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C : N : P stoichiometry at the Bermuda Atlantic Time-series Study station in the North Atlantic Ocean

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BGD

12, 9275–9305, 2015

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Abstract

Nitrogen (N) and phosphorus (P) availability determine the strength of the ocean's carbon (C) uptake, and variation in the N : P ratio in inorganic nutrients is key to phytoplankton growth. A similarity between C : N : P ratios in the plankton biomass and deep-water
nutrients was observed by Alfred C. Redfield around 80 years ago and suggested that biological processes in the surface ocean controlled deep ocean chemistry. Recent studies have emphasized the role of inorganic N : P ratios in governing biogeochemical processes, particularly the C : N : P ratio in suspended particulate organic matter (POM), with somewhat less attention given to exported POM and dissolved organic
matter (DOM). Herein, we extend the discussion on ecosystem C : N : P stoichiometry but also examine temporal variation of stoichiometric relationships. We have analysed elemental stoichiometry in the suspended POM and total (POM + DOM) organic matter (TOM) pools in the upper 100 m, and in the exported POM and sub-euphotic zone (100–500 m) inorganic nutrient pools from the monthly data collected at the Bermuda
Atlantic Time-series Study (BATS) site located in the western part of the North Atlantic Ocean. C : N : P ratios in the TOM pool were more than twice that in the POM pool. Observed C : N ratios in suspended POM were approximately equal to the canonical Redfield Ratio (C : N : P = 106 : 16 : 1), while N : P and C : P ratios in the same pool were more than twice the Redfield Ratio. Average N : P ratios in the subsurface in-
organic nutrient pool were ∼ 26 : 1, squarely between the suspended POM ratio and the Redfield ratio. We have further linked variation in elemental stoichiometry with that of phytoplankton cell abundance observed at the BATS site. Findings from this study suggest that the variation elemental ratios with depth in the euphotic zone was mainly due to different growth rates of cyanobacterial cells. These time-series data have also
allowed us to examine the potential role of climate variability on C : N : P stoichiometry. This study strengthens our understanding of elemental stoichiometry in different organic matter pools and should improve biogeochemical models by constraining the range of non-Redfield stoichiometry.

1 Introduction

Nitrogen (N) and phosphorus (P) are critical elements that control primary production in large portions of the surface ocean. Traditionally, N is considered a proximate and P is an ultimate limiting nutrient in surface waters (Tyrrell, 1999), but P has gained ap-
5 preciation lately as being the proximate limiting nutrient for ocean primary production in some regions such as the North Atlantic Ocean (Wu et al., 2000; Karl et al., 2001; Sañudo-Wilhelmy et al., 2001; Lomas et al., 2010). Alfred C. Redfield first noted the similarity between N : P ratios in surface ocean particulate organic matter (POM) and in deep-water inorganic nutrients; this observation was further extended to include car-
10 bon (Redfield, 1934). Oceanographic studies have consistently found mean plankton biomass to adhere to the Redfield Ratio (C : N : P = 106 : 16 : 1; Redfield, 1958; Copin-Montegut and Copin-Montegut, 1983; Geider and LaRoche, 2002,), and since then this ratio has become a fundamental stoichiometric tenet in marine biogeochemistry. Deviations from the canonical ratio have been used to provide insights into phytoplankton
15 physiology (Goldman et al., 1979; Quigg et al., 2003), nutrient limitation of primary production (e.g., Falkowski and Raven, 1997; Moore et al., 2013), efficiency of biological carbon sequestration in the ocean (Sigman and Boyle, 2000) and the input/output balance of the marine N cycle (e.g., Gruber and Sarmiento, 1997). Geochemists use the Redfield conceptual model to determine the state of the marine N cycle using the
20 N^* proxy (e.g., Gruber and Sarmiento, 1997). In the context of this proxy, subsurface nutrient N : P ratios > 16 : 1 suggest net nitrogen gain, while ratios < 16 : 1 suggest net nitrogen loss (e.g., Gruber and Deutsch, 2014). However, this relatively simple point of view has been shown to yield up to four-fold overestimation of N_2 fixation rates when compared to directly measured rates (Mills and Arrigo, 2010). In part, this overesti-
25 mation is due to the production and sedimentation of non-N_2 fixer biomass that can occur at ratios much greater than Redfield, particularly in the subtropical and tropical oceans (Singh et al., 2013; Martiny et al., 2013; Teng et al., 2014). Furthermore, an ocean circulation model has shown that the N : P ratio of biological nutrient removal

varies geographically, from 12 : 1 in the polar ocean to 20 : 1 in the sub-Antarctic zone, regions where N_2 fixation is not thought to be important (Weber and Deutsch, 2010). With a better understanding of N cycle processes, the validity of the Redfield model for nutrient uptake has been questioned (Sañudo-Wilhelmy et al., 2004; Mills and Arrigo, 2010; Zamora et al., 2010).

Biologically speaking, a fixed N : P ratio, like the Redfield ratio, would suggest that nutrients are taken up in that ratio during production of new organic matter (Redfield, 1958; Lenton and Watson, 2000). This conceptual model has been challenged by the fact that the variability in nutrient requirements is related to the functioning and evolution of microbes (Arrigo, 2005). The N : P ratio in phytoplankton need not be in the canonical ratio and can vary widely from coastal upwelling to transitional to oligotrophic regions of the ocean. The observed ratio varies with taxa and growth conditions (Arrigo et al., 1999; Quigg et al., 2003; Klausmeier et al., 2004). For example, it has been shown that non-Redfield nutrient utilization is common during blooms (Arrigo et al., 1999) and in regions dominated by cyanobacteria (Martiny et al., 2013). The N : P ratio of *Synechococcus* and *Prochlorococcus*, small and abundant phytoplankton cells in the open ocean, varies from 13.3 to 33.2 and 15.9 to 24.4, respectively, during exponential growth, while the ratio can be as high as 100 during PO_4^{3-} limited growth (Bertilsson et al., 2003; Heldal et al., 2003). Another cyanobacteria, the N_2 fixer *Trichodesmium* has an N : P ratio that varies from 42 to 125 (Karl et al., 1992), while in general diatoms have a ratio of $\sim 11 : 1$ (Quigg et al., 2003; Letelier and Karl, 1996; Mahaffey et al., 2005). Excess downward dissolved organic nitrogen (DON) fluxes relative to NO_3^- are associated with elevated *Trichodesmium* abundance (Vidal et al., 1999). Thus the relative abundance of different phytoplankton functional groups may lead to coupling of N and P cycles in non-Redfieldian proportions.

Considerable effort has been made to understand the variability and controls on the N : P ratio in the dissolved inorganic nutrient pool (e.g., Gruber and Sarmiento, 1997; Pahlow and Riebesell, 2000; Arrigo, 2005). In contrast, analysis of C : N : P ratios in particulate organic matter (POM) and dissolved organic matter (DOM) are more

scarce (Karl et al., 2001; Letscher et al., 2013). The C : N : P ratio however, has great relevance in oceanography, as it connects the "currency" of the ocean, i.e., carbon, to some of its controlling variables, N and P. Here, we present a detailed analysis of C : N : P stoichiometry of POM and TOM along with N : P stoichiometry of dissolved inorganic nutrients at the Bermuda Atlantic Time-series Study (BATS) for an eight year period. The observed ratios are correlated with and discussed in the context of co-measured biological parameters such as cell abundances of different phytoplankton groups and chlorophyll a. The goal of this study was to quantitatively assess C : N : P ratios in all (POM, TOM and inorganic nutrients) the pools and their deviations from the Redfield Ratio, and relationships to biogeochemical cycling.

2 Methods

Since 1988, the BATS site, located in the western subtropical North Atlantic Ocean (31°40′ N, 64°10′ W), has provided a relatively unique time-series record of nutrient bio-geochemical cycles. However, data on total organic C (TOC), total organic N (TON) and total organic P (TOP) and particulate organic C (POC), particulate organic N (PON), and particulate organic P (POP) have only been collected concurrently since 2004. These data were collected from seven different depths (5, 10, 20, 40, 60, 80 and 100 m) in the euphotic zone. We obtained these data from the BATS website (bats.bios.edu) and analysed the data record from 2004–2012 in this manuscript.

Samples for nitrate (NO_3^-) and phosphate (PO_4^{3-}) were gravity filtered (0.8 μm) and frozen (−20 °C) in HDPE bottles until analysis (Dore et al., 1996). NO_3^- and PO_4^{3-} were measured using a Technicon autoanalyser with an estimated inaccuracy of ∼ 0.12 and 0.02 μmol kg^{-1}, respectively (Bates and Hansell, 2004). The Magnesium Induced Co-precipitation (MAGIC) soluble reactive P (SRP) method (Karl and Tien, 1997) was used starting in late 2004 to improve both the sensitivity and the accuracy of the inorganic PO_4^{3-} analysis (Lomas et al., 2010). POC and PON samples were filtered on pre-combusted (450 °C, 4 h) Whatman GF/F filters (pore size 0.7 μm) and frozen (−20 °C)

until analysis on a Control Equipment 240-XA or 440-XA elemental analyzer (Steinberg et al., 2001; Lomas et al., 2013). POP was analyzed using the ash-hydrolysis method with oxidation efficiency and standard recovery checks (Lomas et al., 2010). TOC and TON concentrations were determined using high temperature combustion techniques (Carlson et al., 2010). Total P (TP) concentrations were quantified using a high temperature/persulfate oxidation technique and TOP calculated by subtraction of the MAGIC-SRP value (Lomas et al., 2010). Ideally DOM concentrations would have been estimated by subtracting POM from its total organic concentrations, e.g., [DOC] = [TOC] – [POC], but we did not have paired TOC (and TON) and POC (and PON) values; corresponding POC (and PON) values were taken at slightly different depths but on the same sampling day. Nevertheless, subtraction would not have had a substantial impact because, on average, POC and PON values in the upper 100 m were less than 4 % of TOC and TON, respectively (Fig. 1). Both the accuracy and precision of dissolved organic compound concentrations decrease with depth as concentrations of inorganic nutrients increase to dominate total pools.

Chlorophyll *a* pigments were analyzed by HPLC using the method of van Heukelem and Thomas (2001). Samples for flow cytometric enumeration of pico- and nano-plankton were collected on each cruise and analysed as described in Lomas et al. (2013). Export fluxes of POC, PON and POP were estimated using surface-tethered particle interceptor traps (Lomas et al., 2010; Steinberg et al., 2001). Elemental mass of material captured in the sediment trap, its collection surface area and deployment length were used to calculate fluxes (see Lomas et al., 2013 for a more detailed methodology on all the described parameters in the method section).

Our POM and TOM analysis was restricted to the upper 100 m, which also reflects the approximate mean depth of the euphotic zone at BATS (Siegel et al., 2001) and the zone where nutrients are depleted to near analytical detection. All presented elemental ratios are in $mol\,mol^{-1}$ units. We have also temporally aligned our data with respect to the deep winter mixing event each year because the timing of deep mixing varied between January and March during this study (e.g., Carlson et al., 2009). Mixed layer

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depth was defined as a $0.125\,\mathrm{kg\,m^{-3}}$ difference in seawater density from the surface (Gardner et al., 1995).

3   Results

We present time-series data of chemical constitutes in POM and TOM pools (Fig. 1).
5 We further calculated depth-mean ratios of the chemical constitutes. Over the entire length of the time-series, euphotic zone TON : TOP ratios varied between 34 and 130 (Fig. 2a), with a mean and standard deviation of 68 ± 9 (Table 1), TOC : TOP ratios varied between 450 and 1952, with an average of 983 ± 168 (Fig. 2b, Table 1), and TOC : TON varied between 11 and 17, with a mean of 15 ± 0.5 (Fig. 2c, Table 1).
10   Suspended euphotic zone PON : POP ratios were generally lower than TON : TOP ratios (Fig. 2, Table 1). The PON : POP ratio ranged from 7 to 140 with an average of 36 ± 11. Similarly POC : POP ratios were much lower than TOC : TOP, varying from 45 to 532 with an average value of 210 ± 67. The POC : PON ratio ranged between 1 and 19, with an average value of 6 ± 3. Elemental ratios in the TOM and POM were generally
15 above the Redfield Ratio ($p < 0.05$; z test) with the exception of the POC : PON ratio.

3.1   Annual patterns

3.1.1   Concentrations of POM and TOM

There were annual oscillations in POM pools in the upper 100 m (Fig. 1). TOC also showed annual oscillations, however, TON concentrations were relatively constant
20 throughout the study period. The pattern of TOP was an increasing trend during early 2007 until early 2008 (TOP $= 0.0936 \times$ decimal year $- 187.8$; $r^2 = 0.77$, $p < 0.05$). However, there were no long term sustained changes in concentration of POM and TOM.

3.1.2 C : N : P ratios in POM and TOM

There were no discernible trends in the POM stoichiometry. Variation in the C : N : P ratios of POM was less than that in TOM. TON : TOP and TOC : TOP ratios showed a decreasing trend throughout the year 2007 ($r^2 = 0.46$, $p < 0.05$), which was due to an increasing trend in TOP concentration in that year (Fig. 1). There was no annual trend in TOC : TON ratio. Overall, like POM and TOM concentration patterns, there were no long-term sustained changes in TOC : N : P ratios.

3.2 Seasonal variations

Mixed layer depths (MLD) were deepest during winter but the exact timing of the deepest mixing shifted between years (Fig. 3). For example, during 2005, the MLD was deepest in March, while it was deepest during February in 2006. Therefore, we aligned our data to the measured timing of deep mixing and combined all the data to a single 12 month composite. We further divided our data into two depth segments, i.e., 0–25 m and 25–100 m.

3.2.1 Concentrations of POM and TOM

There was larger variability in C and N pools in the 0–25 m range compared to that in the 25–100 m range (Figs. 4 and 6). In the 0–25 m depth range, TOC showed an increasing trend after deep mixing during the following five months and reached a plateau ($\sim 67\ \mu\mathrm{mol\,kg^{-1}}$) after that. POC increased in the first month after deep mixing and then decreased during the next two months and remained constant ($\sim 2\ \mu\mathrm{mol\,kg^{-1}}$) in the rest of the year (Fig. 4a). The pattern in PON was similar to POC, while those in TON and TOC were opposite to each other during the first two months after mixing and increased after that until the sixth month (Fig. 4a and b). These higher values of TOC and TON in the sixth month can be attributed to the occurrence of higher *Trichodesmium* colonies during August at BATS (Orcutt et al., 2001; Singh et al., 2013). There was no

variation with respect to timing of mixing in the TOP and POP values in the upper 25 m depth (Fig. 4c).

3.2.2   C : N : P ratios in POM and TOM

TON : TOP (68±9) and PON : POP (36±11) values were greater than the Redfield Ratio ($p < 0.05$). Patterns in TOC : TOP and TON : TOP ratio, and POC : POP and PON : POP were similar to each other (Fig. 5a and b). TOC : TOP (983±168) and POC : POP (210± 67) values were much higher than the Redfield Ratio of 106 ($p < 0.05$). TOC : TON (15 ± 0.5) increased for the two months following deep mixing and decreased until the seventh month (Fig. 5c). POC : PON (6 ± 3) increased in the next month after deep mixing, but remained around the Redfield Ratio throughout the year. Minimal variability in concentration and ratios in the 25–100 m depth horizon suggests confinement of the more dynamic biogeochemical processes to within the mixed layer, i.e. within 0–25 m (Figs. 6 and 7).

3.2.3   N : P ratios in inorganic nutrients

The NO_3^- : PO_4^{3-} ratio was 25.6 ± 9.1 in the 100–500 m depth at BATS, which is greater than the Redfield ratio (Table 1). We excluded data from the top 100 m in this analysis due to low precision relative to the mean nutrient values which are at or near analytical detection limits due to active biological uptake. NO_3^- and PO_4^{3-} were at their highest concentrations before deep mixing and decreased immediately following the month of deepest mixing and remained constant rest of the year (Fig. 8). The decrease in NO_3^- and PO_4^{3-} concentration could be due to the dilution with low nutrient surface water during mixing and/or rapid biological uptake.

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4 Discussion

From the approximately eight years of BATS data, it is apparent that the total and particulate organic matter C : N : P stoichiometries are not a long-term fixed ecosystem property, but vary seasonally and deviate substantially from the canonical Redfield
5 Ratio. Observed C : N : P ratios in TOM were much greater than Redfield proportions (Figs. 2, 4, 6). Similar patterns were also present in POM except that POC : PON ratios were closer to the Redfield Ratio. Overall, the TOC : TON : TOP ratio was 983 : 68 : 1 and the POC : PON : POP ratio 210 : 36 : 1. To elucidate a link between these ratios and biological activities in the surface ocean, we analysed data on PON and POP flux,
10 chlorophyll *a* and phytoplankton cell abundances in a similar way (i.e., relative to deep mixing) as was done with the elemental ratios (Figs. 8 and 9).

4.1 Connections among POM, TOM and inorganic nutrients

The PON flux increased during and peaked immediately after winter mixing. The POP flux showed elevated values before and shortly after the time of deep mixing
15 (Fig. 8a and b). The N : P ratio of export fluxes was nearly twice that of PON : POP ratio in the suspended matter (upper 100 m; Table 1). Higher N : P ratio in the fluxes than that in the suspended matter can be due to the preferential export of N or remineralisation of P. But similar C : N ratio in the fluxes and suspended matter would suggest preferential remineralisation of P.
20   The N : P ratio of export fluxes was also almost twice that of the dissolved NO_3^- : PO_4^{3-} ratio (Fig. 8c), which would suggest either loss of N or advective flux of low NO_3^- : PO_4^{3-}. However, literature indicates that sub-euphotic water at BATS is a mixture of water originated at the north of the site, which has low NO_3^- : PO_4^{3-} (Bates and Hansell, 2004; Singh et al., 2013).
25   One reason behind the TON : TOP ratio higher than Redfield Ratio could be that TON is less reactive than TOP and broken down mainly in the subsurface layer (Letscher et al., 2013), while TOP is labile or semi-labile and assimilated at a shallower depth

while TOP values do not change (comparing data in the Figs. 4 and 6). Our results on the TON : TOP ratio have important implications in ocean biogeochemistry of olig-
5 otrophic waters where DON and DOP concentrations in the sunlit layers exceed the concentration of inorganic nutrients by an order of magnitude (Church et al., 2002) and therefore DOM components likely sustain phytoplankton growth (Williams and Follows, 1998).

4.2 Linkages of concentrations and ratios of POM and TOM to chlorophyll *a*
10   and phytoplankton

We hypothesize that C : N : P ratios in the phytoplankton community itself changes the elemental stoichiometry of the POM and TOM pools. The C : N : P ratio is different in different phytoplankton communities and their biological uptake and degradation could potentially change the elemental stoichiometry of the particulate and dissolved organic
15 matter. C : N : P ratio varies geographically and its pattern is driven by variations in temperature, nutrients and phytoplankton functional groups. Latitudinal patterns in the C : N : P ratio have been attributed to changes in phytoplankton community as polar (colder) regions have a high abundance of diatoms with low N : P and C : P ratios, in contrast to the directly measured high elemental ratios in the cyanobacteria from
20 warmer regions (Martiny et al., 2013). So how and why does C : N : P ratio vary in phytoplankton communities? Two mechanisms could explain variability in the C : N : P ratios in a phytoplankton community. The first mechanism suggests that the taxonomic composition of a phytoplankton community influences its elemental composition. Elemental ratios inside a cell are controlled by growth strategies (Klausmeier et al., 2004).
25 Several studies have reported low C : P and N : P ratios in fast growing diatoms (Price, 2005), whereas slower growing cyanobacteria have C : P and N : P ratios higher than the Redfield Ratio (Bertilsson et al., 2003; Martiny et al., 2013). More precisely, it is not so much the growth rate that determines the difference, but the machinery invested

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in nutrient acquisition vs. protein production. The second mechanism links the nutrient supply ratio to the cellular elemental ratio (Rhee, 1978). POP remineralisation is faster than PON because POP is more labile than PON (Monteiro and Follows, 2012) and this results in changing PON : POP ratio.

5   Chlorophyll *a* values decreased after the spring bloom that was stimulated by deep mixing (Fig. 9a) and were anti-correlated with TOC values ($r^2 = 0.76$, $p < 0.05$). The gradual increase in Chlrophyll *a* during the four months before deep mixing is due to similar increase in MLD before deep mixing (Fig. 3), which suggests that there may be nutrient flux into the upper layer well before deep mixing. *Prochlorococcus* and
10 *Synechococcus* profiles were correlated to each other in the first seven months of the year ($r^2 = 0.58$, $p < 0.05$) and there was no relation in the rest of the year. Furthermore, *Synechococcus* cell abundance was correlated with POC ($r^2 = 0.67, p < 0.05$), PON ($r^2 = 0.47, p < 0.05$), POP ($r^2 = 0.29, p < 0.05$) and anti-correlated with TOC values ($r^2 = 0.72, p < 0.05$). *Synechococcus* is more abundant during the more produc-
15 tive season whereas *Prochlorococcus* is dominant during the highly oligotrophic part of the year. Such patterns are typically observed in many parts of the ocean. The seasonal pattern of *Picoeukaryote* abundance was similar to that of *Synechococcus* ($r^2 = 0.58, p < 0.05$) and Chlorophyll *a* ($r^2 = 0.81, p < 0.05$). POC : PON : POP ratios in *Prochlorococcus*, *Synechococcus* and *Picoeukaryote* are 234 : 33 : 1, 181 : 33 : 1 and
20 118 : 15 : 1, respectively at BATS site (Martiny et al., 2013; Lomas et al., unpublished data), which clearly suggests imprints of a mixture of *Prochlorococcus*, *Synechococcus* on the observed POM stoichiometry presented in Table 1. Biomass of *Prochlorococcus*, *Synechococcus* and *Picoeukaryote* together contributes $\sim 25\%$ to POM pool with a major contribution ($\sim 15\%$) from *Synechococcus* (Lomas et al., unpublished
25 data). There was no significant variability in *Nanoeukaryotes* (Fig. 9e). Hence, biological parameters could potentially explain up to 25 % variability in the POM and TOM concentration and hence in the elemental ratios. So what else drives the variability in the C : N : P ratios?

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We analysed trends in the TON : TOP and TOC : TOP ratios for December 2006 to January 2008 data along with phytoplankton cell abundances for the top 100 m BATS data (Fig. 10a). Since the variation in TON : TOP and TOC : TOP were due to an increasing trend in TOP, we correlated TOP concentrations with a lag of three months (There is a time lag between phytoplankton and elemental abundance as observed by Singh et al., 2013 at the BATS site) in phytoplankton cell abundances (data during September 2006 to November 2007). We observed significant anti-correlation ($r^2 = 0.61$, $p < 0.001$) between *Nanoeukaryotes* and TOP but the data did not correlate with other phytoplankton cells (Fig. 10a). In the paucity of elemental composition data on *Nanoeukaryotes*, we hypothesize that these cells have less requirement of P. We further analysed this increasing trend in the TOP concentration with climate indices. The Arctic Oscillation is a major climatic phenomenon in the North Atlantic Ocean (Thompson and Wallace, 1999). Positive trends in the Arctic Oscillation lead to higher temperatures, advanced spring, and increased CO_2. This could lead to enhanced uptake of CO_2 during spring as has been found in terrestrial systems (Schaefer et al., 2005). Higher build-up of organic matter would require more P and hence we correlated TOP concentration with monthly Arctic Oscillation index with a lag of a year (monthly Arctic Oscillation indices are from November 2005 to December 2006, because there is a lag of one year before climatic oscillations in the North Atlantic show its impact on surface biogeochemistry; Fromentin and Planque, 1996). We observed a significant correlation ($r^2 = 0.46$, $p < 0.01$) between the Arctic Oscillation and TOP concentrations (Fig. 10b).

Since variations in phytoplankton cells and climate variability could not explain all the variation in the elemental stoichiometry, we hypothesize that physical processes play a role in driving POM and TOM stoichiometries. A decrease in NO_3^- and PO_4^{3-} in the subsurface water (100–500 m) during deep mixing suggests that vertical mixing dilutes the subsurface nutrients values, which would have eventually enhanced nutrient concentrations in the surface waters (Fig. 8). All the above factors potentially contribute to the observed gradients of the TON : TOP ratio. However, other mechanisms are yet to be identified to explain the observed variability in the elemental stoichiometry.

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4.3 Role of DOM in microbial carbon export

Many biogeochemical modelling estimates of export production assume Redfield Stoichiometry in export fluxes but a non-Redfieldian approach has gained appreciation recently (Letscher and Moore, 2015). Net community production is 3–4 mol C m^{-2} yr^{-1} in the BATS region (Jenkins, 1982; Emerson, 2014), which requires a lot more nutrient input than observations suggest (Williams and Follows, 1998). A possible mechanism to sustain such production is the supply of DOM to the sunlit layer.

DOM consists of complex compounds whose chemical characterization is incomplete, but it is evident that its elemental stoichiometry differs drastically from the Redfield Ratio. Differential production and degradation of DON and DOP with lifetimes comparable to the gyre circulation could potentially change the overall stoichiometry of nutrient supply (Voss and Hietanen, 2013). Preferential degradation of DOP rather than DON expands the niche of diazotrophs beyond that created by subsurface denitrification. Diazotrophs, e.g. *Trichodesmium*, can quickly utilize recycled DOP (Dyhrman et al., 2006). Simultaneously, these diazotrophs release newly fixed N$_2$ in the surrounding environment as DON (Mulholland, 2007), which can be used by other phytoplankton, but this DON likely has associated DOP. In the PO$_4^{3-}$ limited Sargasso Sea, DOP contributes up to 50 % of P demand for primary production (Lomas et al., 2010) and up to 70 % to the exported POP (Roussenov et al., 2006; Torres-Valdés et al., 2009).

C : N ratios in TOM were slightly higher than Redfield Ratio but C : P and N : P ratios deviated greatly. N : P ratios in inorganic nutrients were also higher than the Redfield Ratio. Such patterns underscore that productivity in this part of the ocean is limited by PO$_4^{3-}$ availability rather than N (Wu et al., 2000; Karl et al., 2001; Sañudo-Wilhelmy et al., 2001; Lomas et al., 2010).

5 Conclusions

Our time-series analysis suggests temporal and depth variability in the C : N : P ratio in the Sargasso Sea. C : N : P ratios in the TOM were significantly higher than the canonical Redfield Ratio, while C : N was similar to the Redfield Ratio in the POM. We observed seasonal variability in stoichiometry but on average, the TOC : TON : TOP ratio was 983 : 68 : 1 and the POC : PON : POP was 210 : 36 : 1. Such ratios appear to be largely driven by the growth of *Synechococcus* during winter mixing, while flourishing of *Prochlorococcus* cells during the oligotrophic period (fall) could also explain some variability in the stoichiometry. The N : P ratio in subsurface inorganic nutrients was also greater (N : P = 26) than the Redfield Ratio in this region. We observed a significant decreasing trend in TON : TOP and TOC : TOP during 2007, which was due to an increase in TOP concentration and could have been partly driven by the Arctic Oscillation and a decrease in the relative abundance of *Nanoeukaryotes*. Other causes for the observed variations in the elemental stoichiometry need to be explored; however, this elemental stoichiometry analysis may improve biogeochemical models, which have hitherto assumed Redfield stoichiometry to estimate export fluxes.

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Table 1. Average concentration (μmol kg^{-1}), molar ratio of various biogeochemical parameters and particle fluxes (mmol m^{-2} d^{-1}) from the BATS data presented in Fig. 1.

Parameter	$C \pm \sigma$[a]	no of samples	Sampling period
Concentration (C) in the upper 100 m			
TOC	63.81 ± 2.86	714	Jan 2004–Dec 2011
TON	4.43 ± 0.50	712	Jan 2004–Dec 2011
TOP	0.07 ± 0.03	547	Jun 2004–Nov 2011
POC	2.36 ± 1.14	844	Jan 2004–Apr 2012
PON	0.40 ± 0.19	845	Jan 2004–Apr 2012
POP	0.01 ± 0.01	696	Jan 2004–Apr 2012

Parameter	$R \pm \sigma$	no of data points[c]	Sampling period
Ratio (R)[b] in the upper 100 m			
TOC : TON	15 ± 0.5	86	Jul 2004–Dec 2011
POC : PON	6 ± 3	95	Jan 2004–Apr 2012
TON : TOP	68 ± 9	77	Jul 2004–Nov 2011
PON : POP	36 ± 11	88	Jan 2004–Apr 2012
TOC : TOP	983 ± 168	78	Jul 2004–Nov 2011
POC : POP	210 ± 67	88	Jan 2004–Apr 2012

Parameter	(C or R) $\pm \sigma$	no of data points	Sampling period
Inorganic nutrient stoichiometry in 100–500 m			
NO_3^-	2.74 ± 2.40	3425	Oct 1988–Jul 2012
PO_4^{3-}	0.11 ± 0.13	3405	Oct 1988–Jul 2012
$NO_3^- : PO_4^{3-}$	25.6 ± 9.1	2415	Oct 1988–Jul 2012

Parameter	$C \pm \sigma$	no of samples	Sampling period
Particle fluxes at 200 m			
C	1.68 ± 1.07	254	Jan 1989–Dec 2011
N	0.23 ± 0.16	254	Jan 1989–Dec 2011
P	0.008 ± 0.014	64	Oct 2005–Dec 2011

Parameter	$R \pm \sigma$	no of data points	Sampling period
Ratio in particle fluxes at 200 m			
N : P	57 ± 46	61	Oct 2005–Dec 2011
C : P	287 ± 269	62	Oct 2005–Dec 2011
C : N	7.9 ± 2.8	252	Jan 1989–Dec 2011

[a] σ is standard deviation of the samples mentioned in next the column.
[b] Ratios and their standard deviations are derived from the monthly mean values.
[c] one datum would be mean of many values of concentration for a particular month of concentration in the upper 100 m.
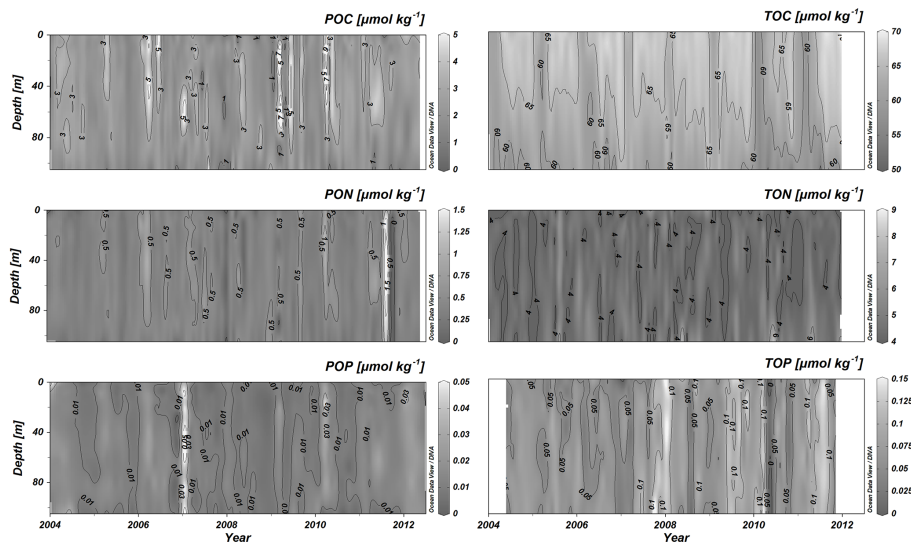
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Figure 1. Monthly BATS data on C, N and P in particulate and total organic matter in top 100 m during January 2004 to April 2012.
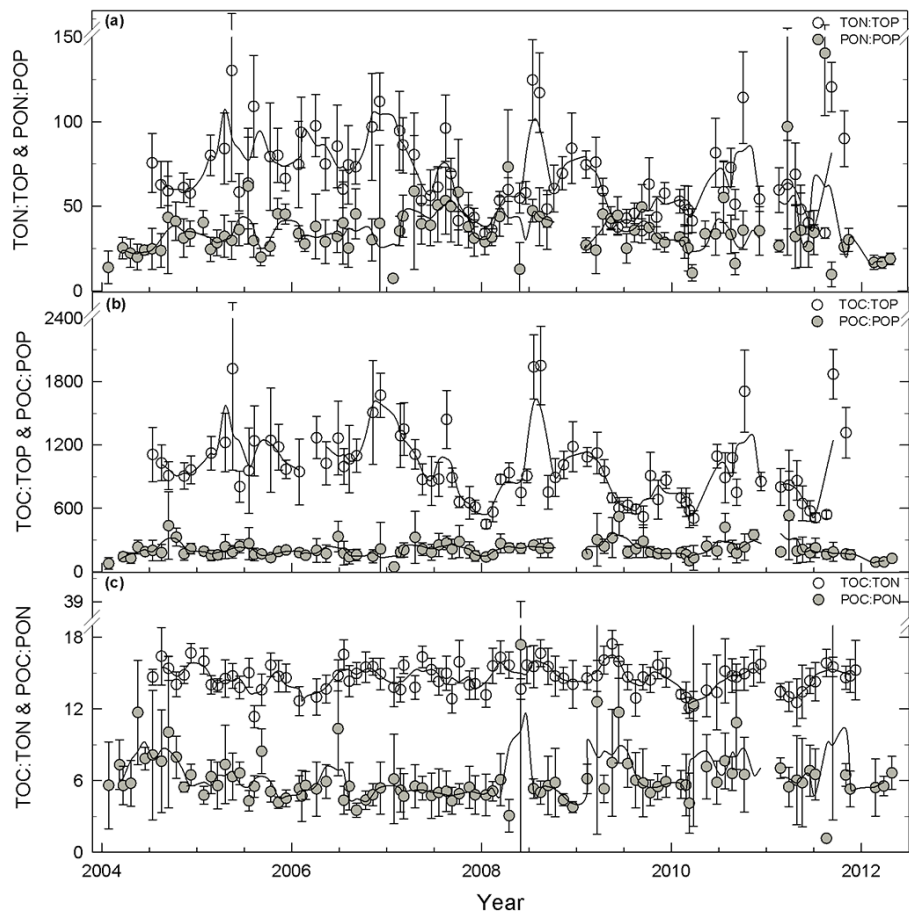
Figure 2. Monthly stoichiometry during 2004–2010 at 0–100 m. Solid lines are three months running mean. Error bars are 1σ standard deviations from the mean values.
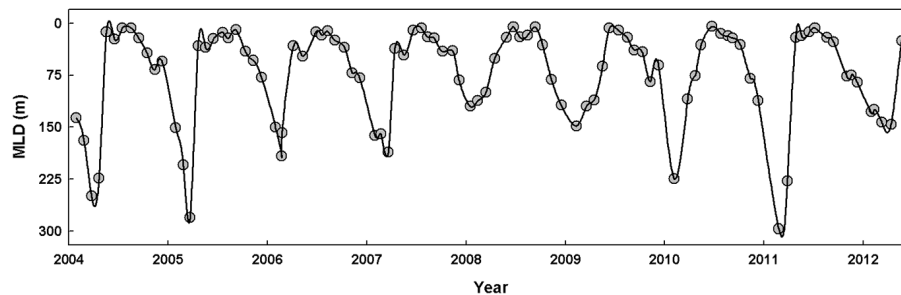
Figure 3. Mixed layer depth (MLD) during the sampling period at BATS site.

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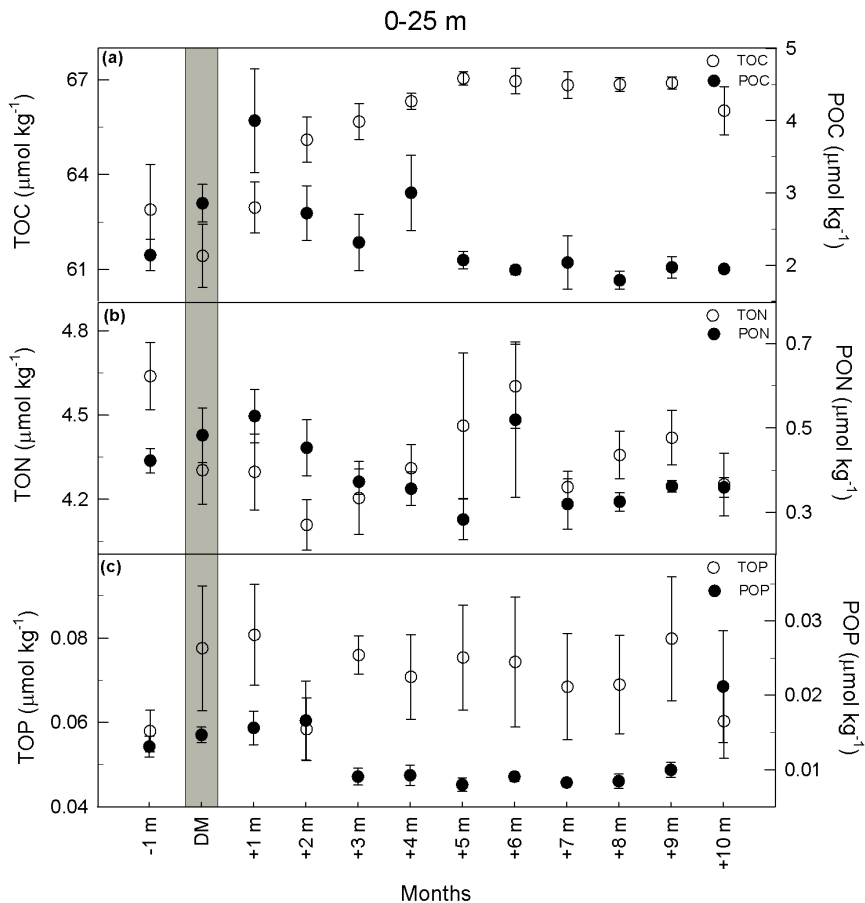
Figure 4. Annual concentrations of total (open circles) and particulate organic matter (filled circles) relative to the deep mixing in 0–25 m depth at BATS (data used from January 2005–December 2011). The gray bar represents the period of deep mixing (DM) for each year.
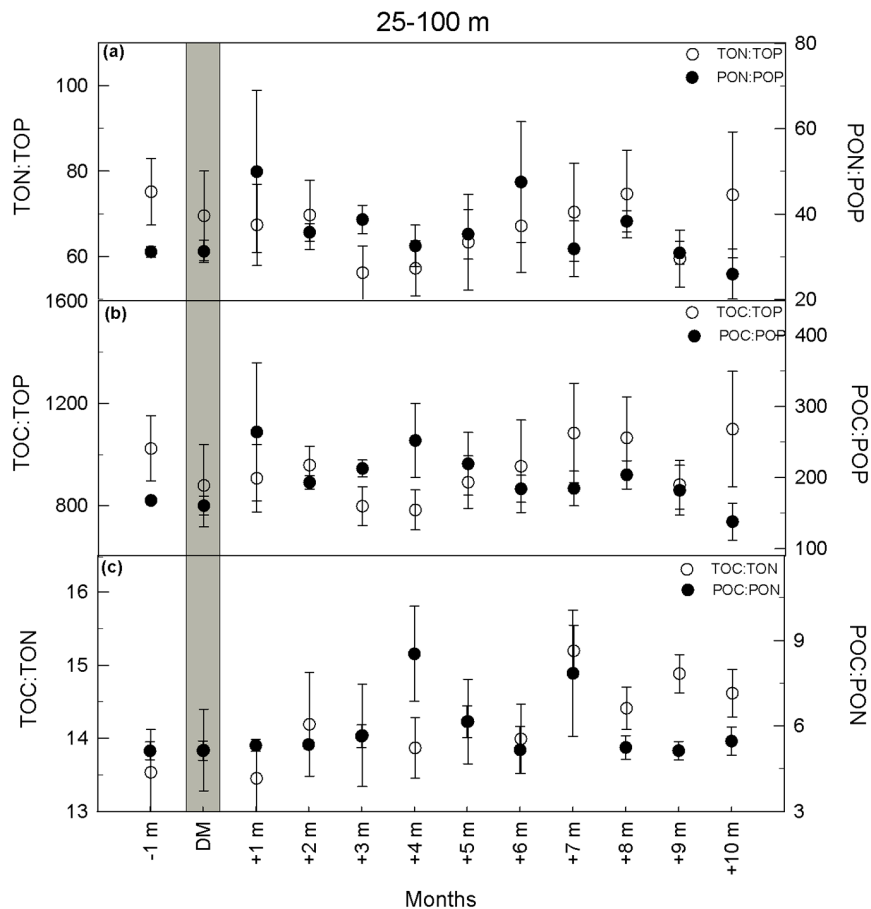
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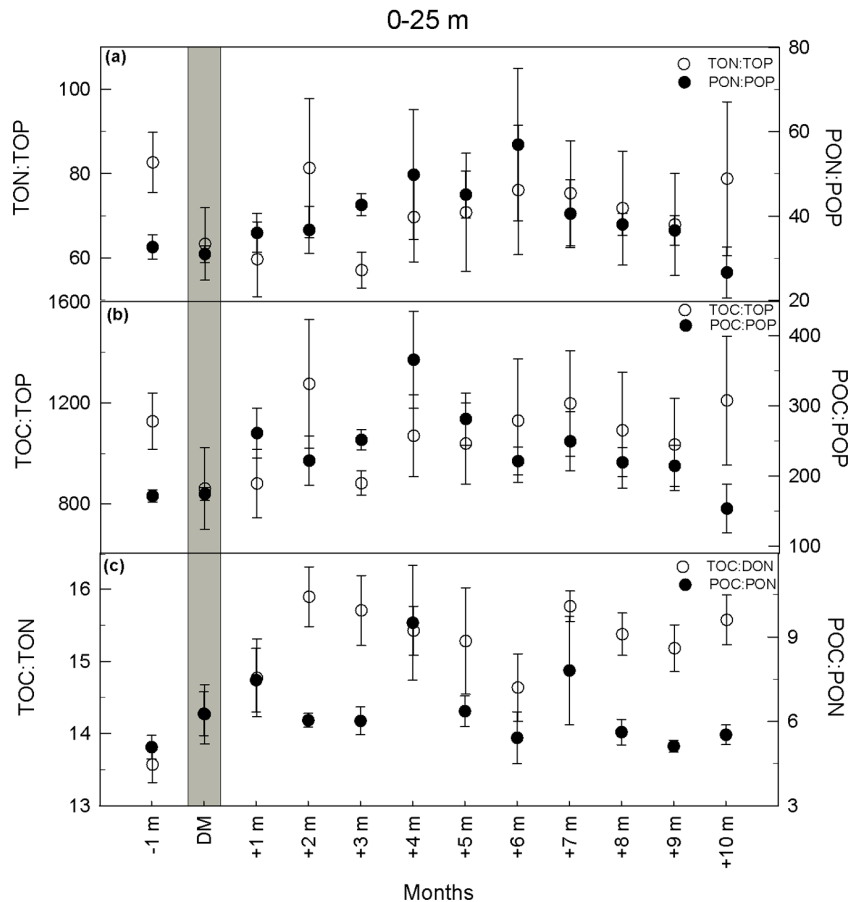
Figure 5. Annual ratios of elemental stoichiometry relative to the deep mixing at 0–25 m depth (data used from January 2005–December 2011). The gray bar represents the period of deep mixing (DM) for each year.
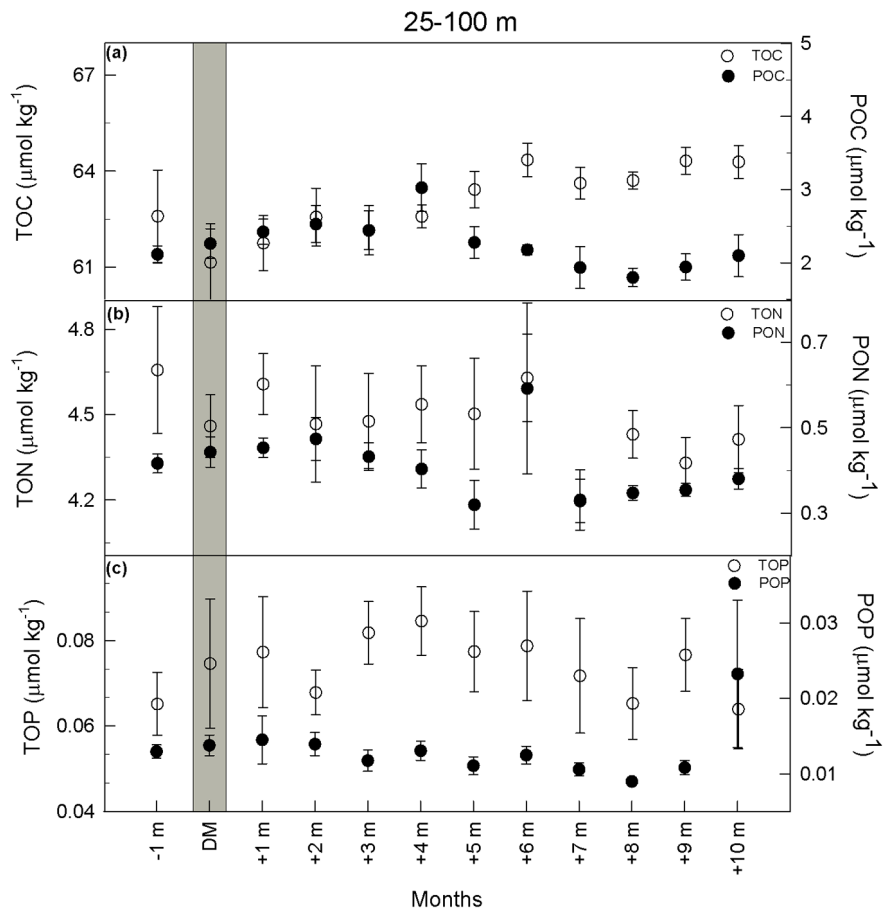
Figure 6. Annual concentrations of total (filled circles) and particulate (open circles) matter relative to the deep mixing at 25–100 m depth (data used from January 2005–December 2011). The gray bar represents the period of deep mixing (DM) for each year.

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Figure 7. Annual ratios of elemental stoichiometry relative to the deep mixing at 25–100 m depth (data used from January 2005–December 2011). The gray bar represents the period of deep mixing (DM) for each year.

Figure 8. Annual variation of NO_3^- and PO_4^{3-} concentrations, N and P fluxes, and their ratios relative to the deep mixing at 100–500 m depth (data used from January 2005–December 2011). The gray bar represents the period of deep mixing (DM) for each year.

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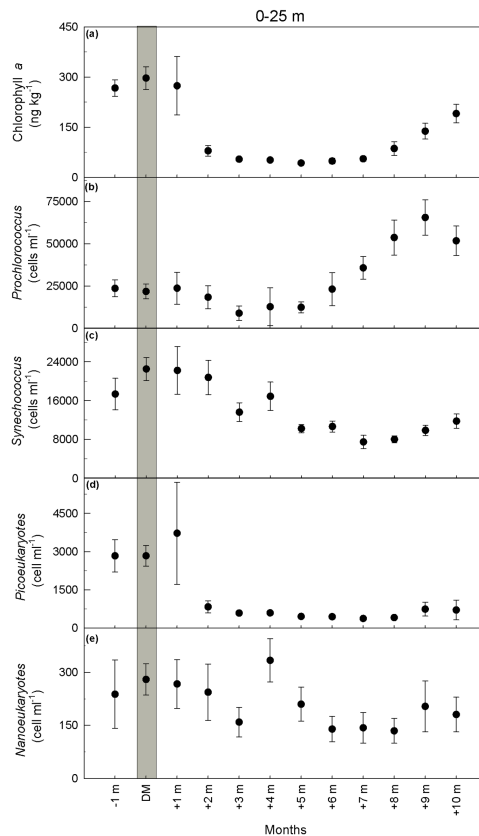
Figure 9. Annual variation in Chlorophyll *a* and cell counts for *Prochlorococcus*, *Synechococcus*, picoeukaryotes, and nanoeukaryotes relative to the deep mixing in 0–25 m depth at BATS (data used from January 2005–December 2011). The gray bar represents the period of deep mixing for each year.
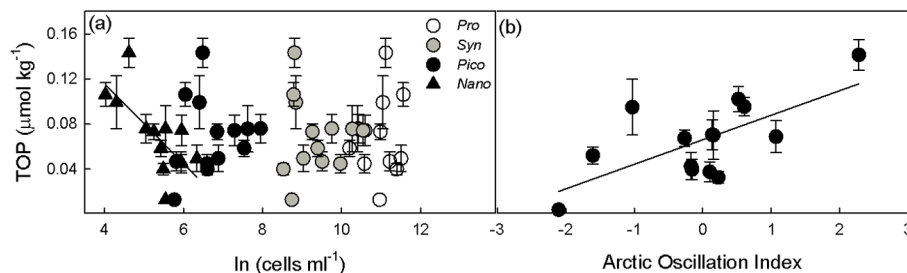
Figure 10. Correlation between TOP (December 2006–January 2008) and **(a)** cell abundances of *Prochlorococcus*, *Synechococcus,* picoeukaryotes and nanoeukaryotes during September 2006–November 2007. Among cell abundances, only nanoeukaryotes showed significant correlation ($r^2 = 0.61$, $p < 0.001$) and **(b)** Arctic Oscillation index during November 2005–December 2006 ($r^2 = 0.46$, $p < 0.01$).