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Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP)

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Abstract

Inorganic phosphorus (SRP) concentrations in the subtropical North Atlantic are some of the lowest in the global ocean and have been hypothesized to constrain primary production. Based upon data from several transect cruises in this region, it has been hypothesized that dissolved organic phosphorus (DOP) supports a significant fraction of primary production. In this study, a time-series of phosphorus biogeochemistry is presented for the Bermuda Atlantic Time-series Study site, including rates of phosphorus export. Most parameters have a seasonal pattern, although year-over-year variability in the seasonal pattern is substantial, likely due to differences in external forcing. Suspended particulate phosphorus exhibits a seasonal maximum during the spring bloom, despite the absence of a seasonal peak in SRP. However, DOP concentrations are at an annual maximum prior to the winter/spring bloom and decline over the course of the spring bloom while whole community alkaline phosphatase activities are highest. As a result of DOP bioavailability, the growth of particles during the spring bloom occurs in Redfield proportions, though particles exported from the euphotic zone show rapid and significant remineralization of phosphorus within the first 50 m below the euphotic zone. Based upon DOP data from transect cruises in this region, the southward cross gyral flux of DOP is estimated to support ~32% of annual primary production and ~100% of phosphorus export. These estimates are consistent with other research in the subtropical North Atlantic and reinforce the hypothesis that while the subtropics may be phosphorus stressed (a physiological response to low inorganic phosphorus), utilization of the DOP pool allows production and accumulation of microbial biomass at Redfield proportions.

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1 Introduction

Phosphorus is a key macronutrient for phytoplankton growth (e.g., DNA, RNA, lipids) and intracellular energy (ATP) and signaling pathways, and as such has the potential to limit oceanic primary production. The traditional paradigm is that marine primary production is nitrogen limited on biologically relevant timescales (Codispoti, 1989; Ryther and Dunston, 1971). However, evidence is mounting that suggests oceanic primary production may be limited by inorganic phosphorus (Karl et al., 2001a; Thingstad et al., 2005), such as in the oligotrophic North Atlantic subtropical gyre (Ammerman et al., 2003; Mather et al., 2008). In the subtropical and tropical North Atlantic, [SRP] determined using the magnesium co-precipitation method (Karl and Tien, 1992), have been found to be consistently <10 nmol l^{-1} and often <1 nmol l^{-1} (Cavender-Bares et al., 2001; Wu et al., 2000) in transect cruises through this region. These consistently low inorganic phosphorus concentrations, along with DIN:SRP ratios much greater than the Redfield Ratio, have been used as evidence for inorganic phosphorus stress of primary production in this region. Phosphorus stress is defined in this manuscript as a physiological response to low [SRP], such as the induction of alkaline phosphatase activity, but microbial cells remain able to grow.

However, phosphorus is also present in a dissolved organic (DOP) pool which often accounts for >80% of the total dissolved phosphorus pool in the North Atlantic Ocean (Ammerman et al., 2003; Cavender-Bares et al., 2001; Mahaffey et al., 2004; Vidal et al., 1999; Wu et al., 2000). [DOP] in the western tropical and subtropical North Atlantic range from 50–100 nmol l^{-1} (Ammerman et al., 2003; Cavender-Bares et al., 2001; Mather et al., 2008; Wu et al., 2000), while in the eastern tropical/subtropical North Atlantic [DOP] are much higher, ranging from 100–300 nmol l^{-1} (Mahaffey et al., 2004; Mather et al., 2008; Vidal et al., 1999). The DOP pool is a diverse assemblage of compounds with the largest fraction, on average ~75% of the DOP amenable to characterization, being esters with much of the remaining fraction being phosphonates (Karl and Bjorkman, 2002; Kolowith et al., 2001; Payan and McLaughlin, 2007). Esters

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are readily hydrolyzed by bacterial and phytoplankton alkaline phosphatases (APase) (Chrost and Overbeck, 1987), and increases in phytoplankton APase activity have been interpreted as an indicator of inorganic phosphorus stress (e.g., Hoppe, 2003). Indeed, assays for the enzyme APase suggest that DOP is readily utilized by the autotrophic community (Dyhrman et al., 2002; Lomas et al., 2004; Mather et al., 2008). Uptake measurements in oligotrophic gyres also indicate that the DOP pool is a potentially important source of P for autotrophs (Benitez-Nelson and Karl, 2002; Bjorkman and Karl, 2003; Bjorkman and Karl, 2005), particularly in the P-depleted North Atlantic (Casey et al., 2009; Orchard et al., 2009).

Despite the mounting evidence for inorganic phosphorus stress and utilization of DOP in the subtropical North Atlantic, relatively little is known about the seasonal variability in phosphorus biogeochemical parameters. The only seasonal study of high-sensitivity [SRP] (using an optimized autoanalyzer with no MAGIC-SRP preconcentration) conducted in the western subtropical North Atlantic at the Bermuda Atlantic Time-series Study (BATS) site (Case, 2001) suggests that there is no seasonal pattern and [SRP] approximate the analytical detection limit of $\sim$12 nmol l^{-1}. Seasonally, euphotic zone (0–100 m) [DOP] at BATS have been shown to decrease from winter through the subsequent fall (Case, 2001). This pattern suggests biological consumption during the spring bloom and into the summer which may explain continued CO_2 drawdown during a period of minimum external inorganic nutrient inputs at BATS (Bates, 2001; Michaels et al., 1994b). Salihoglu et al. (2007), using a one-dimensional multi-component lower trophic level ecosystem model that includes detailed algal physiology, showed an increase in euphotic zone [DOP] at BATS coincident with increased primary production following winter convective mixing, which is consumed during the subsequent summer period. More generally, Salihoglu et al. (2007) observed that the inclusion of an explicit DOP pool, which could be accessed by phytoplankton, significantly improved the fit between modeled and observed carbon fluxes relative to model runs that did not include a DOP pool. This model output implies that DOP may be involved in export production. Using a simplified nutrient cycle and transport model for

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the eastern North Atlantic, Roussenov et al. (2006) hypothesize northward transport of DOP into the subtropics from the gyral boundaries as part of the surface Ekman wind-driven circulation with 70–80% of the phosphorus export in the subtropical North Atlantic supported by DOP. Despite the modeled biogeochemical importance of the DOP, observational data are sparse and additional datasets are required to evaluate model output and prediction. In this manuscript, we present multi-year records of all the major phosphorus pools at the BATS site and bulk alkaline phosphatase activity (APA) and particulate phosphorus export rates.

2 Materials and methods

2.1 Sample collection

Samples for phosphorus pool measurements were collected biweekly from February to April and monthly for the remainder of the year at 12–15 depths in the upper 500 m (roughly 20 m intervals in the upper 200 m and 50 m intervals from 200–500 m) starting in November 2003 (particulate phosphorus; PPhos), March 2004 (MAGIC-SRP) and June 2004 (total dissolved phosphorus; TDP) and continuing to present. Data through the end of 2008 only are presented in this manuscript. Samples (4 l) for PPhos analysis were filtered under low pressure (~50 mm Hg) onto pre-combusted (450°C, 5 h) GF/F filters. Samples were flushed with ~5 ml of 0.17 M Na_2SO_4 and stored at −20°C until analysis. Samples for MAGIC-SRP and TDP analysis were collected in acid-cleaned (10% HCl) 250 ml and 60 ml HDPE bottles, respectively, from the same Niskin bottle. Both samples were left unfiltered and stored frozen at −20°C until analysis.

Samples for whole-community alkaline phosphatase activity (APA) were collected from 10 depths between 0–300 m on monthly cruises from October 2005 to April 2008. Immediately following collection APA assays were conducted. Gravitational phosphorus fluxes were quantified using surface tethered particle interceptor traps (PITs) starting in October 2005 (Knauer et al., 1979). Acrylic tubes (0.0039 m^2 cross sectional

area) were fitted with acid-cleaned (10% HCl) polycarbonate membrane filters (0.8 μm) at the bottom and then filled with poisoned seawater brine (0.7% formaldehyde, ~50 g NaCl l^{-1} above ambient seawater salinity). Triplicate tubes were deployed at each of 150, 200, and 300 m depths for ~72 h on monthly BATS Core cruises. Following recovery, tubes were allowed to stand for several hours and seawater was siphoned off to the brine/seawater interface. Each tube was then drained through the filter at the bottom of the tube with the filter stored damp at 4°C and samples of the brine solution stored at −20°C until further processing as described below.

Other hydrographic and biogeochemical measurements have been collected at the BATS site each month since October 1988. Details on sample collection and analysis for these other parameters can be found in the BATS Method Manual (Knap et al., 1997) or online (http://bats.bios.edu/). Access to all the BATS data is through the BATS web page (http://bats.bios.edu/).

2.2 Sample analysis

2.2.1 Particulate phosphorus

Particulate phosphorus (PPhos) samples were analyzed using the ash-hydrolysis method of Solarzano and Sharp (1980). No efforts were made to separate particulate inorganic from organic phosphorus so data are simply referred to as particulate phosphorus. In addition, there is some evidence that the use of GF/F filters may lead to variable overestimation of PPhos concentrations, presumably due to adsorption of DOP to the filter (Ammerman, unpublished data); no corrections were made to PPhos concentrations for this possibility. For analysis, sample filters were placed in acid-cleaned (10% HCl) and pre-combusted glass scintillation vials along with 2 ml of 0.017 M $MgSO_4$, dried down at 80–90°C and then combusted at 500°C for 2 h. After cooling to room temperature, 5 ml of 0.2 M HCl was added to each vial and hydrolyzed at 80°C for 30 min. After cooling to room temperature, SRP mixed reagent was added (Parsons et al., 1984), sample was clarified by centrifugation, and absorbance read

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at 885 nm. Samples were calculated against a potassium monobasic phosphate standard. Oxidation efficiency and standard recovery was tested with each sample run using an ATP standard solution and a certified phosphate standard (Ocean Scientific International Ltd. Phosphate Nutrient Standard Solution). In our laboratory, the precision of this method is ~9% at 2.5 nmol l^{-1} (the lowest concentrations typically observed well below the euphotic zone), and ~1% at 15 nmol l^{-1} (typical euphotic zone concentrations). The method detection limit, defined herein as three times the standard deviation of the lowest standard (2.5 nmol l^{-1}) is ~0.1 nmol l^{-1}.

2.2.2 Dissolved inorganic phosphate (MAGIC-SRP)

Dissolved inorganic phosphate (SRP) concentrations in the euphotic zone of the Sargasso Sea are below the analytical detection limits (~20 nmol l^{-1}) of standard nutrient autoanalyzers. Data presented here were analyzed using the Magnesium Induced Co-precipitation method (Karl and Tien, 1992; Rimmelin and Moutin, 2005) and referred to as MAGIC-SRP in this manuscript. Several modifications to the method are as follows. Sodium hydroxide (3 M) is added to replicate 50 ml samples at a 1:45 vol:vol ratio, samples are shaken and allowed to react for 5 min shaken again and then centrifuged to form the $Mg(OH)_2$ pellet. The supernatant was decanted and the pellet dissolved in 6 ml of 0.25 M trace metal grade HCl, thus concentrating SRP by 8.3-fold. Arsenate reagent (Johnson, 1971) was added (1:10 vol:vol ratio) to each sample, allowed to react for 15 min and then the SRP mixed reagent added to quantify absorbance at 885 nm (Parsons et al., 1984). It is assumed that following addition of the Arsenate reagent, only SRP remains to react with the color reagents (Karl and Tien, 1997). There is evidence that the MAGIC-SRP method does remove some DOP compounds from solution (whether it be direct scavenging or base hydrolysis of DOP compounds). The potential inclusion of DOP is not accounted for in these calculations and therefore our estimates of MAGIC-SRP concentration may be slight overestimates of actual SRP concentrations. Samples were calculated against a potassium monobasic phosphate standard, made up in phosphate free seawater, and the accuracy of this

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standard checked on each run with a certified standard (Ocean Scientific International Ltd. Phosphate Nutrient Standard Solution). The method detection limit following this protocol is ~1–2 nmol l^{-1} with a precision of±5% at 5 nmol l^{-1}. MAGIC-SRP concentrations compare favorably with BATS autoanalyzer SRP concentrations (MAGIC-SRP = 1.01 × Autoanalyzer – 17.3 nmol l^{-1}).

2.2.3 Total dissolved phosphorus and dissolved organic phosphorus

Total dissolved phosphorus (TDP) concentrations were quantified using the high temperature/persulfate oxidation technique as described by Ridal and Moore (1990) with the following modifications. Samples and standards were autoclaved in polypropylene bottles, and following oxidation were concentrated using the MAGIC-SRP method described above to improve method sensitivity. With each batch of samples, standard solutions of glycerophosphate and phosphonic acid were run to monitor oxidation efficiency. Additional blanks were run with each batch of samples to correct for any contamination associated with the bottles and oxidation and detection reagents. Samples were calculated against a potassium monobasic phosphate standard, made up in phosphate free seawater, and the accuracy of this standard checked on each run with a certified standard (Ocean Scientific International Ltd. Phosphate Nutrient Standard Solution). The method detection limit is 10–15 nmol l^{-1}, with a precision for the 45 nmol l^{-1} standard of ~±4%. Dissolved organic phosphorus (DOP) concentrations are calculated by subtracting MAGIC-SRP from TDP concentrations.

2.2.4 Alkaline phosphatase activity

Whole-community alkaline phosphatase activity (APA) was quantified by following the hydrolysis of the highly sensitive fluorescent substrate 6,8-difluoro-4-methylumbelliferyl phosphate (Invitrogen Inc.), which permits continuous incubation of samples without the need to raise the pH to maximize fluorescence. The assays were conducted according to the methods of Ammerman (1993), except that a saturating substrate

concentration of 10 μmol l^{-1} was used, and therefore the rates presented in this paper are potential hydrolysis rates. All assays were run as a continuous time-course (5–6 h total duration) with samples read hourly on a Turner Designs TD-700 fluorometer with an Alkaline Phosphatase filter set (Long Wavelength UV Filter Kit; P/N 10-302R). Abiotic substrate hydrolysis was accounted for in killed controls that were boiled and cooled prior to substrate addition. APA rates were calculated from the slope of fluorescent intensity over time after subtracting fluorescence changes in killed controls (Ammerman and Glover, 2000).

2.2.5 Phosphorus export fluxes

Samples for particulate phosphorus export (Pflux) were picked free of swimmers following standard BATS protocols (Knap et al., 1997). Samples are examined under both 120× and 250× total magnification and all zooplankton removed with fine-tipped forceps. After picking, using a surgical scalpel, all remaining particulate material was scraped into a bolus in the center of the filter. Deionized water was carefully placed on the bolus dropwise to flush away any residual salt, the bolus was dried overnight at 65°C, and analyzed for phosphorus content as described above for PPhos analyses. Additionally, starting in August 2007, MAGIC-SRP was measured in the trap brine solution to account for dissolution/remineralization during trap deployment. The same protocol was used as above for MAGIC-SRP, except all standards were made up in the initial poisoned seawater brine.

3 Results

3.1 Particulate phosphorus

PPhos samples have been analyzed from November 2003 to November 2008 representing five annual cycles. A clear seasonal signal is present with maximum PPhos

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concentrations occurring throughout the euphotic zone at the time of the spring bloom, and minimum annual concentrations generally occurring in the fall period associated with the deep chlorophyll maximum (Figs. 1, 2 and Table 1). Spring PPhos concentrations (16.4±3.0 nmol l^{-1}) were significantly (P=0.003) greater than fall PP concentrations (9.1±1.7 nmol l^{-1}), but not any other season. Generally, PPhos concentrations ranged from <5 nmol l^{-1} below the euphotic zone to ~20 nmol l^{-1} in the euphotic zone. During the spring in each year, when euphotic zone PPhos was highest, elevated PPhos concentrations were found at depths >100 m consistent with the annual peak in PPhos export, and deeper mixed layers resulting in 'turbulent drainage' during spring blooms (Backhaus et al., 2003). During the stratified summer period, PPhos concentrations at depths >100 m were always <2 nmol l^{-1}, and <10 nmol l^{-1} within the euphotic zone, consistent with the annual minimum in P export fluxes and anticipated increases in P recycling within the upper water column. Integrated euphotic zone PPhos inventories were on average 2- to 3-fold greater than MAGIC-SRP inventories regardless of the season suggesting a high demand on phosphorus pools to support growth of microbial biomass.

3.2 Dissolved inorganic phosphate (MAGIC-SRP)

MAGIC-SRP measurements have been made from March 2004 to November 2008. Generally, concentrations were low and uniform over the euphotic zone (0–100 m) for each season, although occasionally, mean 0–100 m [SRP] exceeded the nominal method detection limit (MDL) for standard autoanalyzer methods (~20 nmol l^{-1}) due to particularly high concentrations at 80–100 m (Fig. 3). No reproducible seasonal cycle in [SRP] was observed due to significant variability in the annual cycle between years (Fig. 3, Table 1). In 2004 and 2005, there was an increase in SRP (albeit for only 1 cruise) during the spring, with easily detectable concentrations observed throughout much of the euphotic zone, that were then depleted throughout the remainder of the year (Fig. 3). In contrast in 2006–2008 seasonal patterns in [SRP] were much less apparent and more variable cruise-to-cruise (Fig. 3).

3.3 Dissolved organic phosphorus

Dissolved organic phosphorus (DOP) was the largest measured phosphorus pool in the Sargasso Sea, and was on average 4- to 7-fold larger than the SRP or PPhos pools (Figs. 1, 4 and Table 1). Due to substantial year-over-year (mid 2004–late 2007) variability, driven by biological demand for phosphorus, [DOP] displayed a weak average seasonal pattern with maximum concentrations in winter that slowly decreased through the summer (Fig. 4, Table 1). [DOP] were statistically similar throughout the euphotic zone (Fig. 1). In 2005 and 2006 [DOP] clearly decreased from winter to summer, but in late 2006 through mid-2007, showed the opposite pattern. These year-over-year patterns were not related to local hydrographic forcing as there were negligible differences in annual minimum and maximum temperatures during this time. Phytoplankton biomass (as Chla) and primary production during the winter/spring of 2007 were ~50% higher than any other winter/spring period during this study period (Fig. 4b), and consequently so was the likely demand for phosphorus, perhaps resulting in the substantial drawdown of DOP observed during this period (Fig. 4).

3.4 Whole-community alkaline phosphatase activity

Whole community alkaline phosphatase activity (APA) was measured from October 2005 to April 2008. Highest potential rates were observed in the euphotic zone, during winter/spring when PPhos and primary production was highest and [DOP] began to decrease. Indeed, integrated and volumetric APA had a clear seasonal signal with significantly higher values in spring ($P<0.05$) than summer and fall seasons (Fig. 5, Table 1). Volumetric rates ranged from 0–14 nmol l^{-1} h^{-1}, although most often rates were <5 nmol l^{-1} h^{-1} (Fig. 5). The similarity in seasonal and depth distributions for [PPhos] and whole-community APA (Pearson Correlation; $r=0.63$, $P=0.002$) suggests that much of the measured whole-community APA is associated with particles and not in solution (i.e., <0.2 μm; Sebastian and Niell, 2004). This is also consistent with our own observations that rates of APA in the <0.2 μm are generally low (<5%)

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relative to the whole-community rates. Furthermore, APA and [DOP] display similar temporal and vertical patterns (cf. Figs. 4 and 5), although this correlation is not significant (Pearson Correlation; r=0.35, P=0.15). Highest APA values were found when [SRP] was <10 nmol l^{-1} (Fig. 5b).

3.5 Phosphorus export fluxes

Particulate phosphorus export fluxes (Pflux) have been measured from October 2005 to November 2008, covering three annual cycles. Particulate phosphorus export has a seasonal pattern with significantly (P=0.05) higher fluxes at 150 m in the spring, 8.2±3.1 μmol m^{-2} d^{-1}, than the fall, 5.8±2.5 μmol m^{-2} d^{-1} (Fig. 6, Table 1). As with the other parameters, year-over-year variability in seasonal signals was substantial, with Pflux in 2007 and 2008 showing a much weaker/non-existent seasonal signal. Solubilization of phosphorus during the trap deployment was extensive. The flux calculated from the accumulation of SRP in the brine ranged from 70–95% of the total (sum of Pflux and SRPflux) flux. Although the SRPflux record is too short to comment on year-over-year variability, for the data available no clear seasonal signal is obvious in the total flux (Table 1). Pflux attenuated with depth as expected, with most of the seasonal signal attenuated by 300 m (Table 1).

4 Discussion

4.1 Seasonality of the Sargasso Sea phosphorus cycle

The northwestern Sargasso Sea, near the BATS site (31°40′ N, 64°10′ W) is at the southern extent of seasonal atmospheric forcing in the subtropical North Atlantic, and has a seasonal signal with a spring phytoplankton bloom that generally occurs between February and April (e.g., Michaels and Knap, 1996; Steinberg et al., 2001). Seasonality of biogeochemical cycles was first studied in the Sargasso Sea near Bermuda in the

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1950's (e.g., Menzel and Ryther, 1960, 1961). However, due to the long entrenched belief that nitrogen is the primary macronutrient controlling rate processes in the ocean (e.g., Ryther and Dunston, 1971), relatively little attention has been paid to seasonality of the phosphorus cycle in the Sargasso Sea (Michaels et al., 1994a, 1996). This has only been reinforced by the low SRP concentrations that are difficult to measure.

The phosphorus concentration data collected as part of this study in the western subtropical North Atlantic compare favorably with other studies that have measured various phosphorus pools in the subtropical North Atlantic (Table 2). Case (2001) conducted a seasonal study at the BATS site from 1996–1998. Due to SRP method limitations, ~12 nmol l^{-1} method detection limit, no seasonal pattern was observed; however, a seasonal pattern was clearly evident in their PPhos, DOP and APA data records. All three parameters were highest during the winter/spring bloom period: PPhos was highest due to growth and accumulation of phytoplankton, which increased demand on the SRP pool resulting in increased P-stress, the induction of APA and ultimately the hypothesized net consumption of DOP in support of primary production. The present study reinforces and expands upon this interpretation of the seasonal pattern in phosphorus biogeochemistry in the western subtropical North Atlantic. Despite nearly an order of magnitude more sensitive SRP analysis, SRP concentrations remain low and invariant over the seasonal cycle (Fig. 3) and are roughly one third of the euphotic zone integrated PPhos pool which is maximal during the winter/spring bloom (Table 1). Maximum PPhos during the winter/spring bloom, coupled with high net phytoplankton growth rates (0.6–0.9 d^{-1}; Malone et al., 1993) and rapid turnover of the ambient SRP pool (3–5 h; Ammerman et al., 2003) during this same time of year strongly suggest that phytoplankton are relying on the much larger DOP pool for growth. Correlation analysis demonstrates a significant negative relationship between euphotic zone integrated stocks of PPhos and DOP, and no relationship with average euphotic zone temperature (as a proxy for convective mixing of deep water and physical dilution of high DOP surface waters with low DOP deep water) supporting our hypothesis that DOP is consumed in support of the winter/spring bloom (Fig. 4, Table 3). This is a pattern

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that repeats over several years, although year-over-year variability is quite large in this region of the subtropical North Atlantic. This variability could be driven by changes in physical forcing on biological productivity, as well as larger scale changes in the gyre circulation patterns and resultant Ekman nutrient fluxes through the gyres. Transect studies by Jakuba et al. (2008) and Mather et al. (2008), also conducted during the spring period in the western subtropical North Atlantic, reach similar conclusions that DOP is an important phosphorus source supporting phytoplankton production, although those studies base conclusions on DOP concentrations and APA activities alone.

4.2 Contribution of DOP to primary and export production in the Sargasso Sea

A common metric for assessing nutrient stress in phytoplankton is the comparison of measured elemental ratios to the Redfield Ratio (Redfield, 1958); a ratio believed to reflect the balanced elemental composition of marine particles. Arithmetic calculation of elemental POC:PPhos and PON:PPhos ratios of suspended euphotic zone particles in the time-series presented here (2004–2007) are consistent with those reported for 1996–1997 (Ammerman et al., 2003) and average 207±69 and 34±13, respectively; twice the canonical Redfield Ratios of 106:1 and 16:1 (Table 4). There are no significant seasonal or year-over-year differences in elemental ratios (one-way ANOVA, all pair-wise comparisons $P>0.1$), although there is a tendency for POC:PPhos ratios to increase in the summer and fall, which is consistent with increasing P-stress during periods of prolonged stratification. Plotting the same data against each other and calculating the least squares linear regression, which also is the POC:PPhos ratio, one would reach a very different and perhaps more ecologically relevant, conclusion. For the period 2004–2007 the linear regression fit of POC vs. PPhos was 100±8 (Fig. 7, Table 4), statistically identical to the ratio of ~106 observed a decade earlier (Case, 2001) and the Redfield Ratio of 106:1. Ratios for PON vs. PPhos were 14±1.4, 16.5 and 16:1 for this study (Fig. 7), Case (2001) and Redfield, respectively. This suggests

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that as plankton grow and accumulate, much of which occurs during the winter/spring bloom, they do so in Redfield proportions, despite very low SRP concentrations.

To better constrain various phosphorus fluxes and quantitatively evaluate the role of DOP in supporting phytoplankton growth and primary production, we construct an approximate flux budget for the BATS region (Fig. 8). For the period 2004–2008, annual primary production at BATS was 13.5±2.1 mol C m^{-2} y^{-1}. Using the linear regression POC:PPhos ratio for particles analyzed during this same period, the estimated annual phosphorus demand is 135±58 mmol P m^{-2} y^{-1}. Estimates of vertical SRP input from convection, diapycnal diffusion and eddy upwelling range from 21–31 mmol m^{-2} y^{-1} based upon nitrogen inputs (McGillicuddy et al., 1998) and measured 100–200 m nitrate:phosphate ratios (Karl et al., 2001b) or modeled inputs (McGillicuddy and Robinson, 1997). Something that has not been considered in previous phosphorus budgets are vertical inputs of DOP. [DOP] are measurable between 100–200 m, but there is little to no gradient in the profiles, so vertical fluxes should be minimal. Overall, these results highlight an imbalance in phosphorus demand and vertical supply that is further exacerbated after accounting for export fluxes.

Sediment trap based export fluxes comprise two components, what remains as particles and what is solubilized during trap deployment. The importance of solubilization of material captured in sediment traps, and its impact on elemental ratios due to differential solubilization has recently been reviewed (Antia, 2005). Antia (2005) concludes from a range of sediment trap deployments that 70–90% of total phosphorus flux and 30% of total organic carbon flux is solubilized during trap deployment. From the current study, the solubilized SRPflux, as a fraction of the total, ranged from 70–95% (Table 1). Carbon solubilization was not measured, so we used the values given in Antia (2005) to estimate a correction for carbon export fluxes so that elemental ratios can be compared between what is produced in the euphotic zone and what is captured in the traps (Table 1). As calculated for suspended particles, exported material trapped at 150 m was found to have POC:PPhos and PON:PPhos ratios that are greater than those of the suspended material in the euphotic zone (Table 4). Indeed, the POC:PPhos

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ratio nearly doubled between the euphotic zone (0–100 m) average and the 150 m trap, suggesting that nearly half of the PPhos had already been remineralized before particles were captured in the trap. This additional remineralization was accounted for to better constrain the amount of phosphorus gravitationally settling from the base of the euphotic zone. The phosphorus flux from the euphotic zone was estimated at 23 mmol m^{-2} y^{-1} with 12.8 mmol m^{-2} y^{-1} exported below 150 m and the remainder remineralized between these two depths, and therefore potentially supporting further euphotic zone phosphorus demand (Fig. 8). While this shallow recycling narrows the imbalance in the phosphorus budget there are still significant gaps between supply and demand.

These observations reinforce the hypothesis that DOP may be a critically important pool supporting primary production in the subtropical North Atlantic (Mather et al., 2008): there are several lines of supporting this hypothesis in the Sargasso Sea. The induction of APA is commonly used as a metric to determine inorganic P-stress and therefore utilization of DOP in support of primary production (e.g., Matheret al., 2008; Sebastian et al., 2004). Using the measured APA results (Fig. 5) and constants derived from kinetic experiments conducted in the Sargasso Sea (Strojsova et al., unpublished data) in situ euphotic zone APA estimates suggest that DOP hydrolysis would provide 82±18 mmol P m^{-2} y^{-1} or ~60% of the estimated annual phosphorus demand. Mather et al. (2008) made the same calculation for the eastern North Atlantic and found that 12–30% of primary production was supported by DOP. This cross-gyre gradient is consistent with observations of much greater DOP drawdown from east to west (Mather et al., 2008). Local seasonal drawdown of DOP at BATS is a tiny fraction (~2%) of this DOP hydrolysis estimate suggesting a required exogenous source of DOP to the subtropical gyre. Roussenov et al. (2006), based upon data originally presented in Mahaffey et al. (2004) from the eastern subtropical North Atlantic, suggest that throughout the subtropical North Atlantic there is net production of DOP (and DON; see also Williams and Follows, 1998) in upwelling areas near the gyral boundaries and that some of the DOP produced is ultimately transported into the subtropical

gyre via surface Ekman flow from the south where it supports a large component of primary and export production.

We have compiled available DOP transect data for the western subtropical North Atlantic. In contrast to the eastern North Atlantic, there is an increasing gradient from 20–38° N (Fig. 9). We do not have data from the equator and 20° N where Mahaffey et al. (2004) show a DOP gradient in the eastern North Atlantic to be from the equator to 10° N. Using the average (1992–2002) Ekman transport from just north of the BATS region $\sim 0.05 \times 10^6\,m^3\,s^{-1}$ (34° N, data from .Gordon and Giulivi, 2008) and the DOP concentration at 34° N, $\sim 150\,\mu mol\,m^{-3}$ (Fig. 8), we estimate the DOP transport rate into the BATS region (here defined as 34–28° N, 70–60° W) as $\sim 43\,mmol\,m^{-2}\,y^{-1}$. This southward Ekman flux of DOP could account for ~32% of annual phosphorus demand at BATS. A similar calculation for SRP (Lomas et al., unpublished SRP concentrations) results in an estimated SRP transport rate of $\sim 22\,mmol\,m^{-2}\,y^{-1}$. The flux of nutrients ($mol\,time^{-1}$) approaches zero with the decrease in Ekman volume flow to 28° N (the BATS site is at 31°40 N). It is worth noting that DOP measurements are needed for the western tropical North Atlantic closer to the equator to determine if there is a northward DOP flux as there is in the eastern North Atlantic.

Compiling all of the terms calculated in this section and data from the literature a first order phosphorus budget can be completed for the BATS region (Fig. 8). The remaining term is atmospheric deposition. Atmospheric inputs of phosphorus, while perhaps important as singular events, are a minor source of phosphorus to the euphotic zone over the year (Baker et al., 2003; Michaels et al., 1996). While all of the input terms in this budget have large uncertainties, their sum ($\sim 96\,mmol\,P\,m^{-2}\,y^{-1}$) balances the biological phosphorus demand of $135 \pm 58\,mmol\,P\,m^{-2}\,y^{-1}$ (Fig. 8). Therefore, we conclude that most of the necessary inputs of phosphorus have been accounted for and that exogenous DOP supports 30–60% of primary production in the western subtropical North Atlantic.

This latter conclusion of an exogenous DOP source is a crucial component in the argument that DOP supports export production; if DOP is recycled locally it can contribute

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to primary production but not to export production. Based upon modeled estimates of DOP flux between gyres, Roussenov et al. (2006) suggest that between 70–80% of the phosphorus export in the western subtropical North Atlantic is supported by a labile DOP pool, although one must point out that they have no data for in their model from the western North Atlantic. Using the data presented in this manuscript, the southward Ekman flux of DOP (~43 mmol P m^{-2} y^{-1}) is sufficiently large to quantitatively support the observed phosphorus export below 150 m (~12.8 mmol P m^{-2} y^{-1}). Based upon this new data, the model of Roussenov et al. (2006) may be correct and applicable across the entire North Atlantic subtropical gyre.

4.3 Long term changes in *P* cycling

Two phosphorus time-series records exist at BATS, this study and that of Case (2001), and they provide a unique assessment of the role of DOP in the western subtropical North Atlantic over the past decade. Mean DOP concentrations in this study were 30–50% lower than measured a decade earlier at BATS (Case, 2001), and similar to recent transects in the western subtropical North Atlantic near BATS (Mather et al., 2008). The microbial community in the western subtropical North Atlantic readily assimilates DOP (e.g., Casey et al., 2009; Dyhrman et al., 2002; Lomas et al., 2004; Orchard et al., 2009) and a large fraction of the total phosphorus export is believed to be supported by DOP, therefore it is plausible that over the past decade DOP concentrations may have been slowly drawn down via the biological pump. If this process is indeed occurring, then there should be some evidence for it in permanent thermocline waters; here defined as σ_θ=26.55–26.65 which is approximately 500 m depth. Based upon the quasi-conservative biogeochemical tracer SRP_{xs} (cf. Bates and Hansell, 2004), SRP_{xs} concentrations have increased significantly (P=0.001) from 1989 through 2008 at a rate of 1.7±0.5 nmol kg^{-1} y^{-1} (Fig. 10). Over the decade between the two datasets discussed, this would account for the accumulation of ~17 nmol kg^{-1} SRP, or roughly the difference in euphotic zone DOP concentrations between this study and that of Case (2001). This increase in SRP_{xs} over the past 2 decades would also bring euphotic

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zone DOP concentrations in the western subtropical North Atlantic right in line with current DOP concentrations in the eastern subtropical North Atlantic which are hypothesized to be higher due to lower total phosphorus demand (Mather et al., 2008) and/or higher SRP inputs and greater recycling (Cianca et al., 2007; Helmke et al., accepted pending revision). More importantly, permanent thermocline waters appear to be returning to Redfield stoichiometry (SRP_{xs}=0) from an SRP depleted state hypothetically driven by nitrogen fixation (e.g., Michaels et al., 2001). We are only beginning to understand these multi-year to decadal changes in elemental stoichiometry in the ocean and the controls exerted on these ratios by the amazing diversity of ocean biota (Karl et al., 2001a).

4.4 Summary

Taken together, the data presented in this manuscript suggest that even if the Sargasso Sea near BATS is inorganic phosphorus stressed, this stress has not, as yet, negatively impacted microbial biomass and rate processes, perhaps it has even allowed for an increase in rate processes given that primary production has doubled from 1997 to present, (Lomas et al., 2009). Maintaining this microbial activity has placed a heavy biological demand on the DOP pool resulting in its decrease over the past decade. The data presented here support the hypothesis first proposed by Roussenov et al. (2006) for the eastern subtropical North Atlantic, that productivity in the subtropical North Atlantic is fueled in part by the exogenous supply of DOP from the tropical and subpolar gyres. However, we cannot completely rule out changes in atmospheric phosphorus inputs supporting primary production due a lack of temporal data (Tian et al., 2008). Based upon the data in this manuscript, we suggest that forecasting models of ocean productivity should consider not only changes in vertical mixing and atmospheric inputs, but also cross gyral organic nutrient inputs to the subtropics which dominate global productivity (e.g., Behrenfeld et al., 2006).

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Table 1. Seasonal mean (±stdev) euphotic zone phosphorus inventories and rates. Integration depths are given with each parameter. Total P export is sum of particulate and SRP fluxes. See text for additional details.

	Seasonally averaged phosphorus inventories			
	Winter (DJF)	Spring (MAM)	Summer (JJA)	Fall (SON)
PPhos(∫0–100 m; mmol m^{-2})	1.8±1.5	1.4±0.4	1.3±0.5	1.0±0.3
MAGIC-SRP (∫0–100 m; mmol m^{-2})	0.5±0.4	0.7±0.7	0.6±0.6	0.4±0.2
DOP (∫0–100 m; mmol m^{-2})	6.1±3.5	5.8±2.0	5.6±1.9	6.9±2.2
	Seasonally averaged phosphorus rate processes			
	Winter (DJF)	Spring (MAM)	Summer (JJA)	Fall (SON)
APA (∫0–140 m; μmol m^{-2} h^{-1})	248±121	300±108	200±99	190±55
$^{33}P_i$ uptake (∫0–140 m; μmol m^{-2} h^{-1})	n.d.	75.8–141	n.d.	25.4
^{33}ATP uptake (∫0–140 m; μmol m^{-2} h^{-1})	n.d.	4.2–8.6	n.d.	2.8
Particulate export at (μmol m^{-2} d^{-1})				
150 m	7.6±7.4	8.2±3.1	6.9±3.7	5.8±2.5
200 m	4.7±2.9	5.4±2.9	4.2±3.0	2.9±1.3
300 m	2.5±1.4	2.7±1.2	2.6±1.5	1.9±0.9
Total P export (μmol m^{-2} d^{-1})				
150 m	39.2±19.9	34.0±22.8	38.8±5.6	24.0±9.4
200 m	41.3±24.2	25.7±22.8	24.7±6.7	25.6±12.2
300 m	31.2±26.6	17.4±14.9	24.1±2.6	14.1±6.9

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Table 2. Summary of published phosphorus stock measurements in the subtropical North Atlantic, separated by season. All concentrations are given in nmol l^{-1} and APA in units of nmol l^{-1} h^{-1}, except where noted in the footnote. Data are given as ranges, means (±stdev) or estimates depending upon how it was presented in the original publication. Eastern subtropical North Atlantic samples are denoted by italics.

Lat/Long	Season	Depth (m)	[SRP]	[PPhos]	[DOP]	APA	Ref.
26–38° N, 65–72° W	Spring (Mar)	~3	0.2–20	–	50–100	–	1
26–32° N, 64–70° W	Spring (Mar)	~0.5	0.48±0.27	–	75±42	–	2
25–32° N, 58–65° W	Spring (Mar)	~2	10–50	–	90–170	0.3–2.1	3
20–35° N, 50–64° W	Spring (Mar/Apr)	~10	<1.4–6.3	–	60.2–196.4	2–14	4
31.7° N, 64.2° W	Spring (Mar–May)	0–100	~15	~15	~75	5–15	5, 15
20–50° N, 20° W	*Spring (Mar/Apr)*	*~3*	*20–300*	–	*50–150*	–	*6*
20–30° N, 20° W	*Spring (Mar/Apr)*	*5*	< 100	*~25*	–	*0–25*	*7, 8*
31–32° N, 59–60° W	Summer (Jun)	~3	10–20	–	–	–	9
31.7° N, 64.2° W	Summer (Jun–Aug)	0–100	~15	~12	~60	1–5	5, 15
22–50° N, 20–40° W	*Summer (Jun)*	*25*	*<5*	–	*50–150*	*0.5–4.5*	*10*
27–28° N, 13–16° W	*Summer (Aug)*	*0–100*	*0.04–0.53*	*1–186*	–	*0.02–0.18*	*11*
30–31° N, 71–72° W	Fall (Nov)	surface	5–7.5	–	–	–	12
41° N, 64° W	Fall (*Sep*)	0–200	–	–	70–100	–	13
31.7° N, 64.2° W	Fall (Sep–Nov)	0–100	~15	~10	~90	1–3	5, 15
20–30° N, 20° W	*Fall (Oct/Nov)*	*~25*	*225–425*	*25–150*	*100–300*	*~5*	*7, 8*
22–50° N, 20–40° W	*Fall (Nov)*	*25*	*<5*	–	*200–325*	*0.5–1.5*	*10*
20–25° N, 20–32° W	*Fall (Sep/Oct)*	*~0.5*	*60±60*	–	*200±50*	–	*14*

References: (1) Cavender-Bares et al., 2001; (2) Wu et al., 2000 – average of all stations, [DOP] is actually [TDP]; (3) Sohm and Capone, 2006; (4) Wisniewski-Jakuba et al., 2008; (5) Case, 2001 – all data estimated from Fig. 6; (6) Mahaffey et al., 2004; (7) Vidal et al., 1999; (8) Vidal et al., 2003; (9) Li et al., 2008; (10) Mather et al., 2008 – APA in units of nmol l^{-1} h^{-1} μgC^{-1}; (11) Sebastian et al., 2004 – APA are at tracer level additions; (12) Dyhrman et al., 2002; (13) Ridal and Moore, 1990; (14) Reinthaler et al., 2008; (15) Ammerman et al., 2003

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Table 3. Correlation matrix of Sargasso Sea euphotic zone (0–100 m) integrated properties. For each comparison, the top number is the correlation coefficient (with the appropriate sign), the second number is the P-value, significant ($P<0.05$) correlations are denoted in bold, and the third number is the number of data points in the correlation. Data categories are: DecYr = decimal year; PPhos = particulate P; DOP = dissolved organic phosphorus; Pflux = particulate P flux at 150 m; PP = primary production; T°C = temperature averaged over 0–100 m; SRP = soluble reactive phophorus; APA = alkaline phosphatase activity.

	PPhos	DOP	Pflux	PP	T°C	SRP	APA
DecYr	**−0.32** **0.02** **58**	0.22 0.20 35	**−0.49** **<0.01** **31**	**−0.50** **<0.01** **52**	**0.76** **<0.01** **41**	−0.18 0.20 55	0.10 0.65 21
PPhos		**−0.32** **0.05** **35**	0.09 0.66 30	**0.40** **<0.01** **51**	**−0.35** **0.03** **41**	0.20 0.15 54	0.34 0.16 19
DOP			**−0.44** **0.04** **21**	−0.19 0.28 34	−0.06 0.74 31	0.11 0.53 35	*0.35* *0.17* *17*
Pflux				0.32 0.11 26	**−0.52** **0.03** **17**	−0.07 0.69 31	0.31 0.20 18
PP					**−0.53** **<0.01** **40**	0.26 0.07 48	−0.17 0.48 19
T°C						−0.20 0.23 37	−0.23 0.46 13
SRP							−0.23 0.31 21

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Table 4. Elemental ratios for euphotic zone suspended particles and particles captured in surface tethered traps at the depths noted. Trap particles: corr. are those corrected for solubilization of nutrient elements during trap deployment. See text for additional details.

Parameter	POC:PPhos (mol mol^{-1})	PON:PPhos (mol mol^{-1})
Suspended Particles		
Arithmetic mean	207±69	34±13
Linear regression	100±8	14±1.4
Trap Particles		
Arithmetic mean		
150 m	359±186	59±34
200 m	443±233	69±42
300 m	499±239	67±40
Linear regression		
150 m	255±57	45±12
200 m	216±66	28±
300 m	364±105	44±
Trap Particles: corr.		
Arithmetic mean		
150 m	259±134	48±27
200 m	320±168	57±34
300 m	361±201	55±33
Linear regression		
150 m	184±42	37±9
200 m	156±48	23±9
300 m	263±76	36±11

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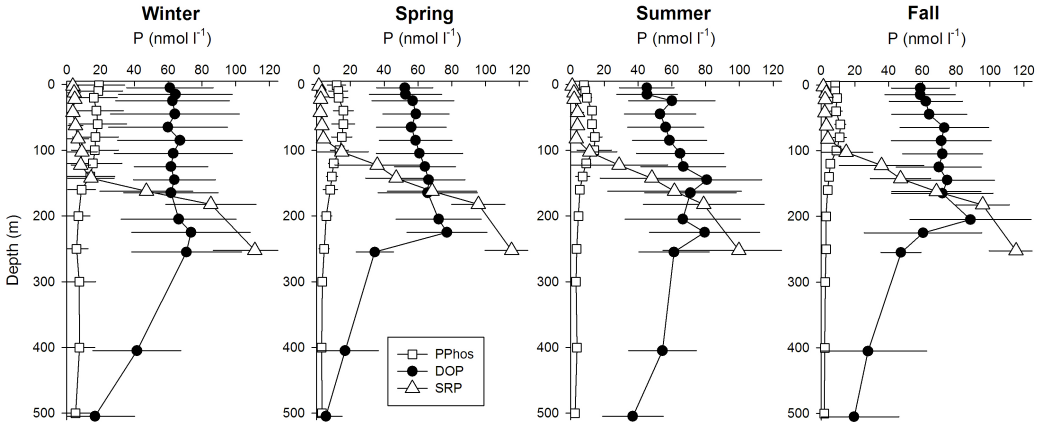

Fig. 1. Seasonal mean (±stdev) profiles of PPhos (squares), DOP (filled circles), and MAGIC-SRP (open triangles) at BATS. All concentrations are in nmol l^{-1}. n=6–15 for each depth depending upon season and phosphorus pool. Depths are slightly offset such that error bars do not overlap.

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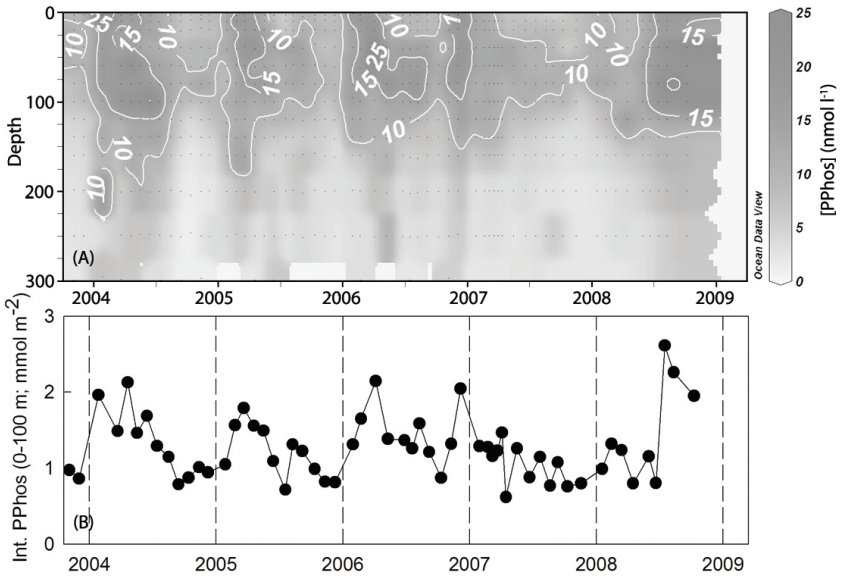

Fig. 2. **(A)** Time-series contour plot of PPhos concentrations (nmol l^{-1}) in the upper 300 m of the Sargasso Sea, and **(B)** time-series of euphotic zone (0–100 m) integrated PPhos inventories (mmol m^{-2}).

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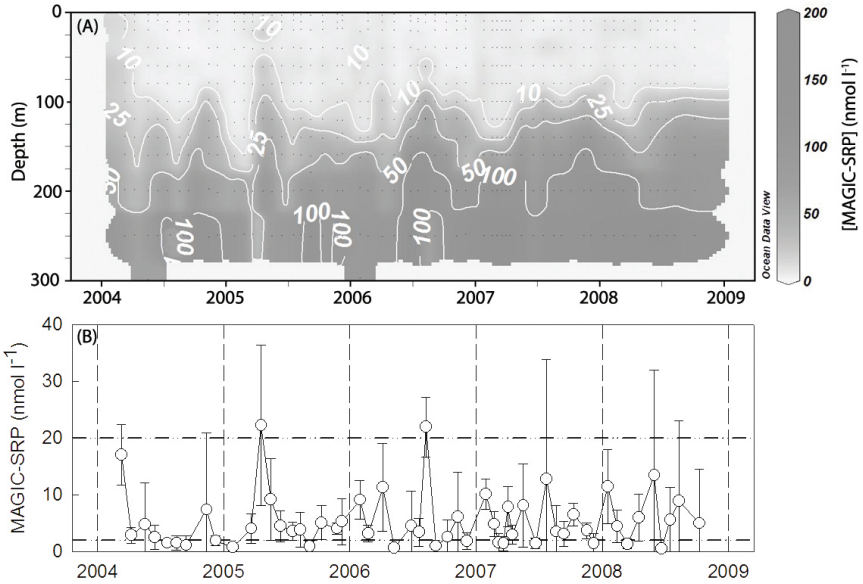

Fig. 3. (A) Time-series contour plot of MAGIC-SRP concentrations (nmol l^{-1}) in the upper 300 m of the Sargasso Sea, and **(B)** time-series of euphotic zone (0–100 m) averaged MAGIC-SRP concentrations (nmol l^{-1}). The dash-dot lines denote the method detection limits (MDL) for standard autoanalyzer methods (~20 nmol l^{-1}) and our MAGIC-SRP method (~1–2 nmol l^{-1}).

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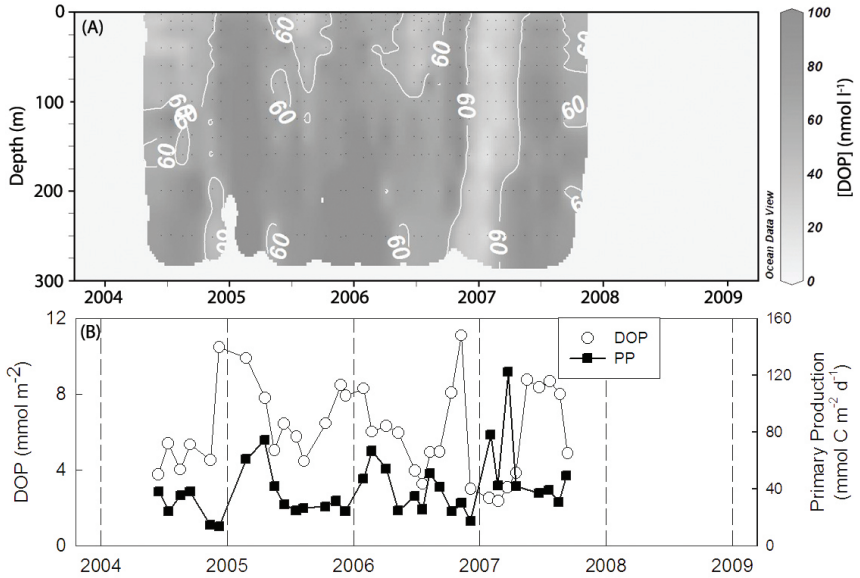

Fig. 4. (A) Time-series contour plot of DOP concentrations (nmol l^{-1}) in the upper 300 m of the Sargasso Sea, and **(B)** time-series of euphotic zone (0–100 m) integrated DOP concentrations (mmol m^{-2}; open circles) and primary production (mmol C m^{-2} d^{-1}; filled squares).

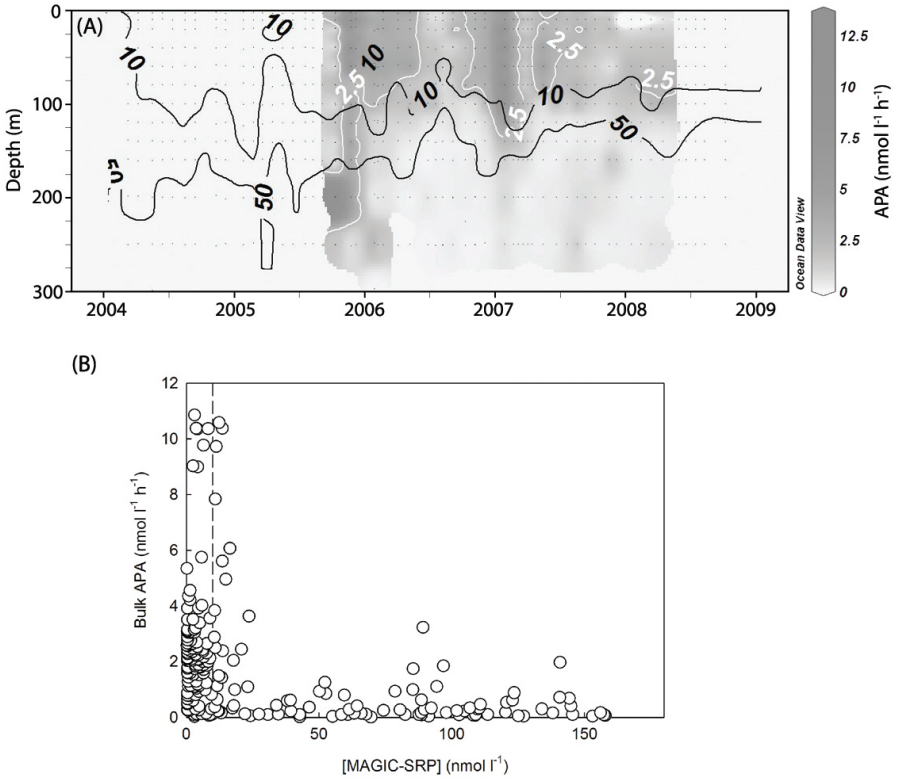

Fig. 5. **(A)** Time-series contour plot of whole-community alkaline phosphatase activity (APA; nmol $l^{-1}\,h^{-1}$). White lines are the contours for APA, and black lines are contours for [SRP] nmol l^{-1}. **(B)** bivariate plot of APA versus ambient SRP concentrations highlighting that the highest APA values are at [SRP] <10 nmol l^{-1} (vertical dashed line).

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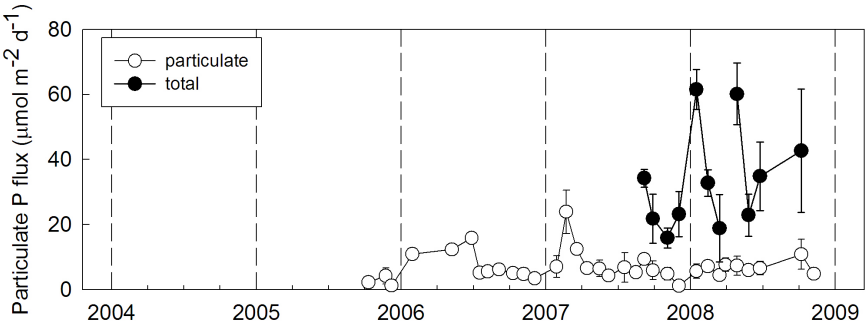

Fig. 6. Time-series of mean (± stdev) particulate phosphorus export fluxes at 150 m (open circles) and the sum of particulate and SRP fluxes (filled circles). See text for description of SRP fluxes. Error bars are stdev of duplicate or triplicate trap tubes.

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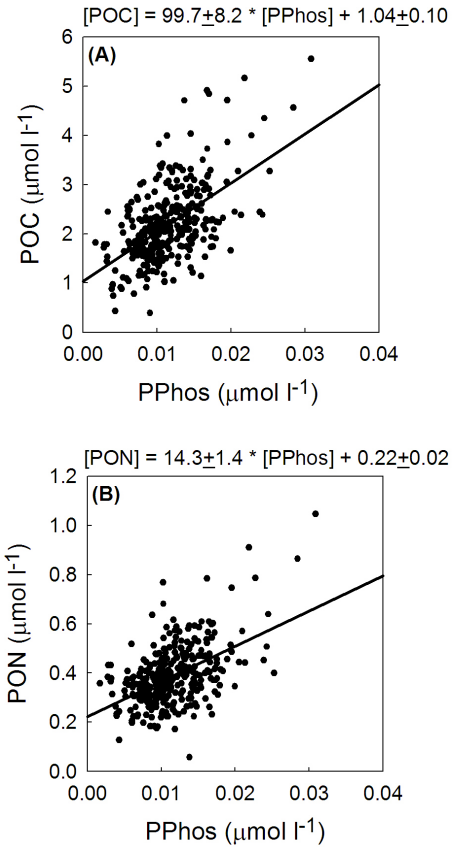

Fig. 7. Bivariate plots of **(A)** particulate organic carbon [POC] vs. [PPhos] and **(B)** [PO] vs. [PPhos] for euphotic zone (0–100 m) particles during this study period. The solid line in each panel is the least squares linear regression. Regression equations are given above each panel.

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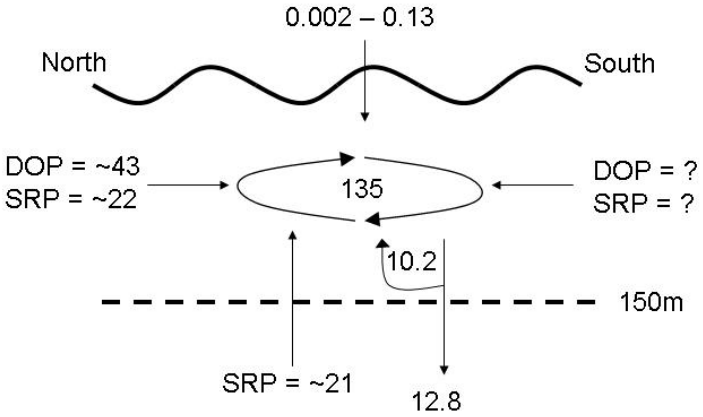

Fig. 8. Phosphorus budget (all fluxes in mmol m^{-2} y^{-1}) for the BATS region. See text for details on flux calculations.

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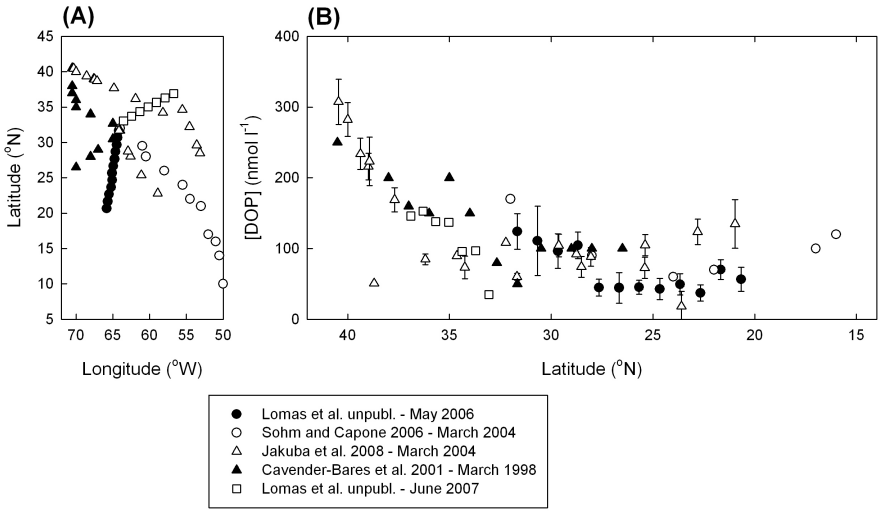

Fig. 9. Compilation of known [DOP] (nmol l^{-1}) from transect cruises in the general BATS area. **(A)** Cruise tracks from which data were collected, and **(B)** [DOP] plotted as a function of latitude. Data were made available by the original author and are identified in the legend.

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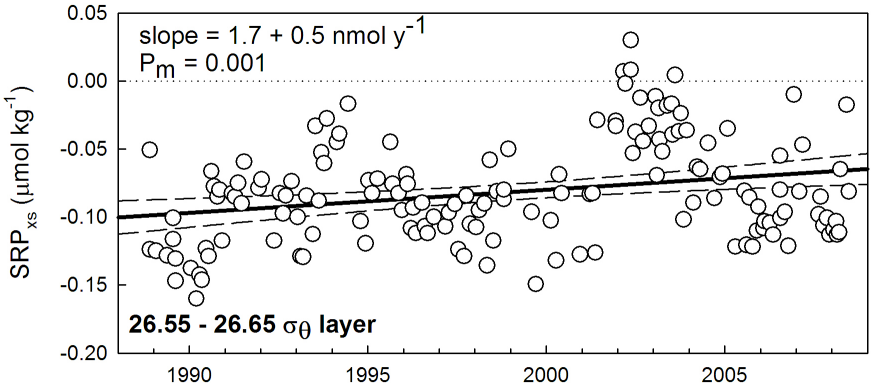

Fig. 10. SRP_{xs} data (calculated as $[SRP_{xs}]=[SRP]-[NO_3]/16$) in permanent thermocline waters at BATS. Data are from the σ_θ=26.55–25.65 kg m^{-3}, which is centered around 500 m.

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