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Title
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Regional variation in the particulate organic carbon to nitrogen ratio in the surface ocean

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[1]   The concept of constant elemental ratios in plankton communities—the Redfield ratio—is of central importance to ocean biogeochemistry. Recently, several studies have demonstrated regional differences in the plankton C:P and N:P ratio. However, less is known about potential systematic variations in the C:N ratio. Here we present an analysis of the particulate organic carbon to nitrogen ratio of 40,482 globally distributed samples from the upper 200 m of the ocean water column. Particulate organic carbon and nitrogen concentrations are highly correlated ($R^2 = 0.86$) with a median value of 6.5. Using an artificial neural network analysis, we find regional variations in the C:N ratio linked to differences in environmental conditions. The ratio is lower in upper latitude cold water as well as upwelling regions in comparison to the warm oligotrophic gyres. We find substantial differences between ocean gyres that might be associated with differences in the nutrient supply ratio. Using cell sorting, we also quantified the C:N ratio of *Prochlorococcus*, *Synechococcus*, and picoeukaryotic field populations. The analysis demonstrates that picophytoplankton lineages exhibit a significantly higher ratio than the bulk particulate material but are only marginally significantly different from each other. Thus, the dominance of picophytoplankton in ocean gyres may contribute to the elevated ratios observed in these regions. Overall, the median C:N ratio derived from 40,482 samples is close to the canonical Redfield ratio, but significant regional deviations from this value are observed. These differences could be important for marine biogeochemistry and the regional coupling between the ocean's carbon and nitrogen cycles.

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1.   Introduction

[2]   Nearly 80 years ago, Alfred Redfield observed that ocean surface plankton and deep dissolved nutrient concentrations shared similar C:N:P ratios [*Redfield*, 1934]. This "Redfield ratio" has later become a central tenet for ocean biogeochemistry and underlies our understanding of the linkages between the nutrient cycles, conditions for nutrient limitation, extent of nitrogen fixation or loss, and other important oceanographic processes [*Deutsch and Weber*, 2012; *Mills and Arrigo*, 2010]. Recently, several studies have demonstrated that the N:P and C:P ratios vary in different ocean regions [*Martiny et al.*, 2013; *Weber and Deutsch*, 2010]. This variation in N:P and C:P is attributed to regional variations in environmental conditions and plankton biodiversity. Despite the importance of elemental ratios in many biogeochemistry and modeling studies, not much is known about systematic regional variations in the C:N ratio.

[3]   The particulate organic carbon to nitrogen ratio (referred to as the C:N ratio) is important for linking the carbon and nitrogen cycles [*Oschlies et al.*, 2008; *Schneider et al.*, 2004; *Tagliabue et al.*, 2011] as well as trophic processing of material [*Sterner et al.*, 1992] and is a basic assumption for many concepts in ocean biogeochemistry like the f-ratio and new production [*Dugdale*, 1967]. Several reviews have reported variations in the C:N ratio but with means above the "canonical Redfield ratio" of 6.63 [*Fleming*, 1940; *Geider and La Roche*, 2002; *Schneider et al.*, 2003; *Sterner et al.*, 2008]. Part of this variation can be linked to an elevated C:N ratio in the deep ocean compared to surface water—possibly due to a preferential remineralization of organic N over C [*Schneider et al.*, 2003]. Moreover, some variation in the C:N ratio has been observed in regional studies. For example, Körtzinger and colleagues observed a ratio ~5 in eutrophic compared to ~7 in nitrogen depleted regions along a North Atlantic transect [*Kortzinger et al.*, 2001]. In contrast, others found little regional variation [*Copin-Montegut and Copin-Montegut*, 1983].

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[4] Despite the progress made, relatively little is yet known about any systematic regional variations in the C:N ratio. The existence of such variations should not be surprising. In general, protein and nucleic acids are both rich in N compared to C (C:N ~ 4). In contrast, lipids in the cell membrane and wall, carbohydrates, and storage molecules like glycogen or polyhydroxy-butyrate are rich in C. Thus, the relative biochemical allocation to different biopolymers can influence the cellular stoichiometry and result in variations in C:N between plankton lineages and environments [*Geider and La Roche*, 2002; *Sterner and Elser*, 2002]. Indeed, at least five different mechanisms can induce variations in the particulate C:N ratio. As a first mechanism, the N cell quota declines when cells are N limited [*Droop*, 1983]. Thus, N limitation commonly results in an increased cellular C:N ratio [*Goldman and Peavey*, 1979; *Vrede et al.*, 2002]. The second mechanism links light limitation with a lower cellular C:N ratio as phytoplankton growing under low light irradiance may accumulate less carbon storage polymers [*Chalup and Laws*, 1990; *Cronin and Lodge*, 2003]. The third mechanism is based on a negative relationship between cellular C:N ratio and growth rate [*Chalup and Laws*, 1990]. This is particularly the case if the growth rate is controlled by nutrient availability [*Bertilsson et al.*, 2003; *Goldman and Peavey*, 1979; *Vrede et al.*, 2002]. Although the exact mechanism for this relationship is unknown, it is likely due to an increase in the concentration of both proteins and nucleic acids compared to other cellular components as well as an increase in nutrient storage in fast-growing cells. The fourth mechanism suggests phylogenetically constrained elemental ratios derived from differences in the structural biochemical composition of the cell. This mechanism has been invoked as contributing to regional differences in the C:P and N:P ratios, whereby coexisting phytoplankton taxa have unique elemental stoichiometries [*Martiny et al.*, 2013]. Phylogenetic differences in the C:N ratio have not been studied in detail. Generally, it is plausible that smaller cells can have a higher C:N ratio compared to large cells—i.e., more skin to flesh [*Kroer*, 1994]. The fifth mechanism is that dead plankton material or detritus can influence the observed particulate elemental ratios. Recently, we observed that living cells constituted the majority of particulate material in open ocean waters [*Martiny et al.*, 2013] but detritus is likely a nontrivial component of the particulate pools in some regions. However, our quantitative knowledge of detritus concentration [*Jackson and Williams*, 1985] and elemental composition [*Verity et al.*, 2000] in the ocean is rather limited. Furthermore, both heterotrophs and autotrophs can preferentially scavenge specific elements from this pool. Thus, processes of both detritus formation and degradation can influence the elemental ratio of marine particles [*Loh and Bauer*, 2000].

[5] While these mechanisms can lead to deviations from the canonical Redfield value of 6.63 among ocean plankton and communities, variations in the global ocean C:N ratio have hitherto not been studied in detail. To address this, we ask the following questions for the global upper ocean: (i) What are the median and (ii) global variation in the C:N elemental ratio?

2. Data Set

[6] To assess the variation in the particulate C:N ratio in the top 200 m of the water column, we compiled a data set of particulate organic carbon (POC) and nitrogen (PON) measurements from 72 previously published and publicly available cruises or time series (Table S1 in the supporting information). Unless otherwise stated, all mathematical operations were done in Matlab (Mathworks, Natick, MA). Our combined dataset contained 40,482 paired samples of POC and PON covering both open-ocean and coastal samples. We combined this information with data on longitude, latitude, temperature, sampling and absolute water column depths, as well as nitrate, phosphate, and chlorophyll concentrations. Missing temperature, nitrate, or phosphate data were estimated from the World Ocean Atlas [*Boyer et al.*, 2006]. The water column depth was estimated based on the ETOPO2v2 bathymetry (National Geophysical Data Center, 2006). Samples with a C:N ratio below 2 and above 20 were excluded from our data set. Based on empirical observations and the ratios of plankton, such values were deemed unrealistically small or large and could corrupt the observed mean ratios and further analysis. We defined a station as a unique depth profile in time (±1 day) and space (within a $1° × 1°$ box). This resulted in 5383 stations. We purposely defined this margin to allow for measurements of different environmental parameters on separate casts at the same station. Note that we assumed our samples to be independent and hence did not correct our data set for spatial autocorrelation.

2.1. Data Analysis

[7] The statistical distribution of POC:PON ratios in our data set is not easily characterized by any standard parametric probability density function (pdf). We therefore used one- and two-dimensional kernel density estimation procedures to construct a density distribution for the POC and PON data and their ratio [*Azzalini and Bowman*, 1997; *Botev et al.*, 2010]. To account for nonsymmetry of the resulting density distribution of the C:N ratio, we computed the mean, mode, and median values. Note that we tested the dependence of these moments on the choice of the kernel bandwidth of the density estimator and found consistent estimates of their values. We also estimated the mean bulk C:N ratio, which was defined as the mean POC to mean PON concentration ratio.

[8] A feed-forward back-propagation artificial neural network (ANN) was used to determine the functional relationships between the various environmental factors (predictors) and the measured C:N ratio. The training data set was created using split sampling and consisted of 50% of the total data set. The remaining data not used for network calibration were used as an evaluation data set. A network with three hidden nodes was found to provide stable performance for both data sets. We evaluated the mean variance described by the model (R^2) for 10 independent ANN calibration trials across all possible combinations of explanatory factors (ranging from individual factors to all eight combined; Table S2). Based on this analysis, we found that longitude, temperature, phosphate, chlorophyll, and absolute depth are the most informative predictors for the C:N ratio. To provide insights into the importance of each input variable for the ANN performance, we calculated the ANN response functions by varying one predictor at a time, while keeping the others at the mean values of the calibration data set.

[9] We found the depth-dependent change in C:N ratio at each station with a minimum of four depth-specific
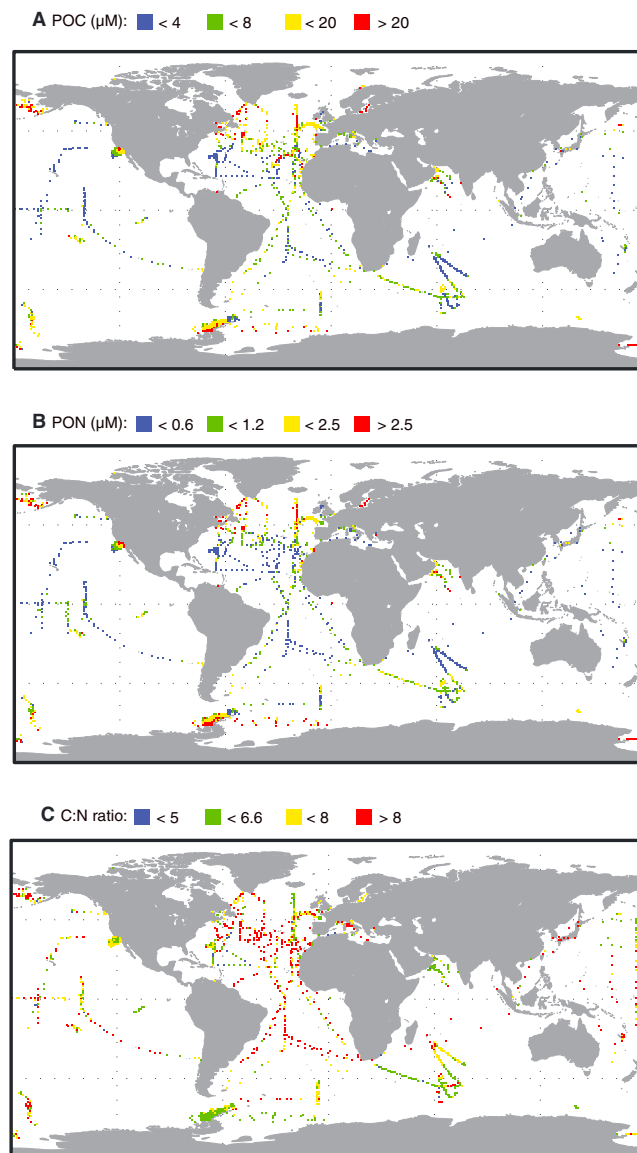
A POC (µM): ■ < 4   ■ < 8   ■ < 20   ■ > 20

B PON (µM): ■ < 0.6   ■ < 1.2   ■ < 2.5   ■ > 2.5

C C:N ratio: ■ < 5   ■ < 6.6   ■ < 8   ■ > 8

Figure 1. Global distribution of (a) particulate organic carbon, (b) particulate organic nitrogen, and (c) their ratio. The data set covers 40,482 samples distributed among 5383 unique stations in time and space. Areas are colored according to the mean concentration or ratio for a 1° × 1° area and the top 30 m in the water column.

measurements. The slope for each station was then calculated by non-linear regression using the relatively simple relationship $C:N = b1 \times \exp(b2 \times depth)$. We evaluated the overall regional influence on the C:N ratio in the gyres using a one-way analysis of variance (ANOVA) and compared the individual gyres using Tukey's honestly significant difference criterion.

2.2. Taxon-Specific Particulate Carbon and Nitrogen Measurements Using Cell Sorting

[10] In addition to bulk samples, we also collected samples for taxon-specific elemental measurements from the western North Atlantic Ocean at three depths (<5, 30, and 100 m) at 15 stations (total of 277 discrete samples; Table S3). Samples were collected in an acid-cleaned Niskin bottle. From the same Niskin bottle, subsamples were taken for taxon-specific elemental content and for community elemental content. For taxon-specific elemental content, seawater samples (1–2 L) were gently concentrated on 0.4 µm polycarbonate filters and kept at 4°C until they could be sorted, within several hours. From the concentrated samples, replicate *Prochlorococcus*, *Synechococcus*, and combined pico/nanoeukaryote populations were sorted using standard protocols [*Casey et al.*, 2007]. Sorted *Synechococcus* and *Prochlorococcus* populations were immediately filtered onto 0.2 µm silver filters, and sorted pico/nanoeukaryote populations and bulk POC/PON samples were filtered on precombusted (450°C, 4 h) Whatman GF/F filters. All samples were frozen at −20°C until elemental analysis [*Lomas et al.*, 2013; *Steinberg et al.*, 2001]. Samples were analyzed on a Control Equipment 240-XA or 440-XA elemental analyzer standardized to acetanilide. The POC analysis included an acidification step to remove inorganic carbonate.
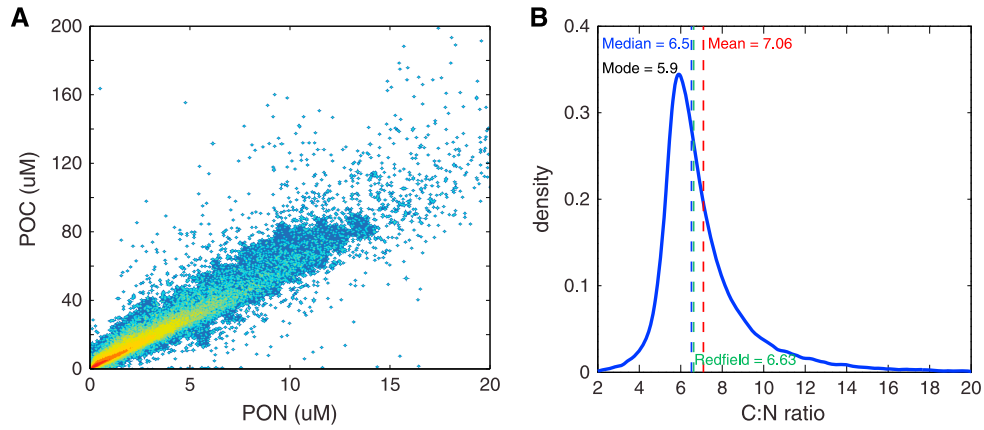
Figure 2. Variation of particulate organic carbon (POC) and nitrogen (PON) concentrations and their ratio. (a) Contour density scatterplot of paired observations. The color coding represents the kernel density. (b) Probability density of the C:N ratio with values of the mode, median, and mean as well as the canonical Redfield ratio of 6.63 [*Fleming*, 1940].
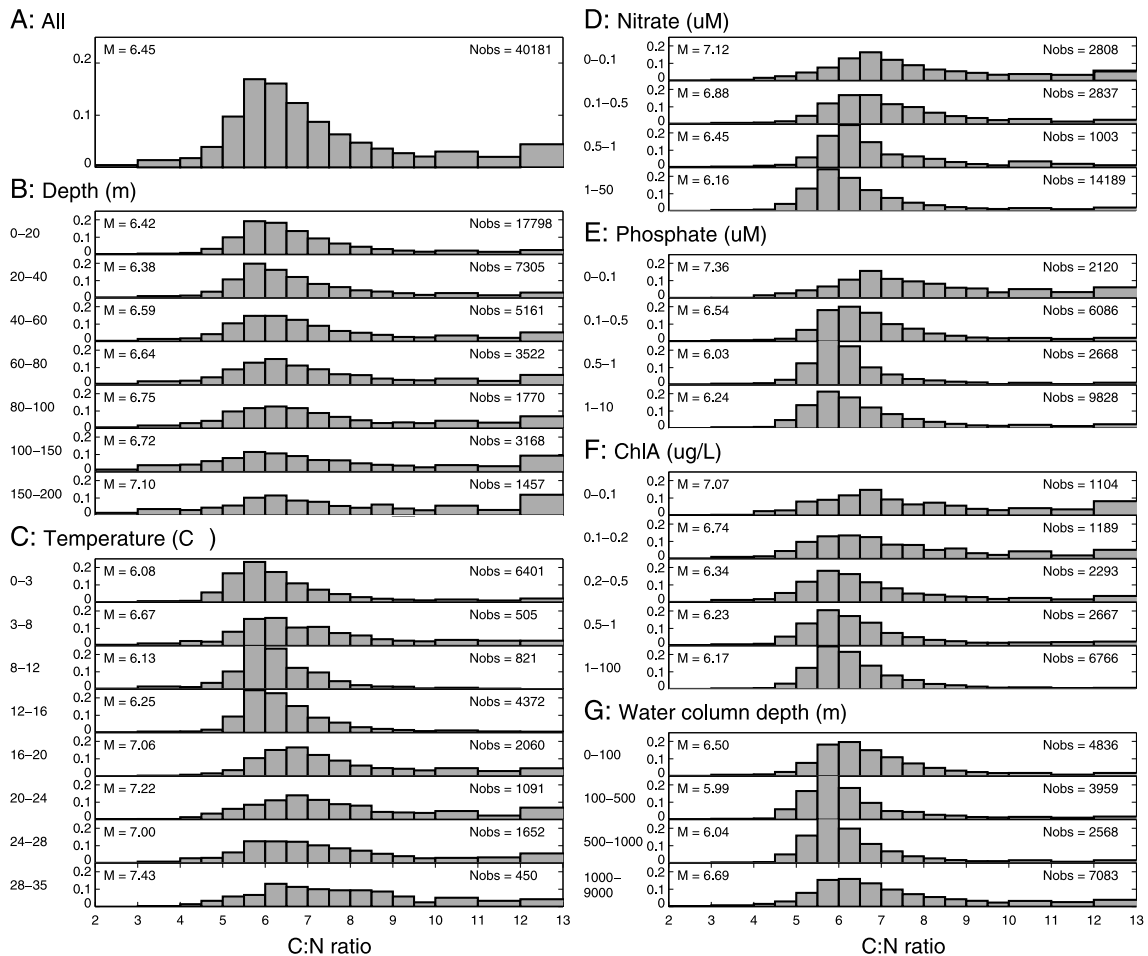

Figure 3. Frequency of the C:N ratios in our samples. Variation in the C:N ratio including all samples (a) from the top 200 m and (b) along a depth gradient. The following figures are for samples from the top 30 m along (c) temperature, (d) nitrate, (e) phosphate, (f) chlorophyll, and (g) absolute water column depth gradients. M is the median ratio.
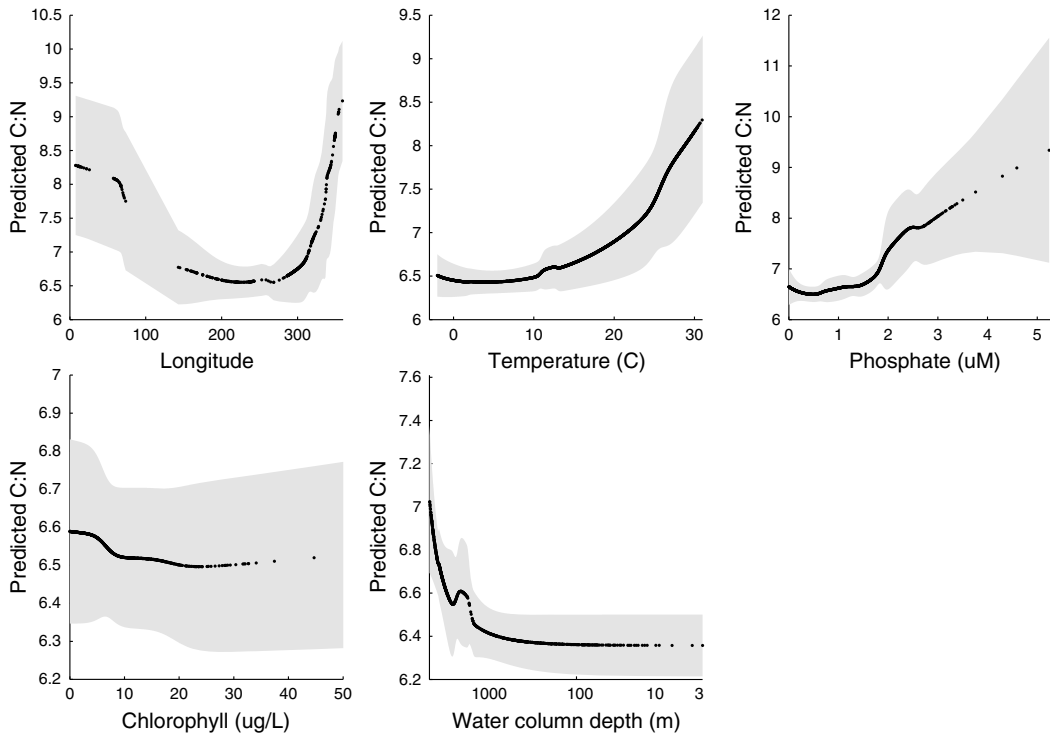
Figure 4. The predicted individual influence of longitude, temperature, phosphate, chlorophyll, and water column depth on the C:N ratio. The C:N is predicted based on a feed-forward back-propagation artificial neural network with three hidden nodes and is the mean of 10 independent runs. The shaded grey areas represent standard deviations among these independent runs.

3. Results

[11] To identify the global surface ocean variation of POC and PON and their ratio, we analyzed globally distributed paired observations from the upper 200 m of the water column (Figure 1). The data were compiled from 72 cruises or time series (Table S1). The POC concentration followed a clear regional pattern with concentrations above $8\,\mu M$ at higher latitudes and in coastal upwelling regions and concentrations below $4\,\mu M$ in the oligotrophic gyres. The PON concentration showed a similar regional pattern with concentrations above $1.2\,\mu M$ in coastal and higher-latitude areas and mainly below $0.6\,\mu M$ in the oligotrophic gyres. Consequently, POC and PON were highly correlated globally with an R^2 of 0.86 (Figure 2a). We next used a kernel density estimation procedure to construct a normalized smoothed histogram of the ratio of POC:PON (Figure 2b). The nonsymmetrical shape of the pdf made it impossible to define a single C:N ratio that adequately characterized the central tendency of the entire distribution. Indeed, the mode of the pdf of the C:N ratio equals 5.90, whereas the median (6.5) and mean (7.1) are considerably larger. We also estimated a mean bulk C:N ratio (i.e., the mean POC to mean PON ratio) of 6.75.

3.1. Global Variation in the C:N Ratio

[12] Despite the striking global agreement between POC and PON, a considerable range in the measured C:N ratio was also detected (Figure 2b). About half of the data set (19,788 samples) exhibited a C:N ratio that differed more than one unit from the canonical Redfield ratio. This included

8656 samples (~21%) with values smaller than 5.6 and 11,132 samples (~27%) with a C:N ratio larger than 7.6. Part of this variation could be attributed to a positive depth dependence of the C:N ratio. A lower C:N ratio was observed near the ocean surface (median C:N$_{0m}$ = 6.4) compared to 200 m depth (C:N$_{200m}$ = 7.1) (Figure 3b). However, this finding was not universal. In low-temperature, high-nutrient

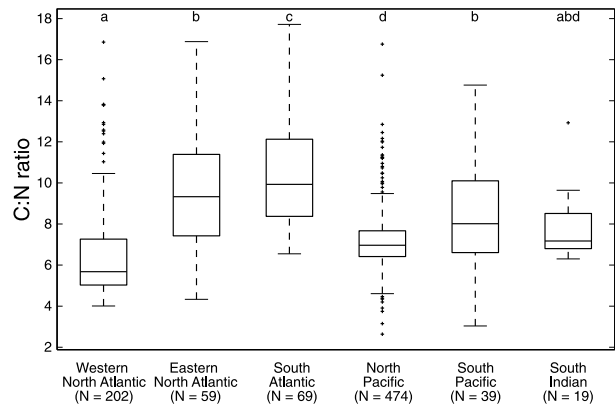**Figure 5.** The C:N ratio in the top 30 m in different oligotrophic gyres. Samples from the oligotrophic gyres are defined geographically as well as with a temperature above 20°C and a nitrate concentration below 0.1 μM. The line in the box represents the median, the box is the 25 and 75 percentile, and the whiskers cover approximately 99.3% of the data. Letters indicate significant groupings.
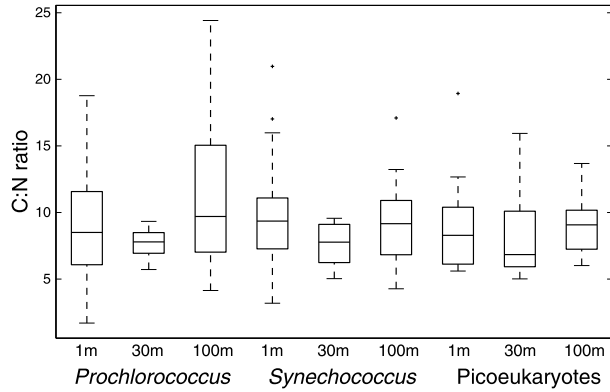
Figure 6. The C:N ratio of *Prochlorococcus* (N = 90), *Synechococcus* (N = 119), and picoeukaryotes (N = 68) field populations at three depths. The samples were taken from the western North Atlantic Ocean and specific taxa were sorted using flow cytometry before the elemental analysis. The line in the box represents the median, the box is the 25 and 75 percentile, and the whiskers cover approximately 99.3% of the data.

ocean regions, the C:N ratio tended to increase with depth down to 200 m. In contrast, the ratio was either constant or decreased with depth in oligotrophic gyres. Finally, upwelling regions had either constant or increasing ratios. Indeed, surface temperature influenced whether the C:N ratio increases or decreases with depth (linear regression, $P \sim 6 \times 10^{-15}$).

[13] To filter out this depth dependence, we summarized our findings for the top 30 m of the ocean water column along gradients of temperature, nutrient and chlorophyll concentrations, and water column depth (i.e., a proxy for coastal and benthic influence; Figures 3c–3g). The median C:N ratio was lower in low-temperature, high-nutrient waters (~6) and higher in elevated temperature and low-nutrient waters (>7). Furthermore, the C:N ratio was higher in low compared to high chlorophyll waters. We then tested if we could explain the observed variation in the observed C:N values based on these environmental factors using feed-forward back-propagation artificial neural networks (ANNs; Table S2). We also added latitude and longitude as proxies to test for relevant yet unknown biological or ecological factors. In the first step, we analyzed the predictive power of all combinations of the environmental factors described above and were seeking an ANN with a minimum number of input variables, and hence computational complexity, but maximum predictive performance. Our analysis convincingly demonstrated that the longitude of measurement contained the most information to explain the observed C:N ratios with a R^2 of 0.08. With a more complex network, repeated trials suggested that a model with five predictors including longitude, chlorophyll and phosphate concentration, temperature, and the absolute depth of the water column provided a network with a R^2 of 0.21 (Table S2). In contrast, a model with any other combination of five predictors (i.e., latitude, depth, chlorophyll and nitrate concentrations, and absolute water column depth) reduced the R^2 to 0.05. Thus, it appeared that this combination best explained the observed C:N ratios. We then identified the individual quantitative effect of each predictor (Figure 4). The relationship between longitude and

C:N showed a generally higher ratio in the Eastern Atlantic Ocean and Indian Ocean (longitude: 300°–80°) in comparison to the Pacific and Western Atlantic Ocean (longitude: 120°–300°; Figure 4a). As seen in Figure 3, we also found a clear positive relationship with temperature and a higher ratio in open compared to coastal ocean samples (Figure 4b and 4e). When this temperature effect was included, there was no additional influence of nutrients at low concentration (i.e., due to a strong covariance of the two factors). However, the presence of very high nutrient concentrations had an additional positive influence on the ratio. Finally, we also saw a negative relationship to chlorophyll concentration.

[14] The regional variation in C:N ratio at different longitudes could be observed in the difference in ratio between the oligotrophic gyres. For example, the Sargasso Sea appeared to have a lower C:N ratio compared to other regions. To address this, we identified the C:N ratio in each gyre but split the North Atlantic gyre into eastern and western parts (Figure 5). As observed in the earlier analyses, most gyres had a ratio above Redfield (with the notable exception of the western North Atlantic). A significant effect of region was apparent (one-way ANOVA, $P \sim 1 \times 10^{-53}$). Furthermore, most regions displayed unique C:N ratios (Tukey's honestly significant difference criterion, $P < 0.05$). For example, we found a C:N ratio in the western North Atlantic Ocean significant lower than that of most other regions (the only exception was the South Indian Ocean gyre, which could be due to a relatively low sample size for this region). In contrast, the C:N ratio was significantly higher in the South Atlantic Ocean gyre compared to all other regions.

3.2. C:N Ratio of Plankton Communities

[15] One factor that might contribute to the observed regional variation in the C:N ratio was differences in plankton biodiversity. To directly assess the impact of community differences, we measured, at multiple depths (0, 30, and 100 m), the taxon-specific elemental composition in flow cytometrically sorted natural populations of *Prochlorococcus*, *Synechococcus*, and small eukaryotic phytoplankton collected from warm nutrient-deplete stations in the western North Atlantic Ocean. The three groups of phytoplankton constituted on average $38 \pm 21\%$ of bulk POC and $42 \pm 25\%$ of bulk PON and were thus important contributors to the pools of particulate organic matter. Overall, we found a high C:N ratio in all three taxa and a mean for *Prochlorococcus*, *Synechococcus*, and small eukaryotic phytoplankton of 10.1 ± 0.5, 9.1 ± 0.3, and 8.7 ± 0.3 ($\pm$S.E.), respectively (Figure 6). Furthermore, the ratios for all three lineages were consistently above the bulk value (Student's t test, $P \sim 3 \times 10^{-21}$). Using a two-way ANOVA, we also observed a significant depth effect ($P \sim 0.01$) on the C:N ratio and less significant taxon effect ($P \sim 0.06$). Yet the influence of depth was not linear. Instead, we observed for all three taxa that the C:N ratio was highest in the 100 m samples followed by the surface and 30 m samples.

4. Discussion

[16] The paired observations of POC and PON analyzed herein present the largest data set assembled to date. Based on this large dataset, we find a median C:N ratio of 6.5 and a mean of 6.75 in ocean bulk surface particles. Both values

are remarkably close to the canonical Redfield ratio of 6.63 but lower than derived in previous studies using smaller data sets [*Geider and La Roche*, 2002; *Schneider et al.*, 2003]. We attribute at least part of this difference to the statistical approach applied including a more accurate characterization of the nonsymmetrical (non-Gaussian) shape of the pdf of the C:N ratio. Indeed, simple averaging of the observed C:N ratios gives a mean ratio above 7 due to a skew of its underlying probability distribution at higher values. This skew is particularly pronounced for samples with low PON concentrations and thus can be biased due measurement uncertainty.

[17] We find a correlation between environmental conditions and the C:N ratio in surface populations. Does this variation in C:N ratio constitute systematic regional differences? In the Pacific Ocean, the C:N ratio is commonly near or below the canonical Redfield value in upper latitude cold, nutrient-rich waters like the Bering Sea (Figure 1c). The ratio is also low in upwelling systems like the California Current or the Eastern Equatorial provinces. In contrast, the ratio is generally above Redfield in both the North and South Pacific Ocean gyres. These trends are also present in the Indian Ocean, where an increase in the C:N ratio is clearly visible when moving from higher latitudes into the gyre. We also detect a relatively low C:N ratio in the Arabian Sea upwelling system. However, we observe more variation in the North Atlantic Ocean region. In the western part (including the Sargasso Sea), the ratio appears near or below Redfield, whereas the eastern part exhibits higher ratios. In the South Atlantic gyre, the ratio is generally above Redfield. Finally, the ratio is higher in the Southern Ocean. Thus, globally cold, nutrient-rich upper latitude waters as well as upwelling regions are characterized by a lower C:N ratio than warm, nutrient-depleted gyres. This pattern is analogous to what we have previously observed for the N:P and C:P ratios [*Martiny et al.*, 2013], yet the magnitude of change is much smaller for the C:N ratio.

[18] In this study, we have analyzed only the spatial variation of the C:N ratio but the dependence of this ratio on the environmental conditions suggests a presence of temporal variations. Thus, we hypothesize that open-ocean middle and upper latitude surface waters are characterized by a seasonal succession in the C:N ratio. Here the ratio may be low in winter and spring but increases as the water column gets more stratified and the surface waters more nutrient depleted during the summer and early fall. Future studies should focus on a more detailed assessment of the temporal variations in the C:N ratio.

[19] There are at least five mechanisms that can lead to this regional variation in the C:N ratio. As a first mechanism, N limitation often leads to a low N cell quota and resulting high C:N ratio. In support of this, we see a clear difference between the eastern and western part of North Atlantic Ocean. The plankton community in this region of the Atlantic Ocean receives an influx of water with a dissolved N:P ratio much greater than the canonical Redfield ratio, whereas most other gyres as well as the eastern Atlantic Ocean have a lower dissolved N:P ratio [*Gruber and Sarmiento*, 1997; *Wu et al.*, 2000]. Thus, the lower N stress in the western North Atlantic may result in a lower C:N ratio and thus provide a link between the observed C:N ratio and the nutrient supply ratio. We also find that the North Pacific has a significantly lower C:N ratio than the South Pacific Ocean, a finding which is

consistent with a much lower input of iron and associated nitrogen fixation [*Moutin et al.*, 2008]. This limited input of fixed nitrogen may cause the observed difference in the C:N ratio between the two gyres in the Pacific Ocean. Overall, differences in the supply of N and P including from N fixation and the resulting degree of N stress may affect the elemental stoichiometry in the oligotrophic gyres and contribute to a regional variation in the C:N ratio in the gyres.

[20] The second mechanism links light limitation with a lower cellular C:N ratio. Based on this mechanism, we should expect to find a decline in the C:N ratio with depth. Our analysis also suggests a depth-dependent variation in both bulk and picophytoplankton C:N ratio. However, we find regional differences in the sign of the depth dependence and see the highest C:N ratio in sorted phytoplankton populations at the base of the euphotic zone. This suggests that light limitation may play an important role but that the mechanisms controlling the observed vertical variation in the C:N ratio are complex, warranting further study and observation.

[21] The third mechanism is based on a negative relationship between the cellular C:N ratio, growth rate, and nutrient stress. This mechanism may be important for the identified latitudinal change in the C:N range, whereby the ratio is generally higher in the warm, nutrient-depleted gyres and lower in upper latitude as well as in upwelling regions. Cells growing in nutrient depleted compared to rich environments may have a higher C:N ratio. This may not directly be a growth rate effect as plankton can have growth rates in the gyres that are comparable to or greater than in cold, nutrient-rich environments [*Doney et al.*, 2009]. Instead, the higher C:N ratio can broadly be related to the nutrient level and corresponding degree of nutrient stress as found in various phytoplankton culture experiments [*Bertilsson et al.*, 2003; *Goldman and Peavey*, 1979; *Vrede et al.*, 2002].

[22] In support of the fourth mechanism, we find that regional differences in the C:P and N:P ratios are at least in part driven by changes in phytoplankton community composition [*Martiny et al.*, 2013]. Cyanobacteria have higher C:P and N:P ratios compared to eukaryotic phytoplankton co-occurring in the same sample. Thus, can differences in community composition also explain the regional variation we observe in the C:N ratio? Our taxon-specific elemental analyses show that the C:N ratio in all three small phytoplankton population are significantly higher than the canonical Redfield ratio which is consistent with phytoplankton culture studies [*Bertilsson et al.*, 2003; *Heldal et al.*, 2003]. In contrast, we only observe slight differences between *Prochlorococcus*, *Synechococcus*, and small eukaryotic phytoplankton. This suggests that the overall presence of small phytoplankton, as opposed to large phytoplankton like diatoms and dinoflagellates, leads to a higher ratio in the gyres. It further suggests that other plankton groups or detrital material has a much lower ratio in the western North Atlantic in order for the bulk to reach the observed value. However, the distribution of individual taxa among the picophytoplankton groups will not have much impact on the C:N ratio. Presently, we do not have data for diatom and other large plankton populations. However, it is known that diatoms can store large amounts of N [*Lomas and Glibert*, 2000] and this may contribute to the low C:N ratio in nutrient replete environments. Thus, a more detailed understanding of the elemental ratios of large

phytoplankton will be important to elucidate the impact of changes in plankton community on the regional C:N ratio.

[23] Not all particulate nitrogen and carbon are of marine origin so it is possible that carbon-enriched terrestrial material delivered from rivers or dust could influence the observed C:N ratio, particularly in coastal regions [*Kononova*, 1966]. We do not observe a high C:N ratio in coastal samples (i.e., a low absolute water column depth; Figure 3g) where the terrestrial impact presumably will be largest. *Schneider et al.* [2003] examined this issue but found that lithogenic material with a high carbon content was a minor component of most open ocean samples. Finally, we observed that small phytoplankton represent nearly half the biomass in open ocean near-surface samples. Combined with other plankton groups, for example heterotrophic bacteria and protistan grazers, it is likely that living cells constitute most of the POC and PON in open ocean surface environments. Thus, it appears that non-marine particles are not the drivers of the observed mean and variation in the C:N ratio.

[24] It is worth noting that we were unable to explain approximately 80% of the observed variation in the C:N ratio using longitude, temperature, phosphate, chlorophyll, and water column depth as predictive factors. This suggests that factors beyond the common oceanographic or geographic factors tested here can influence the linkages between the organic carbon and nitrogen content. This may include iron or other trace metal concentrations, nutrient fluxes rather than nutrient stocks, differences in plankton biodiversity including the ratio of autotrophs to heterotrophs, or biotic/trophic interactions. Also, currently we do not understand the mechanism(s) driving the depth dependence of the C:N ratio. Previous work found a depth dependent increase of the C:N ratio, whereby the ratio rose from 8.3 in the upper surface (< 500 m) to above 9 in the deep ocean [*Schneider et al.*, 2003]. Schneider and colleagues attributed these depth differences to preferential remineralization of nitrogen over carbon. This can possibly also explain some of the changes in the upper 200 m of the ocean water column but our data suggest that the depth dependence is much more complex. Thus, it appears that other, yet unexplored factors may influence the C:N ratio in different ocean environments.

[25] Our results have important biogeochemical implications. We identify a very high correlation between POC and PON, which indicates that a constant C:N ratio remains a reasonable approximation for global ocean biogeochemical studies. However, there are also systematic regional differences in this ratio. These regional differences could influence the link between the nitrogen and carbon cycle [*Oschlies et al.*, 2008; *Schneider et al.*, 2004; *Tagliabue et al.*, 2011]. Biogeochemical models can possibly be improved by allowing for a cellular stoichiometry that varies in response to the overall nutrient and temperature level (i.e., high C:N in low-nutrient, high-temperature environments), the nutrient supply ratio (i.e., higher in P versus N stressed environments in the gyres), and taxonomic differences (i.e., high ratio in small phytoplankton). In summary, we have here identified both a substantial congruence between the concentration of POC and PON but also significant variation in the C:N ratio in different ocean environments. This variation in the coupling between the carbon and nitrogen cycles can in part be described by known mechanisms but it is also clear that additional factors are likely influencing the observed C:N ratio.

Considering the importance of this ratio in the formulation of global ocean carbon-cycle models, elucidating these additional factors should be an important goal of the oceanographic research community.

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