Zonal differences in phosphorus pools, turnover and deficiency across the tropical North Atlantic Ocean

Jill A. Sohm[1] and Douglas G. Capone[1]

Received 24 October 2008; revised 2 September 2009; accepted 4 January 2010; published 13 May 2010.

[1] The oceanic phosphorus (P) cycle is often overlooked in biogeochemical studies because it is dominated by geological processes. However, recent reports indicate that some oceanic regimes are P limited; thus an evaluation of the P pools and the biological cycling of P is warranted in these locations. The subtropical and tropical North Atlantic is one area proposed to be P deficient. A cruise across a wide swath of the tropical North Atlantic (~25–60°W and 0–15°N) allowed us to investigate spatial differences in these parameters, including in waters influenced by the Amazon River plume. The majority of the total P pool was present as dissolved organic phosphorus (DOP, ~80%), with soluble reactive phosphorus (SRP) and particulate organic phosphorus (POP) comprising much smaller fractions. Concentrations of both SRP and POP were elevated in areas influenced by the Amazon River, while DOP was not. The turnover time of the PO_4^{3-} pool was more rapid on the western side of the basin (<10 h) and slower to the east (>100 h). Fast turnover times are indicative of P deficiency, and the observed trend suggests an east to west increase in P deficiency in the tropical North Atlantic. The maximal PO_4^{3-} uptake rate (V_{max}) of *Trichodesmium* spp., a well-studied nitrogen-fixing cyanobacterium, also indicates higher P deficiency in the western compared to eastern basin. These data support the hypothesis that P could be an important nutrient limiting certain biological processes in the North Atlantic, although it may be spatially (as well as temporally) variable in this basin.

Citation: Sohm, J. A., and D. G. Capone (2010), Zonal differences in phosphorus pools, turnover and deficiency across the tropical North Atlantic Ocean, *Global Biogeochem. Cycles*, *24*, GB2008, doi:10.1029/2008GB003414.

1. Introduction

[2] The marine phosphorus (P) cycle is largely free of redox reactions and dominated by the slow geological processes of continental uplift and weathering as the dominant source of P to the ocean via riverine transport, and the burial of marine organic matter as the P sink. Internal cycling of P in the ocean is dominated by the relatively fast biological processes of uptake from and release and degradation to the dissolved inorganic and organic pools [*Benitez-Nelson*, 2000]. Nitrogen (N) has long been held to be the proximate and P the ultimate limiting nutrient for primary production because the P source and sink terms are geological processes, corresponding to a residence time for P in the ocean of ~25,000 years [*Schlesinger*, 1997]. In contrast the N cycle is more dynamic, with a shorter residence time of ~3,000 years [*Codispoti et al.*, 2001], because it can respond to chemical changes in the ocean through the biological processes of nitrogen fixation and denitrification [*Froelich*, 1988]. Additionally, through much of the nitrate (NO^-_3) depleted waters of the oligotrophic upper ocean, there is still a small amount of phosphate (PO_4^{3-}) remaining [*Tyrrell*, 1999]. Because P was thought to limit primary production only in the long-term, biological P cycling has often been overlooked. However, P is a critical macronutrient for protein synthesis (ribosomal RNA), energy generation (ATP), information storage (DNA) and as a component of cell membranes (phospholipids). Moreover, even in putatively N limited waters, certain functional groups such as diazotrophs may be P limited [*Sohm et al.*, 2008]. Finally, new estimates of the residence time of P in the ocean indicate that it could be as short as ~10,000 years [*Benitez-Nelson*, 2000], and several regions of the ocean have been shown to be P limited in the short term for at least parts of the microbial community [*Cotner et al.*, 1997; *Thingstad et al.*, 2005]. This is important because limiting nutrients have the potential to control the strength of the biological pump.

[3] Because the definition and use of the term nutrient limitation can sometimes be ambiguous, it is useful here to discuss some of the terms relating to nutrient status in the ocean. Limitation generally refers to the case when growth rate is determined or controlled by nutrient supply and organisms are acclimated to this condition [*Parkhill et al.*, 2001]. Two terms, starvation [*Parkhill et al.*, 2001] and

[1]Department of Biological Sciences and Wrigley Institute for Environmental Studies, University of Southern California, Los Angeles, California, USA.

0886-6236/10/2008GB003414

deficiency [*Tanaka et al.*, 2006], have been used to define a state where nutrient supply is suboptimal and the physiological status of organisms is altered in response to this reduced supply, but growth is not necessarily limited [*Parkhill et al.*, 2001; *Tanaka et al.*, 2006]. Many assays of nutrient status, such as gene expression, enzyme activity, or nutrient uptake do not specifically measure the effects of potential limiting nutrients on growth, and therefore are measures of nutrient deficiency or starvation in the population being tested. However, these assays are useful in relating the deficiency of samples to each other and have the advantage of being rapid, with low sample perturbation, and using small volumes. Nutrient stress is a generic term that encompasses limitation, starvation and deficiency [*Parkhill et al.*, 2001].

[4] The North Atlantic basin appears to be P deficient [*Ammerman et al.*, 2003]. Upper water column PO_4^{3-} concentrations can be very low here (sometimes < 1 n*M*) compared to other areas of the ocean [*Wu et al.*, 2000], and bacterial growth [*Cotner et al.*, 1997] and respiration [*Obernosterer et al.*, 2003] both respond positively to PO_4^{3-} additions. Another study shows N and P colimitation of bacterial production there [*Mills et al.*, 2008]. The diazotrophic cyanobacterium *Trichodesmium* spp. appears to be P limited in this basin as well [*Sañudo-Wilhelmy et al.*, 2001; *Sohm et al.*, 2008], although N_2 fixation by the entire diazotrophic community (which could include *Trichodesmium* spp.) has been shown to be colimited by P and iron (Fe) in the eastern basin [*Mills et al.*, 2004]. On the other hand, P limitation of primary productivity has not been shown here [*Davey et al.*, 2008]. To the far west in the tropical North Atlantic basin, waters are seasonally influenced by the Amazon River outflow, exhibiting increases in nutrients and productivity where there is a freshwater signal [*Demaster and Aller*, 2001], but it is not well known what nutrients may be limiting in river-influenced areas. Nitrogen limitation has been suggested for the river mouth and shelf areas [*Demaster and Pope*, 1996], and the abundance of nitrogen fixing organisms in plume influenced waters reinforces this theory [*Foster et al.*, 2007; *Subramaniam et al.*, 2008]. Conversely, the prominence of nitrogen fixation in river-influenced waters could drive the system to P limitation. Taken together, this research suggests that the tropical and subtropical North Atlantic is a complex area with regards to nutrient limitation, with different functional groups (e.g., heterotrophic bacteria, primary producers, and diazotrophs) exhibiting limitation by different nutrients and in different parts of the basin, and perhaps varying over seasonal time scales.

[5] Despite the fact that P appears to be an important limiting nutrient for some groups in the North Atlantic, few studies have quantified the different P pools in the water column or examined P cycling across the basin. This study was carried out on a research cruise in the summer of 2006, where the P pools (soluble reactive P (SRP), dissolved organic P (DOP) and particulate organic P (POP)) were quantified in surface waters, the rate of PO_4^{3-} cycling was measured, and P uptake kinetics in the nitrogen fixing cyanobacterium *Trichodesmium* spp. was assessed to determine the spatial patterns in these parameters along the cruise track and infer information on the nutrient status of osmotrophs across the tropical North Atlantic. The affinity (α) of small bulk water samples for PO_4^{3-}, or the biomass specific turnover rate of inorganic P, was also calculated. *Tanaka et al.* [2006] have proposed that P sufficiency, deficiency or starvation, and limitation can be distinguished by this measure.

2. Methods

2.1. Study Site

[6] Samples were collected and experiments performed on a cruise on the R/V Seward Johnson in June and July 2006. The sampling area included the tropical North Atlantic; leg 1 crossed from Barbados to Cape Verde between ~11 and 15° N (stations 3–12) and leg 2 returned from Cape Verde to Barbados while traveling down to the equator (stations 13–23; see Figure 1). Samples were collected in surface waters (3–5 m) for SRP, DOP and POP concentration analysis, uptake and turnover rate measurements of the PO_4^{3-} pool, and PO_4^{3-} uptake kinetics of *Trichodesmium* spp. "River influenced" and "oceanic" stations were distinguished based on salinity data gathered with the CTD. Plume influenced stations are defined here as those with salinity <35, and oceanic stations are defined as stations with salinity >35, with the exception of the equatorial station (17), which was influenced by equatorial upwelling and thus was fundamentally different than other oceanic stations.

2.2. P Pool Analysis

[7] Water was collected with a CTD rosette system, then sampled into acid cleaned 250 mL HDPE plastic bottles, rinsed 3 times with sample water before filling, and frozen at −20°C until analysis on land. Current methods cannot directly measure the ambient PO_4^{3-} pool in a water sample; the molybdenum blue colorimetric method [*Strickland and Parsons*, 1972], routinely used by most researchers, uses acidic conditions for the development of color and thus some PO_4^{3-} is cleaved from DOP during analysis. The pool measured with this method is thus termed the soluble reactive P (SRP) pool, and has a detection limit of ~0.03 μM. To improve our sensitivity in oligotrophic waters, SRP was determined using the magnesium induced coprecipitation (MAGIC) method [*Karl and Tien*, 1992], with slight modifications. A 1 *M* NaOH solution was added at a 1% vol/vol ratio to a 75 mL of sample water. After precipitation and centrifugation, the supernatant was removed and the pellet resuspended in 5 mL Omni-trace clean HCl (0.2 *M*). The SRP concentration was then measured with the molybdenum blue method on a Shimadzu UV-VIS 1600 spectrophotometer equipped with a 10 cm path length cell set to read at 880 nm. With the concentration factor of 15 achieved by the MAGIC precipitation step, the limit of detection is reduced to ~2 n*M*.

[8] Samples for POP analysis were collected using a high-volume water pump connected to clean tubing that was lowered over the side of the boat to 5 m. Water was collected into polycarbonate bottles and 2–3 L was filtered onto 25 mm precombusted GF/F filters using gentle vacuum (<10 psi) filtration. Samples were stored frozen at −20°C and then analyzed using the Hawaii Ocean Time series protocol (http://hahana.soest.hawaii.edu/hot/protocols/protocols.

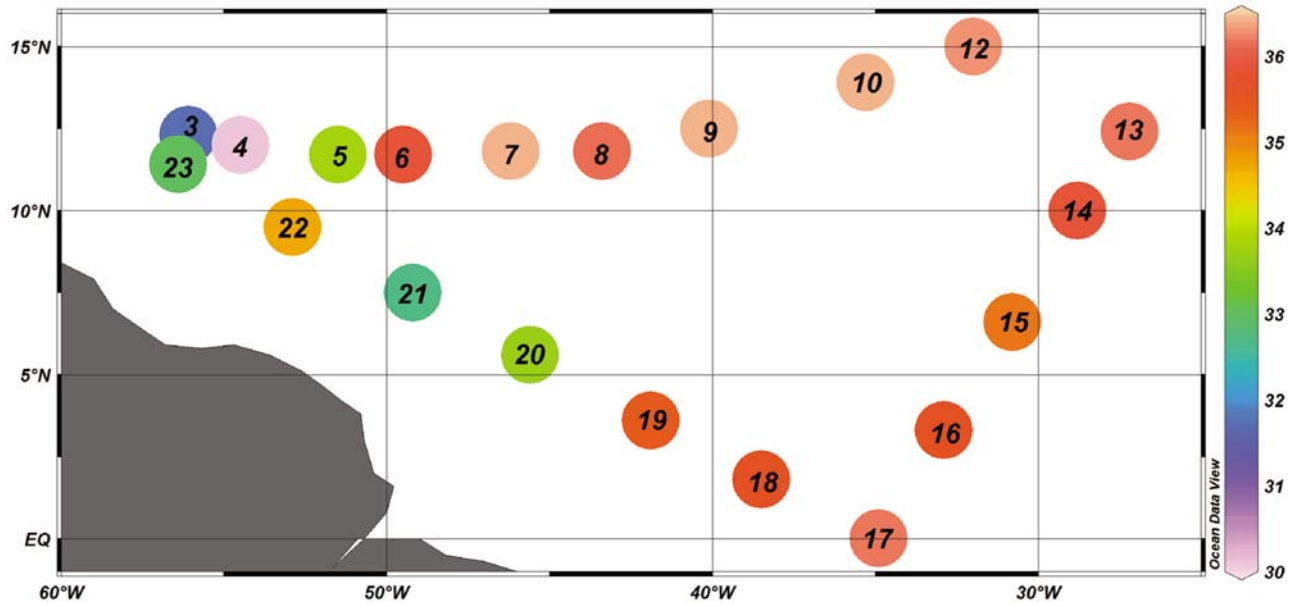

Figure 1. Salinity of surface waters in the tropical North Atlantic, shown in units of ppt. Station numbers are shown for reference.

html): dried filters were combusted at 500°C for 4–5 h, cooled, and then heated to 90°C in 10 mL 1 *M* HCl to convert POP to PO_4^{3-}, followed by the measurement of PO_4^{3-} with the molybdenum blue method as described above.

[9] Total phosphorus (TP) was determined on unfiltered samples using the high-temperature combustion and hot acid digestion method of *Solórzano and Sharp* [1980] to convert organic P to PO_4^{3-}, followed by the measurement of PO_4^{3-} with the molybdenum blue method. DOP was calculated by subtracting SRP and POP concentrations from the TP concentration.

2.3. PO_4^{3-} Uptake and Turnover

[10] PO_4^{3-} uptake was determined on bulk water collected from the high-volume pump system and therefore measurements represent the uptake of PO_4^{3-} of all the picoplanktonic and nanoplanktonic osmotrophs that would dominate such a sample, both heterotrophic and autotrophic. 50 mL of surface water was poured into 60 mL polycarbonate bottles in duplicate (leg 1) or triplicate (leg 2) and 0.1–0.4 μCi of $H_3^{33}PO_4$ added. Samples were incubated on deck in flowing seawater at 40% ambient light for 2–3 h then filtered onto 0.2 μm polycarbonate filters. A pair of controls killed with paraformaldehyde or glutaraldehyde was run to control for abiological adsorption of isotope. Filters were placed in 6 mL plastic ampules, and the activity was determined using an onboard scintillation counter after addition of 5 mL of scintillation fluid. The turnover time of the PO_4^{3-} pool in a sample was calculated as $T = R_t \times t/(R_f - R_k)$, where t is the incubation time and R_t, R_f and R_k are the radioactivity (in counts per minute) of the total pool added, the filter and the killed control, respectively. PO_4^{3-} uptake is calculated as the SRP concentration divided by turnover time.

2.4. *Trichodesmium* spp. PO_4^{3-} Uptake Kinetics

[11] *Trichodesmium* spp. colonies were collected by a surface net tow with a 202 μm mesh net. Colonies were picked from the tow with a plastic bacteriological loop into GF/F filtered seawater (FSW) rinse and then picked into 50 mL FSW in 60 mL polycarbonate bottles. Each bottle contained 5–10 colonies, depending on the density of *Trichodesmium* spp. in the tow, and samples were run in triplicate with two killed controls. Unlabeled PO_4^{3-} was added to incubations in concentrations from 0 to 3 μM along with 0.1–0.4 μCi $H_3^{33}PO_4$ to generate Michaelis-Menton uptake curves. Samples were incubated for ~60 min in on-deck incubators with flowing seawater at 40% ambient light and then filtered onto 8 μm polycarbonate filters. The activity and uptake rate of the samples was determined as described above for bulk measurements. The maximal PO_4^{3-} uptake rate (V_{max}) and the half saturation constant (K_s) were found by fitting the Michaelis-Menton equation to each data set using curve fitting routines in Sigmaplot. The kinetics of nutrient uptake are described by the equation $V = (V_{max} \times S)/(K_s + S)$, where V is the uptake rate at nutrient concentration S.

3. Results

3.1. Salinity and P Pool Composition

[12] Salinity in the surface waters of the tropical North Atlantic was generally high (salinity > 35; Figure 1). In the far western North Atlantic, however, salinity was lower due to inputs from the Amazon River. The influence of the river plume on surface ocean salinity was detected at least 700 km offshore, and > 1500 km away from the mouth of the river (Figure 1).

[13] Surface SRP concentrations were low at both oceanic and plume-influenced stations, but were somewhat higher in

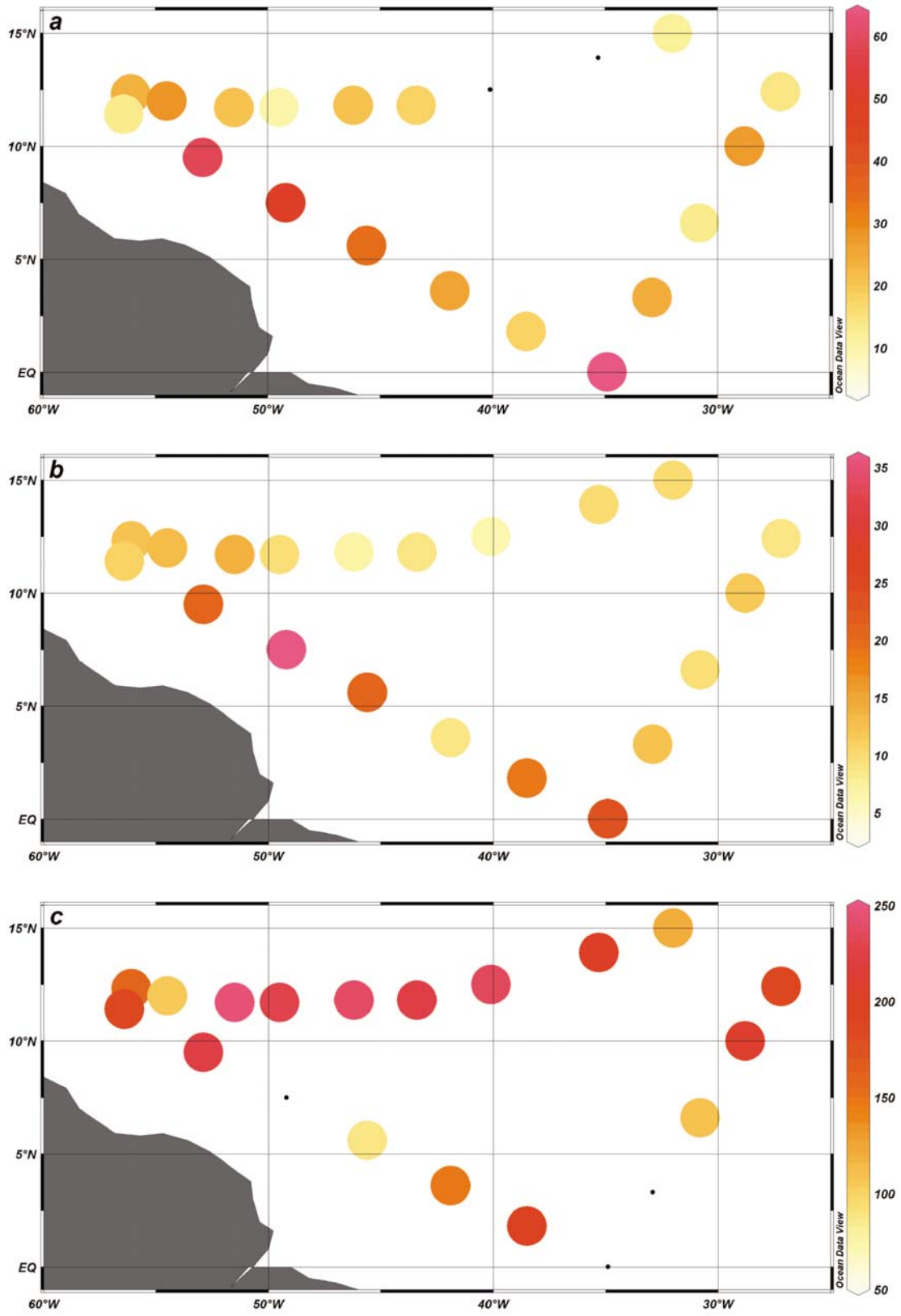

Figure 2. Surface water P pool concentrations, in n*M*, in the tropical North Atlantic: (a) soluble reactive phosphorus (SRP), (b) particulate organic phosphorus (POP), and (c) dissolved organic phosphorus (DOP).

Table 1. Phosphorus Pool Concentrations in Different Regions of the Ocean as Reported Here and in Previous Studies[a]

Location	SRP (n*M*)	DOP (n*M*)	POP (n*M*)	Study
West Mediterranean[b]	<30–200	150–930	3–55	*Tanaka et al.* [2004]
North Pacific (ALOHA)[c]	<10 to >100	<150 to >300	15–17	*Karl et al.* [2001]
North Pacific (off Japan)	50	300	18.2	*Suzumura and Ingall* [2004]
North Pacific (31–48°N)	10–1420	100–220	9–110	*Yoshimura et al.* [2007]
SW Pacific[d]	<30 to 60	211–281	10–25	*Van Den Broeck et al.* [2004]
SE Pacific	<150 to >500	150–400	10–125	*Moutin et al.* [2008]
Sargasso Sea (BATS)	~15	~80	~15	*Ammerman et al.* [2003]
Sargasso Sea	0.2–1	74.5	-	*Wu et al.* [2000]
Sargasso Sea	0.5–18	100	-	*Cavender-Bares et al.* [2001]
Central Atlantic	<100 to >250	<100 to 200	18–39	*Cañellas et al.* [2000]
Tropical North Atlantic	10–64	88–246	6–36	This study

[a]SRP, soluble reactive phosphorus; DOP, dissolved organic phosphorus; POP, particulate organic phosphorus.
[b]Range during period from June to December 2002.
[c]Range of data for 9 year sampling period from 1988–1997.
[d]Range during period from October 2001 to August 2002.

the plume. Oceanic stations averaged 18.4 ± 5.9 n*M* (range: 9.8–26.3) and plume-influenced stations averaged 32.6 ± 16.5 n*M* (range: 13.6–58.4 n*M*) (Figure 2a), a significant difference ($p = 0.023$). The highest SRP concentration in surface waters measured during the cruise was 64.1 n*M*, at the equatorial station 17. These values were within the ranges seen in other oligotrophic areas, and the oceanic values were at the lower end of reported values (Table 1).

[14] The distribution of surface water POP was similar to that of SRP. In oceanic waters, the POP concentration was low and ranged from 6.1–19 n*M* (average 10.2 ± 3.2 n*M*) (Figure 2b). At the equatorial station, however, the POP concentration was notably higher, 23.7 n*M*. POP concentrations in plume-influenced waters were significantly different from POP concentrations at oceanic stations ($p = 0.010$), ranging from 10.8–35.9 n*M* and averaging 18.2 ± 8.8 n*M* (Figure 2b). Across all stations, the concentration of POP was significantly linearly correlated to SRP concentration ($R^2 = 0.62$, $p = 0.042$, Figure 3). Published measurements of POP concentration in the North Atlantic are few, although the values for one study in the central Atlantic (~20–40 n*M*) [*Cañellas et al.*, 2000] and one at the Bermuda Atlantic Time series (~15 n*M*) [*Ammerman et al.*, 2003] were similar to those reported here. Additionally, POP concentrations were similar to, but appear slightly lower than, those found in the North and South Pacific and the Mediterranean Sea (see Table 1).

[15] The concentration of DOP in surface waters was variable, but much greater than either SRP or POP, ranging from 88 to 246 n*M* (Figure 2c) and averaging 182 ± 52 n*M* for the region. DOP concentrations were slightly lower on average in the river-influenced stations than at oceanic stations, although this was not a significant difference. These values are consistent with published values from the North Atlantic, and also from locations around the world (Table 1). When considering the total P pool in the tropical North Atlantic surface waters, DOP is clearly the major form of P. On average, 84 ± 9% of P was in the DOP phase, 10 ± 6% was SRP, and POP was 6 ± 3% of the total P pool. Measurements of all three components of the P pool in oceanic waters, including the North Atlantic, are few, but the relative

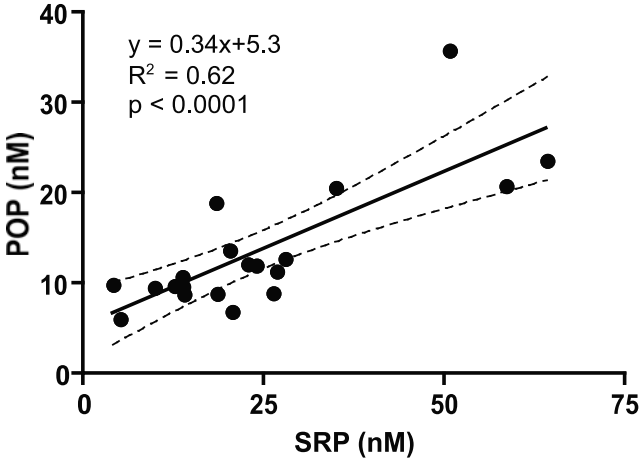

Figure 3. The relationship of SRP to POP in surface water for all stations where both measurements were made. Dashed lines show the 95% confidence interval.

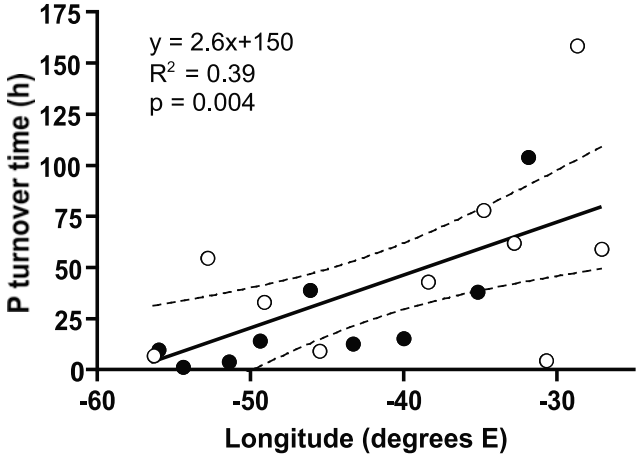

Figure 4. The longitudinal gradient of PO_4^{3-} turnover times in surface water. Closed circles show data from leg 1; open circles show data from leg 2. The regression line shown is for all data combined. Dashed lines show the 95% confidence interval.

Table 2. PO_4^{3-} Turnover Times in Different Regions of the Ocean as Reported Here and in Previous Studies

Location	Turnover Time (h)	Month	Study
East Mediterranean	2–5	May	*Fonnes Flaten et al.* [2005]
East Mediterranean (after PO_4^{3-} addition)	94	May	*Fonnes Flaten et al.* [2005]
East Mediterranean (Levantine Basin)	2–7	Jan	*Zohary and Robarts* [1998]
West Mediterranean (Villefranche Bay)	0.9–90.7	Sep–Dec	*Tanaka et al.* [2003]
North Pacific (ALOHA)	48–969	year round	*Bjorkman et al.* [2000]
SW Pacific	<4 to 400	year round	*Van Den Broeck et al.* [2004]
SE Pacific	~5–300 days	Nov–Dec	*Moutin et al.* [2008]
Sargasso Sea (BATS)	9	Mar/Aug	*Cotner et al.* [1997]
Central Atlantic	38–962	Oct/Nov	*Cañellas et al.* [2000]
Tropical North Atlantic	2–159	Jun/Jul	This study

distribution of P found in this study appears to be consistent throughout the oligotrophic oceans, including oceanic waters offshore of Japan [*Suzumura and Ingall*, 2004], in the North Pacific between 30° and 40° N [*Yoshimura et al.*, 2007], at station ALOHA [*Karl et al.*, 2001], in the SW Pacific near New Caledonia [*Van Den Broeck et al.*, 2004] and in Villefranche Bay in the Mediterranean Sea [*Tanaka et al.*, 2004].

3.2. PO_4^{3-} Uptake and Turnover

[16] The turnover time of the PO_4^{3-} pool varied widely across the North Atlantic, ranging from 2 to 159 h (Table 2). An increase in turnover times from west to east was found for the entire data set, but the pattern is less variable on leg one than leg two (Figure 4), possibly because there was not a concurrent change in latitude on leg 1. Alternatively, some of the variability between leg 1 and leg 2 could be related to relatively short-term temporal shifts in PO_4^{3-} turnover in this system. The turnover time was significantly correlated to longitude, which explained nearly 40% of the variation in turnover time ($R^2 = 0.39$, $p = 0.004$). The uptake rate of PO_4^{3-} in bulk water samples ranged from 2.9–317 n*M* P d^{-1} (average 48.8 ± 74.9 n*M* P d^{-1}). The turnover time of POP was calculated by dividing the POP concentration by the PO_4^{3-} uptake rate. POP turnover time also increased across the basin from west to east, ranging from 1–82 h, and was also significantly correlated to longitude ($R^2 = 0.38$, $p = 0.005$). The affinity (α) of the microbial community for PO_4^{3-} indicates biomass specific demand and can be calculated as $\alpha = 1/(PO_4^{3-}$ turnover time × POP) (see *Thingstad and Rassoulzadegan* [1999] for discussion). The affinity of the microbial community for PO_4^{3-} on this cruise was much higher when turnover time was low (Table 3). These data indicate very efficient recycling of P in the western tropical North Atlantic, although it is not clear if this is due to cellular release, or efficient recycling through grazing.

[17] The maximum PO_4^{3-} uptake rate in colonies of *Trichodesmium* spp. was also found to vary widely across the basin, ranging from ~10–300 pmol P col^{-1} h^{-1} (Figure 5). *Trichodesmium* spp. V_{max} decreased across the basin from east to west, and, similar to PO_4^{3-} turnover times, was correlated to longitude ($R^2 = 0.44$).

Table 3. Relationship of PO_4^{3-} Turnover Times With Affinity for PO_4^{3-}[a]

Turnover Time (h)	α (L nmol P^{-1} h^{-1})	Number of Measurements
<10	0.021 (0.005)	4
10–20	0.0075 (0.0009)	5
20–60	0.0018 (0.0006)	5
60–160	0.0010 (0.0002)	5

[a]Error is shown as standard error.

4. Discussion

4.1. P Pool Composition and Distribution

[18] Midsummer is a high-flow period for the Amazon River and the effect of the river on surface salinity in the tropical North Atlantic could be seen far away from the mouth of the river during this cruise. As expected, the average SRP concentration was somewhat higher in the plume than out of the plume (Figure 2a); the Amazon River is known to deliver high concentrations of nutrients to the shelf area off Brazil, and >90% of the river-derived inorganic P is transported off the shelf to the open ocean [*Demaster and Pope*, 1996]. However, the SRP concentrations were low both in and out of the plume compared to data from around the globe (see Table 1), but were generally higher than values reported in two studies of the Sargasso Sea. *Wu et al.* [2000] found SRP to be 0.2 to 1 n*M*, and *Cavender-Bares et al.* [2001] reported values of 0.5 to 18 n*M*. These studies were both far north of our study, suggesting that SRP in the subtropical

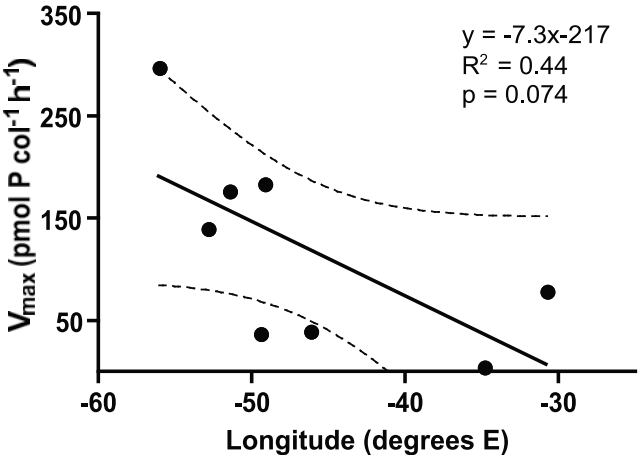

Figure 5. The maximal PO_4^{3-} uptake rate (V_{max}) by colonies of *Trichodesmium* spp. in the tropical North Atlantic. V_{max} of PO_4^{3-} uptake in *Trichodesmium* spp. increases with P depletion [*Fu et al.*, 2005]. Dashed lines show the 95% confidence interval.

Sargasso Sea may be consistently and considerably lower than in the tropical North Atlantic. A recent survey of SRP in the North and South Atlantic supports this view of SRP in the subtropical and tropical North Atlantic basin [*Mather et al.*, 2008].

[19] The significant correlation found between SRP and POP measurements (R^2 = 0.60, p = 0.042; Figure 3) indicates that the SRP concentration in surface waters plays an important role in determining POP concentration. This result was predicted, as POP is largely composed of living biomass [*Faul et al.*, 2005], and PO_4^{3-} is the preferred form of P for osmotrophs. However, the SRP concentration alone does not explain POP concentrations. Standing stocks do not indicate fluxes, and differences in supply and demand could affect the instantaneous SRP and POP pool concentrations. It is also possible that SRP, which is an analytically defined pool, may not be representative of the bioavailable inorganic P pool. Alternatively, DOP could be acting as a source of P for some organisms. DOP makes up the large majority of the dissolved P pool in this area and picoplankton and nanoplankton in the North Atlantic have been shown to produce the enzyme alkaline phosphatase [*Sohm and Capone*, 2006; *Vidal et al.*, 2003] that cleaves the PO_4^{3-} moiety from many organic P molecules [*Ammerman*, 1993]. Indeed, $\delta^{18}O$ of PO_4^{3-} values (K. McLaughlin et al., Phosphate cycling in the Sargasso Sea: Investigation using the oxygen isotopic composition of phosphate, enzyme labeled fluorescence, and turnover times, submitted to *Geophysical Research Letters*, 2009) and seasonal comparisons of DOP concentrations and APA in the North Atlantic [*Mather et al.*, 2008] indicate that substantial DOP utilization occurs in this area. Phosphonates (direct C to P bonds), may also be a source of P to some microbes in the North Atlantic, e.g., *Trichodesmium* spp. contains the operon for phosphonate utilization and was shown to express one of these genes in colonies collected in the North Atlantic [*Dyhrman et al.*, 2006].

4.2. P Cycling and the Cross Basin Pattern in P Deficiency

[20] In general, PO_4^{3-}turnover times were rapid in the North Atlantic on this cruise, averaging ~40 h. Short PO_4^{3-} and POP pool turnover times (<1 day) in the western side of the basin indicate very efficient cycling of P in this area. Shorter PO_4^{3-} turnover times generally indicate greater demand and thus a greater degree of P deficiency [*Fonnes Flaten et al.*, 2005; *Zohary and Robarts*, 1998], thus it appears that the osmotrophic plankton communities on the western side of the basin were more P deficient during our cruise than those on the eastern side of the basin. A survey of PO_4^{3-} turnover times from different regions shows that the turnover times in the western basin are consistent with those found in the P limited area of the Mediterranean Sea [*Thingstad et al.*, 2005] while the turnover times in the eastern basin are more similar to values reported from the North and South Pacific (Table 2), where P limitation of microbial activity is not apparent [see *Moutin et al.*, 2008; *Van Mooy and Devol*, 2008]. This pattern was not only seen in the general osmotrophic plankton community, but also when looking at one specific prokaryote, *Trichodesmium* spp., that plays an important role in the N cycle in this region [*Capone et al.*, 2005]. The maximal PO_4^{3-} uptake rate (V_{max}) of *Trichodesmium* spp. has been shown to be an order of magnitude greater in P deficient versus P replete cultures [*Fu et al.*, 2005], and has been used in the field as an indicator of P deficiency [*Sohm et al.*, 2008]. During the cruise reported here, *Trichodesmium* spp. V_{max} values were nearly an order of magnitude higher in the western basin, decreasing to the eastern side of the basin (Figure 5), and indicating greater P deficiency of colonies in the western compared to the eastern basin. Taken together, these data strongly indicate greater P deficiency in the western tropical North Atlantic during the time of our cruise, decreasing toward the eastern tropical North Atlantic. These are some of the few data mapping nutrient status in this area of the North Atlantic and on such a wide spatial scale (see *Davey et al.* [2008] for another example). This cross basin pattern could be due to an imbalance in the delivery of dissolved inorganic N (DIN) and SRP, thereby increasing the demand for P in the western basin. While DIN was below the colorimetric detection limit of 30 n*M* in surface waters during this study, it was elevated compared to SRP (i.e., higher than the Redfield ratio of 16:1) in subsurface waters (120–150 m) of the western basin, while the DIN:SRP was $\leq$ 16 in the eastern basin (J. Montoya, personal communication, 2007). We hypothesize (as others have) [see *Michaels et al.*, 1996; *Gruber and Sarmiento*, 1997] that this subsurface DIN:SRP > 16:1 is caused by nitrogen fixation and that elevated nitrogen fixation rates and the subsequent remineralization of diazotrophic biomass led to the accumulation of DIN and SRP in ratios > 16:1 in subsurface waters of the western tropical North Atlantic around the time of our cruise. There is some evidence to support this hypothesis. The abundance of *Trichodesmium* spp. on leg one of our cruise was highest in surface waters on the western side of the basin (stations 3–6) and nearly zero in the east (stations 9, 10, and 12; Ian Hewson, personal communication, 2007), while *Davis and McGillicuddy* [2006] showed that *Trichodesmium* spp. abundance was more than 5 times greater in the western than eastern North Atlantic. *Capone et al.* [2005] found that nitrogen fixation by *Trichodesmium* spp. averaged 247 μmol N m^{-2} d^{-1} to the west of 40°W and 100 μmol N m^{-2} d^{-1} to the east of 40°W (see supplemental Table 1 in the work of *Capone et al.* [2005]). The western basin average is a fairly robust number, as ~90% of the 158 observations were collected there and include measurements from all seasons, while the eastern basin average is from one cruise with substantially fewer data points and is thus a much more uncertain value. More research is needed to discern zonal patterns of nitrogen fixation in the North Atlantic.

[21] While PO_4^{3-} pool turnover is considered an indicator of P deficiency [*Zohary and Robarts*, 1998], it is important to recognize that the turnover time is related to both biological demand and biomass. If the turnover time is high simply because there is high biomass in the water (i.e., the demand of each individual cell is low), fast turnover times do not indicate P deficiency. The affinity (α) of the microbial community for PO_4^{3-} indicates biomass specific demand and is higher when cells are P starved, approaching a theoretical maximum where uptake is limited by the diffusion of PO_4^{3-}

molecules to the cell surface and every molecule that hits the cell surface is taken up. The affinity of the osmotrophic microbial community for PO_4^{3-} on this cruise was much higher when turnover time was rapid (Table 3), indicating that the populations at stations with the fastest turnover times were, in fact, the most P deficient. In fact, at these stations, the mixed community was approaching diffusion limitation for PO_4^{3-} uptake in a 1 μm cell, 0.046 L nmol P^{-1} h^{-1} [*Thingstad and Rassoulzadegan*, 1999]. *Tanaka et al.* [2006] proposed that a PO_4^{3-} affinity > 0.01 nmol P^{-1} h^{-1} indicates P limitation of growth, while affinity > 0.001 nmol P^{-1} h^{-1} indicates P deficiency. Using their criteria, this would suggest that the entire area over which we sampled was P deficient at the time of sampling, and that the stations with the fastest turnover times were P limited. Four out of five stations with α > 0.01 nmol P^{-1} h^{-1} were in the western basin (west of 40°W).

5. Conclusions

[22] The Amazon River plume affects a large area of the tropical western North Atlantic, far off the continental shelf, as shown by depressed surface ocean salinities, and elevated SRP and POP in this region. P cycling was rapid, indicating very efficient recycling of P in surface waters of the tropical North Atlantic, particularly in the western basin. Bulk water PO_4^{3-} turnover times were faster and maximal PO_4^{3-} uptake by *Trichodesmium* spp. was higher in the western compared to eastern basin, indicating high P deficiency in the west, decreasing to the east, a trend which, to our knowledge, has not been previously shown. This suggests that P deficiency of the osmotrophic microbial community in the tropical North Atlantic is zonally and possibly temporally variable. More research is required to further define and understand this phenomenon and its temporal and spatial variability, as well as to determine if the microbial community in the tropical western basin is P limited for growth.

[23] **Acknowledgments.** We would like to express our thanks to Joseph Montoya and Jon Zehr for providing support and ship time and to Ian Hewson for logistical support. We would also like to thank the captain and crew of the R/V *Seward Johnson*. Angela Knapp provided stimulating discussion and advice on this manuscript. Two anonymous reviewers helped to significantly improve the manuscript. This work was supported by NSF grant OCE 0452765 to D.G.C. and travel support from a Gordon and Betty Moore Foundation grant to J.P. Zehr.

References

Ammerman, J. A. (1993), Microbial cycling of inorganic and organic phosphorus in the water column, in *Handbook of Methods in Aquatic Microbial Ecology*, edited by P. F. Kemp et al., pp. 621–631, Lewis Press, Boca Raton, Fla.

Ammerman, J. W., R. R. Hood, D. A. Case, and J. B. Cotner (2003), Phosphorus deficiency in the North Atlantic: An emerging paradigm in oceanography, *Eos Trans. AGU*, *84*, 165, doi:10.1029/2003EO180001.

Benitez-Nelson, C. R. (2000), The biogeochemical cycling of phosphorus in marine systems, *Earth Sci. Rev.*, *51*, 109–135, doi:10.1016/S0012-8252(00)00018-0.

Björkman, K., A. L. Thomson-Bulldis, and D. M. Karl (2000), Phosphorus dynamics in the North Pacific subtropical gyre, *Aquat. Microbial Ecol.*, *22*, 185–198.

Cañellas, M., S. Agusti, and C. M. Duarte (2000), Latitudinal variability in phosphate uptake in the central Atlantic, *Mar. Ecol. Prog. Ser.*, *194*, 283–294, doi:10.3354/meps194283.

Capone, D. G., J. A. Burns, J. P. Montoya, A. Subramaniam, C. Mahaffey, T. Gunderson, and E. J. Carpenter (2005), Nitrogen fixation by *Trichodesmium* spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, *Global Biogeochem. Cycles*, *19*, GB2024, doi:10.1029/2004GB002331.

Cavender-Bares, K. K., D. M. Karl, and S. W. Chisolm (2001), Nutrient gradients in the western North Atlantic Ocean: Relationship to microbial community structure and comparison to patterns in the Pacific Ocean, *Deep Sea Res., Part I*, *48*, 2373–2395, doi:10.1016/S0967-0637(01)00027-9.

Codispoti, L. A., J. A. Brandes, J. P. Christensen, A. H. Devol, S. W. A. Naqvi, H. W. Paerl, and T. Yoshinari (2001), The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene?, *Sci. Mar.*, *65*, 85–105.

Cotner, J. B., J. W. Ammerman, E. R. Peele, and E. Bentzen (1997), Phosphorus-limited bacterioplankton growth in the Sargasso Sea, *Aquat. Microb. Ecol.*, *13*, 141–149, doi:10.3354/ame013141.

Davey, M., G. A. Tarran, M. M. Mills, C. Ridame, R. J. Geider, and J. LaRoche (2008), Nutrient limitation of picophytoplankton photosynthesis and growth in the tropical North Atlantic, *Limnol. Oceanogr.*, *53*, 1722–1733.

Davis, C. S., and D. J. McGillicuddy (2006), Transatlantic abundance of the N_2 fixing cyanobacterium *Trichodesmium*, *Science*, *312*, 1517–1520.

Demaster, D. J., and R. C. Aller (2001), Biogeochemical processes on the Amazon Shelf: Changes in dissolved and particulate fluxes during river/ocean mixing, in *The Biogeochemistry of the Amazon Basin*, edited by M. E. McClain et al., pp. 328–357, Oxford Univ. Press, New York.

Demaster, D. J., and R. H. Pope (1996), Nutrient dynamics in Amazon shelf waters: Results from AMASSEDS, *Cont. Shelf Res.*, *16*, 263–289, doi:10.1016/0278-4343(95)00008-O.

Dyhrman, S. T., P. D. Chappell, S. T. Haley, J. W. Moffett, E. D. Orchard, J. B. Waterbury, and E. A. Webb (2006), Phosphonate utilization by the globally important marine diazotroph *Trichodesmium*, *Nature*, *439*, 68–71, doi:10.1038/nature04203.

Faul, K. L., A. Paytan, and M. L. Delaney (2005), Phosphorus distribution in sinking oceanic particulate matter, *Mar. Chem.*, *97*, 307–333, doi:10.1016/j.marchem.2005.04.002.

Fonnes Flaten, G. A., et al. (2005), Studies of the microbial P-cycle during a Lagrangian phosphate-addition experiment in the eastern Mediterranean, *Deep Sea Res., Part II*, *52*, 2928–2943, doi:10.1016/j.dsr2.2005.08.010.

Foster, R. A., A. Subramaniam, C. Mahaffey, E. J. Carpenter, D. G. Capone, and J. P. Zehr (2007), Influence of the Amazon River plume on distributions of free-living and symbiotic cyanobacteria in the western tropical North Atlantic Ocean, *Limnol. Oceanogr.*, *52*, 517–532.

Froelich, P. N. (1988), The problem with phosphorus, *Eos Trans. AGU*, *69*, 760–761, doi:10.1029/88EO01041.

Fu, F. X., Y. H. Zhang, P. R. F. Bell, and D. A. Hutchins (2005), Phosphate uptake and growth kinetics of *Trichodesmium* (Cyanobacteria) isolates from the North Atlantic Ocean and the Great Barrier Reef, Australia, *J. Phycol.*, *41*, 62–73, doi:10.1111/j.1529-8817.2005.04063.x.

Gruber, N., and J. L. Sarmiento (1997), Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cycles*, *11*, 235–266, doi:10.1029/97GB00077.

Karl, D. M., and G. Tien (1992), Magic: A sensitive and precise method for measuring dissolved phosphorus in aquatic environments, *Limnol. Oceanogr.*, *37*, 105–116.

Karl, D. M., K. M. Bjorkman, J. E. Dore, L. Fujieki, D. V. Hebel, T. Houlihan, R. M. Letelier, and L. M. Tupas (2001), Ecological nitrogen-to-phosphorus stoichiometry at station ALOHA, *Deep Sea Res., Part II*, *48*, 1529–1566, doi:10.1016/S0967-0645(00)00152-1.

Mather, R. L., S. E. Reynolds, G. A. Wolff, R. G. Williams, S. Torres-Valdes, E. M. S. Woodward, A. Landolfi, X. Pan, R. Sanders, and E. P. Achterberg (2008), Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres, *Nat. Geosci.*, *1*, 439–443, doi:10.1038/ngeo232.

Michaels, A. F., D. Olson, J. L. Sarmiento, J. W. Ammerman, K. Fanning, R. Jahnke, A. H. Knap, F. Lipschultz, and J. M. Prospero (1996), Inputs, losses and transformations of nitrogen and phosphorus in the pelagic North Atlantic Ocean, *Biogeochemistry*, *35*, 181–226, doi:10.1007/BF02179827.

Mills, M. M., C. Ridame, M. Davey, J. LaRoche, and R. J. Geider (2004), Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature*, *429*, 292–294, doi:10.1038/nature02550.

Mills, M. M., C. M. Moore, R. Langlois, A. Milne, E. Achterberg, K. Nachtigall, K. Lochte, R. J. Geider, and J. LaRoche (2008), Nitrogen and phosphorus co-limitation of bacterial productivity and growth in the oligotrophic subtropical North Atlantic, *Limnol. Oceanogr.*, *53*, 824–834.

Moutin, T., D. M. Karl, S. Duhamel, P. Rimmelin, P. Raimbault, B. A. S. Van Mooy, and H. Claustre (2008), Phosphate availability and the

ultimate control of new nitrogen input by nitrogen fixation in the tropical Pacific Ocean, *Biogeosciences*, *5*, 95–109.

Obernosterer, I., N. Kawasaki, and R. Benner (2003), P-limitation of respiration in the Sargasso Sea and uncoupling of bacteria from P-regeneration in size-fractionation experiments, *Aquat. Microb. Ecol.*, *32*, 229–237, doi:10.3354/ame032229.

Parkhill, J., G. Maillet, and J. J. Cullen (2001), Fluorescence-based maximal quantum yield for PSII as a diagnostic of nutrient stress, *J. Phycol.*, *37*, 517–529, doi:10.1046/j.1529-8817.2001.037004517.x.

Sañudo-Wilhelmy, S. A., A. B. Kustka, C. J. Gobler, D. A. Hutchins, M. Yang, K. Lwiza, J. A. Burns, D. G. Capone, J. A. Raven, and E. J. Carpenter (2001), Phosphorus limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic Ocean, *Nature*, *411*, 66–69, doi:10.1038/35075041.

Schlesinger, W. H. (1997), *Biogeochemistry: An Analysis of Global Change*, 2nd ed., Academic, London.

Sohm, J. A., and D. G. Capone (2006), Phosphorus dynamics of the tropical and subtropical North Atlantic: *Trichodesmium* spp. versus bulk plankton, *Mar. Ecol. Prog. Ser.*, *317*, 21–28, doi:10.3354/meps317021.

Sohm, J. A., C. Mahaffey, and D. G. Capone (2008), Assessment of relative phosphorus limitation of *Trichodesmium* spp. in the North Pacific, North Atlantic, and the north coast of Australia, *Limnol. Oceanogr.*, *53*, 2495–2502.

Solórzano, L., and J. H. Sharp (1980), Determination of total dissolved phosphorus and particulate phosphorus in natural waters, *Limnol. Oceanogr.*, *25*, 754–758, doi:10.4319/lo.1980.25.4.0754.

Strickland, J. D. H., and T. R. Parsons (1972), *A Practical Handbook of Seawater Analysis*, 2nd ed., *Bull.* 167, 311 pp., Fish. Res. Board of Can., Ottawa, Ont.

Subramaniam, A., et al. (2008), Amazon River enhances diazotrophy and carbon sequestration in the tropical North Atlantic Ocean, *Proc. Natl. Acad. Sci. U. S. A.*, *105*, 10,460–10,465, doi:10.1073/pnas.0710279105.

Suzumura, M., and E. D. Ingall (2004), Distribution and dynamics of various forms of phosphorus in seawater: Insights from field observations in the Pacific Ocean and a laboratory experiment, *Deep Sea Res., Part I*, *51*, 1113–1130, doi:10.1016/j.dsr.2004.05.001.

Tanaka, T., F. Rassoulzadegan, and T. F. Thingstad (2003), Measurements of phosphate affinity constants and phosphorus release rates from the microbial food web in Villefranche Bay, northwestern Mediterranean, *Limnol. Oceanogr.*, *48*, 1150–1160.

Tanaka, T., F. Rassoulzadegan, and T. F. Thingstad (2004), Orthophosphate uptake by heterotrophic bacteria, cyanobacteria, and autotrophic nanoflagellates in Villefranche Bay, northwestern Mediterranean: Vertical, seasonal, and short-term variations of the competitive relationship for phosphorus, *Limnol. Oceanogr.*, *49*, 1063–1072.

Tanaka, T., P. Henriksen, P. Lignell, K. Olli, J. Seppala, T. Tamminene, and T. F. Thingstad (2006), Specific affinity for phosphate uptake and specific alkaline phosphatase activity as diagnostic tools for detecting phosphorus-limited phytoplankton and bacteria, *Estuaries Coasts*, *29*, 1226–1241.

Thingstad, T. F., and F. Rassoulzadegan (1999), Conceptual models for the biogeochemical role of the photic zone microbial food web, with particular reference to the Mediterranean Sea, *Prog. Oceanogr.*, *44*, 271–286, doi:10.1016/S0079-6611(99)00029-4.

Thingstad, T. F., et al. (2005), Nature of phosphorus limitation in the ultraoligotrophic eastern Mediterranean, *Science*, *309*, 1068–1071, doi:10.1126/science.1112632.

Tyrrell, T. (1999), The relative influences of nitrogen and phosphorus on oceanic primary production, *Nature*, *400*, 525–531, doi:10.1038/22941.

Van Den Broeck, N., T. Moutin, M. Rodier, and M. Le Bouteiller (2004), Seasonal variations of phosphate availability in the SW Pacific Ocean near New Caledonia, *Mar. Ecol. Prog. Ser.*, *268*, 1–12, doi:10.3354/meps268001.

Van Mooy, B. A. S., and A. H. Devol (2008), Assessing nutrient limitation of *Prochlorococcus* in the North Pacific subtropical gyre by using an RNA capture method, *Limnol. Oceanogr.*, *53*, 78–88.

Vidal, M., C. M. Duarte, S. Agusti, J. M. Gasol, and D. Vaque (2003), Alkaline phosphatase activities in the central Atlantic Ocean indicate large areas with phosphorus deficiency, *Mar. Ecol. Prog. Ser.*, *262*, 43–53, doi:10.3354/meps262043.

Wu, J. F., W. Sunda, E. A. Boyle, and D. M. Karl (2000), Phosphate depletion in the western North Atlantic Ocean, *Science*, *289*, 759–762, doi:10.1126/science.289.5480.759.

Yoshimura, T., J. Nishioka, H. Saito, S. Takeda, A. Tsuda, and M. L. Wells (2007), Distributions of particulate and dissolved organic and inorganic phosphorus in North Pacific surface waters, *Mar. Chem.*, *103*, 112–121, doi:10.1016/j.marchem.2006.06.011.

Zohary, T., and R. D. Robarts (1998), Experimental study of microbial P limitation in the eastern Mediterranean, *Limnol. Oceanogr.*, *43*, 387–395.

D. G. Capone and J. A. Sohm, Department of Biological Sciences and Wrigley Institute for Environmental Studies, University of Southern California, Los Angeles, CA 90089, USA. (sohm@usc.edu)