

Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres

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Despite similar physical properties, the Northern and Southern Atlantic subtropical gyres have different biogeochemical regimes. The Northern subtropical gyre, which is subject to iron deposition from Saharan dust¹, is depleted in the nutrient phosphate, possibly as a result of iron-enhanced nitrogen fixation². Although phosphate depleted, rates of carbon fixation in the euphotic zone of the North Atlantic subtropical gyre are comparable to those of the South Atlantic subtropical gyre³, which is not phosphate limited. Here we use the activity of the phosphorus-specific enzyme alkaline phosphatase to show potentially enhanced utilization of dissolved organic phosphorus occurring over much of the North Atlantic subtropical gyre. We find that during the boreal spring up to 30% of primary production in the North Atlantic gyre is supported by dissolved organic phosphorus. Our diagnostics and composite map of the surface distribution of dissolved organic phosphorus in the subtropical Atlantic Ocean reveal shorter residence times in the North Atlantic gyre than the South Atlantic gyre. We interpret the asymmetry of dissolved organic phosphorus cycling in the two gyres as a consequence of enhanced nitrogen fixation in the North Atlantic Ocean⁴, which forces the system towards phosphorus limitation. We suggest that dissolved organic phosphorus utilization may contribute to primary production in other phosphorus-limited ocean settings as well.

The physical characteristics of the extensive subtropical gyres restrict the supply of inorganic nutrients to surface waters, producing an oligotrophic environment⁵. Nitrogen (N) and phosphorus (P) are essential micronutrients for oceanic primary production and occur in the ratio of ~16:1 (ref. 6). However, comparisons of global ocean nitrate and phosphate show that nitrate is exhausted before phosphate⁷. Thus, in oligotrophic systems where inorganic nutrients are depleted and nitrate is exhausted, a residual phosphate pool should remain. There is, however, a clear contrast between the North Atlantic subtropical gyre (NASG) and the South Atlantic subtropical gyre (SASG; Fig. 1a), where our recent field measurements during seven cruises show contrasting values of surface (25 m depth) phosphate, with mean values of 9 and 210 nM, respectively. This contrast is probably

due to the greater role of nitrogen fixation in the NASG (ref. 4) (Fig. 2a), providing an alternative source of N and driving complete draw-down of the residual phosphate pool.

A possible alternative source of P to phytoplankton in the NASG is dissolved organic phosphorus (DOP). Our observational surveys, incorporating data from seven cruises between April 2000 and November 2005, show that in the surface (25 m depth) of the oligotrophic Atlantic, DOP represents a large fraction of total dissolved phosphorus of $66 \pm 23\%$ (s.d.) (see Supplementary Information, Table S1, for individual cruise transects and dates). There are significantly lower absolute concentrations of DOP in the NASG (80 ± 140 nM (s.d.)) than in the SASG (150 ± 70 nM (s.d.)), where the distribution is more homogenous (Fig. 1b). This gyre-scale contrast in the mean DOP is a robust signal and statistically significant, with a concentration \pm standard error (s.e.m.) of 80 ± 10 nM in the NASG and 150 ± 10 nM in the SASG (s.e.m. = s.d./ $\sqrt{(n-1)}$, where s.d. is the standard deviation and n is the number of independent data points; $P < 0.01$; T -test). Given the apparent nutrient asymmetry between the NASG and SASG, we now investigate the role of DOP within the system by examining its turnover and bioavailability in the two gyres, and explore the implications for their biogeochemistry.

The turnover of the DOP pool can be assessed through the measurement of the activity of the P-specific enzyme alkaline phosphatase (APA). This enzyme, which releases P bound in DOP, has been found associated with bacteria and phytoplankton and free in the water⁸, and its activity can limit DOP decomposition and plankton growth⁹. Extracellular APA has also been found to be expressed in a large range of phytoplankton taxa in response to P limitation⁸.

During June and November, the contrasts between three distinct oceanic dynamical regimes were investigated, identified through chlorophyll *a* and inorganic nutrient concentrations (see the Methods section below): the downwelling NASG (15° N–40° N), the region of equatorial and wind-induced upwelling (15° N–10° S) and the downwelling SASG (10° S–40° S). Michaelis–Menten kinetics were additionally used during spring in

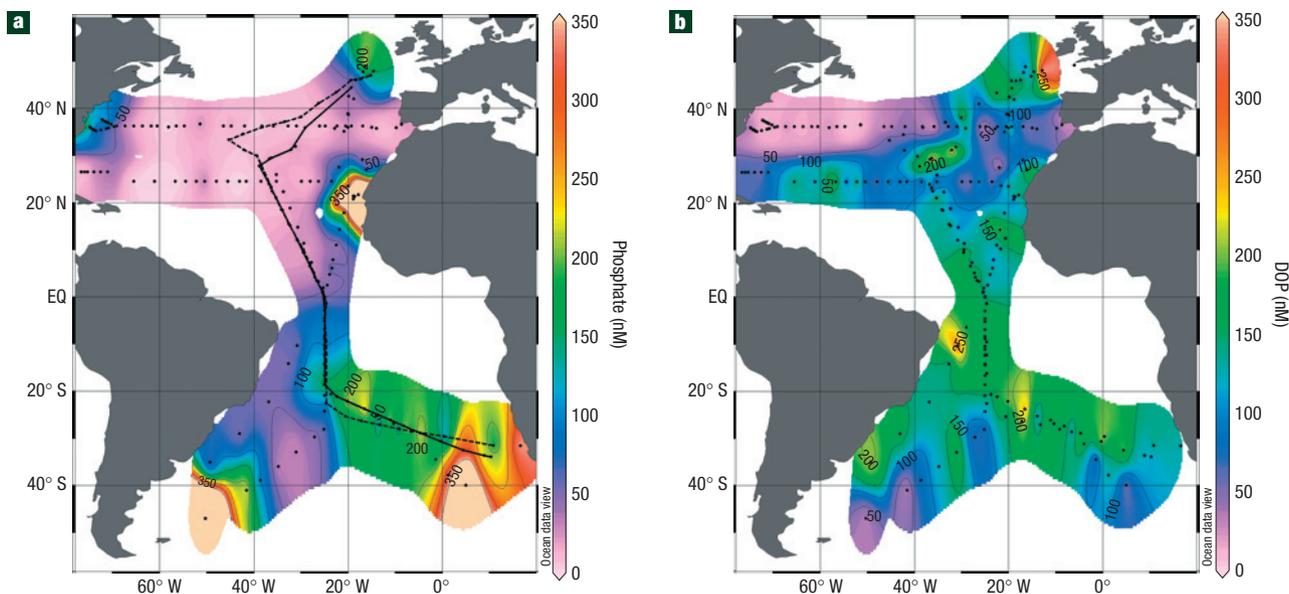


Figure 1 Phosphorus data from cruises AMT10 (April 2000), D279 (April 2004), AMT14 (May 2004), AMT15 (Oct 2004), CD171 (May 2005), AMT16 (June 2005) and AMT17 (Nov 2005). **a**, 25 m phosphate concentrations (nM) and AMT16 (dashed line) and AMT17 (solid line) ship transects. **b**, 25 m DOP concentrations (nM). Stations are marked as black dots.

each gyre to assess the turnover time and lability of the DOP pool through this season.

Our measured APA activities indicate a significantly greater utilization of the DOP pool in the NASG compared to the SASG over June and November (Fig. 2c). In the NASG, APA activities were ~3-fold higher in June, with a maximal rate of $4.65 \text{ nM P h}^{-1}/\mu\text{g C}$ (mean $2.44 \text{ nM P h}^{-1}/\mu\text{g C}$), compared to a mean of $0.84 \text{ nM P h}^{-1}/\mu\text{g C}$ in November. The higher activities correspond to a significantly smaller DOP pool size, which was ~60% lower in June compared with November (Fig. 2d). These seasonal APA activities and DOP concentrations are significantly different, as indicated by the contrast in their means \pm standard errors (Table 1; $P < 0.05$; T -test). Phytoplankton community production and growth are higher during spring in both hemispheres³. We interpret the higher APA activities and lower DOP concentrations in the NASG as reflecting phosphate limitation (Fig. 2b), which leads to a greater utilization of the DOP pool to maintain production.

In contrast to the seasonality of the NASG, APA activities of the SASG were lowest in spring (November), with activities of $0.20 \text{ nM P h}^{-1}/\mu\text{g C}$ (Fig. 2c). Within these waters, phosphate concentrations were higher in spring (Fig. 2b), likely through winter mixing of the water column. Phosphate is a more bioavailable nutrient source than DOP; hence we observe a reduction in enzyme activities and an accumulation of DOP in the water column (Fig. 2d).

Plots of APA versus phosphate (Fig. 3a) and DOP (Fig. 3b) for the NASG and SASG highlight the differences for spring in the two systems, as there are lower phosphate concentrations in the NASG and subsequently higher APA and lower DOP compared to the SASG. At a confidence level of 98% ($P < 0.02$; T -test) \log_{10} plots of APA versus phosphate and APA versus DOP for all data show significant negative correlations (coefficient of determination $r^2 = 0.54$ and 0.45 , respectively; data not shown). APA activities do not directly represent DOP uptake, as enzyme activities are measured using an artificial substrate present at

Table 1 APA and DOP \pm their standard errors for cruises AMT16 and AMT17.

Province/Month	Season	Cruise	APA \pm s.e.m.		DOP \pm s.e.m.	
			<i>n</i>	($\text{nM P h}^{-1}/\mu\text{g C}$)	<i>n</i>	(nM)
SASG June	Autumn	AMT16	4	0.84 ± 0.16	6	170 ± 20
NASG June	Spring	AMT16	7	2.44 ± 0.66	8	80 ± 10
NASG Nov	Autumn	AMT17	5	0.84 ± 0.13	8	210 ± 10
SASG Nov	Spring	AMT17	10	0.20 ± 0.04	13	240 ± 10

a higher concentration than the naturally occurring DOP pool. This is probably responsible for the low r^2 values reported. It is clear however that the NASG and SASG are biogeochemically different throughout spring owing to the severely depleted levels of phosphate in the NASG.

It is possible to estimate the amount of primary production potentially supported by the DOP pool in spring using the Michaelis–Menten equations. By combining these with the ambient DOP concentrations we can calculate the *in situ* APA activity. Integrating these activities over the euphotic zone shows the DOP pool to contribute $0.015 \pm 0.005 \text{ mol P m}^{-2} \text{ y}^{-1}$ to the NASG in spring compared with $0.003 \pm 0.001 \text{ mol P m}^{-2} \text{ y}^{-1}$ in the SASG. Combined with euphotic-zone rates of carbon fixation for the same season³, and applying the Redfield ratio, we estimate the DOP pool to support 20% (range of 12–30%) of production in the NASG and only 5% (range of 3–7%) in the SASG. Estimates of production in the NASG do vary, however; for example, geochemical estimates of new production in the Sargasso Sea show the P demand to be $0.031 \pm 0.009 \text{ mol P m}^{-2} \text{ y}^{-1}$ (ref. 10). Using this estimate, the DOP pool would support up to 90% of production.

Given the different utilization rates of DOP in each gyre in spring, we now consider the biological availability of the DOP pool using the Michaelis constant (K_m). Bulk dissolved organic matter is often viewed as a series of pools, representing a continuum

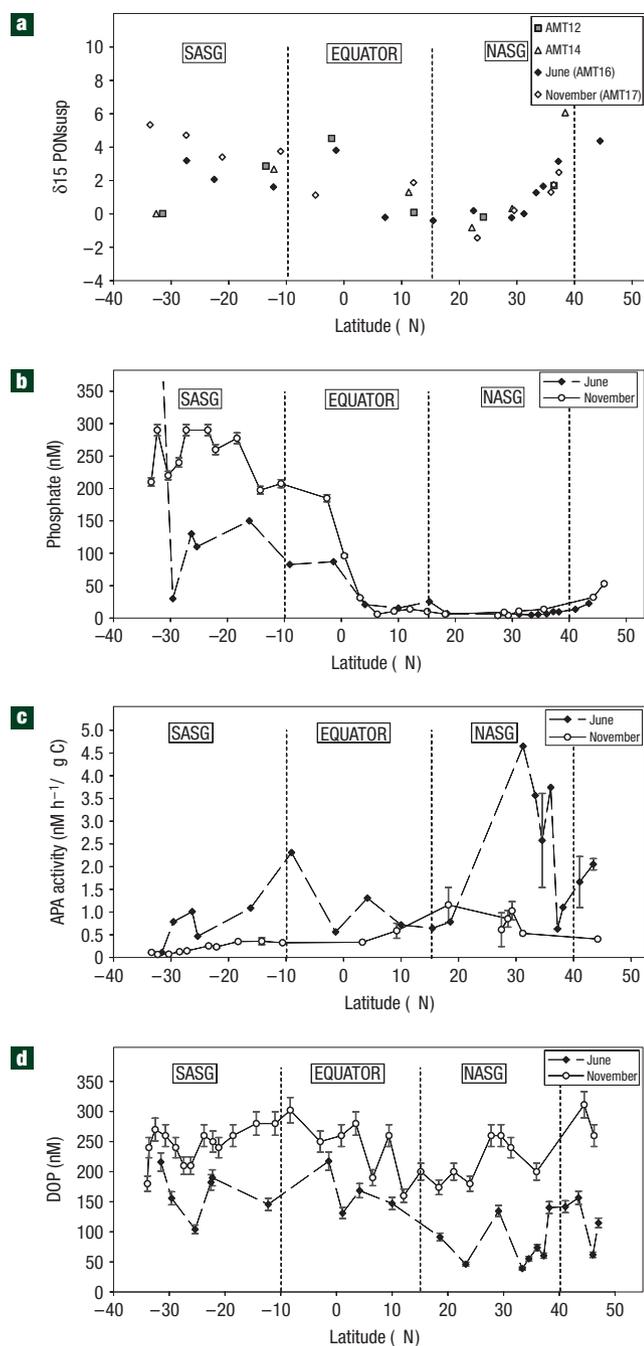


Figure 2 Biogeochemical results. **a**, Meridional variations in $\delta^{15}\text{PON}_{\text{susp}}$ above the nitricline (values averaged) for cruises AMT12, AMT14, AMT16 and AMT17 (ref. 4), with depleted values of $\delta^{15}\text{PON}_{\text{susp}}$ indicating N_2 fixation. **b**, Phosphate concentrations from AMT16 (June; dashed line) and AMT17 (November; solid line). Precision and reproducibility are shown as error bars ($\pm 3\%$). **c**, APA activities normalized to total carbon. Error bars of duplicate measurements are shown as \pm percentage range. **d**, DOP concentrations. Reproducibility is shown as error bars ($\pm 7\%$).

of biological lability, from refractory material turning over on timescales of centuries to millennia, to very labile material turning over on timescales of minutes to days¹¹. K_m provides a measure of the binding strength between the enzyme and DOP; low K_m values

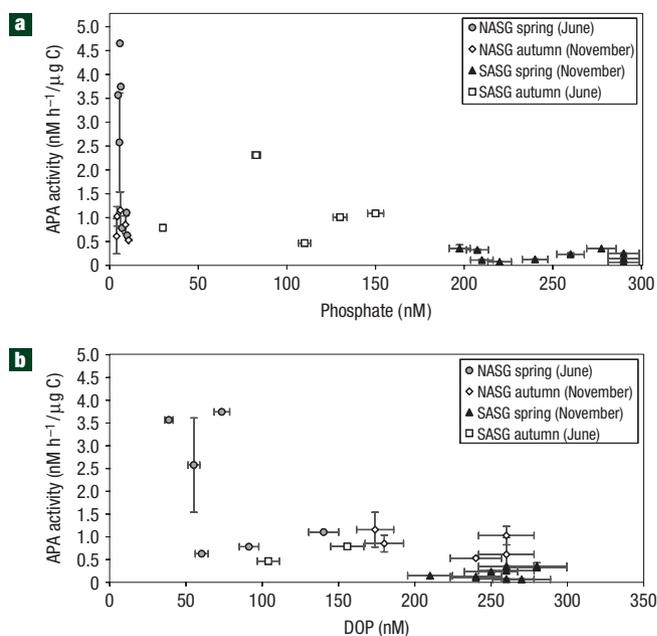


Figure 3 Seasonal data for the NASG and the SASG. **a**, APA activities versus phosphate concentrations. **b**, APA activities versus DOP concentrations. NASG spring is represented as grey circles, NASG autumn as white diamonds, SASG spring as black triangles and SASG autumn as white squares. Error bars of duplicate APA measurements are shown as \pm percentage range. Error bars of phosphate and DOP measurements are shown as reproducibility errors ($\pm 3\%$ and $\pm 7\%$ respectively).

indicate that labile DOP is scarce and that it is strongly bound by enzymes.

In spring between the NASG (June) and the SASG (November) the variations in K_m are not significantly different, with a mean \pm s.e.m. of $789 \pm 387 \mu\text{M}$ ($n = 3$) and $565 \pm 114 \mu\text{M}$ ($n = 10$) respectively (see Supplementary Information, Table S2 for individual station locations). The high K_m values reveal the presence of similar pools of labile DOP in both gyres during spring, presumably due to increased production resulting in the release of fresh, labile DOP compounds, via excretion, exudation, grazing and cell lysis¹².

The turnover time of the DOP pool (T) is diagnosed using the Li parametrization, equation (1) (ref. 13), from the ratio of K_m and V_{max} , the measured activity ($\mu\text{M h}^{-1}$):

$$T = \frac{K_m}{V_{\text{max}}} \quad (1)$$

The turnover times of the DOP pools are only 5.5 ± 2.3 months (s.d.) in the NASG, but much longer in the SASG with 10.5 ± 6.8 years (s.d.). In turn, these different turnover rates between the northern and southern gyres imply contrasting DOP distributions over the NASG and SASG. Model studies reveal that high concentrations of DOP produced in the tropics may be transported into the subtropical gyre as part of the wind-driven Ekman and gyre circulation¹⁴. A typical advective timescale for a transient tracer to cross the entire NASG within the upper thermocline is 7–10 years (ref. 15). Consequently, short DOP turnover times of less than a year in the NASG imply that there is insufficient time for the DOP to be transported over the entire gyre, resulting in consistently lower concentrations within the interior of the gyre as seen in the observations (Fig. 1b). Conversely, in the SASG, the DOP turnover times of typically 10 years are sufficiently

long for DOP to be advected over the entire gyre and become relatively uniform.

These experimental diagnostics reveal opposing biogeochemical regimes in the NASG and the SASG, with the DOP pool acting as an important nutrient source to marine plankton in the NASG as a result of severely depleted phosphate concentrations. The NASG is documented for its atmospheric, synoptic-scale dust inputs and resulting deposition of iron¹. Studies of the distribution of the stable isotopes of nitrogen in suspended particulate organic matter likewise reveal a depleted signal over the central and eastern side of the NASG, between 10° N and 30° N, consistent with regions of N₂ fixation⁴ (Fig. 2a). Furthermore, the nitrogen-fixing cyanobacteria *Trichodesmium spp.* occur extensively within the warm waters of the North Atlantic¹⁶, are uniquely adapted for scavenging P from organic sources¹⁷ and have been shown to contribute substantially to total APA in the water¹⁸. Viewed together, these observations suggest that N₂ fixation leads to the observed depleted surface phosphate concentrations and subsequent raised levels of APA activity and DOP utilization in the NASG. The opposing biogeochemistry of the NASG and SASG probably reflect marked differences in the atmospheric delivery of dust, implying that this asymmetry might vary with the ongoing, long-term changes in the atmospheric winds¹⁹.

The contrast in P cycling has wider significance in the ocean export of organic carbon, because half the global export of organic carbon is estimated to occur over these extensive, oligotrophic subtropical gyres²⁰. This export of organic matter is sustained through a supply of new nutrients to the sunlit, surface ocean, which we show over the NASG to be partly achieved through the enhanced utilization of DOP. The asymmetry of the P cycling in the NASG and SASG probably reflects the enhanced levels of nitrogen fixation in the NASG, forcing⁴ the system towards P limitation. The enhanced utilization of DOP in the NASG might therefore also be relevant to other extensive, oligotrophic P-limited parts of the global ocean, such as the Mediterranean Sea²¹ and, possibly, the North Pacific subtropical gyre²². Thus, utilization of DOP potentially sustains levels of carbon fixation over much of the global oligotrophic ocean whenever there is phosphorus limitation.

METHODS

Seven cruises were conducted between April 2000 and November 2005. Seawater samples were collected from Niskin bottles mounted on a SeaBird CTD/Rosette system.

ALKALINE PHOSPHATASE ACTIVITIES

APA activities in the photic zone were determined at a total of 37 stations along two Atlantic meridional transects (AMTs) in boreal spring (AMT16; 19 May–29 June, referred to as June) and autumn in 2005 (AMT17; 15 Oct–28 Nov, referred to as November; Fig. 1a). Reported activities were normalized to biomass. The fluorogenic substrate 4-methylumbelliferylphosphate was used to assess the alkaline phosphatase activities, using substrate additions of 250 μM for AMT17 and 200 μM for AMT16. Michaelis–Menten kinetics were used for the NASG in June and the SASG in November on cruises AMT16 and AMT17. The key parameters from these experiments were V_{max} , the maximum rate of turnover of DOP by the enzyme, and K_m , the concentration of DOP at which the enzymes are half saturated. Michaelis–Menten kinetic experiments were conducted with three to six 10 ml seawater samples inoculated with 1–750 μM substrate, in acid-washed polypropylene pots. All experiments were incubated in the dark, at *in situ* temperature, for 24–48 hours. Details of station experiments and locations are included in the Supplementary Information, Table S2, which accompanies this paper.

NORMALIZATION

Activities were normalized to total carbon, assessed through chlorophyll *a* concentrations and bacterial counts, using conversion factors of 1 g chl *a* = 50 g C (ref. 23) and 12 fg C/bacterial cell (ref. 24). Chlorophyll *a*

concentrations were determined using a fluorometric assay of the acetone extract of particulate material collected on a GF/F filter²⁵. Errors were estimated at ±5%. Bacterial counts were carried out by flow cytometry, using a 15 mW laser set to excite at 488 nm (ref. 26). Errors were estimated at ±2.5%. The patterns we report were found to be significant regardless of the method of normalization used, that is, no normalization, bacterial numbers only, chlorophyll concentrations only or total carbon.

NUTRIENT CONCENTRATIONS

Phosphate concentrations were analysed using standard colorimetric techniques^{27,28}, with an analytical precision of ±3%. DOP samples from cruises AMT10, CD171 and AMT17 were filtered immediately on collection using ashed GF/F filters and a glass filtration unit, and stored frozen in sterile high-density polythene 60 ml bottles. Samples from cruises D279, AMT14, AMT15 and AMT16 were unfiltered and therefore represent total organic phosphorus, which is appropriate in oligotrophic waters, where the particulate pool is generally considered negligible (<10%) (ref. 29), and has hence been referred to as DOP throughout the text. DOP was calculated as the difference of total dissolved phosphorus and phosphate, measured by standard colorimetric techniques following ultraviolet photo-oxidation³⁰ with a Metrohm 705 ultraviolet digestion system. Reproducibility errors were ±7% on the basis of duplicate measurements from AMT16.

STATISTICS

Statistical analysis of the data sets was carried out by Excel data analysis (one-tailed *T*-test) and Sigma plot and Sigma-stat analytical tools (test of normal distribution). See Supplementary Information, Table S3–S7 for individual *P* values.

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Author contributions

R.L.M., S.E.R., G.A.W. and R.G.W. wrote the paper. G.A.W. and R.G.W. designed the research programme. R.L.M., S.E.R., S.T.V., E.M.S.W., A.L., X.P., and R.S. carried out the field work. R.S. and E.P.A. oversaw the analysis of the organic nutrients.

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