Ala becomes
468 relatively more enriched than Asp. The DI, originally derived from sediment samples of
469 different degradation states (Dauwe et al., 1999; Dauwe and Middelburg, 1998), decreases from
470 positive values in fresh plankton and most sinking particles to negative values in sediments as
471 it integrates the products of Asp and Gly multiplied with negative factors, and the products of
472 Glu, Met, Ile, Leu, Tyr and Phe multiplied with positive factors (Dauwe et al., 1999).

473 In contrast, the AA in SPM evolve along a different path than the sedimentation pathway (Gaye
474 et al., 2013b). The increases in Mol% Ser, His and Orn and the decreases in Mol% Asp from
475 shallow (<200 m) to deep SPM (>200m) and even further in TCAA of sea water and pore water
476 are either not depicted or even contrary to the trends depicted by the common biogeochemical
477 indicators (Fig. 4b). The striking difference in AA distribution of SPM (Fig. 4) on the one hand
478 and sinking particles and sediments on the other hand as well as the different depth dependent
479 trends (Fig. 4, 5) suggest that there is little exchange between the two types of particles in the
480 ocean. Sinking particles build up sediments and the degradation pathways evident in the water
481 column - namely the accumulation of degradation products and acidic AA often absorbed to
482 carbonates - continue in the sediments. Novel biogeochemical indicators are required for SPM
483 and possibly also DOM to characterize their AA changes.

484

485 **4.2 Results of a PCA: two new biogeochemical indicators**

486 A PCA of individual AA (Mol %, Fig. 6a) of all samples compiled in this study results in two
487 factors which explain 59 % of the total variance within the data set. The first factor delineates
488 the well-known changes along the degradation pathway from plankton via sinking particles to
489 sediments. Phe, Ile, Leu, Glu and Tyr (enriched in fresh plankton) have the highest F1 loadings
490 while Asp, β -Ala and γ -Aba (accumulating during degradation) have the lowest negative F1
491 loadings. Highest F2 loadings are found for Asp, Thr, Lys and Val while Gly, Orn, His and Ser
492 have the most negative F2 loadings. Factor scores of the individual samples (Fig. 6b) plot in a
493 triangular shape with plankton and fresh organic matter from surface waters at the apex with

494 highest F1 and F2 scores. The diverging sides of the triangle mark sinking particles and
 495 sediments decreasing in F1 scores on one side and SPM with decreasing F2 scores on the other
 496 side (Fig. 6b). Similar trends were observed in earlier studies based on local data sets (Nagel et
 497 al., 2016; Gaye et al., 2013b). That samples from greatly different environments reveal the same
 498 divergence between sinking particles and SPM with only little overlap (Fig. 4) suggest a general
 499 mechanism operating globally. Most of the overlap encompasses SPM and sediment trap
 500 samples from the Kara Sea all sampled at water depths below 100 m. The Kara Sea is
 501 characterized by sediment resuspension related to strong riverine input in combination with sea
 502 ice dynamics so that many of the Kara Sea SPM and trap samples are mixed with resuspended
 503 sediments (Gaye et al., 2007; Unger et al., 2005). TDAA analyzed in water and pore water form
 504 a cluster with significantly different AA composition from particulate matter, but instead
 505 recapitulating the enrichments of Mol% Ser, His and Orn observed in SPM (Fig. 6b).

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

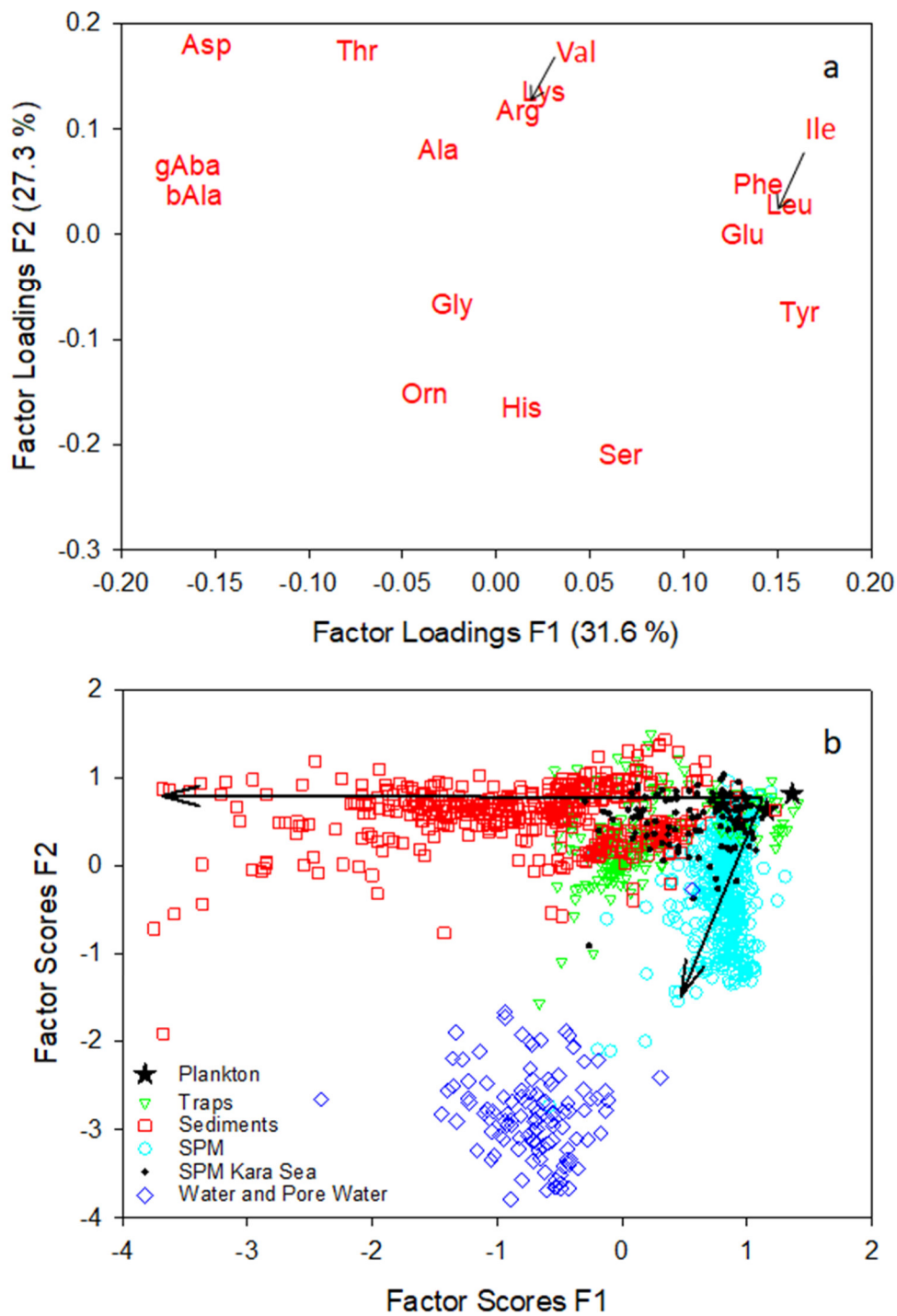
$$509 \quad SDI = \sum_i \left(\frac{var_i - AVG.var_i}{STD.var_i} \right) \times Loadings . F1_i \quad (4)$$

510 where var_i is the original mole percentage of each AA_i , $AVG.var_i$ and $STD.var_i$ are the mean and
 511 standard deviations, respectively, and $Loading.F1_i$ is the factor loading of the first axis (F1) of
 512 the PCA of the individual amino acid_i shown in Table 2. Most of the F1 loadings resemble those
 513 of the DI of Dauwe et al. (1999) (Table 2) and the SDI and DI thus are significantly correlated
 514 (Table 3).

515 The second factor (F2) - normalized in the same way with the averages and standard deviations
 516 of the same PCA - can be used as an indicator of changes in the AA composition of SPM
 517 possibly related to the residence time or renewal time of the water mass they are transported
 518 with (see discussion in 4.2.2). With longer residence time in the ocean the organic matter in
 519 SPM is likely to become more recalcitrant and the indicator and is therefore named residence
 520 time index (RTI)

$$521 \quad RTI = \sum_i \left(\frac{var_i - AVG.var_i}{STD.var_i} \right) \times Loadings . F2_i \quad (5)$$

522 and is calculated in the same way as the SDI but the factor loadings of the second axis (F2) of
 523 the PCA of the individual amino acid_i (Table 2) is inserted for the term $Loadings.F2_i$.



525

526 Figure 6: Results of a PCA of AA (Mol%) of all samples of this study with factor loadings of
 527 amino acids for the first and second factor (a) and factor scores of samples (b). Small arrows in
 528 (a) point to the positions of Val and Ile, respectively. Arrows in (b) indicate progressive
 529 deviation in composition from the plankton source, essentially with increasing water and
 530 sediment depths.

531

532 The SDI allows a separation of trap samples from shallow water depth from those of greater
 533 depths (Figure S1). All samples from deep sediment traps have SDI values below 0.5. Likewise,
 534 SPM from >200 m depths have lower RTI than most of the samples from shallower depths.
 535 Deep trap samples and deep SPM samples form two clearly separated clusters with different
 536 SDI and RTI (see Figure S1 for further details).

537 Table 2: Factor loadings of F1 and F2 for calculating the SDI and RTI, respectively, average
 538 [Mol%] and standard deviations (Std. Dev.) of AA of samples used for the PCA shown in Figure
 539 5 in comparison with the factor loadings (named factor coefficients) of the DI published by
 540 Dauwe et al (1999) and their averages [Mol%] and standard deviations used for the DI based
 541 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

542

544 4.2.1 The SDI as an indicator of degradation and oxic vs. anoxic diagenetic conditions of 545 sinking particles and sediments

546 In order to test the performance of our new degradation indices, we separated SPM samples
 547 from sinking particles and sediments and correlated the common biogeochemical indicators and
 548 individual AA (Mol %) of SPM with the RTI of individual samples while we correlated the
 549 same variables of sinking particles and sediments with the SDI (Table 3). We assume that
 550 correlations with Pearson correlation coefficients $R > 0.50$ can be considered as “strong
 551 correlations” (Cohen, 1988). The SDI correlates moderately to strongly with the common

552 degradation indicators and the best positive correlation is found between SDI and the DI (Table
553 3). The strong correlation among the degradation indicators with POC contents indicates that
554 this common and often measured variable is a good indicator of relative organic matter quality
555 in sinking particles and sediments and all other degradation indices do not perform better than
556 POC concentrations (see correlation coefficients in Table 3). The DI and the SDI, which are to
557 some extent interchangeable, allow a fine tuning of degradation intensities. The most significant
558 negative correlation of the ox/anox ratio with the SDI is preconditioned, as the ox/anox is the
559 quotient of AA enriched by degradation to those enriched in fresh plankton. It should be noted
560 that this negative correlation is even better than the positive correlation of the DI and the SDI.
561 A close look at the SDI and ox/anox in sediment samples suggests that the SDI can be used to
562 distinguish between oxic and anoxic diagenetic conditions (Fig. 7). The sediment samples
563 deposited in regions of bottom water anoxia (surface samples from Namibian shelf at < 200 m
564 depths; a core from the Arabian Sea slope at 775 m) have lower ox/anox ratios and distinctly
565 higher SDI values compared with the samples from similar depths and oxygenated bottom water
566 (e.g. Mediterranean Sea, Kara Sea) (Fig 7a). The SDI performs better than the DI to determine
567 diagenetic conditions as the DI less significantly correlates with the ox/anox indicator (Figure
568 S2). The best fit between the SDI and the ox/anox in sediment samples is an exponential
569 correlation with a correlation coefficient of $R=-0.95$ while the DI and the ox/anox correlate
570 exponentially with an $R=-0.79$ (Fig. 7a, Figure S2). The SDI better depicts the spectral changes
571 in samples deposited under anoxic diagenetic conditions such as those from the Namibian shelf
572 (Nagel et al., 2016) and the Arabian Sea mid-water oxygen minimum zone (Suthhof et al., 2001)
573 while the ox/anox ratio better resolves variations in samples of strong oxic degradation so that
574 the SDI is in fact better suited to determine the threshold of anoxic vs. oxic diagenesis. Another
575 indication of this quality of the SDI is that the anoxic sediments have SDI values in the range
576 of sediment trap samples from the water column while they decrease under oxic diagenetic
577 conditions (Fig. 7b). Further, the SDI also correlates with other indicators of oxic vs. anoxic
578 conditions. The core SO90-111 KL from within the mid-water oxygen minimum impinging on
579 the Pakistan margin, was used to reconstruct changes in oxygenation during the last 60 ka BP
580 based e.g. on $\delta^{15}\text{N}$ values of total N (Suthhof et al., 2001). The $\delta^{15}\text{N}$ values fluctuated between
581 enhanced values in warm phases due to denitrification in the mid-water oxygen minimum and
582 lower values in cold phases when the oxygen minimum zone was weaker or absent (Suthhof et
583 al., 2001). The SDI very precisely tracks these changes (Fig. 7c) and in accordance with the
584 threshold discernable in Fig. 7a and b we propose that the divide between oxic and anoxic

585 diagenetic conditions is at SDI values between 0 and -0,2 with SDI<-0.2 indicating oxic and
 586 SDI >0 indicating anoxic diagenetic conditions (Fig. 7a, b) and we propose to use this indicator
 587 to reconstruct redox conditions from sediment cores. The work of (Carr et al., 2016) - relying
 588 on the DI – suggests that signals of changes in redox conditions can be preserved even down to
 589 200 m core depth.

590

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

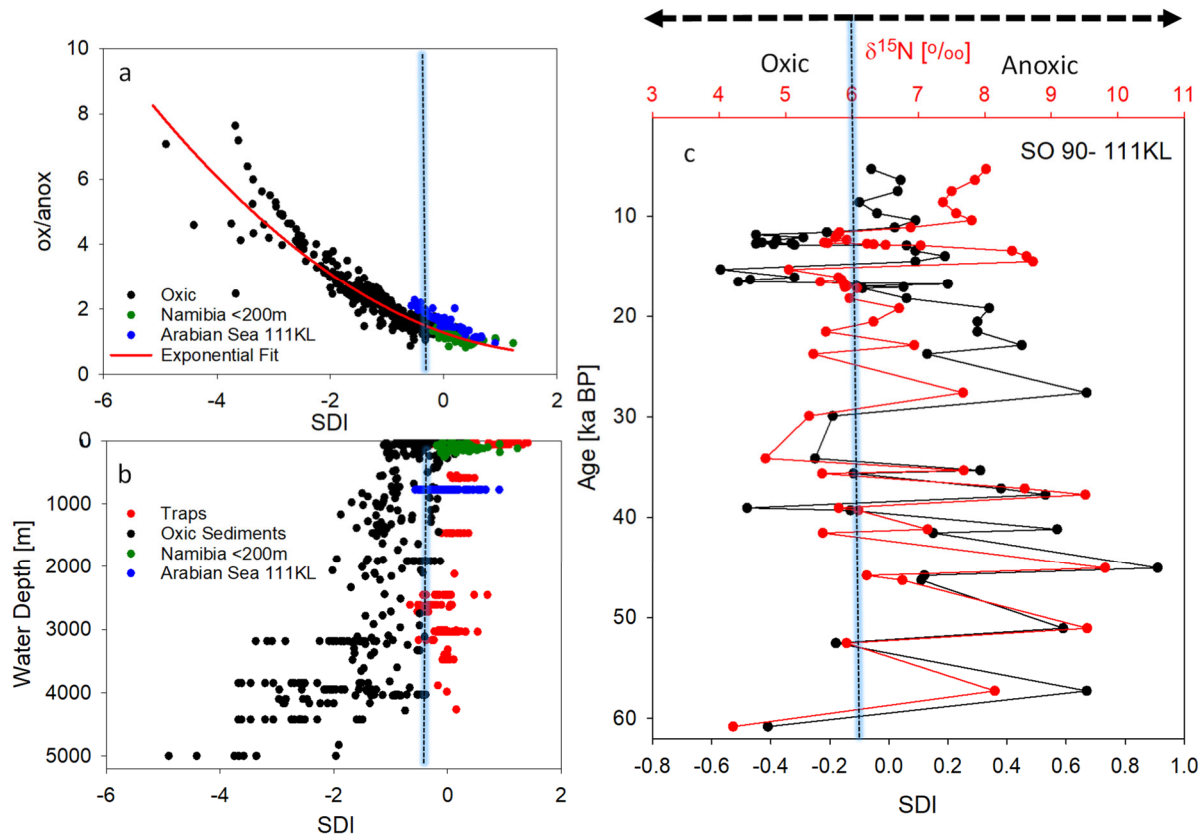
598 * Only AA with a correlation coefficient $R \geq 0.50$ with at least one of the indicators are shown.

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

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601



602

603 Figure 7: SDI indicator plotted against the ox/anox ratio with dots indicating oxic sediments
 604 (black) and suboxic to anoxic sediments from Namibia (green) and the Arabian Sea (blue), the
 605 red line marks the exponential fit to all sediment samples with an $R=0.95$ (a). SDI plotted with
 606 water depth (in m) of sediment trap deployment (red) and of sediment sampling (see color code
 607 of a) (b). SDI and the $\delta^{15}\text{N}$ of total N with sediment depth in sediment core SO90-111 KL
 608 correlated with an $R=0.71$ (c); the blue bar marks the threshold of the SDI delimiting oxic and
 609 anoxic diagenetic conditions at an SDI value of about -0.1.

610

611 4.2.2 The RTI as an indicator of suspended matter residence time

612 Changes in SPM composition between shallow and deep waters (Fig. 4b) are depicted by a
 613 decrease of the RTI which is due to the relative depletion of Asp, Thr, Lys and Val with highest
 614 positive factor loadings and the enrichment of Ser, His and Orn with the most negative factor
 615 loadings (Table 2). Both, Ser and Gly (Mol %) are strongly linearly anticorrelated with the RTI
 616 ($R=-0.91$ and -0.90) showing that they can be used instead of the RTI to characterize SPM if
 617 not all AA used for the RTI can be measured. The anticorrelation of the RTI with water depths
 618 ($R=-0.55$; Table 3) is due to the RTI decrease in the upper 200 m only. Below this depth there
 619 is no further trend in the RTI and values scatter between -0.5 and -1.5 (Fig. 8).

620 The results of our PCA also show that below 200 m SPM becomes distinctly decoupled from
621 sinking aggregates (Fig. 7, Figure S1). Both, sinking particles and SPM sampled in the upper
622 ocean mixed layer and euphotic zone resemble fresh plankton whereas below the surface mixed
623 layer they follow different pathways and the chance that SPM and sinking particles interact
624 obviously decreases with water depth which could be due to the scarcity of both types of
625 particles in the deep ocean (McCave, 1984). Our AA results support previous studies on SPM
626 (using e.g. thorium isotopes, radiocarbon and biomarkers) which found that the interaction
627 between sinking particles and SPM by aggregation and disaggregation strongly decreases from
628 the euphotic zone to the meso- and bathypelagic zone and that SPM rather interacts with DOM
629 due to the long residence time of both in the deep ocean (Lam and Marchal, 2015). The observed
630 constant AA composition of SPM below 200 m water depth could be explained by a recalcitrant
631 nature making the AA barely accessible to further microbial degradation. Alternatively, and in
632 analogy to observations of DOC, it could be due low concentrations of SPM which rather than
633 their recalcitrance limits prokaryotic growth and thus organic matter degradation in the deep
634 ocean (Arrieta et al., 2015). The age of the water masses in the upper ocean mixed layer is less
635 than 100 years while deeper waters have ages of several 100 years to maxima of 1600 years in
636 the deep Indian and Pacific Oceans (England, 1995; Gebbie and Huybers, 2012). The constantly
637 low RTI below the mixed layer is thus related to the long residence time of deep SPM in the
638 deep ocean. An earlier study using detailed ventilation ages available from the Atlantic and
639 Pacific subtropical gyres at stations BATS and respectively, HOT showed that changes in AA
640 composition of SPM took place within a few decades (Kaiser and Benner, 2009).

641 Solubilization of particulate matter by exoenzymes and the subsequent uptake in dissolved form
642 (Carlson and Hansell, 2015; Aristegui et al., 2009) leads to an almost complete turnover of
643 originally diverse surface derived organic matter. It is thus feasible that bacterial biomass
644 comprises a large amount of organic matter in compartments of long residence times. However,
645 fresh bacteria and fungi have quite similar AA composition as plankton (Cowie and Hedges,
646 1992) while SPM AA composition is fundamentally different. The high AA/HA ratios not
647 having a clear trend with water depth also suggest that the contribution of bacterial biomass to
648 SPM is small and does not increase with water depth (Table 1; Fig. 5a, b). The observed changes
649 in SPM are thus more likely related to adsorption processes and macromolecule formation of
650 material not digestible to deep sea organisms and resistant to their enzymes. DOM was shown
651 to become adsorbed to mineral surfaces (Keil and Kirchman, 1993; Keil and Kirchman, 1994;
652 Keil et al., 1994; Arnarson and Keil, 2005, 2007). However, degradation of adsorbed AA

653 proceeds on particles (Satterberg et al., 2003; Taylor, 1995). Thus, the constant AA composition
654 in SPM at depths >200 m may indicate that SPM is in equilibrium with TDAA which likewise
655 show no clear depth dependent changes in AA composition (Figure S3, S4). Feasible candidate
656 processes to explain the homogeneity are AA scavenging by SPM or formation of gels (3D
657 networks = biopolymers) which can anneal to larger sizes so that part of the dissolved AA can
658 be passed from the dissolved to the particulate organic carbon pool (Druffel and Williams,
659 1990; Orellana and Leck, 2015). This process is, however, reversible so that there is probably
660 an exchange between the gel and particulate matter phase as well as between gels of different
661 sizes and complexities depending on pH, temperature, the presence of ligands, pollutants or UV
662 radiation (Orellana and Leck, 2015). Generally, hydrophobic AA (Ala, Val, Met, Ile, Leu, Phe,
663 Pro, Trp) and aromatic AA (His, Tyr) are more likely to form gels and aggregates (Orellana and
664 Leck, 2015). Our results indicate that an equilibrium may be attained between the dissolved
665 phase and SPM after a relatively short time so that the AA composition of SPM is constant
666 below 200 m water depth. If there is no further significant scavenging of SPM by sinking
667 particles and no degradation of AA on SPM, their abundance could increase due to further
668 adsorption of DOM with increasing age on the ocean conveyor belt. However, large
669 zooplankters may be able to utilize the SPM pool (Koppelman et al., 2009; Gloeckler et al.,
670 2018; Hannides et al., 2013) and further studies are required to elucidate the fate of SPM in the
671 ocean.

672

673 **4.3 Contents and composition of total dissolved amino acids in sea water and pore water**

674 **The TDAA concentrations show a decrease from the epi- to the mesopelagic ocean similar to**
675 **many earlier findings (Davis et al., 2009; Kaiser and Benner, 2009; Kim et al., 2017) whereas**
676 **the spectra of TDAA sampled in the oligotrophic Indian Ocean Subtropical Gyre and the deep**
677 **Pacific are uniform with water depth. This is also reflected in the DOM-DI which does not**
678 **show any trend neither with depth in the water column nor in sediments (Figure S4).** Further,
679 the difference between water and pore water samples is small and Ser, Gly and His are
680 uniformly the major TDAA in sea water and pore water. It is possible that the selective
681 accumulation of these AA in the dissolved phase is due to their excretion or their association
682 with exoenzymes. Ser is present in N-acyl homoserine lactone (AHLs) which is a class of
683 bacterially produced signaling molecules involved in bacterial quorum sensing; these
684 compounds serve to regulate growth by changing gene expressions, for example, in order to

685 influence population density or phenotype (Parsek et al., 1999; Klein et al., 2009). His changes
686 from its protonated to deprotonated form at a pH of 6 and is therefore often present at the active
687 sites of enzymes. Ser and Gly may simply remain dissolved in sea water as they are hydrophilic.
688 Once mixed into the deeper ocean the scarcity of bacteria or the incorporation of AA into gels
689 could be the reason for their recalcitrance. However, we do not assume that a considerable part
690 of the TDAA belong to dissolved free AA. Because the differences between samples from
691 different regions are much smaller than the difference between the molecular weight fractions
692 and sea water vs. pore-water (Figure S3), we surmise that the formation and transformation
693 processes of DOC are very uniform in the ocean. This assumption is based on limited data so
694 that these results are rather preliminary. We also do not have enough spatial coverage of SPM
695 and TDAA data in the deep ocean to detect AA utilization by organisms or sorption and
696 desorption processes. Both these organic matter pools are large (see below), so that such
697 investigations are important to estimate the possible role of these pools in oceanic carbon
698 sequestration and the reactions to global change (Ridgeway and Arndt, 2015; Lonborg et al.,
699 2018).

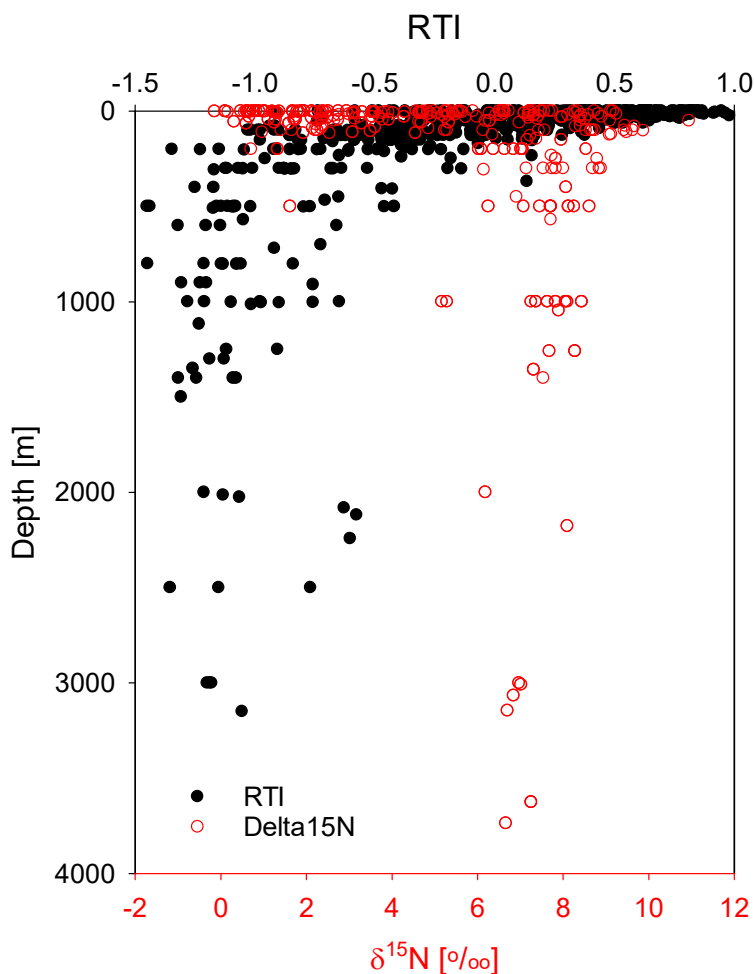
700 Our AA yield with AA-C/C of $10.1 \pm 6.5\%$ are in the high range of studies from the literature.
701 In some of the previous studies AAC/C was between 0.4 and 4 % with a reduction from 1-4 %
702 AAC/C in surface waters to 0.4-0.8 % in waters >1.000 m. This reduction was moreover,
703 associated with a progressive AA degradation reflected in the DI and the DOM-DI at some of
704 the sampling stations (Kim et al., 2017; Davis and Benner, 2005; Kaiser and Benner, 2009).
705 These lower yields may however, be due to different hydrolysis conditions as these studies used
706 water vapor hydrolysis at higher temperatures (150°C) but for a much shorter duration (32.5
707 minutes). Studies using the same hydrolysis conditions as this work reported AAC/C of 5-10
708 % (Ittekkot, 1981; Keil and Kirchman, 1999; McCarthy et al., 1997).

709

710 **4.4 $\delta^{15}\text{N}$ values in sinking and suspended matter and evidence for nitrogen sources and** 711 **transformation processes**

712 The $\delta^{15}\text{N}$ values in sediments can preserve information on N sources throughout the geological
713 history (Sun et al., 2019; Gaye et al., 2018; Kienast et al., 2008). However, $\delta^{15}\text{N}$ values may be
714 modulated by organic matter cycling and diagenetic processes which are replicated and thus
715 traceable in the AA composition not least because AA are the main identifiable contributors to
716 N in particulate organic matter. The increase of $\delta^{15}\text{N}$ values by about 2 ‰ on average during

717 organic matter burial and early diagenesis in the upper sediments (Robinson et al., 2012; Tesdal
 718 et al., 2013) is corroborated by a parallel shift in AA based degradation indicators (Gaye-Haake
 719 et al., 2005; Möbius et al., 2010). In contrast to sediments, there are no clear depth related trends
 720 in $\delta^{15}\text{N}$ values of sinking particles in the water column of the epi- to mesopelagic ocean (Gaye-
 721 Haake et al., 2005; Yang et al., 2017; Altabet, 2006). AA based biogeochemical indicators
 722 revealed degradation with depth at specific trap sites (Haake et al., 1993a) and $\delta^{15}\text{N}$ analyses of
 723 individual amino acids showed that degradation is proceeding on sinking particles with $\delta^{15}\text{N}$
 724 changes of “trophic” AA while $\delta^{15}\text{N}$ of “source” AA remained constant (McCarthy et al., 2007).
 725 However, degradation of sinking particles is much smaller than degradation at the sediment
 726 water interface and in our large data set that integrates many different areas of study the small
 727 to moderate changes in AA degradation are obviously obliterated, as neither AA concentrations
 728 (Fig. 3), nor the SDI (Fig. 7), the AAC/C % (Figure S5) nor AAN/N % (not shown) reveal any
 729 significant trends in sinking particles in the deep ocean.



730
 731 Figure 8: The RTI (black dots) and the $\delta^{15}\text{N}$ values of SPM with water depths [m] (red circles).

732 AA composition of SPM as expressed in the RTI is constant and SPM is rather recalcitrant at
733 water depths >200 m. Paralleling this, the $\delta^{15}\text{N}$ values of SPM are about 6-8 ‰ on average in
734 all our studies carried out (Fig. 8). In previous studies $\delta^{15}\text{N}$ values of SPM were reported to
735 increase from ≤ 5 ‰ in surface waters to values between 6-8 ‰ below 200 m water depth which
736 was attributed to organic matter degradation on SPM (Yang et al., 2017; Altabet et al., 1991;
737 Hannides et al., 2013; Emeis et al., 2010). However, SPM samples from the Arabian Sea
738 upwelling area show decreasing $\delta^{15}\text{N}$ values from an average of 8.6 ‰ at water depth above
739 200 m to 7.4 ‰ at depths below 200 m (Gaye et al., 2013b). It is thus reasonable that SPM has
740 a constant $\delta^{15}\text{N}$ value in the mesopelagic and bathypelagic ocean. This is an additional indicator
741 of a common process determining the AA composition and their $\delta^{15}\text{N}$ values of SPM and
742 probably also of DOM sampled below water depths of 200 m (equivalent to an age of ≥ 100
743 years; (England, 1995; Gebbie and Huybers, 2012).

744

745 **4.5 Abundance of amino acids in the ocean**

746 Based on POC, TN and AA fluxes and the area of the open ocean and shallow seas (Costello et
747 al., 2010) we can estimate annual downward fluxes (Table S6). Average POC flux of
748 compilations of trap fluxes were between $1.65 \text{ g m}^{-2} \text{ a}^{-1}$ (Wilson et al., 2012) and $2.74 \text{ g m}^{-2} \text{ a}^{-1}$
749 (Rixen et al., 2019a) while our subset of trap samples from the open ocean (>2000 m water
750 depth) averages to $3.06 \text{ g m}^{-2} \text{ a}^{-1}$. For open ocean traps this results in total fluxes of 0.51-0.94
751 PgC a^{-1} . Our average flux estimates for TN are 0.13 PgN a^{-1} and for AAC are 0.15 PgAA a^{-1} .
752 The flux rates over the shelves and slopes bear, however, large uncertainty because productivity
753 is by several orders of magnitude higher than in offshore areas and spatially variable. Our first
754 estimate, simply based on an average of our fluxes caught in traps deployed in areas of water
755 depth < 2000 m arrives at POC fluxes of 5.4 PgC a^{-1} , TN fluxes of 0.9 PgN a^{-1} and AAC fluxes
756 of $1.36 \text{ Pg AAC a}^{-1}$. Thus 85-90 % of fluxes occur in near shore environments corroborating
757 that 95 % of the total marine organic carbon is buried in these environments (Hedges and Keil,
758 1995). The total sinking fluxes in the proximal plus distal ocean add up to 6.3 PgC a^{-1} , 1.0 PgN
759 a^{-1} and, respectively, $1.51 \text{ Pg AAC a}^{-1}$ (see Table S6 for further details).

760 The largest organic carbon pool in the ocean is DOC with an inventory of $632 \pm 32 \text{ PgC}$ (Carlson
761 and Hansell, 2015; Hansell et al., 2009) and the largest N pool is DON with $77 \pm 23 \text{ PgN}$ (Gruber,
762 2008; Bronk, 2002). Dissolved AA are thus the largest AA pool in the ocean even if AA
763 comprise only a minor amount of DOC. We have only few measurements of AA concentrations,

764 which range between 0.1-0.2 mg/L with an average of 0.16 mg/L in all water samples excluding
765 bottom water. Based on these data we can estimate that AA comprise about 200 ± 70 Pg which
766 would contribute about 35 ± 11 Pg AAN and about 89 ± 29 Pg AAC to the oceanic DON and,
767 respectively, DOC pools. Accordingly, AAC contributes about 14 % to DOC while AAN
768 contributes 45 % to total oceanic DON. This is in the low range of an estimate of 45-86 % AAN
769 based on NMR spectroscopy with acid hydrolysis suggested to recover about half of this AAN
770 pool (Aluwihare et al., 2005).

771 The constant composition of TDAA throughout the ocean indicates that it belongs to the
772 recalcitrant or refractory pool of DOC; this pool is hardly removed in the deep sea and may
773 only be degraded by photochemical reactions as it is returned into surface waters in the course
774 of ocean circulation (Legendre et al., 2015). Our TDAA data reveal no depth dependent trend
775 but our data coverage is not sufficient to detect any spatial variation. The distribution of DOC
776 is, however, well known with its maximum in surface water with $40-80 \mu\text{mol C kg}^{-1}$ and
777 depletion in deep water with DOC concentrations from $>50 \mu\text{mol C kg}^{-1}$ in the North Atlantic
778 to $39 \mu\text{mol C kg}^{-1}$ in the North Pacific deep water (Carlson and Hansell, 2015; Hansell et al.,
779 2009). Due to our limited number of measurements we may have missed spatial variations
780 which could elucidate TDAA sources and cycling processes in the ocean as is the case for DOC.
781 Respiration of DOC may be an important removal process in shallower waters (Reinthal et
782 al., 2006) while a large proportion of the DOC reduction on its way to the Pacific on the deep
783 conveyor belt could be related to adsorption to POC, partly via gel formation (Druffel and
784 Williams, 1990).

785 TDAA may be among the constituents of DOC, which interact with SPM as both are transported
786 with their specific water masses by the ocean conveyor belt. Interaction with SPM is suggested
787 by the relative similarity in AA composition of TDAA and SPM. Moreover, SPM carries the
788 second largest pool of POC and AA in the ocean which has not been accounted for in carbon
789 budgets and which role in oceanic biogeochemical cycling has received little attention. The
790 total abundance of POC, TN and AA in SPM can be calculated using average concentrations
791 (Table 1) in the ocean volume between 0-200 m and between 200 m and the sea floor (Costello
792 et al., 2010). These calculations show that there are 443 Pg of total suspended matter in the
793 ocean of which organic carbon comprises 48 PgC, amino acids 35 PgAA and, total nitrogen 6
794 PgN. The relative similarity of AA spectra in SPM and TDAA suggests interaction between the
795 two pools at shallower depths and the build-up of an equilibrium, so that both pools remain

796 constant in concentrations and composition with depths. Like DOC, which was suggested to be
797 recalcitrant in the deep sea (Hansell and Carlson, 2013), SPM may only be affected by
798 degradation and repackaging into aggregates as it is reintroduced into surface water by ocean
799 circulation. Several studies, however, suggest that SPM may be an important food source for
800 deep living zooplankton (Koppelman et al., 2009; Hannides et al., 2013; Gloeckler et al.,
801 2018). If there are no removal processes in the deep ocean, we would expect SPM and their
802 organic constituents to be exported from the Atlantic via the deep ocean circulation and to
803 accumulate in the Pacific.

804

805 **5 Conclusions**

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

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

822 A novel biogeochemical indicator derived from the second factor of the PCA named Residence
823 Time Indicator (RTI) depicts the transformation of SPM enriched in plankton derived AA in
824 the epipelagic ocean to a constant composition in the meso- and bathypelagic ocean. The deep
825 SPM is probably the residue of microbial processing and is not utilizable by enzymes under the

826 present oceanic conditions. This constant composition of SPM is corroborated by a constant
827 $\delta^{15}\text{N}$ value below 200 m irrespective of the area of study.

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

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

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

848

849 **Data Availability**

850 Excerpts of the data were used in previous publications (i) from the Kara Sea in Gaye et al.
851 (2007) Nagel et al. (2005) and Unger et al. (2009), (ii) from the northern Indian Ocean in Gaye
852 et al. (2013), Gaye-Haake et al. (2005), Möbius et al. (2011) and Suthhof et al. (2001), (iii) from
853 the Mediterranean Sea in Möbius (2013) and Möbius et al. (2010), (iv) from the Namibian
854 upwelling in Nagel et al. (2016) and (v) from the Pacific in Paul et al. (2018). The entire set of
855 amino acid data was submitted to PANGAEA. Data from the Pacific are available at:
856 <https://doi.pangaea.de/10.1594/PANGAEA.885391>, <https://doi.pangaea.de/10.1594/PANGAEA.881804>,
857 <https://doi.pangaea.de/10.1594/PANGAEA.881813> and for TOC at

858 <https://doi.pangaea.de/10.1594/PANGAEA.884975>, <https://doi.pangaea.de/10.1594/PANGAEA.885023>,
859 <https://doi.pangaea.de/10.1594/PANGAEA.884981>.

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861

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879 Mediterranean Sea (MEDNIT), the Namibian upwelling (GENUS) and the Kara Sea (SIRRO).

880

881 **Author Contribution**

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

886

887

888 **Competing interests**

889 The authors declare that they have no conflict of interest.

890

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