

## Depth-dependent elemental compositions of particulate organic matter (POM) in the ocean

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[1] For the determination of the elemental composition of particulate organic material (POM) and its impact on the marine carbon cycle, we assembled C:N data for POM from many different sources into a single data collection for joint evaluation. The data set contains 10,200 C:N values, encompassing all major oceans and trophic levels, showing that C:N ratios are highly variable with values below the traditional Redfield ratio (C:N = 6.6) to values greatly exceeding it. On a global mean, C:N ratios of marine sinking particles from the surface water amount to  $7.1 \pm 0.1$ , and there is a systematic increase of C:N ratios with depth of  $0.2 \pm 0.1$  units per 1000 m. The discrepancy with results from analyses of dissolved nutrient fields, yielding constant C:N ratios close to the Redfield value, can be explained by the implicit depth averaging caused by depth variations of the surfaces under consideration. Additionally, due to preferential remineralization of nitrogen compared to carbon, the C:N ratio of the dissolving component, which is seen on dissolved nutrient fields, is smaller than the C:N ratio of the remaining particles. For carbon flux estimations, elevated and depth dependent C:N ratios should be implemented in biogeochemical models to correctly represent relative strengths of downward carbon and nitrogen fluxes. *INDEX TERMS*: 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4863 Oceanography: Biological and Chemical: Sedimentation; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; *KEYWORDS*: particulate organic matter (POM), carbon to nutrient relationship, Redfield ratio, biological pump, particle flux, remineralization of organic matter

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### 1. Introduction

[2] Organic carbon is the basic component of all living organisms, thus it has a key function in biogeochemical cycles. In its gaseous phase, as carbon dioxide (CO<sub>2</sub>), it is next to water vapor and methane the most important greenhouse gas in the atmosphere. During photosynthesis in the surface water dissolved inorganic carbon (DIC) and nutrients are removed from the water and fixed into particulate and dissolved organic matter (POM, DOM). Larger particles sink down, whereby carbon is exported from the euphotic zone into the deeper ocean, whereas DOM export is tightly linked to deep water formation. The corresponding loss of DIC in the surface water is replaced by upwelling of

carbon enriched deep waters and by equilibration with atmospheric CO<sub>2</sub> due to gas exchange. Both mechanisms, production and sinking of organic matter (biological pump) and solubility of CO<sub>2</sub> and deep water formation (physical pump), are the main processes leading to a CO<sub>2</sub> exchange between ocean and atmosphere [Volk and Hoffert, 1985]. Since the beginning of industrialization, the atmospheric pCO<sub>2</sub> has increased from 280 ppm to 370 ppm. Approximately 7 Gt C are emitted annually by burning of fossil fuels and changes in land use [Siegenthaler and Sarmiento, 1993; Schimel et al., 2001]. Currently, approximately 2 Gt C/yr are taken up by the ocean [Siegenthaler and Sarmiento, 1993; Takahashi et al., 1999], but there is large uncertainty about this value. The oceanic carbon reservoir is about 60 times larger than that of the atmosphere [Ittekkot, 1993], therefore the oceans are of fundamental importance in the global carbon cycle.

[3] The downward flux of particulate organic matter (POM) and export of dissolved organic matter (DOM) by deep water formation are important parts of the biological pump. Sinking matter exports carbon and nutrients from the surface into the deep ocean, where carbon and dissolved inorganic nutrients are released during remineralization, maintaining vertical gradients in the distributions of DIC and nutritional elements. The C:N:P element ratios of organic matter determine the relative magnitude of carbon and nutrient fluxes and they are key factors for estimates of the global ocean's capacity as a sink for atmospheric CO<sub>2</sub>. Redfield [1934] and Redfield *et al.* [1963] supposed that POM is produced in constant molar element ratios of C:N:P:O of 106:16:1:–138, i.e., during particle production dissolved inorganic carbon, nitrogen and phosphorus are fixed into organic particles while oxygen is released. Even though Redfield *et al.* [1963] also reported species specific, seasonal and regional variations, they concluded that this ratio is valid on a global annual mean for the formation of marine plankton. This classical Redfield ratio is generally accepted as constant in space and on recent time scales, and it is applied as such in biogeochemical modeling.

[4] Several more recent studies based on the analysis of dissolved inorganic nutrient fields supported or slightly revised the constant Redfield ratio. These studies determined changes in dissolved inorganic nutrient concentrations either due to remineralization in carefully selected water masses [Takahashi *et al.*, 1985; Peng and Broecker, 1987; Minster and Boulahdid, 1987; Boulahdid and Minster, 1989; Anderson and Sarmiento, 1994] or the draw-down of dissolved carbon and inorganic nutrients by particle formation [Arrigo *et al.*, 1999]. Whereas restricted regions with special climatic conditions and nutrient levels can exhibit strong non-Redfieldian behavior at least temporarily [e.g., Arrigo *et al.*, 1999], most studies using basin-wide or global dissolved nutrient, carbon and oxygen distributions, even though they might have revealed deviations from the classical Redfield ratio, concluded that their results are constant (in space and time) with element ratios in agreement with the Redfield ratio. Significant differences were mainly found for the ratios of oxygen to carbon and nutrients, respectively.

[5] A direct approach for the study of element ratios of POM is the determination of the C, N and P content of particulate material obtained by filtrations and sediment trap sampling. The most common sampling method is filtration of small volumes of sea water (1–4 L) over filters of a pore size between 0.2 and 0.7  $\mu\text{m}$ . Such filtration data are relatively easy to obtain and allow a good regional and vertical data coverage. However, due to the small amounts of filtered water, the yield of particulate material is generally low, and the levels of particulate organic nitrogen (PON) and phosphorus (POP) are often close to detection limit or affected by contamination. Moran *et al.* [1999] reported that with decreasing volumes of sampled water (<2 L) and also with decreasing POC concentrations (<5  $\mu\text{mol/L}$ ), the contribution of sorbed DOM to the filters increases, which is then quantified as POC and PON, erroneously. This may lead to an overestimation of POC concentrations up to a factor of five, and consequently to an overestimation of the

C:N ratio, requiring a correction by measuring sorption blanks.

[6] The problems of DOM sorption onto the filters and overall too small sample sizes, as it is described above, do not apply to the large volume filtrations using in situ pumps [Druffel *et al.*, 1998; Bishop *et al.*, 1999; Loh and Bauer, 2000], where several hundred to several thousand liters of sea water are filtered. These samples yield relatively large amounts of particulate material and are therefore supposed to be of very high quality.

[7] Sediment traps, usually deployed for some months or up to two years, collect larger sinking material. While filter samples represent conditions at the time of sampling, sediment trap data provide integrated information over the whole deployment period with a temporal resolution between a few days to months. Thereby seasonal variability near the surface or in deeper water masses can be detected. However, sediment traps might not capture the vertical particle flux quantitatively due to non-ideal trapping efficiencies and the composition of the material might be altered due to remineralization in the sampling cups [Gardner *et al.*, 1983; Wakeham *et al.*, 1993; Gust *et al.*, 1994; Noji *et al.*, 1999; Kähler and Bauerfeind, 2001; Scholten *et al.*, 2001]. These problems mainly refer to shallow sediment trap deployments (<1000 m) and poisoning of the water in the cups is often applied to reduce this problem.

[8] There is a general difference in the types of particles gained either by filtrations or by sediment traps [Altabet, 1988; Druffel *et al.*, 1992, 1998], which have to be distinguished, because they cycle very differently in the ocean. Below the euphotic zone filter samples largely consist of suspended particles that are very small (<2  $\mu\text{m}$ ), and partially old and nutrient depleted as a consequence of preferential nutrient remineralization [Müller, 1977; Sambrotto *et al.*, 1993]. Sediment trap samples predominantly contain larger, fast sinking particles that are relatively fresh, as has been determined by  $\Delta^{14}\text{C}$  measurements [Druffel *et al.*, 1998]. Consequently, sediment trap data referring to truly sinking material are most suitable to estimate C:N ratios of sinking particles.

[9] However, all usual methods collect bulk material which consists of a large number of different components, with probably different element ratios. There is, for example, phytoplankton, zooplankton, living matter and detritus at different stages of decomposition [Edwards, 2001], and sinking aggregates may also contain considerable amounts of DOM [Alldredge and Gotschalk, 1989; Kjørboe *et al.*, 1994]. In addition, the sampled particles also may carry nonmarine material from eolian dust input, river discharge and resuspension from the sea floor [Banse, 1974; Müller, 1977; Ratmeyer *et al.*, 1999; Hebel and Karl, 2001], which indicates a wide variety of factors influencing the elemental composition of sinking particles in the ocean. In any case, data obtained from measurements of sampled particles represent a direct measure of the elemental composition of POM, which most probably yields better estimates of marine carbon fluxes than the indirect method of analyzing effects of remineralization rates on dissolved nutrient fields.

**Table 1.** General Overview and References of Individual Data Sets Used for This Study

Name	Cruise/Station	Type	No. of Samples	Project	References
AESOPS	MS-1, MS-2, MS-3, MS-4, MS-5	traps	58	JGOFS	<i>Honjo et al.</i> [2000]
Arabian Sea	ttn 043, ttn 045, ttn 049, ttn 053	filter	944	JGOFS	<a href="http://usjgofs.whoi.edu/jg/dir/jgofs/">http://usjgofs.whoi.edu/jg/dir/jgofs/</a>
Arctic	ARK XIII/2	filter	227	AWI	unpublished data
BATS	BATS trap 150, OFP 500, OFP 1500, OFP 3200, SCIFF/OFP	traps	922	JGOFS	<a href="http://www.bbsr.edu/users/ctd/traplist.html">http://www.bbsr.edu/users/ctd/traplist.html</a>
BATS	BATS bloom, BATS core, BATS valid	filter	2896	JGOFS	<a href="http://www.bbsr.edu/users/ctd/batdataex.html">http://www.bbsr.edu/users/ctd/batdataex.html</a>
EQPAC	tt007	filter	287	JGOFS	<a href="http://usjgofs.whoi.edu/jg/dir/jgofs/">http://usjgofs.whoi.edu/jg/dir/jgofs/</a>
EQPAC	eqpac	traps	305	JGOFS	<i>Honjo et al.</i> [1995]
HOT	HOT	traps	206	JGOFS	<a href="http://usjgofs.whoi.edu/jg/dir/jgofs/">http://usjgofs.whoi.edu/jg/dir/jgofs/</a>
Line P	Line P	pump	769	JGOFS	<a href="http://www.meds-sdmm.dfo-mpo.gc.ca/jgofs/jgofs_cd/datasets/varela/readme.htm">http://www.meds-sdmm.dfo-mpo.gc.ca/jgofs/jgofs_cd/datasets/varela/readme.htm</a>
North Atlantic	Nabe atl II, Meteor 10-1, Meteor 10-2	filter	727	JGOFS	<a href="http://usjgofs.whoi.edu/jg/dir/jgofs/">http://usjgofs.whoi.edu/jg/dir/jgofs/</a> (Nabe); and unpublished data
Peru/Chile	CH1-3, CH3-1, CH3-2, CH 4-1	traps	80	JGOFS	<i>Hebbeln et al.</i> [2000]
Ross Sea	NBP 96-4A, NBP 97-1, NBP 97-3	filter	728	JGOFS	<a href="http://usjgofs.whoi.edu/jg/dir/jgofs/">http://usjgofs.whoi.edu/jg/dir/jgofs/</a>
SFB 261	BO1, BO2, BO3, CB1, CB2, CB3, CB4, CB5, C11, C12, C13, C14, CV1, CV2, EA1, EA2, EA3, EA4, EA5, EA8, GB2, GBN3, GBN6, GBZ4, GBZ5, KN1, KN3, PF3, PF5, WA1, WA2, WA3, WA4, WR1, WR2, WR3, WR4, WS3, WS4	traps	897	SFB 261	<i>Fischer et al.</i> [1996]; <i>Wefer and Fischer</i> [1993] and unpublished data
Weddell Sea	ANT III/3, ANT V/2, ANT VII/2, ANT X/6	filter	1009	AWI/JGOFS	<i>Nöthig</i> [1987]; <i>Scharek</i> [1990]; <i>Bianchi et al.</i> [1992]; <i>Rutgers van der Loeff et al.</i> [1997]

[10] A large number of studies have been published where element ratios were explicitly derived from particles [*Holm-Hansen et al.*, 1966; *Gordon*, 1971; *Copin-Montégut and Copin-Montégut*, 1978; *Honjo*, 1980; *Knauer and Martin*, 1981; *Honjo*, 1982; *Wefer et al.*, 1982; *de Baar et al.*, 1983; *Copin-Montégut and Copin-Montégut*, 1983; *Karl et al.*, 1984, 1988; *Martin et al.*, 1987; *Tréguer et al.*, 1990; *Haake et al.*, 1993; *Hecky et al.*, 1993; *Bauerfeind et al.*, 1994; *Honjo et al.*, 1995; *Arrigo et al.*, 1999; *Honjo et al.*, 1999, 2000; *Hebbeln et al.*, 2000; *Hebel and Karl*, 2001; *Hernes et al.*, 2001]. Although variations in particle compositions were found, these studies concluded that results were not significantly different from the classical Redfield ratio and/or spatial limitations did not allow broader conclusions on a basin-wide or global scale.

[11] Other studies discuss probable reasons for variations in the element ratios of POM and come up with mainly two ways of explanation: deviations from the Redfield ratio during particle production and changes during subsequent remineralization processes. During particle production, variations in the elemental compositions may be related to ambient CO<sub>2</sub> concentrations and/or nutrient availability [*Sakshaug and Holm-Hansen*, 1977; *Burkhardt and Riebesell*, 1997; *Burkhardt et al.*, 1999]. While there is no uniform trend between CO<sub>2</sub> availability and carbon incorporation by the organisms, ample supply of phosphorus and nitrate can lead to luxury consumption, for example, particles may incorporate more nitrogen than essentially necessary, leading to low C:N ratios [*Droop*, 1973; *Elfiri and Turpin*, 1985; *Roelke et al.*, 1999]. Under nutrient limitation (nitrate), particles may take up less nitrogen; that is, they are able to incorporate relatively more carbon, resulting in elevated C:N ratios [*Copin-Montégut*, 2000; *Gervais and Riebesell*, 2001]. Changes of element ratios

during remineralization are described as preferential remineralization of nutrients; that is, phosphorus and nitrogen are released more easily from the particles than carbon and become available again for new production faster. This was supported by measuring significant differences between dissolved inorganic and particulate element ratios [*Sambrotto et al.*, 1993; *Thomas et al.*, 1999; *Hupe and Karstensen*, 2000; *Osterroht and Thomas*, 2000; *Körtzinger et al.*, 2001].

[12] While variations in particle compositions have been found in numerous previous investigations, as it was described above, the spatial and/or temporal limitations of the respective studies did not allow to draw general conclusions on basin-wide and/or global scales. For the present study, we have compiled many independent data sets for C:N ratios of particulate material into a large data collection for joint evaluation to achieve a new global perspective on the C:N elemental composition of POM in the ocean.

## 2. Data Set

[13] In this study we compiled more than 10,200 C:N measurements on particulate material from sediment trap and filter samples covering large parts of the global ocean. Detailed information about the individual data sets and their sources are given in Table 1. All data sets include data for particulate organic carbon (POC) and particulate organic nitrogen (PON). Several data sets also include dissolved nutrients, chlorophyll concentrations and particle fluxes. The global distribution of the resulting data set is shown in Figure 1 overlain on a global productivity map based on satellite observations [*Behrenfeld and Falkowski*, 1997], which shows that many different hydrographic and biogeochemical provinces are covered by the data collection.

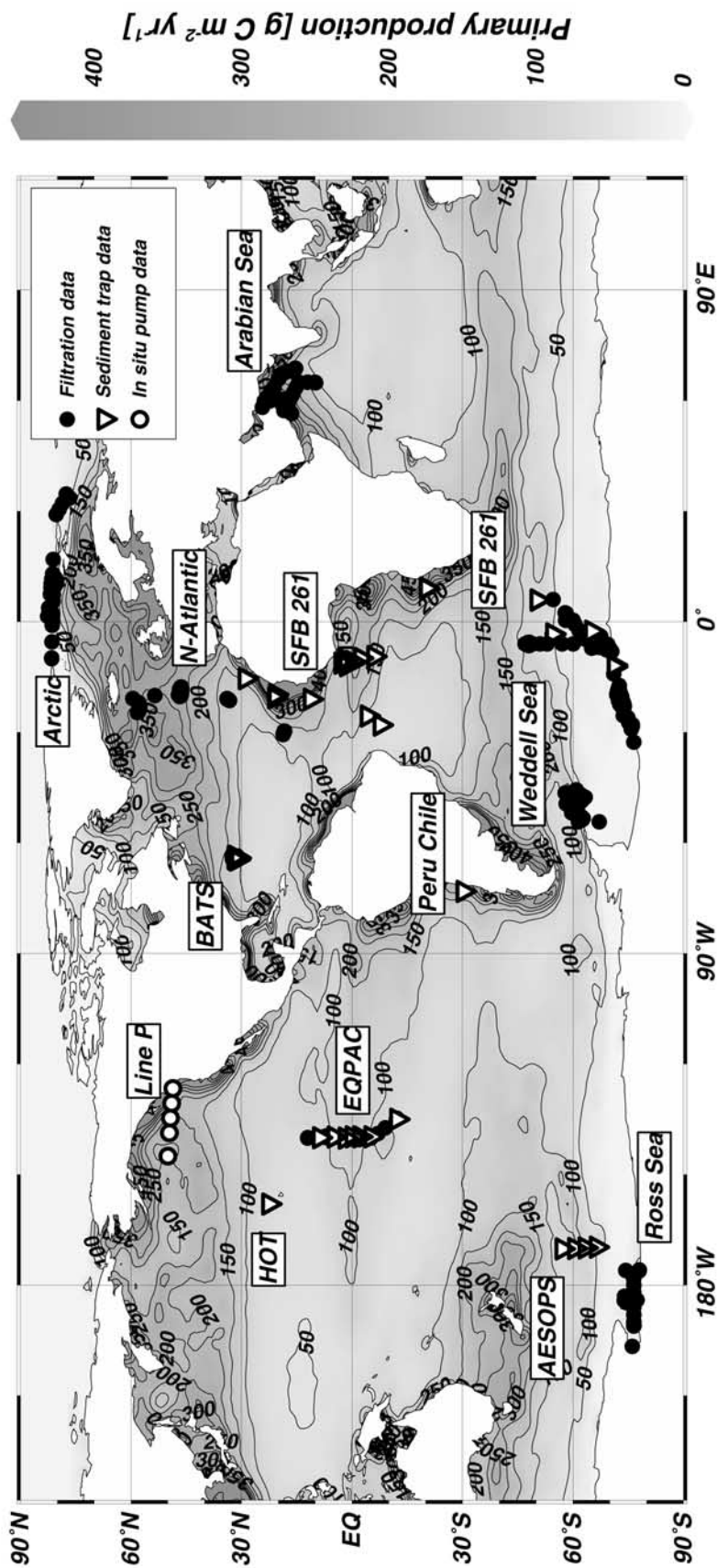
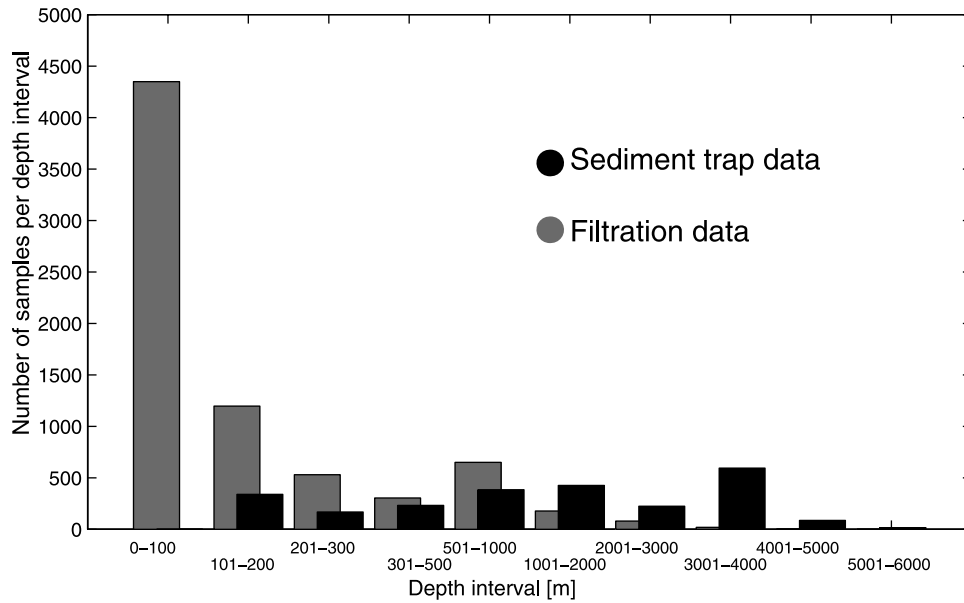


Figure 1. Sample locations of the C:N data collection overlain on the marine primary production map of Behrenfeld and Falkowski [1997].



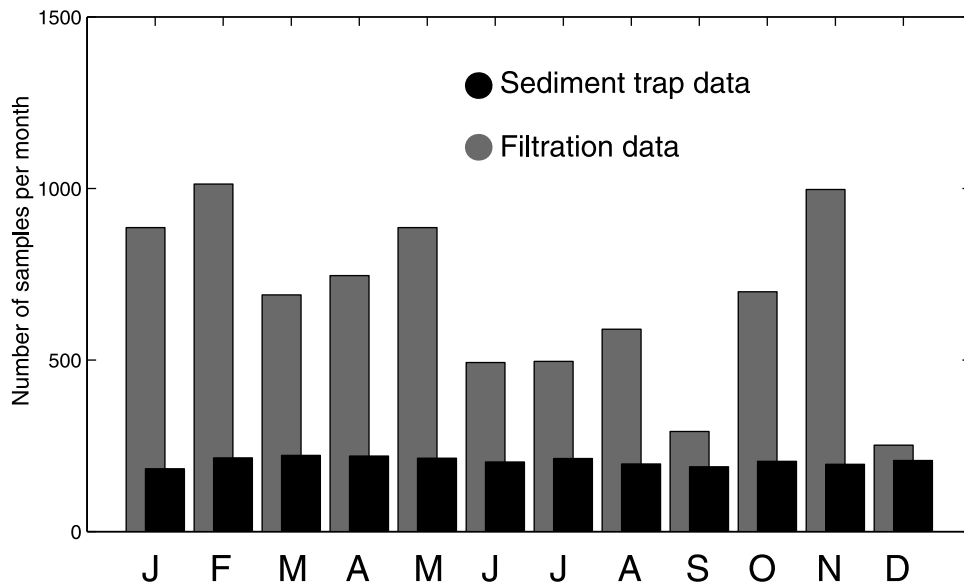


**Figure 2.** Sample distribution over depth in the water column.

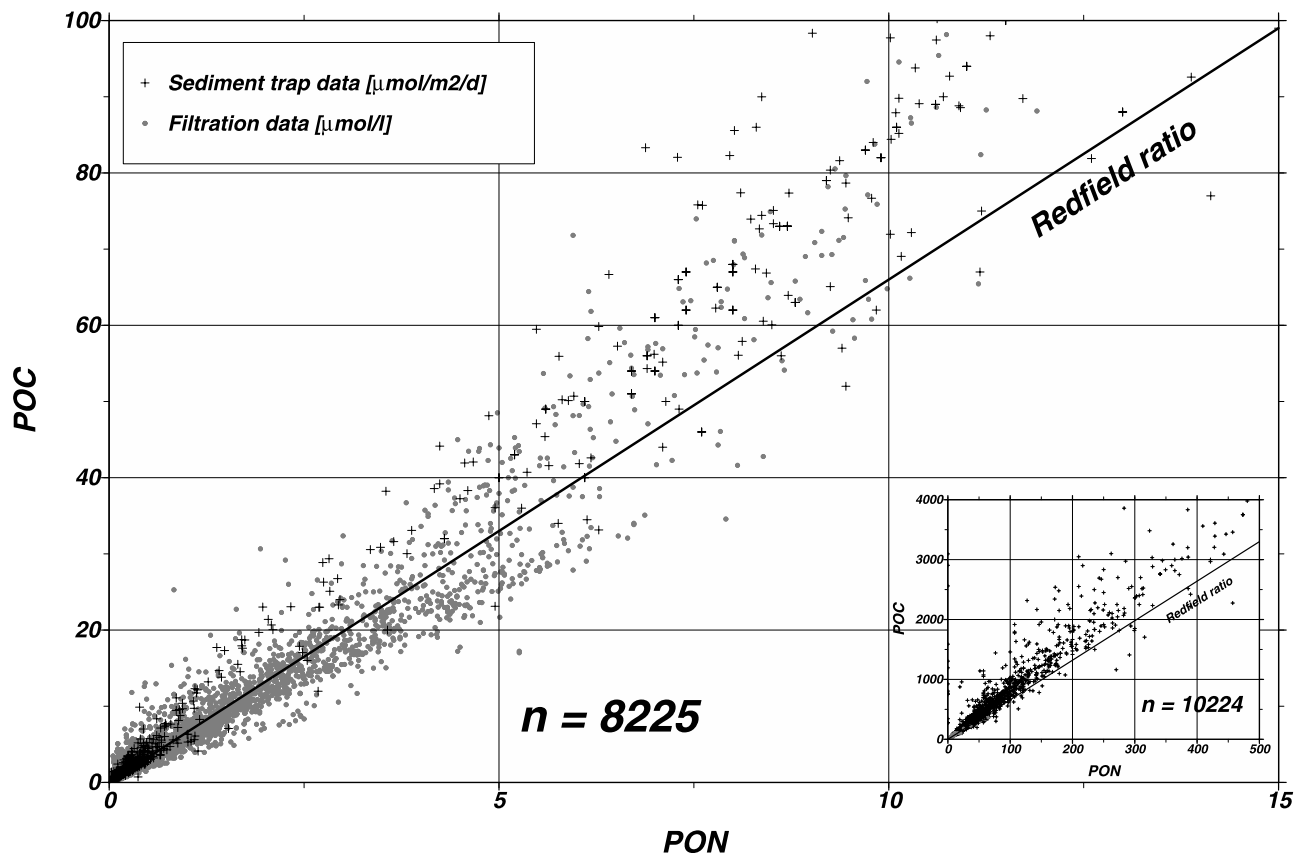
There are oligotrophic regions like the Sargasso Sea as well as high productive areas in coastal and equatorial upwelling regions, in the Pacific, Indian and the Atlantic Ocean, respectively. Zones with seasonal ice cover in polar regions, areas of high nutrient low chlorophyll (HNLC) in the South Atlantic and the northeast Pacific and furthermore the monsoon region of the Arabian Sea are also represented in the data set.

[14] The data collection contains data from sediment trap samples as well as from filter samples obtained from both small and large volumes (in situ pumps) of sea water. Figure 1 shows the regional distribution of samples obtained by each collection method. Approximately 75% of the values in our data set are from filtrations while 25% are sediment

trap data. Filtration data are mostly from the upper water column with a mean depth of 200 m. Sediment trap samples are taken at deeper levels with an average depth of 1700 m (Figure 2). Sediment traps are typically deployed over time periods of months to 1 or 2 years, and thus can yield temporal variability and mean values over the deployment period. Filtration data, on the other hand, represent point measurements in space and time, and thus exhibit spatial and temporal variability of individual production and remineralization events. Figure 3 shows the number of samples per month for both methods. Sediment trap samples are distributed relatively homogeneously over the whole year, whereas samplings by filtration show large differences between single months.



**Figure 3.** Number of samples per month.



**Figure 4.** Particulate organic carbon (POC) displayed versus particulate organic nitrogen (PON) for all data over all depths. The solid line indicates the classical C:N Redfield ratio of 6.6. The small inset shows the whole range of data, whereas the large panel displays the range of low POC and PON values, only.

[15] For the current analysis, all data were transferred from their original formats into ODV-Collections (R. Schlitzer, Ocean Data View, available online at <http://www.awi-bremerhaven.de/GPH/ODV>) to facilitate joint evaluation. The following analysis focuses on the C:N ratios of POM, because these data are most abundant. Throughout the paper, C:N ratios are given in molar units. Weight ratios in the original data sets were converted to molar units using the atomic weights for carbon (12) and nitrogen (14). Arithmetic means ( $\bar{x}$ ) of C:N ratios, standard deviations (s) and standard mean errors ( $s_{\bar{x}}$ ) were calculated for different depths or regional data subsets. A t-test was applied to check whether differences from the classical Redfield ratios and between different data subsets, respectively, are significant [Sachs, 1997; Lozan and Kausch, 1998].

[16] Measurements of organic material from low volume filtrations may be questionable due to the possible sorption of DOM on the filter material [Moran *et al.*, 1999], as was mentioned above. For most of the small volume filter analyses in the current study the JGOFS standard procedures have been applied; that is, at least 2 L of sea water were taken for samples from the upper 250 m of the water column and 4 L for samples below 250 m water depth. Furthermore, sorption blanks were determined and DOM contributions on the POC and PON values were corrected. There are 539 filtration values in the current study (8%), for

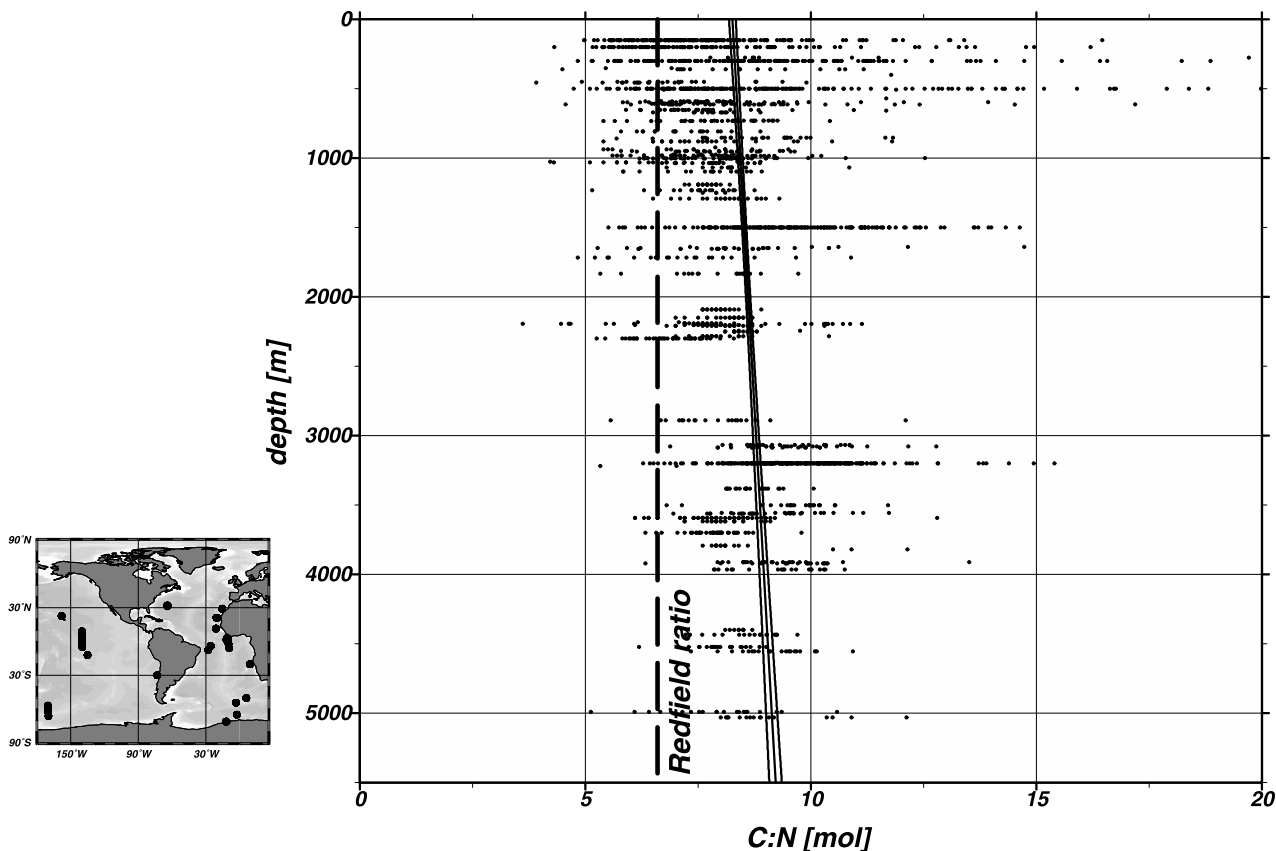
which POC concentrations are low ( $<10 \mu\text{mol/L}$  POC) and the sorption blank correction possibly has not been performed. This applies to ANT X/6 data from the Weddell Sea and to some data from the North Atlantic Nabe, Met 10-1 and Met 10-2. However, analysis of the present data set shows that the mean C:N ratios of these possibly uncorrected data are not significantly different from the C:N ratios of the corrected filter data.

[17] Comparing mean values and standard deviations of C:N ratios from low volume and large volume filtrations also does not reveal significant differences. The mean C:N ratio for the small volume filter values in the data set is 8.00, with a standard mean error of  $\pm 0.04$  ( $n = 7288$ ), which is even lower than the error of the large volume

**Table 2.** Comparison of Sediment Trap Data With Filtration Data at the BATS Site, 150–500 m Depth<sup>a</sup>

Depth	Filtration Data			Sediment Trap Data			Level of Significance
	C:N	s	n	C:N	s	n	
150 m	7.7	2.8	164	7.0	1.4	115	0.01
200 m	8.0	2.8	141	7.6	2.8	113	n.s.
300 m	9.8	3.0	110	8.9	2.8	112	0.05
500 m	9.9	3.1	118	8.1	3.2	124	0.001

<sup>a</sup>Mean C:N ratios, standard deviation (s), number of samples (n) and level of significance.



**Figure 5.** C:N ratios from sediment trap samples versus depth. The dashed line indicates the Redfield ratio of C:N (6.6), the solid line is the regression line for the increase of C:N ratios with depth. The curved lines mark the mean error of the regression line.

filtrations, which have a mean C:N ratio of 7.98 with a standard mean error of  $\pm 0.16$  ( $n = 752$ ). There are obviously no systematic differences between the results of both types of filtration, large volume and low volume, and also the low volume filtration data in the current data collection seem to be of good quality. Therefore, in this study the values obtained from small and large volume filtrations are treated alike.

[18] The possible alteration of material in the sample cups of sediment traps due to dissolution and zooplankton feeding (swimmers) has been described to be a potential problem of sediment trap analyses [Noji *et al.*, 1999; Kähler and Bauerfeind, 2001], especially in shallow trap deployments. However, it is unclear whether zooplankton feeding on particles in the traps is likely to alter the element ratio of the remaining material or if only the amount of bulk material is changed. A plot of trap material C:N ratios versus time since deployment for sediment trap data from the Atlantic Ocean ( $n = 870$ ; data not shown) revealed no shift in the element ratios over time, which would be expected if dissolution in the sampling cups was important. Furthermore, the seasonal C:N signal in shallow traps (not shown) from the BATS site in the Sargasso Sea coincides closely with the pattern obtained for filter data from the same time and location. Again, if dissolution in the traps was important, one would expect systematic differences

with the filter data and a weakening/smoothing of seasonal trends.

### 3. Results

[19] For a first overview of general trends in the elemental composition of POM, all data are analyzed together. To differentiate between element ratios of suspended and sinking particles, filter and sediment trap data from the same time and location are compared. Suspended matter does not sink in the water column and thus it has a long residence time in the water column, whereas sinking particles support a fast export of carbon and nutritional elements from the surface to depth, being the most important mechanism of the biological pump. Therefore, the further interpretations refer to sediment trap data only, because unlike filtered material, trap samples contain truly sinking material. The sediment trap data are more evenly distributed over depth than filter data, and they span longer time intervals, allowing the calculation of annual mean values.

#### 3.1. General Trends

[20] The investigation of data on the elemental composition of POM reveals that C:N ratios are highly variable with deviations from the classical Redfield ratio into both direc-

**Table 3.** Mean Values of C:N Ratios, Standard Deviations (s) and Number of Samples (n) for Sediment Trap Data From Selected Regions<sup>a</sup>

Depth, m	E-Atlantic (SFB 261)			W-Atlantic (SFB 261)			S-Atlantic (SFB 261)		
	C:N	s	n	C:N	s	n	C:N	s	n
0–500							7.77	2.32	58
501–1500	<b>8.13</b>	1.06	276	<b>7.39</b>	0.72	92	<b>8.75</b>	2.23	45
1501–2500	<b>8.31</b>	1.66	93				6.12	1.79	12
2501–3500	<b>9.00</b>	1.19	98				11.91	7.34	8
3501–4500	<b>9.28</b>	1.07	139						
4501–5500	<b>8.01</b>	0.63	20	<b>8.72</b>	1.23	56			

Depth, m	Sargasso Sea (BATS)			S-Pacific (Peru/Chile)			N-Pacific (HOT)		
	C:N	s	n	C:N	s	n	C:N	s	n
0–500	<b>7.92</b>	2.93	480				<b>10.24</b>	4.6	206
501–1500	<b>9.54</b>	1.76	183						
1501–2500				<b>6.83</b>	0.71	40			
2501–3500	<b>9.69</b>	1.35	259						
3501–4500				<b>7.84</b>	0.61	40			
4501–5500									

Depth, m	S-Pacific (AESOPS)			Equation Pacific (EQPAC)			All Sediment Trap Data		
	C:N	s	n	C:N	s	n	C:N	s	n
0–500							<b>8.55</b>	3.58	744
501–1500	6.7	1.0	58	<b>7.7</b>	0.7	68	<b>8.28</b>	1.62	722
1501–2500				<b>8.0</b>	0.6	140	<b>7.87</b>	1.26	285
2501–3500							<b>9.55</b>	1.71	365
3501–4500				<b>8.0</b>	0.8	97	<b>8.63</b>	1.14	276
4501–5500							<b>8.53</b>	1.15	76

<sup>a</sup>Bold numbers indicate significant deviations from the Redfield ratio of 6.6.

tions. For a global overview, all available values of POC versus PON ( $n = 10224$ ) are displayed in Figure 4, where the black line represents the classical Redfield C:N ratio. Despite large scatter, the data show that C:N ratios are generally higher than the classical Redfield ratio, which is evident especially for higher concentrations and flux rates of POC and PON, respectively. The global mean C:N ratio for all data over all included depths (data are not evenly depth distributed; see Figure 2) is about 8.2 with values reaching from 3 to up to 60. In some cases, values below 3 were found ( $n = 45$ ), which is even lower than C:N ratios of pure bacterial biomass. As we do not know any organisms existing with C:N ratios lower than 3, these data are most probably artifactual and they were excluded from further analyses.

[21] The large data base comprising data from different sampling techniques permits both, a detailed evaluation of the data themselves and a comparison of the sampling methods applied. As mentioned above, data from different sampling strategies gather different types of particles, exhibiting systematic variations in their elemental compositions. A direct comparison of data from the two approaches, filtrations and sediment trap data, can be made at the site of BATS in the Sargasso Sea, where both methods were used at the same time and location. In Table 2 mean C:N ratios of data from the 1989–1999 period for both sample types are outlined on four depth levels, 150 m, 200 m, 300 m and 500 m ( $n = 997$ ), respectively. Sediment

trap data are representative for the given depth, while filtration samples were taken from a depth range 10 m above and below the reference level. For both methods and all respective depth levels the mean C:N ratios are significantly higher than the classical Redfield ratio. Furthermore, the C:N ratios from filter samples turn out to be systematically higher than those obtained from sediment traps. The differences between both methods are statistically significant on all examined depth layers except for 200 m depth. Both types of data show standard deviations of similar magnitude, suggesting that the variability in the data is mostly due to natural variability and not caused by analytical procedures.

### 3.2. C:N Depth Dependence

[22] For the study of depth dependencies, all available sediment trap C:N ratios ( $n = 2462$ ) are plotted versus depth as shown in Figure 5. Also shown is the C:N versus depth regression line (solid line) and the classical C:N Redfield value of 6.6 (dashed line). Despite the relatively large scatter, the regression line clearly shows an increase of C:N values with depth, and it can also be seen that the scatter decreases with depth. The increase of particulate C:N ratios with depth in the water column (based on 2462 sediment trap samples) can be described by the equation

$$C : N(z) = 8.26(\pm 0.1) + 0.17(\pm 0.1) \cdot z[\text{km}]. \quad (1)$$

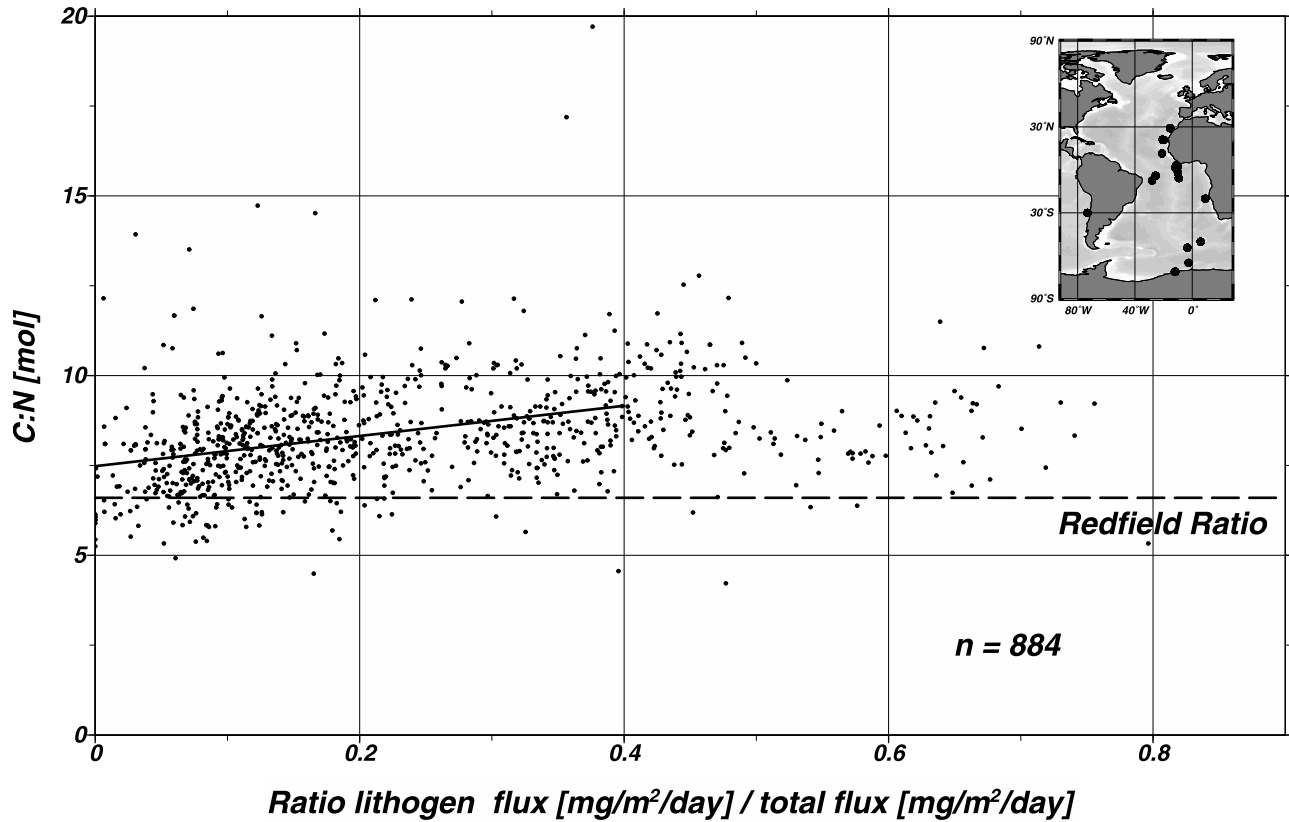
[23] From equation (1) it follows that the mean C:N ratio of sinking POM in the surface water is about 8.3, which is significantly higher than the classical Redfield ratio. Additionally, C:N ratios are increasing over depth with a rate of roughly 0.2 units per 1000 m water depth. Because the shallowest traps were deployed in 150 m water depth, the C:N value for the surface water is obtained by extrapolation of deeper values.

[24] As a consequence of spatially uneven data distribution, individual regions may influence the global mean values disproportionately, as, for example, the BATS data, which make up roughly 35% of all sediment trap data points. Also, there are numerous data from the HOT time series in the subtropical North Pacific, with a low vertical extent, but a significant impact on the global mean values. These data cover the depth interval between 150 and 500 m only, but with a total of 206 single data points they amount to 10% of all sediment trap data. Furthermore, the mean C:N ratio of the HOT data amounts to  $10.2 \pm 0.3$  (see Table 3), which is much higher than both, the classical Redfield ratio and other data from similar depth intervals. This high average value results in a significant shift of the

**Table 4.** Linear Least Squares Fits of C:N Ratios as Functions of Depth for Sediment Trap Data From Selected Regions With Large Vertical Data Coverage

Name	Depth Range, m	Regression Line, km	n
Sargasso Sea	150–3200	C:N = $7.9 + 0.6 \cdot z$	922
Atlantic (30°N–20°S)	570–5030	C:N = $7.8 + 0.3 \cdot z$	774
South Atlantic	275–3220	C:N = $7.9 + 0.5 \cdot z$	123
Equatorial Pacific	880–4400	C:N = $7.7 + 0.1 \cdot z$	305





**Figure 6.** C:N ratios of sediment trap samples versus relative flux of lithogenic material. The dashed line indicates the classical Redfield ratio of 6.6, while the solid line is the regression line for particles fluxes with less than 40% lithogenic contribution.

global mean C:N ratio for particles in the subsurface water towards higher values, and simultaneously it reduces the rate of increasing C:N ratios over depth markedly. Excluding the HOT data from the data set results in a C:N depth dependence of

$$C : N(z) = 7.85(\pm 0.1) + 0.31(\pm 0.1) \cdot z[\text{km}]. \quad (2)$$

[25] Compared to equation (1), the C:N values for particles at the sea surface are now significantly lower and the rate of increase with depth is higher. For a comparison of regional differences, Table 3 shows mean C:N ratios of sinking particles (sediment trap samples) from selected regions and depth levels. Higher-than-Redfield C:N ratios are found almost everywhere, and increasing C:N ratios over depth are also detected in most cases. However, there is a statistically significant decrease of C:N ratios in the bottom layer for samples from the East Atlantic and for the sum of all sediment trap data.

[26] There are regional differences in the rates of increase of particulate C:N ratios over depth. In Table 4 these increases are listed for some regions that exhibit larger than average depth increases of C:N values, such as the Sargasso Sea (0.6 units per 1000 m), the South Atlantic (0.5 units per 1000 m) and the low-latitude Atlantic (0.3 units per 1000 m). The equatorial Pacific, which is also shown in Table 4, reveals a lower than average increase of

C:N ratios versus depth with 0.1 units per 1000 m water depth.

### 3.3. Lithogenic Contribution

[27] Sinking particles are not necessarily pure marine particulate organic matter, but may carry substantial amounts of lithogenic material with them, which can influence the element ratios significantly [Wefer and Fischer, 1993]. In Figure 6, C:N ratios of sinking POM are displayed versus the relative contribution of lithogenic material to the total flux for data from the Atlantic Ocean and the southeast Pacific Ocean. In some cases lithogenic fluxes reach up to 90% of total flux rates while the mean lithogenic contribution is about 25%. Figure 6 shows an increase of C:N ratios with increasing relative lithogenic contributions, especially for small lithogenic contributions below 40%. The increase is attributed to terrigenous organic matter with elevated C:N ratios, attached to lithogenic particles; for example, the C:N ratio of organic soils can reach up to values of 50–60 [Scheffer and Schachtschabel, 1992]. To separate marine from lithogenic signals and to obtain a reliable estimate of the elemental composition of pure marine material, a correction procedure was applied and effects of lithogenic components were eliminated. In a first step, all data with lithogenic fluxes higher than 40% were omitted. For the remaining data, the C:N signal of the lithogenic contribution was derived from the slope of the

**Table 5.** Comparison of Lithogenic and Corresponding Aluminum Fluxes From Sediment Trap Data Between Different Regions

Name	Lith. Fluxes, g/m <sup>2</sup> /yr	Al Fluxes, mg/m <sup>2</sup> /yr	Percent Lithogenic of Total Fluxes	Reference
AESOPS	0.05–0.12	4.1–59.4	0.2–6.9	<i>Honjo et al.</i> [2000]
EQPAC		1.2–42.4		<i>Honjo et al.</i> [1995]
NE-Atlantic (lowest)	4.2–7.7		22–70 <sup>a</sup>	<i>Ratmeyer et al.</i> [1999]
NE-Atlantic (highest)	11.4–20.5		22–70 <sup>a</sup>	<i>Ratmeyer et al.</i> [1999]
Arabian Sea	2.9–10.5	219–284	9–13	<i>Honjo et al.</i> [1999]

<sup>a</sup>From this analysis.

regression line of C:N ratio versus relative lithogenic flux, corresponding to a rate of 0.4 C:N units per 10% lithogenic fluxes (Figure 6), and the initial C:N values were corrected to zero lithogenic contribution.

[28] For some data of more open marine sites, that did not include appropriate parameters for lithogenic fluxes, this correction procedure could not be applied (BATS, HOT, AESOPS, EQPAC). However, there is evidence from associated aluminum measurements (used as a proxy for lithogenic contributions) that most of these data do not need correction due to very low lithogenic fluxes; that is, they can be used as such for the derivation of a C:N depth dependence. This argument seems to be applicable for the AESOPS data set, where in addition to detailed aluminum flux rates, lithogenic fluxes were given as annual mean values and for the EQPAC sediment trap data, where only aluminum fluxes were measured. A comparison of these two data sets with aluminum and lithogenic flux rates of data from the literature [*Honjo et al.*, 1995, 1999; *Ratmeyer et al.*, 1999; *Honjo et al.*, 2000] reveals that lithogenic fluxes in these two sub data sets are in fact negligible, which is displayed in Table 5, where aluminum fluxes in both cases (AESOPS and EQPAC) are in the range of 1.2–60 mg/m<sup>2</sup> yr<sup>1</sup>. At the site of AESOPS this corresponds to annual lithogenic fluxes between 0.05 and 0.12 g/m<sup>2</sup> yr<sup>1</sup>. The comparison with data from the subtropical Northeast Atlantic [*Ratmeyer et al.*, 1999] and data from the Arabian Sea [*Honjo et al.*, 1999] shows that the relatively low lithogenic fluxes from the Northeast Atlantic exceed those from AESOPS by far, and secondly, the amount of aluminum fluxes from the Arabian Sea is also much higher than aluminum fluxes from the AESOPS and EQPAC data sets. Therefore, lithogenic fluxes at these sites can be neglected in the following approach for the investigation of pure marine particulate organic matter.

[29] The corrected C:N ratios and those that did not need correction ( $n = 1123$ ) are displayed in Figure 7 versus depth in the water column. It is found that there is still an increase of C:N ratios with depth of about the same rate as for the uncorrected values shown in Figure 5. However, the corrected C:N values are now closer to the classical Redfield ratio as compared to the uncorrected values. The increase of pure marine sinking particulate C:N ratios corresponds to the equation

$$C : N(z) = 7.14(\pm 0.1) + 0.18(\pm 0.1) \cdot z[\text{km}]. \quad (3)$$

[30] The C:N ratio of what is supposed to be pure marine sinking particles for the surface water is about 7.1 and the

increase over depth amounts to 0.2 per 1000 m. As the shallowest trap for this analysis is in 275 m depth the C:N ratio for particulate material at the surface was extrapolated. It is significantly different from the Redfield ratio and also from the uncorrected value for particles at the surface as given by equation (1).

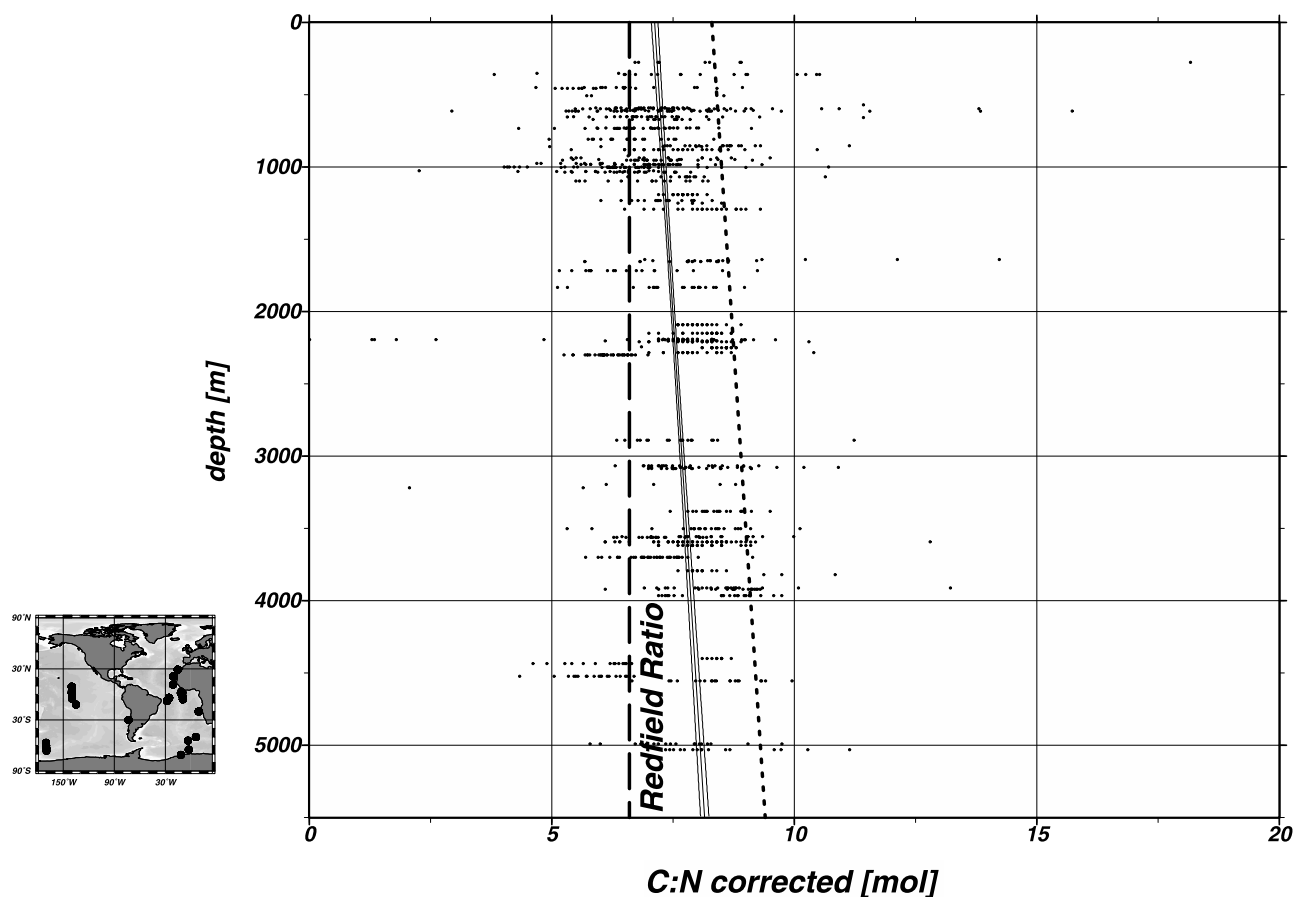
[31] Another way to determine the depth dependence of C:N ratios free from lithogenic effects is the application of uncorrected data, where lithogenic contributions are negligible. Therefore, all samples with lithogenic fluxes lower than 10% were chosen from the global data collection and only the data from the AESOPS and EQPAC sites were added, where lithogenic fluxes are low as it was explained above. The resulting increase of C:N ratios with depth is of comparable magnitude to the corrected data with a slightly higher surface value of 7.4 and again a rate of increase with depth of 0.2 units per 1000 m depth. Although the number of samples has further decreased ( $n = 867$ ) the increase of C:N ratios towards depth is undoubtedly present and it is equal to

$$C : N(z) = 7.4(\pm 0.1) + 0.22(\pm 0.1) \cdot z[\text{km}]. \quad (4)$$

#### 4. Summary and Discussion

[32] The analysis of data on the elemental composition of POM has shown that systematic deviations from the classical C:N Redfield ratio appear. In most of the data compiled here, C:N ratios are higher than the classical Redfield ratio, although large deviations in both directions are detected. There is a systematic offset between particulate matter obtained by different sampling techniques. For instance, at the BATS site, C:N ratios in filtered particles are significantly higher than in sinking material from sediment traps, which is most probably due to the fact that filter samples contain large amounts of suspended matter that can be relatively old, as it was determined by *Druffel et al.* [1998] using radiocarbon measurements, and nitrogen depleted.

[33] When considering the long-term sequestration of carbon in the deep ocean and its implications on the marine carbon cycle, it has clearly to be distinguished between different types of organic matter including sinking and suspended particles and dissolved organic matter (DOM). These have different sinking properties and they cycle differently in the ocean and have different element ratios [*Loh and Bauer*, 2000] and residence times in the ocean. DOM, which has a mean age of 4000–6000 years in the Pacific deep waters [*Williams and Druffel*, 1987:



**Figure 7.** C:N ratios of sediment trap samples corrected for lithogenic contributions (see text) versus depth. The dashed line indicates the Redfield ratio of C:N (6.6); the solid line is the regression line for the increase of C:N ratios with depth. The curved lines mark the mean error of the regression line. The dotted line shows the increase of C:N ratios with depth of uncorrected sediment trap data.

Bauer *et al.*, 1992], indicates a very long residence time of DOM in the ocean. Its downward export is associated to deep water formation, as largely occurring in the North Atlantic Ocean, and with a C:N ratio of 10–20 [Benner, 2000; Loh and Bauer, 2000], DOM is relatively carbon enriched. But the global significance of DOM export, compared to export fluxes by sinking particles and CO<sub>2</sub> solubility is probably low. Suspended particles are very small and have a residence time of 5–10 years in the open ocean [Bacon and Anderson, 1982]. This long residence time may be the cause for the predominant nutrient depletion, explaining the systematic higher C:N ratios found for filter samples compared to sediment trap samples at the BATS site. It also shows that suspended particles are of minor importance for fast carbon export from the surface to depth. Sinking particles with a mean sinking velocity of about 10–280 m per day [Diercks and Asper, 1997; Pilskaln *et al.*, 1998] have only a short residence time on the order of weeks to months. Thereby they are able to maintain a fast export of carbon from the surface into the deep ocean. The relative ages of the above mentioned forms of organic matter have also been demonstrated by  $\Delta^{14}\text{C}$  measurements reported by Druffel *et al.*

[1998], showing an increase in the depletion of  $\Delta^{14}\text{C}$  from sinking particles, which are least depleted and thus relatively fresh, over suspended matter to dissolved organic matter, which is most depleted in  $\Delta^{14}\text{C}$ .

[34] To investigate the downward carbon export by particle fluxes, sediment trap data are most suitable, because traps collect truly sinking material in contrast to filter samples. In this study we found C:N ratios significantly increasing with depth in the water column for the total (uncorrected) POM in sediment traps, with a rate of increase of 0.2 units per 1000 m water depth. After correcting for lithogenic effects, the element ratios of pure marine material are significantly closer to the classical Redfield ratio than those from bulk sinking material, but the rate of increase over depth remains unchanged (0.2 units per 1000 m). Shallow sediment traps show that C:N ratios of particulate material are above the traditional Redfield value, even at the base of the euphotic zone, indicating elevated C:N values for the particle export flux.

[35] Elevated and sometimes depth dependent particle C:N ratios have also been found in previous investigations, where the higher than Redfield C:N values were explained by preferential remineralization of nitrogen and phosphorus

in contrast to carbon [Gordon, 1971; Copin-Montégut and Copin-Montégut, 1983; Martin *et al.*, 1987; Tréguer *et al.*, 1990, Anadón *et al.*, 2002]. Anadón *et al.* [2002] investigated particle compositions from shallow sediment traps (65 m) in the Bellingshausen Sea, close to the Antarctic Peninsula. The sampling interval covered one summer season and particulate C:N ratios showed large variations reaching from values of 5.5 to 16.4, leading to the conclusion that nitrogen and carbon exports are not strictly coupled. Gordon [1971] found increasing C:N ratios with depth for particulate matter collected by filtrations in the central Pacific, near Hawaii, during a time series study of 18 months. In his study, the depth range from the surface to 4000 m depth was included and C:N ratios increased from 7.5 (weight ratios; = 8.8 molar ratios) in 0–250 m depth to 15.1 (weight ratios; = 17.6 molar ratios) for the depth range between 3000 and 4000 m. Gordon [1971] concluded that the increasing C:N values are due to preferential remineralization of nitrogen-rich proteins in contrast to a slower degradation of carbohydrates. Martin *et al.* [1987] found similar C:N ratios for particulate material from sediment trap deployments in the Northeast Pacific Ocean. The C:N ratios in 100 m water depth amount to 7.1, increasing to a value of 11.8 in 5000 m water depth. The subsurface value is identical with the results from our analyses. The increase over depth however, is significantly stronger with a rate of 0.96 units per 1000 m water depth. Comparable results were presented by Copin-Montégut and Copin-Montégut [1983], who examined particulate C:N ratios from filtration data collected in the northeastern equatorial Atlantic, the southwestern tropical Indian Ocean, the Antarctic Ocean and the western Mediterranean Sea. They found surface water particulate C:N ratios varying between 5 and 8, and explained this variability with changes in species composition. For deep waters they found increased C:N ratios between 8 and 15 and larger variances as compared to the surface. Again, the increase of C:N values with depth and the higher variances were explained by preferential remineralization of nitrogen. Tréguer *et al.* [1990] investigated particle element ratios during autumn 1987 in the Scotia Sea by filter analyses. They measured C:N ratios from surface water particles close the Redfield ratio. However, several profiles from the surface to 4500 m depth revealed increasing C:N ratios from surface values of 6.4 to deep water values of 10.1. From their results, Tréguer *et al.* [1990] also suggested that nitrogen recycling is more rapid than that of carbon due to a preferential loss of nitrogen from the particles during decomposition. Preferential remineralization of nitrogen and phosphorus has also been proposed by studies of dissolved nutrient fields [Sambrotto *et al.*, 1993; Anderson and Sarmiento, 1994; Shaffer *et al.*, 1999; Thomas *et al.*, 1999; Hupe and Karstensen, 2000; Osterroht and Thomas, 2000].

[36] While changes in the elemental composition of particulate organic material due to preferential remineralization of nitrogen and phosphorus seem to be well documented by available data, there is also the possibility of obtaining non-Redfield element ratios during particle production. Several studies describe deviations from the Redfield ratio during exponential phytoplankton growth, where

high C:N ratios are achieved under nitrogen and phosphorus limitation [Gervais and Riebesell, 2001]. On the other hand, significantly lower C:N ratios, may result from luxury consumption in situations when plenty of nitrogen and phosphorus is available [Droop, 1973; Elfiri and Turpin, 1985; Roelke *et al.*, 1999]. As the shallowest sediment trap data in this study are from 150 m water depth, which is below the euphotic zone, all material collected can be affected by deviations from the classical Redfield ratio at particle formation as well as during remineralization.

[37] As shown in Figure 6 the bulk sampled particles contain considerable amounts of lithogenic components, which can be either mineral material or terrestrial organic matter. Based on the compiled sediment trap data, lithogenic fluxes appear to be negligible far away from continents or the seafloor, they amount to less than 40% of the total flux for most of the data set (95%), and large contributions up to 90% of the total flux are found in rare and extreme cases, only. Mineral lithogenic material mainly consists of clay particles originating from fluvial and/or eolian input and from resuspension from the seafloor. Organic rich material, which is attached to lithogenic inputs, consists of terrestrial organic matter, which is introduced mainly by river discharge [Ittekkot and Laane, 1991], but also from eolian dust input [Fischer and Wefer, 1996; Wefer and Fischer, 1993]. These contributions have different C:N element ratios, affecting the C:N signals of POM. Clay minerals like illite are able to incorporate ammonia [Müller, 1977], whereas montmorillonite can adsorb inorganic nitrogen. Thus, contributions of clay minerals are likely to lead to a decrease of C:N ratios, because of the additional inorganic nitrogen incorporated by these minerals. On the other hand, river water may carry large amounts of terrigenous organic material. Organic soil C:N ratios are higher than those in marine organic matter [Kononova *et al.*, 1966], therefore, contributions of terrestrial organic material, attached to lithogenic particles, will lead to increasing C:N ratios. Extrapolating the regression line in Figure 6 to 100% lithogenic material leads to a C:N ratio of 11.7, which corresponds very well to the C:N ratio of organic soils, which are in the range of 10 for soils with high biological activity, reaching up to values of 50–60 for organic soils as found in fens [Scheffer and Schachtschabel, 1992]. The abundance of terrestrial organic matter attached to lithogenic particles will be responsible for the increase of C:N values with increasing lithogenic contributions, as given by Figure 6. The lower near-bottom C:N values, compared to values from above, for sediment trap data from the East Atlantic and for the whole sediment trap data set, as shown in Table 3, can be explained by resuspension of clay minerals from the sea floor sediments.

[38] We conclude that the elemental composition of pure marine sinking particles in the ocean is mainly determined by two factors, the initial composition obtained during particle production, which may deviate from the classical Redfield ratio, and changes during subsequent remineralization, where nitrogen is preferentially depleted. As all the sediment trap data analyzed in the current study were taken below the euphotic zone, the material most probably has been affected by both processes, and it was not possible to



reconstruct the relative contribution of each factor by the available data. In the surface water the elemental composition of marine particles largely depends on the predominant species composition and nutrient availability. A significant shift towards the Redfield ratio for shallow sediment trap data after correction for effects of lithogenic material, indicates that probably on a global mean the Redfield ratio is valid for a description of freshly produced material in the surface water. For sinking matter (detritus), however, the element ratios have shifted significantly towards higher relative carbon contents, which is a consequence of preferential remineralization of nitrogen compared to carbon. Preferential remineralization is also responsible for the further increase of C:N ratios over depth. A regional comparison of the increase rates of C:N ratios over depth, as given in Table 4 shows that different trophic regions exhibit different vertical changes in the element ratios, which most probably is a result of different food web patterns. The higher C:N gradient in the Sargasso Sea and the South Atlantic with 0.6 and 0.5 units per 1000 water depth indicate a faster preferential remineralization than, for example, in the equatorial Pacific, where the increase is almost negligible.

[39] The main conclusions of this study, namely that C:N ratios of particulate organic matter increase significantly with depth and are above the classical Redfield value even at the base of the euphotic zone, are in contrast to results from studies based on dissolved nutrient fields that yield C:N values independent of depth and/or in close agreement with the traditional Redfield value of 6.6 [Takahashi *et al.*, 1985; Anderson and Sarmiento, 1994]. According to Anderson and Sarmiento [1994] the remineralized C:P ratio is  $117 \pm 14$ , corresponding to a C:N ratio of  $7.3 \pm 0.9$ . This ratio is in good agreement with the results of the current study. However, Anderson and Sarmiento [1994] stated that their results are not significantly different from the Redfield ratio as they are not corrected for a possible contribution of anthropogenic carbon, and thus the carbon to nutrient values may be overestimated. Furthermore, they discussed a number of possible explanations for a discrepancy between results from particle measurements and studies of regenerated nutrients. One possibility is the continued degradation of the particulate material within the sample cups of sediment traps that could lead to an increase of C:N values after sampling, which results in higher C:N ratios. Plots of the C:N ratios from our database versus sample sequence have not shown any trend of systematically higher C:N values for the first samples of a sequence, which would be expected if dissolution in the cups was altering C:N ratios. In addition, results from short term trap deployments [von Bodungen *et al.*, 1987] which should be much less affected by degradation in the sampling cups also show C:N ratios that are higher than the Redfield ratio, which supports our findings. Noji *et al.* [1999] and Kähler and Bauerfeind [2001] measured dissolved organic material (DOM) from the supernatant of sediment trap samples, and concluded that dissolution happens as a consequence of zooplankton feeding on particles in the cups, especially in shallow trap deployments. Kähler and Bauerfeind [2001] suggest a substantial change in particle compositions due to such

dissolution processes; however, the amount of these changes is not precisely determined. Seasonal signals with very similar annual patterns were found for both sediment trap and filtration data at the BATS site for data from the same time and depth interval, as was briefly mentioned above. A probable effect of dissolution in the cups obviously has not masked this seasonal progression, therefore if there is any effect of dissolution in the cups, this must be a systematic error leading to an overestimation of measured C:N ratios. Therefore, data from shallow sediment traps may have to be corrected towards the Redfield ratio, which in turn would increase the depth dependence. As our analyses are largely from deeper traps where intense grazing by zooplankton is not expected, and as data from suspended material also show both elevated C:N ratios in contrast to the Redfield ratio and increasing values over depth, we are convinced that our approach for a description of marine carbon fluxes remains applicable.

[40] Another argument used by Anderson and Sarmiento [1994] is that high C:N ratios would in general be associated with low vertical particle fluxes and would thus not be important for vertical budgets. They argue that the large downward particle fluxes found in high productive regions were essentially equal to the Redfield ratio. To test this hypothesis, we used our compiled data set and plotted C:N ratios versus downward flux (not shown). We find that even for strong POM fluxes, greater than  $150 \text{ mg/m}^2 \text{ d}^1$  (Peru/Chile, Namibia, Northwest Africa and equatorial Pacific upwelling regions and Southern Ocean), the average C:N ratio amounts to  $8.1 (\pm 0.1, n = 253)$ , which is significantly higher than Redfield's value. Another general difference between the two approaches, measurements on particles and regeneration rates, is that the latter refer to all organic matter that has been remineralized. This includes also DOM and will affect the rates of regenerated nutrients especially in the upper 400 m of the water column, where most DOM is remineralized.

[41] We believe that the sediment trap data shown in this study adequately represent the C:N element ratio of sinking material. These ratios are significantly higher than the traditional Redfield value in the upper water column, and they increase further with depth. In order to reconcile these findings with the results from dissolved nutrient distributions that yielded no depth dependence and essentially Redfieldian values, it is important to realize that in case of preferential remineralization, the elemental C:N ratio of the component that goes into dissolution (and affects dissolved nutrient distributions) is different from the C:N ratio of the remaining particulate material being remineralized. As a consequence, the C:N ratios based on the analysis of changes in dissolved nutrient distributions do not reflect the composition of sinking particles themselves, but rather the change of particle composition due to remineralization. If particulate C:N ratios increase over depth due to preferential remineralization of nitrogen and phosphorus, the C:N ratio of the remineralized component is smaller than the C:N value of the remaining particles, which explains the lower (compared to POM) C:N values obtained from dissolved nutrient fields. Furthermore, the method applied by Anderson and Sarmiento [1994] and Takahashi *et al.* [1985]

exploits dissolved property changes on isopycnal or neutral surfaces over basin scales. Because these surfaces are not level but cover relatively large depth ranges, the method implicitly involves averaging over the depths of the respective surface under investigation. Therefore, any existing C:N depth dependence is likely to be masked because of depth integration. For the deeper surfaces, the uncertainties of the method grow because of only small gradients in the nutrient fields due to only low particle fluxes and remineralization rates. In addition, because of an unrealistic, assumed correlation between remineralization of organic carbon and  $\text{CaCO}_3$  (introduced for numerical stability), the Anderson and Sarmiento [1994] results may be questioned especially in the deep ocean.

[42] Our results for the C:N ratio of particulate material can be extrapolated to the carbon to phosphorus ratio. Assuming a constant value equal to the Redfield ratio of N:P = 16, leads to a surface water C:P ratio of 114 (traditional Redfield C:P = 106), which increases with depth to C:P = 130 in 5000 m water depth. Presently, none of the major global physical/biogeochemical models used to simulate marine nutrient and carbon cycles takes into account the preferential remineralization of nitrogen and phosphorus and the increase of POM C:N ratios with depth, as implied by this and other studies. In contrast, all these models implement depth independent C:N ratios for particulate organic matter, which, according to the results of this study will result in a too large export into the deep ocean of nitrogen relative to carbon. As a consequence, these models might underestimate nitrate concentrations in the upper ocean that might cause too small productivity and downward carbon fluxes in the models. One model approach by Shaffer *et al.* [1999] concluded that fractionation during remineralization reduces atmospheric  $\text{pCO}_2$  by 20 ppm below the level it would have without fractionation. Compared to the results from the current study, the implemented C:P ratios by Shaffer *et al.* [1999] are too low with a C:P value of 100 until 750 m water depth, increasing to a value of 130 in 1500 m depth and staying constant further downwards. However, the results give evidence that the implementation of depth dependent C:N ratios according to equation (3) is likely to increase the vertical carbon gradient and would also change the regional patterns of surface  $\text{pCO}_2$  values and thus the uptake of  $\text{CO}_2$  by the ocean.

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