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Key Points:
- The elemental composition of marine particulate matter is temporally dynamic
- Marine regions display unique temporal trends in particulate elemental concentrations and ratios
- A simple temperature and nutrient limitation model only partially explains temporal changes

Supporting Information:
- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Figure S7
- Figure S8

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Seasonal and long-term changes in elemental concentrations and ratios of marine particulate organic matter

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Abstract What is the temporal variability of the elemental stoichiometry of marine microbial communities across ocean regions? To answer this question, we present an analysis of environmental conditions, particulate organic carbon, nitrogen, and phosphorus concentrations and their ratios across 20 time series (3–25 years duration) representing estuarine, coastal, and open ocean environments. The majority of stations showed significant seasonal oscillations in particulate organic elemental concentrations and ratios. However, shorter-term changes contributed most to overall variance in particulate organic matter concentrations and ratios. We found a correlation between the seasonal oscillations of environmental conditions and elemental ratios at many coastal but not open ocean and estuarine stations. C:N peaked near the seasonal temperature minimum and nutrient maximum, but some stations showed other seasonal links. C:N ratios declined with time over the respective observation periods at all open ocean and estuarine stations as well as at five coastal station but increased at the nine other coastal stations. C:P (but not N:P) declined slightly at Bermuda Atlantic Time-series Study but showed large significant increases at Hawaii Ocean Time-series and Arendal stations. The relationships between long-term changes in environmental conditions and particulate organic matter concentrations or ratios were ambiguous, but interactions between changes in temperature and nutrient availability were important. Overall, our analysis demonstrates significant changes in elemental ratios at long-term and seasonal time scales across regions, but the underlying mechanisms are currently unclear. Thus, we need to better understand the detailed mechanisms driving the elemental composition of marine microbial ecosystems in order to predict how oceans will respond to environmental changes.

1. Introduction

The cellular quotas and ratios of carbon (C), nitrogen (N), and phosphorus (P) in marine phytoplankton are emerging as important features of ocean biogeochemistry. For many decades, the ratios of these elements were assumed static at Redfield proportions (i.e., C:N:P = 106:16:1) [*Redfield*, 1958]. However, variability in plankton nutritional requirements can influence many core ocean features including patterns of nutrient limitation and stress [*Bonachela et al.*, 2013; *Alexander et al.*, 2015], nitrogen fixation rates [*Mills and Arrigo*, 2010; *Weber and Deutsch*, 2012], the link between nutrient supply and C export [*Teng et al.*, 2014], and atmospheric CO_2 levels [*Galbraith and Martiny*, 2015].

Recent work has demonstrated extensive regional differences in the elemental stoichiometry of marine communities [*Weber and Deutsch*, 2010; *Martiny et al.*, 2013a, 2013b]. This work has suggested elevated C:N:P in the low nutrient, high-temperature oligotrophic gyres, near Redfield proportions in low- to middle-latitude upwelling regions, and low C:N:P in high nutrient, colder high-latitude environments. Multiple theories describing these regional differences have been proposed [*Sterner and Elser*, 2002; *Deutsch and Weber*, 2012]. First, phytoplankton nutrient limitation in oligotrophic regions can lead to elevated carbon-to-nutrient ratios [*Rhee*, 1978; *Mouginot et al.*, 2015]. Second, plankton can have elevated C:P when growing slower [*Sterner and Elser*, 2002; *Garcia et al.*, 2016]. Third, plankton may have a lower demand for ribosomes and associated phosphorus when growing at a higher temperature [*Toseland et al.*, 2013]. Fourth, there may be phylogenetically constrained differences in the elemental composition of phytoplankton [*Quigg et al.*, 2003],

whereby smaller lineages like marine Cyanobacteria have elevated carbon-to-nutrient ratios in comparison to larger lineages like diatoms [*Arrigo et al*., 2002; *Martiny et al*., 2013b]. Regardless of the exact mechanism, the regional patterns suggest that low-nutrient, warm environments with a high abundance of marine Cyanobacteria have elevated ratios. In contrast, communities dominated by diatoms and other large phytoplankton growing in low-temperature and high-nutrient environments display lower ratios. However, we know less about how seasonal and/or long-term shifts in environmental conditions and associated phytoplankton community composition affect the temporal evolution of the relative elemental concentrations of marine organic particles.

Most ocean regions experience temporal changes in multiple environmental conditions that lead to community shifts [*Lomas et al*., 2009b; *Church et al*., 2013; *Hatosy et al*., 2013]. On a seasonal time scale, temporal changes commonly include annual oscillations in temperature and light availability. Changes in temperature and light often lead to an opposite phased oscillation in nutrient availability, whereby nutrient concentrations are low during the summer and early fall due to consumption exceeding supply. In addition to seasonal changes, ocean regions may also experience longer-term climate variability such as the El Niño–Southern Oscillation (ENSO) or the North Atlantic Oscillation (NAO). Finally, most coastal areas are characterized by strong episodic (e.g., tidal shifts) or stochastic (e.g., rain or clouds) events that can affect local environmental conditions. Such multiyear, seasonal, and short-term variations in environmental conditions influence the composition of marine plankton communities that subsequently may affect the concentrations and ratios of the particulate organic matter (POM).

A few studies have examined seasonal and/or long-term changes in marine POM elemental ratios [*Karl et al*., 2001; *Frigstad et al*., 2011; Frigstad *et al*., 2013; *Singh et al*., 2015; *Martiny et al*., 2016]. It was demonstrated that C:P and N:P but not C:N display seasonal oscillations [*Frigstad et al*., 2011; *Singh et al*., 2015; *Martiny et al*., 2016]. In addition, several sites displayed long-term variability that might be linked to lower frequency climate cycles [*Karl et al*., 2001; *Frigstad et al*., 2013; *Martiny et al*., 2016]. However, the temporal variability in environmental conditions may vary regionally. First, high—in contrast to low—latitude areas will experience stronger seasonal amplitudes in light, temperature, and nutrients. Second, different ocean regions are subject to unique multiyear cycles (e.g., ENSO in the Pacific or NAO in the Atlantic Ocean). Third, coastal regions are differentially influenced by temporally varying shoreline processes (e.g., runoff of freshwater and/or nutrients) and POM inputs [*Savoye et al*., 2012]. Such local differences in terrestrial inputs and environmental forcing could lead to unique temporal changes in POM concentrations and ratios. Specifically, we hypothesize that seasonal periods of high-temperature and low surface water nutrients should lead to low POM concentrations and elevated carbon-to-nutrient ratios. Analogously, long-term, low-frequency modes of environmental variability of temperature and nutrient availability will also influence POM concentrations and ratios. Hence, the same environmental controls we have observed on regional scales may influence temporal shifts in POM concentrations and ratios. Some coastal stations may nevertheless display unique dynamics due to terrestrial inputs.

To identify the temporal variability and controls of POM concentrations and elemental ratios across different ocean regions, we here compare data on environmental conditions (temperature and phosphate) with POM concentrations and elemental ratios from 20 time series representing a diverse set of ocean environments. Based on this data set, the present study aims at addressing three main questions: (i) how do temperature, phosphate, POM concentrations, and elemental ratios covary at different time scales, (ii), are temporal trends similar across different marine systems, and (iii) do temporal changes in environmental conditions, POM elemental concentrations, and elemental ratios relate across regions?

2. Methods

2.1. Location and Sampling of the Times Series

The time series considered in this study were chosen because they were located in different oceanic regions subjected to a variety of trophic and physical regimes and at different latitudes across the Northern Hemisphere (Table 1 and Figure S1 in the supporting information). Quality-controlled data sets gathered for this study spanned 3 to 25 years (Table 1, between 1987 and 2013) of near-surface ($<$25 m) data on temperature, phosphate concentration (viewed as representing macronutrient levels), particulate organic matter concentrations (carbon (POC), nitrogen (PON), and phosphorus (POP)), and molar ratios. We also analyzed

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Table 1. Station Overview[a]

Station	Latitude	Longitude[c]	Duration (Year)	Sampling Frequency (*d*)	Salinity (‰)	Temperature (°C)	Phosphate (μ*M*)	Bottom Depth (m)	POC (μ*M*)	PON (μ*M*)	POP (μ*M*)	[b]C:N	[b]C:P	[b]N:P	Reference
							Open Ocean								
BATS	31.7	−64.1	23.4	27	36.3 ± 0.8	23.3	0.0045	4680	2.21	0.33	0.010	7.1	212	36	*Singh et al.* [2015]
HOT	22.8	−158	24.6	31	34.9 ± 0.4	25.1	0.051	4760	2.05	0.30	0.013	7.0	157	23	*Karl et al.* [2001]
CARIACO	10.5	−64.7	18.8	30	36.5 ± 0.2	25.4	0.05	1400	9.56	1.10	0.04	8.5	237	28	*Scranton et al.* [2014]
							Coastal Ocean								
Astan	48.8	−3.9	14.0	15	35.3 ± 0.2	13.0	0.28	60	9.42	1.13	NA	8.5	NA	NA	*Goberville et al.* [2010]
Estacade	48.7	−4.0	14.0	15	35.2 ± 0.2	12.9	0.24	3	13.8	1.76	NA	8.1	NA	NA	*Goberville et al.* [2010]
Frioul	43.2	5.3	18.4	14	38.1 ± 0.3	16.3	0.06	60	8.08	1.06	NA	7.2	NA	NA	*Goberville et al.* [2010]
Point B	43.7	7.3	14.8	7	38.0 ± 0.4	17.9	0.04	95	9.04	1.13	NA	8.4	NA	NA	*Goberville et al.* [2010]
Point L	50.7	1.4	16.9	18	34.7 ± 0.4	12.8	0.24	50	22.2	6.64	NA	4.5	NA	NA	*Goberville et al.* [2010]
Point C	50.7	1.5	16.9	17	34.1 ± 0.5	12.4	0.27	26	36.1	6.71	NA	5.8	NA	NA	*Goberville et al.* [2010]
Portzic	48.4	−4.6	17.2	8	34.7 ± 0.6	13.4	0.19	2	13.6	1.99	NA	6.8	NA	NA	*Goberville et al.* [2010]
Bouee13	44.6	−1.2	10.4	14	34.6 ± 0.8	14.9	0.16	25	27.9	4.07	NA	6.8	NA	NA	*Goberville et al.* [2010]
Luc-Sur-Mer	49.3	−0.3	7.2	15	32.6 ± 0.9	12.1	0.68	6.5	33.1	4.18	NA	8.2	NA	NA	*Goberville et al.* [2010]
Antioche	46.1	−1.3	3.3	15	33.9 ± 1.1	15.9	0.18	40	18.0	2.73	NA	6.6	NA	NA	*Goberville et al.* [2010]
SOLA	42.5	3.1	11.9	7	37.7 ± 1.5	16.4	0.03	27	7.72	0.98	NA	7.8	NA	NA	*Goberville et al.* [2010]
Comprian	44.7	−1.1	10.4	15	31.7 ± 2.6	15.5	0.18	6	25.8	3.98	NA	6.7	NA	NA	*Goberville et al.* [2010]
Eyrac	44.7	−1.2	17.7	15	32.5 ± 2.9	14.9	0.17	8	25.3	3.76	NA	6.5	NA	NA	*Goberville et al.* [2010]
Arendal	58.4	8.8	20.4	15	29.5 ± 3.3	9.3	0.16	80	11.9	1.68	0.11	7.3	107	15	*Frigstad et al.* [2011]
							Estuary								
pk86	45.5	−1.0	17.8	34	21.7 ± 6.8	16.2	0.93	8.2	64.9	6.79	NA	8.4	NA	NA	*Savoye et al.* [2012]
pk52	45.3	−0.7	18.1	31	4.8 ± 4.0	18.8	1.99	7	291	34.2	NA	8.4	NA	NA	*Savoye et al.* [2012]
pk30	45.1	−0.7	18.1	34	0.9 ± 2.0	17.2	1.83	8	320	40.7	NA	8.6	NA	NA	*Savoye et al.* [2012]

[a]Sampling frequency, environmental, POC, PON, and POP data represent median values for upper 25 m samples across full time series. Variation in salinity represents one standard deviation. NA: not applicable.
[b]Molar ratios.
[c]Positive longitude values are east and negative values are west.

salinity to determine the freshwater input and variability. If multiple samples from this depth interval were collected, an average was used. The analytical techniques to measure these factors were very similar across data sets. Temperature was measured using a standard thermal-conductive probe. Phosphate concentration was determined using the molybdenum blue method [*Murphy and Riley*, 1962] although at oligotrophic sites, phosphate was preconcentrated first using the MAGIC protocol [*Karl and Tien*, 1992]. POC and PON were measured using an elemental analyzer from particles collected on precombusted GF/F filters [*Steinberg et al*., 2001]. POP was estimated from particles collected on precombusted GF/F filters using an ash-hydrolysis method [*Lomas et al*., 2010]. Only POM samples from Arendal were prescreened with a cloth of pore size of 180 μm before filtration. Particulate matter is listed as organic material but particles may contain inorganic forms of each element.

The time series cover open ocean, coastal, and estuarine systems. The three ocean stations include the oligotrophic Bermuda Atlantic Time-series Study (BATS) in the Northwestern North Atlantic Ocean [*Singh et al*., 2015], the oligotrophic Hawaii Ocean Time series program (HOT) in the central North Pacific Subtropical Gyre [*Karl et al*., 2001], and the productive CArbon Retention In A Colored Ocean time series program (CARIACO) in the Cariaco Basin, north of Venezuela [*Scranton et al*., 2014]. The 17 coastal stations are Arendal in Northern Skagerrak [*Frigstad et al*., 2011], 5 stations in the English Channel (Point L and Point C in the northern end, Luc-sur-Mer in the central part, and Estacade plus Astan by the north coast of Bretagne), 8 stations in coastal systems of the Bay of Biscay (Portzic in the outer end of the Bay of Brest, Antioche in the Pertuis Charentais, Bouee 13, Eyrac, and Comprian in the semienclosed Bay of Arcachon), and 3 stations in the Mediterranean Sea (SOLA and Frioul in the Gulf of Lion and Point B offshore in the Bay of Villefranche-sur-mer). Three estuarine sites are in the Gironde Estuary (pk86, pk52, and pk30—in order from the estuary mouth). The estuary is a large macrotidal estuary with a typical depth of 7–10 m and is well mixed. Marine water can reach the upper Gironde Estuary and enter the rivers, but the overall salinity of the inner estuary ranges between 0 and ~32, depending on location, river flow and tide. The latter 16 stations are part of the French monitoring network Service d'Observation en Milieu LITtoral (SOMLIT) [*Goberville et al*., 2010; *Savoye et al*., 2012]. Neighboring stations were included in this study in order to test whether or not there were similarities in the magnitude and frequency of the temporal changes they experience. Such stations should be equally affected by global-scale phenomenon and thus improve the detection of changes in POM concentrations and ratios.

At BATS and HOT, specific particulate organic elements (i.e., POP versus PON + POC) were commonly determined from different casts. Thus, elemental ratios were determined by first interpolating POM values at the applied sampling frequency, and interpolated values were subsequently used to estimate ratios.

2.2. Temporal Decomposition

All analyses were done in MATLAB (Mathworks, Natick, MA). A decomposition of the temporal variability in temperature, phosphate concentration, particulate organic matter concentrations, and ratios was found by using ordinary least squares fitting of equation (1) to the observed data:

$$Y_t = a^*t + b_m^*\mathrm{M} + c \tag{1}$$

where Y_t is the observed value at time t, a is the estimated linear long-term trend, t is the time (in days) from the beginning of time series, b_m are the 12 monthly (M) contribution coefficients, and c is the residual variance. Following, we estimated the variance contribution (sum of squares) and significance ($p < 0.05$) of multiyear changes, summed monthly (seasonal) variation, and combined short-term and error contribution using an analysis of variance (ANOVA). The magnitude of monthly variability was subsequently estimated as the difference between $b_{m,\mathrm{min}}$ and $b_{m,\mathrm{max}}$ for a given station and factor. We also tested an additional model:

$$Y'_t = a_{\mathrm{yr}}^*\mathrm{Y} + b_m^*\mathrm{M} + c \tag{2}$$

where Y'_t is the observed value at time t, a_{yr} are the yearly (Y) contribution differences, b_m are the 12 monthly (M) contribution coefficients, and c is the residual variance.

Significant seasonal oscillations were found by applying the Lomb-Scargle algorithm to determine the spectral periodogram of each factor and subsequently the localized maxima at the 90% confidence level between 0.85 and 1.2 cycles yr^{-1} [*Scargle*, 1982]. This algorithm was chosen as it allowed for uneven sampling intervals and test for significance against the probability that a peak in the spectrum is due to random fluctuations. A

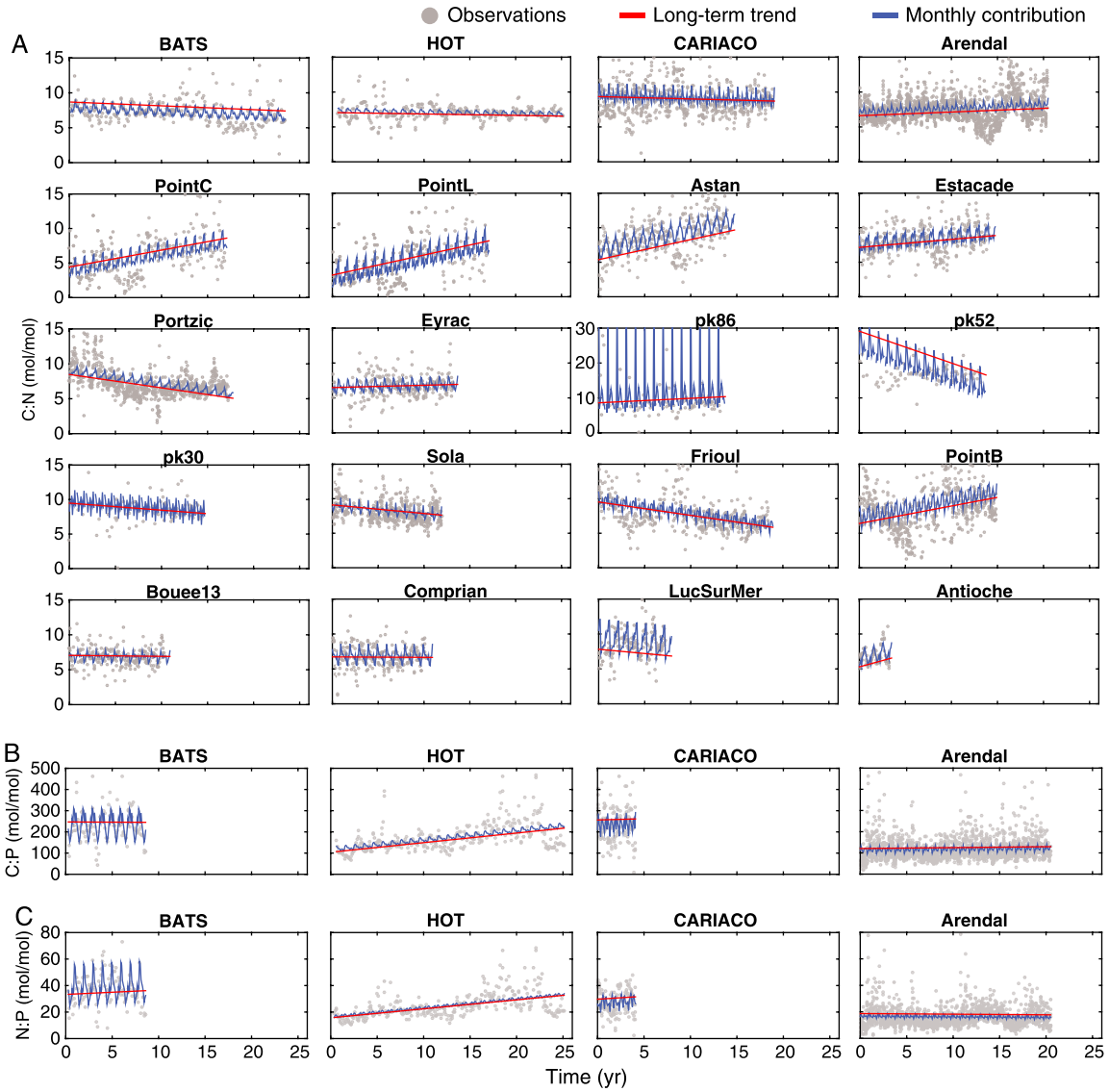


Figure 1. Temporal changes in particulate organic elemental ratios including (a) POC to PON, (b) POC to POP, and (c) PON to POP ratios. Superimposed on observed ratios are the best fit of linear models with a long-term linear trend (in red) and 12 monthly contributions (in blue, equation (1)). The ratios are molar.

link between long-term trends in POM concentrations and ratios against temperature and/or phosphate concentration was determined using a multivariate linear regression containing individual and interaction terms. Correlations between monthly contributions of all factors were estimated using Pearson correlations. The means of correlation coefficients for combination of factors were compared to zero using a Student's *t* test at the 95% confidence level.

3. Results

3.1. Overview of Sites

To understand the temporal variability of particulate organic matter concentrations and ratios, we compiled near-surface (<25 m) data from 20 stations (Table 1 and Figure S1). The 20 stations represented a diverse set of environments from oligotrophic ocean gyres to coastal to estuarine systems (median phosphate concentration (P) ranging from 4.5 nmol L^{-1} to 1.99 μmol L^{-1}), and temperate to tropical (median temperature (*T*) ranging from 9.3 to 25.4°C) ocean waters. All stations displayed strong temporal changes at multiple time scales for temperature and phosphate (Figures S2 and S3), POM concentrations (Figures S4–S6), and POM

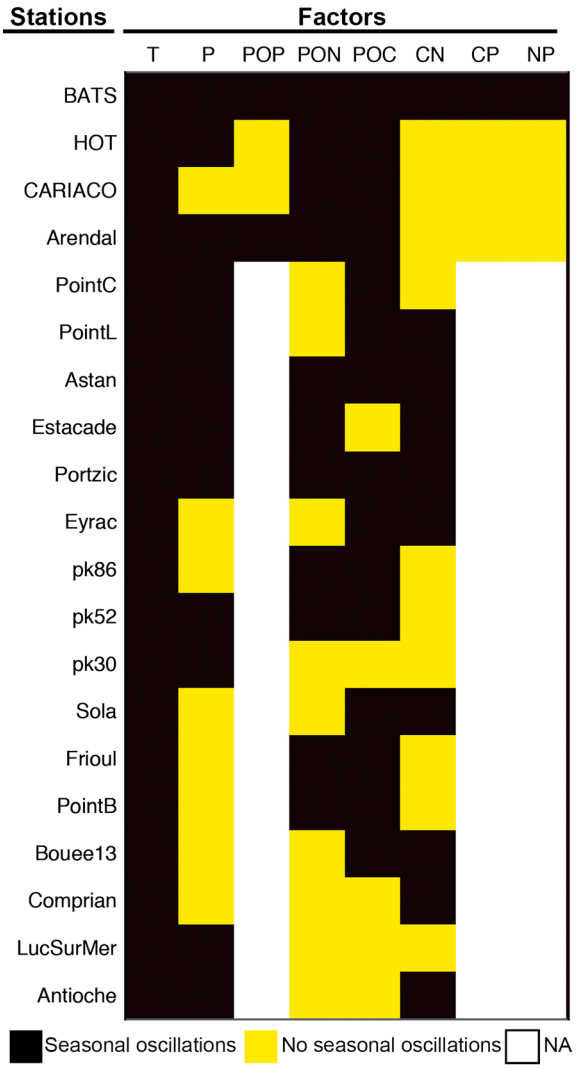


Figure 2. Presence of seasonal oscillations in temperature (*T*), phosphate (P), particulate organic phosphorus (POP), nitrogen (PON), and carbon (POC) and concentrations as well as molar ratios. The frequency distribution was estimated using the Lomb-Scargle algorithm [*Scargle*, 1982]. Significant annual oscillations were identified as peaks at the 90% power-level threshold at a frequency of 0.85–1.2 yr^{-1}.

ratios (Figure 1). We specifically only evaluated the seasonal and long-term trends as we lacked clear expectations of additional signals and wanted to avoid reporting spurious trends in the data.

3.2. Seasonal Variation

As expected, we observed strong seasonal *T* changes at all stations (Figure S2). This was supported by a spectral analysis, whereby we saw significant cycles with a period of 1 year at all stations (Figure 2). However, the individual stations displayed substantial differences in seasonal *T* variability, with a median seasonal peak-to-peak amplitude of ~11°C (Figure S7a). At the lower extreme, there was a 3°C mean seasonal difference in *T* at the tropical open ocean site HOT. In contrast, two estuarine sites, pk52 and pk30, varied by 17.5°C. Many stations also experienced strong seasonal changes in P (Figure S3), and 60% of the stations had significant repeating oscillations (Figure 2). The magnitude of P differed among sites (Figure S7b), but the magnitude of *T* and P changes were significantly correlated ($p_{spearman} < 0.001$). The two oligotrophic open ocean sites, HOT and BATS, as well as two offshore coastal sites (SOLA and Point B) displayed low seasonal amplitudes for P. In contrast, several coastal and estuarine sites were characterized by strong oscillations (i.e., peak-to-peak amplitude) > 1 $\mu mol\,L^{-1}$ P.

We detected strong seasonal changes in POM concentrations (Figures S4–S6). POC and PON oscillated significantly at 75% and 55% of the stations, respectively (Figure 2). Similarly, POP oscillated significantly at both BATS and Arendal, but not HOT and CARIACO. The amplitudes of seasonal changes in POM concentrations differed starkly between stations and were significant positively correlated to amplitudes in *T* and P ($p_{spearman} < 0.001$). Stations with riverine inputs oscillated by up to 235 $\mu mol\,L^{-1}$ POC and 106 $\mu mol\,L^{-1}$ PON (Figures S7c and S7d). In contrast, the seasonal amplitude at the open ocean sites was much lower (but often significant). A similar pattern was observed for POP (Figure S7f), whereby we saw more intense seasonal changes at the coastal or productive (CARIACO and Arendal) versus oligotrophic (HOT and BATS) stations.

Many stations showed seasonal variability in elemental ratios (Figure 1); 50% of the stations displayed significant oscillations for C:N (Figure 1a), and the amplitude was significantly positively related to changes in both environmental conditions and POM concentrations ($p_{spearman} < 0.001$). The estuarine sites showed high seasonal changes in C:N, but most sites had modest changes in this ratio (median = 2.2, Figure S7e). C:P and N:P

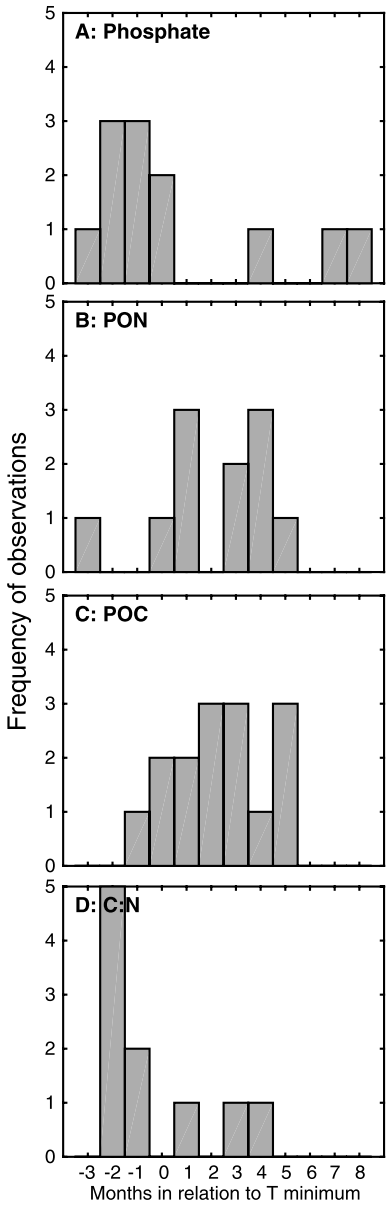


Figure 3. Histograms of temporal separation between the seasonal maximum of (a) phosphate concentration, (b) particulate organic nitrogen (PON) concentration, (c) particulate organic carbon (POC) concentration, and (d) C:N and the seasonal minimum of temperature. Only stations with significantly oscillating factors (Figure 2) are included in the histograms.

ratios also varied on a seasonal time scale (Figures 1b and 1c), but we only observed significant annual oscillations at BATS (Figure 2). This station was also characterized by the largest amplitude, whereby C:P and N:P seasonally varied by 158 and 31, respectively (Figures S6g and S6h). CARIACO also displayed strong (but not significant) seasonal oscillations, whereas Arendal and HOT showed less seasonal variability in these ratios.

We found links between the timing of seasonal oscillation of environmental conditions and POM concentrations and ratios (Figures S8 and 3). The *T* and P cycles were for the most part significantly anticorrelated (Figure S8), whereby P was low during warm periods and vice versa (Figure 3a). The exceptions to this anticorrelation occurred at stations with strong riverine inputs (Figure S8a) as phosphate concentrations did not significantly oscillate here (Figure 2). We expected the seasonal period following the *T* minimum and nutrient maximum to be characterized by elevated POM concentrations (essentially a spring bloom), and this was generally observed (Figures 3b and 3c). Examples of this pattern could be seen in places like BATS, Arendal, Point C, and Portzic, but we did see some exceptions as the maximum biomass at HOT was during the warm period and at the *T* minimum at CARIACO and estuarine sites.

We also observed a clear linkage between the seasonal cycles of C:N, temperature, and phosphate. For the subset of stations with significant oscillations in C:N, we found that C:N peaks late in the season (between the maximum and minimum temperature) (Figure 3d). This is seen at many coastal stations in the English Channel, Bay of Biscay, and Mediterranean Sea (Figure S8a). Although CARIACO did show significant oscillations, the highest C:N was also generally observed at this period. BATS was the only open ocean station with significantly oscillating C:N, and here we observed a different pattern. At this station, C:N peaked in the early summer. HOT did not show significant oscillations but did have the highest C:N coinciding with the temperature maximum. BATS was the only station with significant oscillations in C:P and N:P ratios. The peaks of these two ratios overlapped with C:N and appeared in the early summer, trailing the *T* maxima.

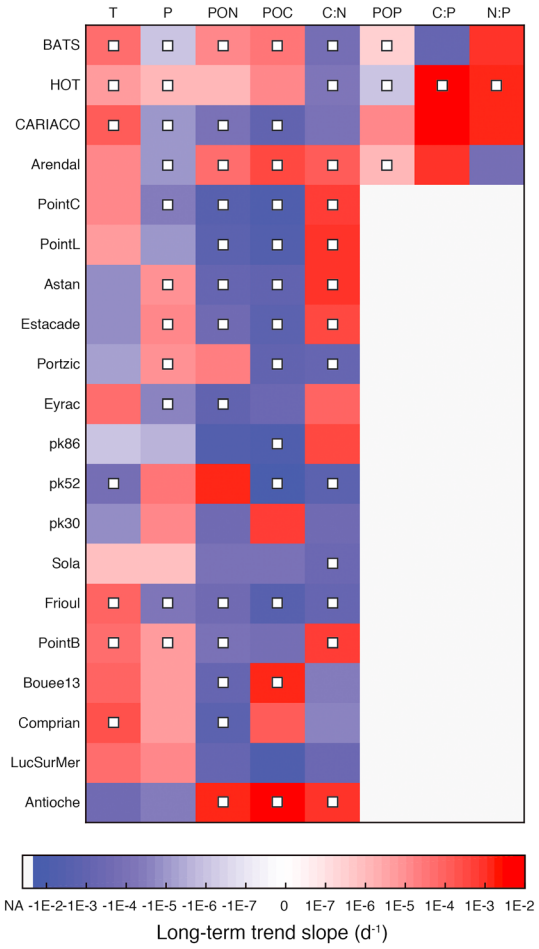


Figure 4. Direction, magnitude, and significance (marked with white squares) of long-term linear trends in temperature (*T*), phosphate (P), particulate organic nitrogen (PON), carbon (POC), and phosphorus (POP) concentrations as well as their molar ratios. The slope and significance ($p < 0.05$) are based on a linear model with linear trends and monthly terms (equation (1)). The unit of the slope is the factor per day—e.g., °C d^{-1}.

3.3. Long-Term Trends

We observed significant long-term linear trends in *T*, *P*, POM concentrations, and POM ratios (ANOVA, $p < 0.05$). *T* increased significantly at all open ocean and many coastal stations, but a few stations also experienced declines (Figures S2 and 4). The *T* change was accompanied by an opposite change in P at 60% of the sites (and 82% of the sites with a significant long-term change in *P*). Thus, most sites experienced substantial long-term environmental changes characterized by rising *T* and declining nutrient availability or vice versa (Figure 4). However, some coastal stations faced environmental changes in other directions, whereby *T* and nutrient concentrations increased (e.g., at HOT) or decreased in parallel (e.g., Antioche).

POM concentrations displayed complex significant long-term trends (Figures S4–S6 and 4). Individual POM elements generally changed in parallel—albeit with a few exceptions among coastal stations (significant only at Bouee 13). POC and PON concentrations increased at the open ocean stations BATS and HOT but declined at CARIACO. Among coastal stations, Arendal and Antioche displayed significant increases, but the majority showed long-term declines in POC and PON. POP showed significant changes at 75% of the stations and increased at BATS, CARIACO, and Arendal but decreased (by nearly 50% over 25 years) at HOT (Figures 1 and 3).

The changes in POM concentrations lead to long-term trends in elemental ratios at multiple stations (Figure 4). C:N declined at all open ocean stations as well as at five coastal stations but increased at 12 stations. C:P (but not N:P) declined slightly at BATS but showed large increases at HOT (significant), CARIACO, and Arendal. Multiyear trends in C:P and N:P at HOT and BATS were primarily driven by opposite changes in POP, whereas POC and PON concentrations increased faster than POP at Arendal.

The relationships between long-term trends in environmental conditions and POM concentrations or ratios varied among stations (Figure 5). We did observe a weak but significant negative relationship between phosphate concentrations and long-term linear trends in POC concentrations, whereas *T* had a lesser role across stations. For example, all open ocean stations (i.e., BATS, HOT, and CARIACO) experienced *T* increases, and BATS and HOT had rising POC concentrations, while they declined at CARIACO. We also observed a strong interaction between *T* and P for describing changes in POC (Figure 5a). A positive interaction between *T* and phosphate was also observed for C:N (Figure 5c) but not PON (Figure 5b). This suggested that multiyear changes in C:N were primarily driven by POC. Based on our limited number of time series

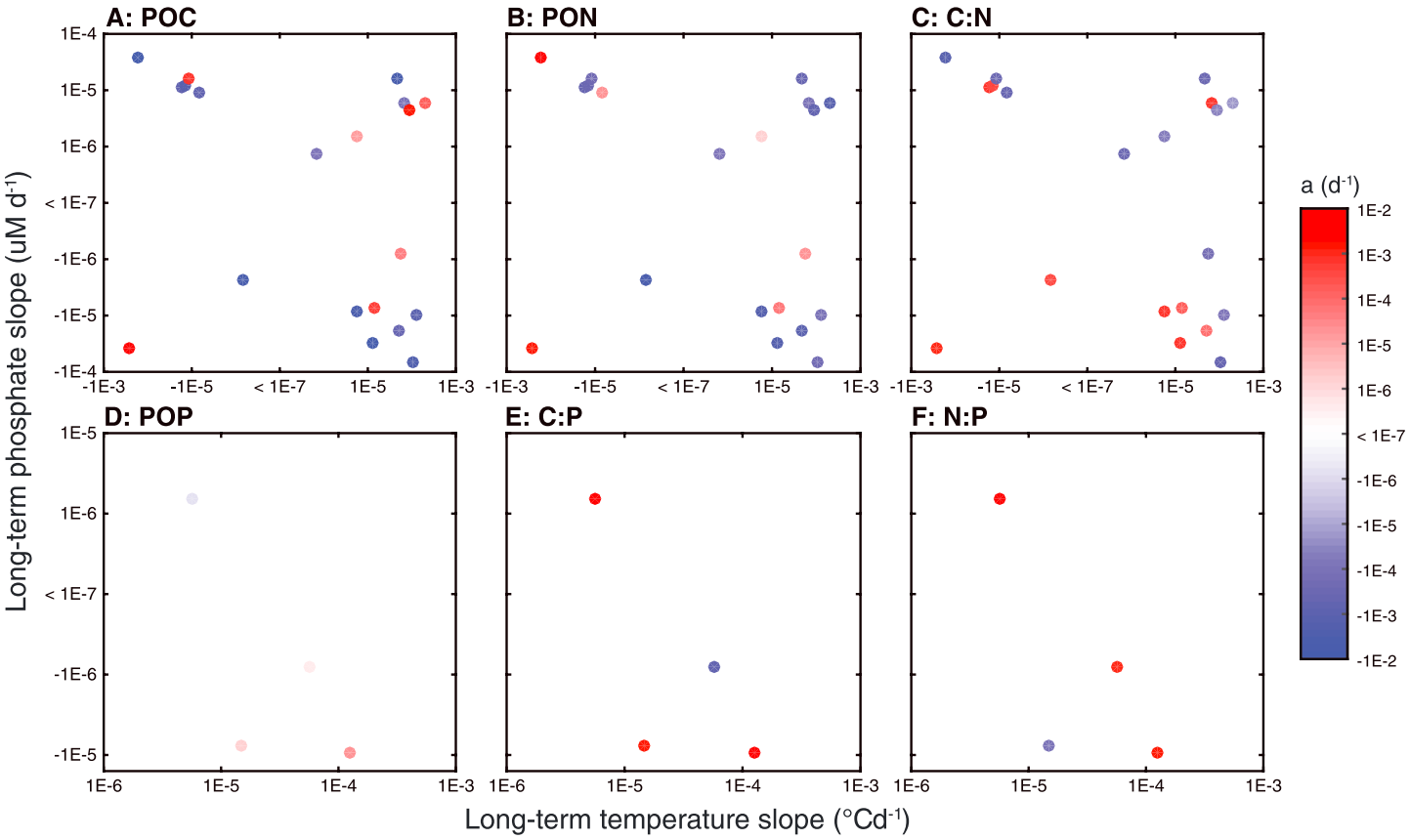


Figure 5. Correlation between long-term linear trends for temperature and phosphate versus (a, b, and d) particulate organic carbon (POC), nitrogen (PON), and phosphorus (POP) concentrations or (c, e, and f) ratios. The linear trends are derived from equation (1), and the absolute values are $\log_{10}$ transformed; *a* is the slope.

including POP data, it appeared that changes in POP were negatively related to changes in phosphate concentrations, and C:P and N:P were positively related to temperature (in three out of four stations, Figures 5d–5f).

3.4. Variance Distribution

We next examined the distribution of the variance between long-term trends (model 1) or annual contributions (model 2), seasonal, and residual changes (Figure 6). Most of the variance in *T* occurred at the seasonal time scale, whereas long-term trends and residual changes made small contributions. For other factors including POM concentrations and ratios, the residual signal was the predominant source of variation (Figure 6c), with the median long-term and seasonal contributions to variation being 2% and 11%, respectively. In contrast, we observed a wide range in the seasonal contribution to variation for P (Figure 6b). Some stations were strongly affected by seasonal oscillations in P (accounting for up to 78% of the variance), whereas other stations had much less seasonal cycling. For model 1, the residual variance encompasses variance associated with annual variance not associated with a linear trend, short-term variation, and measurement errors. For model 2, the residual variance only covers the variance associated short-term variation and measurement errors. In both models, the residual variance is high for all factors but temperature, which suggests that short-term signals and measurement errors are the main sources of this variance. Measuring errors may be minor for some factors (*T*, *P*, and POM concentrations) but can be large for POM ratios [*Martiny et al.*, 2016]. The high contribution of residual variance across all factors further suggests that short-term changes are a big source of variance.

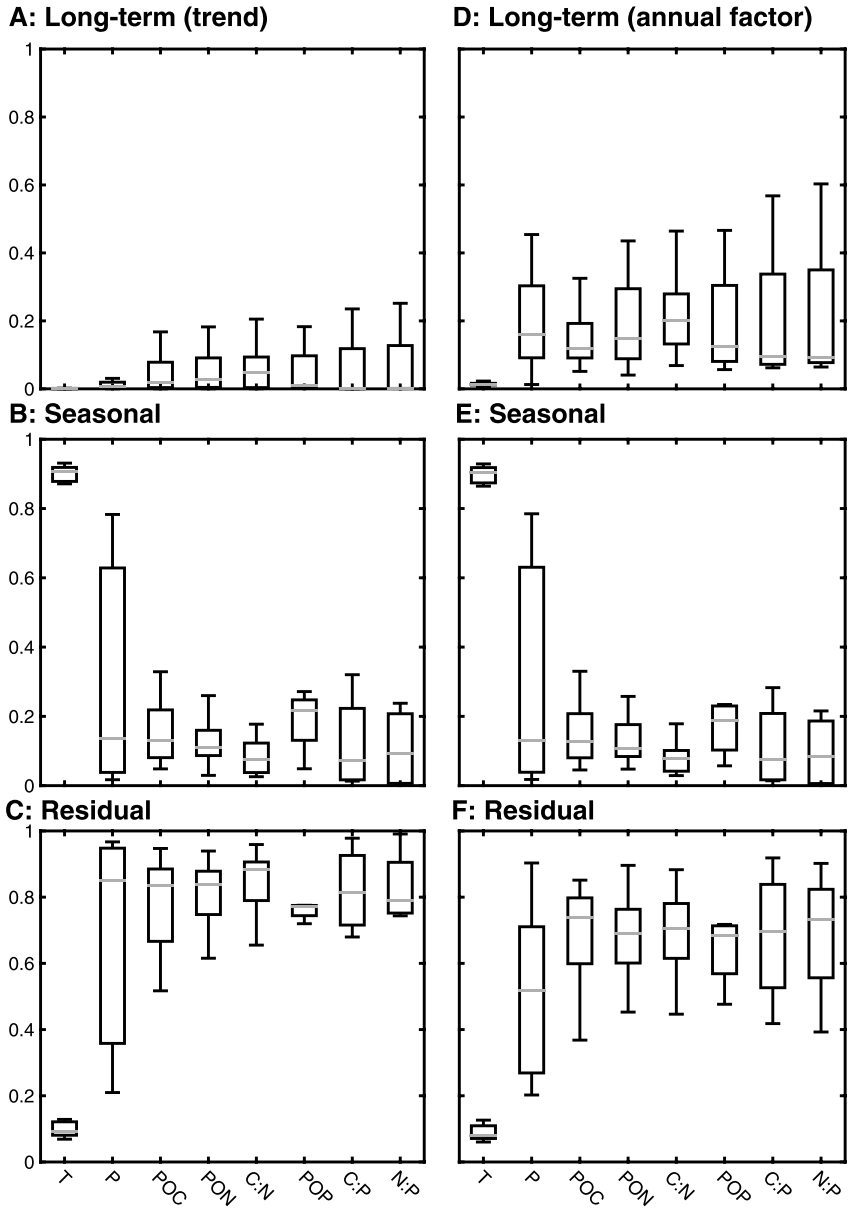


Figure 6. Distribution of variation. Variance associated with (a) interannual trends, (b) seasonal changes, and (c) residual across all time series using model 1. Variance associated with annual contributions (d), seasonal changes (e), and short-term + measuring errors (f) using model 2. For each box plot, the centerline represents the median, the box covers the 25th to 75th percentiles, and the bar covers approximately 99.3% of data.

4. Discussion

Our analysis demonstrates that POM elemental stoichiometry is not temporally static. Instead, we observe significant changes in elemental ratios at long-term, seasonal, and short-term time scales in different marine systems. Our recent work has demonstrated clear macroecological regional patterns in POM ratios that appear linked to some combination of temperature, growth physiology, overall nutrient availability, and phytoplankton community structure [*Martiny et al.*, 2013a, 2013b]. We hypothesized that rising sea surface temperatures and declining P should lead to decreasing ocean biomass and associated POM concentrations—and vice versa. In a seasonal context, we predicted the same mechanisms at play and thus C:N ratios peaking later in the season and connected to high-temperature and low-nutrient conditions [*Martiny et al.*, 2013a]. We

did not find clear support for this hypothesis in stations with significant oscillations in C:N. Instead, it appeared that C:N peaked during colder periods with maximum phosphate concentrations at many coastal sites. At BATS, C:N peaked in the early summer before the temperature maximum and the nutrient minimum. This could be due to the timing and strength of spring blooms as well as the overall contribution of phytoplankton biomass to the total POM pools. For C:P and N:P, the seasonal pattern is even murkier, and three out of four stations with POP data did not display significant oscillating patterns.

We observed significant long-term trends in POM ratios across many stations. Analogously, we predicted that long-term increases in temperature and/or declines in nutrient availability should lead to increasing ratios. Again, such a putative link between environmental conditions and POM ratios is observed at some stations (e.g., Arendal), but temperature increases lead to different trajectories in POM ratios at open ocean sites (e.g., HOT). Thus, this work supports a simple temperature/nutrient model by partially predicting the temporal changes in POM ratios at some stations, but it also suggests that additional factors are at play.

Our study reveals that large fractions of the total temporal variability of POM concentrations and ratios are associated with time scales shorter than the season. Part of this may be due to measurement errors, but the finding is consistent with multiple recent studies of marine physical, chemical, and biological factors showing extensive short-term variability of carbon and nutrient uptake [*Marrec et al*., 2014; *Martz et al*., 2014] as well as particulate matter accumulation and elemental ratios [*Martiny et al*., 2016]. This includes strong diel changes in the physiology and elemental composition of phytoplankton [*Hunter-Cevera et al*., 2014; *Lopez et al*., 2016]. In coastal systems, short-term variability can also be driven by tides, resuspension of sediment or changes in terrestrial inputs (e.g., following rain events), and processes other than the local biological activity [*Savoye et al*., 2012]. In oceanic systems (like HOT and BATS), mesoscale eddies [*McGillicuddy et al*., 2007] or storms [*Lomas et al*., 2009a] can influence elemental ratios. Such features are important and can lead to short-term changes (here included in the residual signal) in primary productivity, nutrient input and C, and may be drivers of the observed C:N:P variability in yet unknown ways.

There are several important factors that could lead to variability in POM concentrations and ratios beyond a *T*/nutrient concentration model. First, many coastal systems get substantial fluvial loading of particulate matter [*Smith and Hollibaugh*, 1993]. A terrestrial input can contribute up to 96% of the total POC at the three estuarine sites [*Savoye et al*., 2012]. Another source is entrainment of benthic POM in coastal zones during periods of high wind stress. These potentially C-rich POM sources may in part explain why some coastal stations observe high C:N during cold periods (Figure 5). With the exception of estuarine stations, phytoplankton largely contributes to the POC at most other stations and has to be a major driver of the overall POM concentrations and ratios [*Frigstad et al*., 2011; *Martiny et al*., 2013b; Martiny *et al*., 2016]. Nutrient availability and their control on phytoplankton elemental composition and ratios may not be fully described by ambient nutrient concentration level alone [*Karl*, 2014]. In most open ocean systems, newly supplied nutrients are immediately assimilated. As has been demonstrated in chemostat experiments and model simulations, the phytoplankton elemental stoichiometry reflects the nutrient supply rather than residual nutrients [*Rhee*, 1978; *Klausmeier et al*., 2004; *Bonachela et al*., 2013; *Mouginot et al*., 2015]. Furthermore, the growth and physiology of the analyzed marine communities—and associated POM concentrations and ratios—will commonly be influenced by other nutrients than P (e.g., N or Fe). Thus, nutrient availability may contribute to the observed temporal trends in ways not captured by our analysis. A third mechanism that needs to be evaluated in future studies is the role of specific phytoplankton populations. Several studies have demonstrated that coexisting phytoplankton lineages can have unique elemental requirements [*Arrigo et al*., 2002; *Quigg et al*., 2003; *Martiny et al*., 2013b; *Alexander et al*., 2015], which in turn may influence the elemental ratio of particulate organic matter and nutrient drawdown [*Weber and Deutsch*, 2010; *Martiny et al*., 2016]. Thus, our study demonstrates that we still do not fully understand the drivers of elemental ratios in marine communities and that there is a clear need to further understand how variation in phytoplankton composition and physiology affect these key ratios.

Our study has clear biogeochemical implications. Spatially and temporally static elemental ratios are often a key assumption in biogeochemical concepts and models. For example, concepts of nutrient limitation and links between nutrient supply, primary productivity, and C export (e.g., "new production") all rely on assumptions about elemental ratios in plankton [*Dugdale and Goering*, 1967]. In coastal and open ocean systems,

changes in the elemental composition of plankton can have a substantial influence on nutrient controls of primary production and C export. Globally, nearly all climate models predict a future decline in open ocean primary productivity and export production [*Bopp et al*., 2001, 2013]. The underlying mechanism for this prediction links temperature with increased stratification, a decline in the phosphorus supply, and—if assuming a constant C:P ratio—a decline in the abundance of diatoms and thus C export [*Ducklow et al*., 2001]. Although the time series are too short for detecting any trends related to the rise in atmospheric CO_2, our work demonstrates that POM concentrations and ratios are highly dynamic in all examined marine regions and would likely be affected by climate change. For example, we observed an upward overall trend at HOT in C:P of $0.012\,d^{-1}$. This rise corresponds to an increase in C:P of 90 over 20 years. Such a change in C:P can support a large increase in C export production and have a profound impact on biogeochemical cycles [*Karl*, 2014; *Galbraith and Martiny*, 2015]. Thus, we need to incorporate such mechanisms into global biogeochemical models in order to improve our predictive ability and realism of future levels of primary production and export.

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