Evidence for production and lateral transport of dissolved organic phosphorus in the eastern subtropical North Atlantic

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Abstract The concentration of phosphate and dissolved organic phosphorus (DOP) is chronically low and limits phytoplankton growth in the subtropical North Atlantic relative to other ocean basins. Transport of phosphate and DOP from the productive flanks of the gyre to its interior has been hypothesized as an important phosphorus supply pathway. During a cruise in the eastern Atlantic in spring 2011, the rates of phosphate uptake, alkaline phosphatase activity (APA), and DOP production were measured in the northwest African shelf region, subtropics, and tropics. Rates of DOP production were sixfold higher in the shelf region (43 ± 41 nM d⁻¹) relative to the subtropics (6.9 ± 4.4 nM d⁻¹). In contrast, APA was threefold higher in the subtropics (8.0 ± 7.3 nM d⁻¹), indicative of enhanced DOP utilization, relative to the shelf region (2.6 ± 2.1 nM d⁻¹). Hence, observations suggest net production of DOP in the shelf region and either net consumption of DOP or a near balance in DOP production and consumption in the gyre interior. Eddy-permitting model experiments demonstrate that (i) DOP accounts for over half the total phosphorus in surface waters, (ii) DOP is transported westward from the shelf region by a combination of gyre and eddy circulations, and (iii) advected DOP supports up to 70% of the particle export over much of the subtropical gyre. Our combined observational and modeling study supports the view that the horizontal transport of DOP from the shelf region is an important mechanism supplying phosphorus to the surface subtropical North Atlantic.

1. Introduction

The subtropical Atlantic Ocean is characterized by extensive oligotrophic gyres, where the winds induce large-scale downwelling and reduced inorganic nutrient supply and primary productivity. Surrounding the subtropical gyres, there are regions of upwelling in the tropics, along the coastal boundaries and subpolar gyres, which supply nutrients to the surface and enhance primary productivity [Williams and Follows, 1998]. Despite comparable rates of carbon fixation [Poulton et al., 2006], there are striking contrasts in phosphorus dynamics between the subtropical gyres in the North and South Atlantic: there are relatively low concentrations of phosphate and dissolved organic phosphorus (DOP) in the northern gyre compared to the southern gyre [Mather et al., 2008; Moore et al., 2009], despite the concentrations of nitrate and dissolved organic nitrogen (DON) being similar [Reynolds et al., 2007]. This north-south contrast in phosphorus specifically has been attributed to the prevalence of dinitrogen (N₂) fixing phytoplankton or diazotrophs in the subtropical North Atlantic. Diazotrophs are not limited by nitrogen, but their distribution and activity is (co-)limited by iron and phosphorus [Mills et al., 2004]. There is an enhanced supply of iron-rich dust from the Sahara into the subtropical North Atlantic, which fuels diazotrophic activity subsequently leading to the drawdown of phosphorus [Mahaffey et al., 2003, 2005; Mather et al., 2008; Moore et al., 2009]. In contrast, the lack of a significant aeolian iron input into the subtropical South Atlantic restricts the growth of diazotrophs and thus prevents phosphorus from being assimilated to such low concentrations. This addition of nitrogen via diazotrophic activity in the northern subtropical gyre leads to elevated nitrate:phosphate ratio in the thermocline, as described by geochemical proxies such as N* [Gruber and Sarmiento, 1997] and DINs [Hansell et al., 2004]. Subsequently, the nutrients transported within the subtropical gyre and supplied to the euphotic zone contain excess nitrate relative to phosphate, requiring an additional supply of excess phosphorus relative to nitrogen to support activity of both diazotrophs and non-diazotrophs [Deutsch et al., 2007; Moore et al., 2009].

A possible solution to this problem of how the necessary phosphorus is supplied to sustain productivity in the northern subtropical gyre involves the lateral transport and cycling of DOP [Mahaffey et al., 2004;
Roussenov et al., 2006; Mather et al., 2008; Torres-Valdés et al., 2009). Our hypothesis is that there is a local imbalance between the production and consumption of DOP, which provides a phosphorus supply over the northern subtropical gyre. Along the boundaries of the subtropical gyre, coastal or tropical upwelling provides a local supply of nutrients to the euphotic zone and enhances primary productivity, causing a net production of DOP. This DOP is transported toward the interior of the subtropical gyre and is consumed where phosphate concentrations are chronically low, through the extant plankton (including diazotrophs, non-diazotrophs, and bacteria) accessing labile fractions of DOP. This viewpoint is supported by numerical model studies revealing a DOP supply to the northern subtropical gyre via horizontal advection [Roussenov et al., 2006; Torres-Valdés et al., 2009]. Unlike phosphate, which is readily available to plankton, up to 50% of DOP is not easily accessible or is “refractory” [Björkman and Karl, 2003; Lonberg et al., 2009]. The remaining labile and semilabile fractions of DOP are available on time scales of hours to days and days to weeks, respectively [Björkman and Karl, 2003], implying that semilabile DOP is transported further into the gyre than phosphate.

The transport of DOP into the gyre has been proposed as an important phosphorus supply pathway in both the eastern [Mahaffey et al., 2004; Roussenov et al., 2006; Mather et al., 2008; Torres-Valdés et al., 2009] and western [Lomas et al., 2010] subtropical North Atlantic. In addition, DOP has been identified as an important phosphorus source to both the diazotrophic [Sohm and Capone, 2006; Sohm et al., 2008] and non-diazotrophic plankton community [Orchard et al., 2010; McLaughlin et al., 2013]. However, there are no direct and concurrent measurements of the production and consumption of DOP in the subtropical Atlantic. Here, using data collected from an east-west and north-south transect in the eastern North and South Atlantic in spring 2011, we provide the first direct measurements of the rates of DOP production together with measurements of the concentration of phosphorus pools, including phosphomonesters, and the rates of phosphate uptake and alkaline phosphatase activity. Using a coupled isopycnic circulation and simplified nutrient model (as in Roussenov et al. [2006] and Torres-Valdés et al. [2009]), the transport pathways of DOP offshore from the northwest African shelf region are identified, as well as the sensitivity of the particle export to the cycling of DOP.

2. Methods From Observational Campaign

2.1. Sampling Protocol

Samples were collected in February and March 2011 on board the RRS Discovery (D361) across a zonal transect (12°N) from the shelf region off the Senegalese coast (18°W) to open ocean waters (25°W) and a meridional transect (25°W to 29°W) from the South to the North Atlantic subtropical waters (7°S to 20°N) (Figure 1a). At 21 stations, samples were collected from 6 to 12 depths between 0 and 500 m predawn using a stainless steel rosette frame fitted with a Seabird Electronics conductivity-temperature-depth (CTD) package and 24–20 L Niskin bottles. Concentration and rate parameters were integrated then averaged within the mixed layer, where the mixed layer depth (MLD) is defined by where the temperature decreases by 1°C from the surface.

Sampling and storage bottles were precleaned with 10% hydrochloric acid and rinsed with deionized water before sample collection. Samples for determination of phosphate, DOP, and phosphomonoesters (PME) were unfiltered, filtered through a combusted and acid-rinsed glass fiber filter, and filtered through a 0.22 μm hydrophilic polyethersulfone filter, respectively. All samples were stored in high-density polyethylene bottles at –20°C. One liter of seawater was filtered through a combusted and acid-rinsed glass fiber for determination of particulate organic phosphorus (POP).

2.2. Phosphorus Concentrations

Phosphate concentration was determined onboard within 3 h of sample collection using a Bran and Luebbe AAIII segmented flow autoanalyzer following the molybdenum blue method or using a 2 m liquid waveguide capillary cell when the phosphate concentration was less than 30 nM [Law et al., 2005]. DOP concentrations were determined in triplicate by measuring the difference in phosphate concentration before
The rate of production of DOP (nM d$^{-1}$) was measured using $^{33}$P-phosphate as a tracer following Björkman et al. [2000]. DOP exuded by phytoplankton and bacteria was labeled with $^{33}$P, which was achieved by incubating 125 mL of unfiltered seawater with 20 kBq of $^{33}$P-phosphate for 8 to 10 h in on-deck incubators. The incubated sample was filtered through a 0.2 μm polycarbonate filter, the filtrate was placed into a 50 mL centrifuge tube, and a white precipitate was produced after the addition of 150 μL of 1 M sodium hydroxide [Thomson-Buildis and Karl, 1998]. After centrifugation (1 h at 3500 rpm), the activity of 1 mL of the supernatant was measured as above. The rate of DOP production and DOP turnover, defined as DOP concentration divided by DOP production rate, was then diagnosed [Björkman et al., 2000]. The efficiency of removal of $^{33}$P-phosphate via precipitation was better than 96% ($n = 16$).

The measured rate of DOP production represents a net rate [Björkman et al., 2000]. Assuming that APA approximates the consumption of a fraction of the semilabile DOP pool, the measured rate of DOP production plus the rate of APA provides an estimate for gross DOP production. To estimate the proportion of DOP exuded relative to the phosphate consumed, the gross rate of phosphate uptake was estimated as the rate of phosphate uptake plus the rate of gross DOP production, and the rate of gross DOP production was compared to this value.

### 3. Results From Observational Campaign

#### 3.1. Hydrography, Distribution, and Partitioning of Phosphorus

The eastern tropical North Atlantic Ocean is influenced by wind-driven Ekman upwelling occurring off the western coast of North Africa and along the equator [Williams and Follows, 1998]. Surface waters are
The rate of phosphate uptake is almost sixfold higher in the northwest African shelf region (188 ± 7 nM d⁻¹) relative to the subtropics (33 ± 22 nM d⁻¹) and tropics (33 ± 16 nM d⁻¹).
mostly likely due to the higher phosphate availability. Biomass normalized phosphate uptake was almost double in the subtropics (158 ± 100 nmol μgc h l⁻¹/C₀₁) relative to the northwest African shelf region (97 ± 39 nmol μgc h l⁻¹/C₀₁) (Table 2), reflecting the enhanced efficiency of the autotrophic community to assimilate the phosphate at low concentrations observed in the subtropics.

Rates of PME hydrolysis, as estimated via APA in unfiltered seawater samples, were 2.6-fold higher in the subtropics (8.0 ± 7.3 nM d⁻¹) and tropics (5.4 ± 3.0 nM d⁻¹), compared to the northwest African shelf region (2.6 ± 2.1 nM d⁻¹) (Figures 4c and 4d and Table 2). Biomass-normalized APA was 24-fold higher in the subtropics (38 ± 31 nmol μg chl a d⁻¹) relative to the northwest African shelf region (1.5 ± 1.5 nmol μg chl a d⁻¹) (Table 2). The westward increase in APA from low rates in the northwest African shelf region (<4 nM d⁻¹) to higher rates in the subtropics (1 to 23 nM d⁻¹) (Figure 4d) reflects the increased reliance of plankton on semilabile DOP compounds as phosphate becomes scarce.

Further evidence of the utilization of semilabile DOP can be observed in the PME turnover time, defined by the concentration of PME divided by the rate of APA. The PME turnover time was longer in the northwest African shelf region (53 ± 46 days) than in the tropics (9 ± 5 days) and subtropics (10 ± 12 days) (Table 2).

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Figure 3. Variation in the contribution of dissolved organic phosphorus (DOP) to total dissolved phosphorus (TDP) along (a) the north-south transect and (b) the east-west transect and contribution of phosphomonoesters (PME) to DOP along (c) the north-south transect and (d) the east-west transect in the tropics, subtropics, and northwest African shelf (NWAS) region in the eastern Atlantic Ocean. Parameters are expressed as percent (%). Error bars represent 1 standard deviation.

Figure 4. Variation in mixed layer-averaged (a and b) rate of phosphate uptake (nM d⁻¹); (c and d) rate of alkaline phosphatase activity (APA, nM d⁻¹); and (e and f) rate of DOP production (nM d⁻¹) along the north-south (latitude) and east-west (longitude) transect in the tropics, subtropics, and northwest African shelf (NWAS) region of the eastern Atlantic Ocean. Error bars represent 1 standard deviation.
Furthermore, assuming that phosphate uptake and rates of APA provide a lower estimate of total phosphorus uptake, in the subtropics and tropics, APA provides 15 ± 10% and 15 ± 9%, respectively, of total phosphorus demand. In contrast, in the northwest African shelf region, APA provides only 1.4 ± 1.0% of total phosphorus demand, indicating the importance of phosphate in sustaining productivity in the northwest African shelf region.

Our estimates of the consumption of semilabile DOP via APA only considers the assimilation of PME and thus provides a lower bound, since our observations do not take into account the assimilation of phosphorus from compounds accessed by other phosphohydrolytic enzymes, such as polyphosphate or phosphonates. Our APA rates (1 to 24 nM d⁻¹/C₀) were similar to those found in other studies (0.42 to 4.32 nM d⁻¹/C₀ [Sebastián et al., 2004] and 7 to 50 nM d⁻¹/C₀ [Sohm and Capone, 2006]) in which lower concentrations of MUFP were used (<1000 nM).

Examination of DOP production rates also demonstrates the differences between the three regions. The volumetric rate of DOP production is sixfold higher in the northwest African shelf region (43 ± 41 nM d⁻¹/C₀, reaching a maximum of 89 ± 29 nM d⁻¹/C₀) compared to that in the subtropics (6.9 ± 4.4 nM d⁻¹/C₀) and tropics (4.5 ± 2.9 nM d⁻¹/C₀) (Figures 4e and 4f and Table 2). Rates of DOP production were also elevated (>10 nM d⁻¹/C₀) on the northern edge of the north-south transect between 15° to 18°N (Figure 4e; see section 3.4). There are very few direct measurements of DOP production in the open ocean. DOP production rates in the tropics and subtropics in our study were comparable to those measured in the subtropical North Pacific (0.6 to 2.5 nM d⁻¹/C₀ [Björkman et al., 2000]), and the DOP production rates in the northwest African shelf region were similar to observations from the coastal waters off of Manzanillo, Mexico (38 to 77 nM d⁻¹/C₀, reaching a maximum of ~200 nM d⁻¹/C₀ [Orrett and Karl, 1987]).

### Table 2. Comparison of Volumetric and Biomass-Normalized Rates Including Phosphate Uptake, Alkaline Phosphatase, and DOP Production Between the Stations in the North West African Shelf Region (NWAS), Tropics, and Subtropics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NWAS</th>
<th>Tropics</th>
<th>Subtropics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volumetric Rates</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Phosphate uptake rate (nM d⁻¹)</td>
<td>188 ± 7</td>
<td>33 ± 16</td>
<td>33 ± 22</td>
</tr>
<tr>
<td></td>
<td>(183–193)</td>
<td>(16–66)</td>
<td>(12–68)</td>
</tr>
<tr>
<td>APA rate (nM d⁻¹)</td>
<td>2.6 ± 2.1</td>
<td>5.4 ± 3.0</td>
<td>8.0 ± 7.3</td>
</tr>
<tr>
<td></td>
<td>(1.2–4.1)</td>
<td>(2.3–10.3)</td>
<td>(1.1–23.7)</td>
</tr>
<tr>
<td>APA relative to total phosphorus uptake (%)</td>
<td>1.4 ± 1.0</td>
<td>15 ± 9</td>
<td>15 ± 10</td>
</tr>
<tr>
<td></td>
<td>(0.6–2.1)</td>
<td>(8–32)</td>
<td>(8–35)</td>
</tr>
<tr>
<td>DOP production rate (nM d⁻¹)</td>
<td>43 ± 41</td>
<td>4.5 ± 2.9</td>
<td>6.9 ± 4.4</td>
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<tr>
<td></td>
<td>(10–89)</td>
<td>(1.5–10)</td>
<td>(1.7–14)</td>
</tr>
<tr>
<td>Gross DOP production/phosphate uptake (%)</td>
<td>19 ± 19</td>
<td>28 ± 15</td>
<td>39 ± 18</td>
</tr>
<tr>
<td></td>
<td>(6–33)</td>
<td>(16–52)</td>
<td>(20–62)</td>
</tr>
<tr>
<td><strong>Biomass Normalized Rates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate uptake rate (nmol P μg chl a d⁻¹)</td>
<td>97 ± 39</td>
<td>236 ± 147</td>
<td>158 ± 100</td>
</tr>
<tr>
<td></td>
<td>(70–125)</td>
<td>(96–456)</td>
<td>(79–353)</td>
</tr>
<tr>
<td>APA rate (nmol P μg chl a d⁻¹)</td>
<td>1.5 ± 1.5</td>
<td>35 ± 14</td>
<td>38 ± 31</td>
</tr>
<tr>
<td></td>
<td>(0.4–2.6)</td>
<td>(15–54)</td>
<td>(7–95)</td>
</tr>
<tr>
<td>DOP production rate (nmol P μg chl a d⁻¹)</td>
<td>24 ± 29</td>
<td>34 ± 26</td>
<td>37 ± 32</td>
</tr>
<tr>
<td></td>
<td>(4–58)</td>
<td>(9–70)</td>
<td>(9–93)</td>
</tr>
<tr>
<td><strong>Turnover</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate turnover (day)</td>
<td>2.6 ± 2.2</td>
<td>2.0 ± 1.4</td>
<td>1.6 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>(1.0–4.2)</td>
<td>(0.5–4.3)</td>
<td>(0.6–3.2)</td>
</tr>
<tr>
<td>DOP turnover (day)</td>
<td>18 ± 13</td>
<td>39 ± 17</td>
<td>30 ± 21</td>
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<tr>
<td></td>
<td>(9–28)</td>
<td>(13–60)</td>
<td>(11–67)</td>
</tr>
<tr>
<td>DOP turnover (day)</td>
<td>5 ± 5</td>
<td>8 ± 4</td>
<td>6 ± 6</td>
</tr>
<tr>
<td></td>
<td>(1–10)</td>
<td>(3–14)</td>
<td>(2–15)</td>
</tr>
<tr>
<td>PME turnover (day)</td>
<td>53 ± 46</td>
<td>9 ± 5</td>
<td>10 ± 12</td>
</tr>
<tr>
<td></td>
<td>(20–86)</td>
<td>(5–13)</td>
<td>(3–28)</td>
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</tbody>
</table>

aData reported is mean ± 1 standard deviation.

Assuming that all DOP is turned over.

Assuming that only the semilabile fractions of DOP are turned over, equivalent to 21% in the subtropics and tropics and 37% in the NWAS shelf waters.
When normalized to biomass, the DOP production rate was higher in the subtropics (37 ± 32 nM/μg chl a d⁻¹) and tropics (34 ± 26 nM/μg chl a d⁻¹) relative to the northwest African shelf region (24 ± 29 nM/μg chl a d⁻¹) (Table 2). However, the differences were statistically insignificant, implying that the partitioning of organic matter between dissolved and particulate pools is relatively constant irrespective of biomass (see section 4).

Gross DOP production ranged from 6 to 62% of phosphate uptake (Table 2 and Figure 5). Despite the significant differences in phosphate concentration and biomass between the northwest African shelf region, tropics, and subtropics, the proportion of DOP exuded relative to phosphate uptake was similar between the subtropics (11 to 62% or 39 ± 18%) and tropics (16 to 47% or 28 ± 15%) and northwest African shelf region (6 to 33% or 19 ± 19%) (Figures 5a and 5b) and within the range of measurements from the subtropical North Pacific (10 to 40%) [Björkman et al., 2000]. The highest DOP production relative to phosphate uptake (47 to 62%) was measured at stations in the tropics (at 1° and 8°N; Figure 5a) and subtropics (12°, 15°, and 17°N; Figures 5a and 5b).

Gross DOP production is estimated by the sum of the measured rates of net DOP production plus APA. It is likely that we have underestimated gross DOP production and subsequent parameters because analysis of production of ³²P-labeled DOP measures the total amount of DOP produced, whereas APA measures consumption of only one fraction of the semilabile DOP pool. We did not measure consumption of other fractions of the DOP produced locally. Therefore, we have used an upper bound value of 50% to present the fraction of DOP produced relative to phosphate uptake in the model study (see section 4).

### 3.3. Comparison of Production and Consumption of DOP

Using our estimates for the magnitude of phosphorus pools and rates of phosphorus cycling, we now examine and discuss the balance between production and consumption of DOP in the northwest African shelf region, subtropics, and tropics. Any mismatch in production and consumption implies the region is a source or sink of DOP, although there is always the possibility of seasonal aliasing and caveats regarding interpretation of rate measurements as mentioned above. In the northwest African shelf region, the rate of APA was 2.6 ± 2.1 nM d⁻¹ (range 1.2 to 4.1 nM d⁻¹) and the rate of DOP production was 43 ± 41 nM d⁻¹ (10 to 89 nM d⁻¹) (Table 2). This difference implies that there is ~40 nM (or between 9 and 85 nM) of DOP produced per day that is in excess of the phosphorus requirements of the extant plankton community. Indeed, the concentration of phosphate in the northwest African shelf region is sufficiently high to support 99% of the phosphorus demand, allowing DOP to reach relatively high concentrations of 222 ± 33 nM.

In contrast to the northwest African shelf region, the production and consumption of DOP in the tropics and subtropics appear to be more tightly coupled. At seven stations, the rate of APA is significantly greater than DOP production, implying that there is a deficit in DOP (up to 19 nM), requiring an exogenous source to meet the phosphorus demands of extant plankton community. At four stations sampled in the tropics (1° and 8°N) and subtropics (15° and 17°N), the rate of DOP production is higher than the rate of APA, implying a small excess in DOP (<12 nM) relative to the DOP requirements implied by APA. However, at 3 out of the 14 stations sampled in the tropics and subtropics, the rate of APA and DOP production in the subtropics were not significantly different (p < 0.05).
There may be a number of factors causing the decoupling of DOP production and consumption in the northwest African shelf region, but instead a tighter coupling of these processes over much of the subtropics and tropics. High phosphate concentrations in the shelf region (168 to 675 nM) are likely to have suppressed alkaline phosphatase activity, as previously observed in this region [Sebastián et al., 2004] and in the coastal upwelling system off of the Oregon coast where phosphate concentrations were > 500 nM [Ruttenburg and Dyhrman, 2012]. Indeed, Sebastián et al. [2004] observed a 50% decrease in APA upon the addition of only 0.1 μM phosphate. Suppressed APA and perhaps other phosphohydrolytic enzymes reduce consumption of DOP, allowing DOP to accumulate. Although the mean rate of DOP production relative to phosphate uptake was lower in the northwest African shelf region (19 ± 19%) relative to the subtropics (39 ± 18%) and tropics (28 ± 15%), the higher phosphate concentration in the northwest African shelf region caused volumetric DOP production rates to be higher reflecting luxury uptake of phosphate and exudation of DOP under bloom-type conditions, as has been previously observed for DOM [Wetz and Wheeler, 2003].

Similar observations of excess DOP production has been reported in nutrient addition experiments in the coastal upwelling system along the Oregon coast [Ruttenburg and Dyhrman, 2012]. Based on their observations, Ruttenburg and Dyhrman [2012] hypothesize that the nitrate to phosphate ratio may control DOP production rates due to the influence of phosphate on hydrolytic enzyme activity. In our study, the nitrate:phosphate ratio of surface waters in the shelf region ranged from 5:1 to 10:1, implying an excess of phosphate and thus supporting this hypothesis.

In the subtropics and tropics, the production and consumption of DOP were coupled or there was a slight over-consumption in DOP. While the half saturation constant for phosphate uptake by the biological community living in the oligotrophic gyres is low (e.g., 57 ± 81 nM) [Orchard et al., 2010], weak vertical fluxes of phosphate require that phosphate is rapidly turned over on time scales of hours, as has been reported [McLaughlin et al., 2013] and/or phosphorus is sourced from organic matter through activity of enzymes such as alkaline phosphatase, which are widespread [Dyhrman et al., 2007; McLaughlin et al., 2013]. Thus, any freshly produced DOP, which is likely to be labile to semilabile on the sliding scale of bioavailability [Lonberg et al., 2009], will be rapidly hydrolyzed to phosphate to meet the phosphorus demand of the local bacterial and autotrophic community. While there are a number of caveats associated with our rate measurements (e.g., measurement of only one phosphohydrolytic enzyme, APA), the fact that PME concentrations were below our limits of detection of 15 nM at more than 50% of the sites sampled in the tropics and subtropics lends further support to the tight coupling between production and consumption of these labile compounds.

### 3.4. Impact of Community Structure on DOP Dynamics

Enhanced DOP production in the northern edge of the north-south transect (15 to 18°N) coincided with two stations where the lowest rate of APA was measured, causing excess DOP production relative to consumption. Analysis of the community structure shows that there was a switch in the diazotrophic community structure at ~ 15°N from a system dominated by *Trichodesmium* to the south of 15°N to a system dominated by uncultured unicellular diazotrophs to the north of 15°N (R. Langlois, unpublished data, 2012). While *Trichodesmium* spp. are known to rely heavily on DOP as a phosphorus source [Sohm et al., 2008] and the unicellular diazotroph, *Crocosphaera*, are known to be able to grow on phosphate and PME [Dyhrman and Haley, 2006], the phosphorus demands and acquisition strategies of uncultured unicellular diazotrophs are currently unknown. We speculate that the switch in community structure from a DOP-demanding community to a community that is less reliant on DOP may explain our observed excess production in DOP. This idea needs to be further explored but suggests that the nutrient distributions respond to and shapes the phytoplankton community.

In summary, our observations support our hypothesis that there is significant net DOP production relative to consumption in the northwest African shelf region and net consumption of DOP within the gyre, thus requiring an external source of DOP to meet phosphorus demands of the plankton community. However, our observations are snapshots and extend over a limited area of the eastern Atlantic. Therefore, our hypothesis is now assessed by a modeling study extending over the Atlantic basin.

### 4. Model Assessment of DOP Pathways

The hypothesis that DOP is preferentially transported offshore from the shelf and sustains productivity over the subtropical gyre is now assessed using a coupled isopycnic circulation and simplified nutrient
model; full models details are provided in Roussenov et al. [2006] and Torres-Valdés et al. [2009]. Based on our observational analyses, the formation of organic matter is now chosen to be equally partitioned between the formation of POP and DOP (see section 3.2). The model formulation is briefly reviewed, the background nutrient distributions are similar to that previously reported in Torres-Valdés et al. [2009], and additional model experiments are included to reveal the sensitivity of the modeled productivity to the DOP closures. The model is then employed to illustrate the pathways and mechanisms by which phosphate and DOP in the northwest African shelf region are transported offshore into the subtropical gyre, so as to provide a wider context to the observational data.

4.1. Formulation of the Physical Model

The physical model is eddy permitting, with a horizontal resolution of 0.23°, configured for an Atlantic basin, extending from 35°S to 65°N and from 98.5°W to 19°E, with realistic bottom topography from ETOP05 [General Bathymetric Chart of the Oceans (GEBCO), 2003]; there are sponge layers on the southern and northern boundaries, relaxing isopycnals and salinity to climatology, and a relaxation of salinity close to a closed Strait of Gibraltar. The physical model adopts an isotopycnal formulation (MICOM 2.7) [Bleck and Smith, 1990] designed to provide an improved representation of ventilation and tracer transport; there are 15 isopycnal layers in the vertical ($\sigma_2$, potential density referenced to 2 km) plus a surface mixed layer with variable density. Outside the mixed layer and the sponge layers, there is only a weak diapycnal diffusivity, $\kappa$, typically of $4 \times 10^{-5} \text{m}^2 \text{s}^{-1}$ in the main thermocline, inversely dependent on buoyancy frequency. There is also an isopycnal mixing of tracers and thickness diffusion, and deformation-dependent momentum mixing.

The dynamical model is initialized from Levitus climatology [World Ocean Atlas, 1998] and integrated for 60 years forced by National Centers for Environmental Prediction (NCEP) monthly mean winds and surface fluxes in a repeating climatological mean year mode; rivers are added as freshwater fluxes at corresponding coastal grid points. The modeled surface temperature reveals a westward warming across the subtropical gyre, a consequence of the warm waters swept northward along the western boundary current and cool waters upwelled along the eastern boundary (Figure 6a). The mixed-layer thickness typically ranges from 100 m to 200 m during March (Figure 6b) and is thickest along the path of the extension of the Gulf Stream and North Atlantic Current due to the accumulated surface heat loss to the atmosphere.

4.2. Phosphorous Model Formulation and Phosphorus Distributions

The physical model after 60 years integration is coupled with the phosphorus model, including phosphate and DOP, and integrated for another 20 years. Organic matter in the model is only formed within the euphotic zone, which has a constant thickness of 100 m. Particulate organic matter (POM) is assumed to sink and be remineralized in the interior with a vertical remineralization scale of 200 m. The phosphate and semilabile and refractory components of DOP are transported by the circulation with lifetimes in the euphotic zone of typically 6 months for the semilabile and 6 to 12 years for the refractory components, depending on the short wave irradiance. The labile components are excluded from the model due to their turnover time (days) being fast relative to the model time scales (months to years).

The rate of consumption of the inorganic nutrients follows Michaelis-Menten kinetics with a dependence on the radiation intensity and the inorganic nutrient concentrations. The consumed fraction of inorganic nutrients is split into POP- and DOP-related parts in a 50:50 ratio. Here and in our previous work [Torres-Valdés et al., 2009], we assume that only a small fraction of recently exuded DOP is refractory (5%), implying that 95% of DOP produced by plankton is semilabile. Between 50 and 100% of DOP is considered to be semilabile or bioavailable with turnover times of weeks to months. We assume that the composition of recently exuded DOP must be similar to or more bioavailable than what is measured in the bulk DOP pool. This choice is supported by our observations that imply tight coupling between the production and consumption of DOP, meaning that DOP must be biologically available on short time scales. In addition, a recent experimental study by Lonberg et al. [2009] lends support to this split as they found that 73 ± 15% of DOP exuded by heterotrophic microbes was bioavailable.

The initial phosphate concentration and distribution is taken from climatology [Conkright et al., 1994], while the semilabile DOP is initialized to be 0 nM and the refractory DOP as 40 nM. Along the southern closed boundary, nutrients are continuously relaxed to the initial condition within the buffer zones, and there are no atmospheric or riverine inputs of nutrients, nor any loss of nutrients on the seafloor through burial.
Nutrient distributions are determined by the interplay of the formation of organic matter, the regeneration into dissolved inorganic nutrients, and the physical transport and mixing of the inorganic and dissolved organic nutrients [Williams and Follows, 2003]. The model shows that over the tropical Atlantic and subtropical North Atlantic, phosphate and DOP concentrations within the mixed layer are typically less than 300 nM (Figure 6c) and up to 160 nM (Figure 6d), respectively. An exception is along part of the African shelf (between 10°N and 30°N), where there are higher phosphate concentrations (>500 nM) and low DOP concentrations (<120 nM), coincident with cooler waters. This narrow boundary signal is probably

Figure 6. Model distributions in the surface mixed layer in March: (a) surface temperature (°C); (b) mixed-layer thickness (m); (c) phosphate (nM); (d) DOP (nM); (e) percentage of DOP relative to the total dissolved P (phosphate plus DOP); and (f) percentage of semilabile DOP relative to total DOP (semilabile plus refractory).
formed by equatorial winds driving an offshore Ekman cell and upwelling phosphate-rich and DOP-depleted, colder waters to the surface.

In the surface mixed layer, the DOP represents from 40% to 70% of the TDP in the model, apart from that in the coastal upwelling along the African shelf where that fraction is less than 30% due to the low DOP concentrations in deep waters (Figure 6e). The semilabile proportion of DOP varies from 35% in the central part of the subtropical gyre up to 65% offshore of the northwest African shelf region (Figure 6f). While the model closure assumes that 95% of freshly formed DOP is semilabile, the fraction of semilabile DOP diminishes as this component is consumed.

4.3. Production of Organic Matter and Sensitivity to DOP Cycling and Transport

The production of organic matter in the euphotic zone is sustained by the supply of phosphate, which is formed by the regeneration of both POM below the euphotic zone and DOP throughout the water column. There is high productivity (~50 mmol P m$^{-2}$ yr$^{-1}$) along and offshore of the northwest African shelf region (Figure 7a), where there are phosphate-rich surface waters (between 10°N and 30°N). Elsewhere the productivity ranges from typically 15 to 40 mmol P m$^{-2}$ yr$^{-1}$ over much of the subtropical gyre (Figure 7a). The model closures assume that 95% of the production of organic matter then forms DOP. The production of organic matter is partly sustained by the inclusion of semilabile DOP, which enhances the...
production by up to 35 mmol P m$^{-2}$ yr$^{-1}$ over the eastern side of the subtropical gyre and by 10 to 20 mmol P m$^{-2}$ yr$^{-1}$ over the western side of the subtropical gyre (Figure 7b); this estimate is based on the difference between two model simulations with and without semilabile DOP included. In turn, much of the particulate export is likewise sustained by the semilabile DOP, accounting for 70% of the particle export over much of the basin (Figure 7c). This regional enhancement in particle export (Figure 7c) is more extensive than the region of high DOP concentration (Figure 6d), due to the transport of DOP over the entire subtropical gyre. When the model experiments are repeated at coarse resolution of 1.4° on a Mercator grid, DOP sustains 70 to 80% of particle export over the central part of the subtropical gyre (Figure 7d), a slightly higher percentage, although over a more confined region, than when eddy stirring is incorporated.

The sensitivity of the production of organic matter is now assessed by modifying the choices made within the DOP closures for the production and lifetime of semilabile DOP formed and the partition of phosphorus production between DOP and POP. The sensitivity experiments are conducted using a coarse-resolution variant of the circulation model solving for the phosphate and DOP distributions at 1.4° in the horizontal [Roussenov et al., 2006]. Each sensitivity experiment has been integrated for 40 years after a 60-year dynamical spin-up, the same as for the default integration.

Reducing the proportion of semilabile DOP produced from the default choice of 95% to 80% leads to a reduction in total production over much of the subtropical gyre, typically being reduced by 8% over much of the oligotrophic subtropical gyre and reduced by up to 15% over the center of the subtropical gyre (Figure 8a, left). This reduction is due to the more limited role that DOP plays in sustaining production given its reduced semilabile fraction.

Reducing the lifetime of the semilabile DOP from the default choice of 6 months to 2 months leads to a slight increase in total production by up to 5% over parts of the subtropical gyre due to the more rapid regeneration into phosphate (Figure 8b, left). At the same time, there are localized regions with a slight reduction in the total production, such as in the western side of the subtropical gyre, due to the reduced supply of DOP from the sources along the eastern boundary.

Changing the partitioning of phosphorus production between DOP and POP from the default choice of 50:50 to 60:40 leads to an enhancement in total production by typically 15% over the central and western parts of the subtropical gyre (Figure 8c, left). This enhancement in total production is due to the increased availability of DOP to help sustain productivity in phosphate-depleted surface waters of the subtropical gyre.

For each of these sensitivity experiments, there are only slight changes by ±10% in the proportion of particle production sustained by semilabile DOP over the subtropical gyre (Figures 8a–8c, right); their maxima range from 65–70% to 75–80%, is broadly in accord with that obtained for the previous coarse-resolution default case (Figure 7d). Hence, while there are significant uncertainties and perhaps variability as to the appropriate parameters chosen for the DOP closures, these model sensitivity experiments support the view that the cycling and transport of semilabile DOP acts to sustain particle export over much of the subtropical gyre, supporting up to 70% of the particle export (Figures 7c and 7d and 8a–8c).

### 4.4. Transport Pathways and Fluxes of DOP and Phosphate

Our data study suggests that within the surface mixed layer, phosphate is preferentially utilized in the northwest African shelf region, forming DOP, which is then transported offshore. The DOP is then utilized when the phosphate is exhausted in the subtropics. This process is now assessed within the high-resolution version of the model.

Circulation actively redistributes phosphate and DOP over the basin. The transport pathways are revealed by the time integral of the horizontal nutrient fluxes, $\mathbf{U}$ phosphate and $\mathbf{U}$ DOP, evaluated from the product of the horizontal transport vector, $\mathbf{U}$, and nutrient concentrations (Figures 9a and 9b). There are westward components of the transports of phosphate between 15°N and 20°N and DOP between 10°N and 15°N from the eastern boundary (Figures 9a and 9b). Ultimately, this westward transport of phosphate and DOP is either utilized, sustaining the productivity in the interior of the subtropical gyre (Figure 7a), or fed into the western boundary currents, sustaining the strong northward nutrient transports, referred to as nutrient streams [Pelegrí and Csanady, 1991; Williams et al., 2011].
Figure 8. Sensitivity experiments for the effect of DOP cycling on (left) total production change (%) relative to a default coarse model and the (right) proportion of particle production (%) from semilabile DOP. The set of experiments employ a coarse-resolution model integrated for the nutrients for 40 years after a dynamical spin-up of 60 years, each including separate changes to the DOP cycling: (a) proportion of semilabile DOP produced is reduced to 80% (compared with a default choice of 95%); (b) lifetime of semilabile DOP reduced to 2 months (compared with a default choice of 6 months); and (c) increased ratio of DOP production, organic production made up of 60% DOP, and 40% POP (rather than a default choice of 50% DOP and 50% POP).
The westward transport of phosphorus in the mixed layer from the shelf region on the African coast (10°N to 30°N) is initially dominated by that of phosphate, reaching 2.5 kmol s⁻¹ at 17°W compared with a smaller westward DOP transport there of almost 1 kmol s⁻¹ (Figure 9c). In the basin interior, the westward transport of phosphate and DOP becomes comparable at 34°W, but then the westward DOP transport dominates, exceeding 2 kmol s⁻¹ at 60°W and with typically half of that transport for semilabile DOP. These east-west
changes in the phosphate and DOP transports reflect how surface phosphate is mainly utilized offshore, while DOP is both produced and consumed offshore within the surface mixed layer.

The offshore transport of DOP and phosphate is achieved through a combination of the time-mean and time-varying eddy circulations, given by the thickness-weighted flux of tracer over the mixed layer, which written for the transfer of DOP is given by

$$\bar{u}h \cdot \text{DOP} = \bar{uh} \cdot \text{DOP} + \bar{u}h^\prime \cdot \text{DOP} + (uh) \cdot \text{DOP},$$

(1)

which consists of an advection by the time-mean velocity, $$\bar{u}$$ (first term on right-hand side), an advection by the time-varying eddy velocity, $$\bar{u}h^\prime/\bar{h}$$ (second term on the right-hand side), and an effective diffusive transfer (third term on the right-hand side of (1)); $$h$$ is the thickness of the mixed layer, the overbar represents a time average, and the prime is a departure from the time mean. Most of the DOP transport is facilitated by the advection by the time-mean flow transfer with the time-varying advective and diffusive transfers (second and third terms on right-hand side of (1)) being only 10% the magnitude of the time-mean advection. In contrast, each of the contributions to the phosphate transport are comparable, a strong offshore transport by the time-mean flow, an opposing on-shore transport by the time-varying eddy velocity, and an offshore diffusive transfer. Thus, there is a partial cancellation of the phosphate transport by the time-mean and time-varying circulations, as previously modeled for eastern boundaries and discussed in terms of how eddies oppose the wind-driven upwelling circulation [Gruber et al., 2011; Williams, 2011].

In summary, the model diagnostics illustrate the phosphate and DOP pathways, confirming a lateral transfer from the northwest African shelf region, and revealing how this tracer transfer is achieved via combination of advection by the time-mean velocity and eddy velocity, and lateral diffusion.

5. Discussion

While there are detailed differences in the model and observed distributions of phosphorus, the model experiment broadly supports our observations and our hypothesis of how DOP is cycled and transported: (i) on-shelf and shelf edge processes, as well as coastal upwelling, supplies water with high phosphate and low DOP concentrations along part of the northwest African shelf region; (ii) phosphate is utilized resulting in net production of DOP; (iii) excess phosphate and DOP is transported offshore into the subtropics; and (iv) the surface phosphate is rapidly depleted in the subtropics through biological consumption, leading to an increased importance in the labile and semilabile fractions of DOP as a source of phosphorus.

Although the importance of DOP as a nutrient source has been previously reported from both observations and model studies, the novel aspects of this study are (a) the observational evidence for the net production of DOP in the northwest African shelf region (Figures 4e and 4f) relative to the subtropics and (b) the increased importance of DOP transported from the northwest African shelf region into the subtropics (Figure 4d), both in terms of contribution to the phosphorus pool and in sustaining productivity. In addition, our model study highlights the distinct east-west contrast in phosphorus regime between the eastern subtropical Atlantic and Sargasso Sea, where there are relatively high versus low proportions of semilabile DOP, respectively, and provides new estimates of DOP and phosphate transport from the northwest African shelf region into the northern subtropical gyre.

5.1. East-West Comparison of Phosphorus Dynamics

Our model output (Figures 6 and 7) and cross-basin observations [Torres-Valdés et al., 2009; Sohm and Capone, 2010] highlight an east-west contrast in phosphorus dynamics between the Sargasso Sea and eastern subtropical Atlantic, in terms of the extent of semilabile DOP. Although the volumetric rates of phosphate uptake in our study region (12 to 68 nM d⁻¹) were similar to those reported in the Sargasso Sea (3 to 78 nM d⁻¹ [Orchard et al., 2010]), the phosphate turnover time in the eastern Atlantic was much longer (0.5 to 4 days, or 12 to 96 h) compared to the Sargasso Sea (<10 h [Lomas et al., 2010]; see references in Sohm and Capone [2010]). Biomass-normalized phosphate uptakes (70 to 456 nmol µg chl d⁻¹) were lower than those reported in the Sargasso Sea (72 to 3120 nmol µg chl d⁻¹ [Orchard et al., 2010] and 600 to 3720 nmol µg chl d⁻¹ [McLaughlin et al., 2013]). Biomass-normalized APA (0.4 to 95 nmol µg chl d⁻¹) was at least an order of magnitude lower than that reported by Orchard et al. [2010] (504 to 2256 nmol µg chl d⁻¹) and by McLaughlin et al. [2013] (74 to 2014 nmol µg chl d⁻¹) in the Sargasso Sea.
The shorter turnover time and higher rate of biomass-normalized uptake rates in the western Atlantic compared to our study region in the eastern Atlantic probably reflect the greater degree of phosphate deficiency and lower biomass observed in the western Atlantic [Sohm and Capone, 2010]. In our study region and during the time of sampling, the concentration of phosphate (12 to 100 nM) and DOP (83 to 215 nM) was higher than that typically observed in the Sargasso Sea (4 to 7 nM and 56 to 69 nM, respectively) [Lomas et al., 2010]. The chlorophyll concentration in the western tropical Atlantic tend to be much lower (<0.05 μg L⁻¹ [Lomas et al., 2010; Orchard et al., 2010]) than the concentrations measured in our study (>0.50 μg L⁻¹).

In studies by Lomas et al. [2010] and Orchard et al. [2010], both phosphate uptake and APA rates are reported (volumetric rates calculated from published data sets). If we assume that 50% of phosphate assimilated is exuded as DOP (see section 3.2), then the rate of DOP production is estimated to be between 7 and 12 nM d⁻¹ [Lomas et al., 2010] (spring only) and 0.6 to 16 nM d⁻¹ [Orchard et al., 2010]. If we compare the rate of DOP production to the rate of APA reported by Lomas et al. [2010], (51 ± 19 nM d⁻¹, spring only) and Orchard et al. [2010] (19 to 47 nM d⁻¹), the rate of DOP consumption far exceeds the rate of DOP production, implying a deficit relative to the daily phosphorus requirements. There is accumulating evidence for the importance of DOP as a nutrient source in both the eastern [Mather et al., 2008; this study] and western subtropical Atlantic [Sohm and Capone, 2006; Lomas et al., 2010; Orchard et al., 2010; McLaughlin et al., 2013] where DOP is estimated to support between 20 and 80% of phosphorus demand required to sustain primary production. McLaughlin et al. [2013] argues that local regeneration of DOP can supply up to 70% of phosphate, while in our view, there is a combination of local regeneration and transport of DOP into phosphate-depleted regions of the subtropical gyre.

### 5.2. Wider Context for the Phosphate and DOP Transports

The transport of DOP provides an important supply of phosphorus and also an associated transport of DON. Using data published by Torres-Valdés et al. [2009], typical concentrations of DON and DOP in the northwest African shelf region are 5.1 μM and 0.22 μM, respectively. The DON:DOP ratio is therefore 23, implying the supply of excess N relative to P. However, DON and DOP contain variable fractions of biologically available material. Only 10 to 16% of DON is considered to be semilabile, whereas at least 35% of DOP is semilabile [Torres-Valdés et al., 2009]. Therefore, using 16% and 35% to represent the semilabile pools of DON and DOP results in an DON:DOP ratio of 10, implying the transport of DOM provides an excess of available P relative to N.

In section 4.4, our model experiments suggest that the westward transport of phosphate from the eastern shelf reaches 2.5 kmol s⁻¹ and the westward transport of DOP at 35°W reaches 1.5 kmol s⁻¹ (Figure 9c). There is a comparable near-surface, northward phosphate transport along the Gulf Stream, ranging from 2.1 to 1.6 kmol s⁻¹ within the lightest waters, α₀ < 26.2, decreasing with latitude from the Florida Strait at 27°N to the separation at Cape Hatteras, 36.5°N [Williams et al., 2011], as well as a smaller Ekman phosphate transport across the Gulf Stream (0.5 ± 0.3 kmol s⁻¹) [Palter et al., 2011]. There are also comparable phosphate transports from the Arctic through flow (0.63 kmol s⁻¹ [Yamamoto-Kawai et al., 2006] and 0.98 ± 0.29 kmol s⁻¹ [Torres-Valdés et al., 2013]) and via northward spreading of Subantarctic Mode water and Antarctic Intermediate Water (0.63 to 2.22 kmol s⁻¹ [Moore et al., 2009]).

### 6. Conclusion

This combined observational and modeling study supports our hypothesis that the horizontal transport of DOP across the boundary of the North Atlantic subtropical gyre is an important mechanism supplying phosphorus to the gyre interior. Our observational analyses provide the first direct evidence for the net production of DOP on the northwest African shelf region. Model output provides estimates of westward horizontal transport of DOP and phosphate from the northwest African shelf region over the equatorial flank of the subtropical gyre. As the supply of phosphate decreases westward from the northwest African shelf region, our observations highlight increased consumption of DOP. DOP is transported far into the interior and may reach the western side of the subtropical Atlantic, where phosphate limitation is even more acute than on the eastern side. There is a much higher proportion of semilabile DOP over the eastern versus the western side of the subtropical gyre.
The potential for a lateral supply of organic nutrients from coastal upwelling systems or shelf seas to the open ocean is not confined to the subtropical North Atlantic. Wind-induced upwelling is likely to enhance the surface supply of macronutrients and form dissolved organic nutrients along the eastern boundaries of other ocean basins. A combination of the gyre and upwelling circulations is likely to transport organic nutrients, albeit at different spatial or seasonal scales, away from the site of formation. Indeed, there is growing observational evidence of this mechanism, specifically excess DOP production and subsequent lateral transport, in the northwest African shelf region [Sebastián et al., 2004; this study] and the upwelling system off the Oregon coast [Ruttenburg and Dyhrman, 2012]. However, a unique feature of the subtropical North Atlantic is that the surface waters have the lowest phosphate concentrations of the global ocean due to drawdown of phosphate by nitrogen fixing organisms, and thus, the lateral supply of DOP is disproportionately important as a phosphorus source to diazotrophs and non-diazotrophs in the North Atlantic basin and important in sustaining productivity. In other ocean basins, lateral transport of other macronutrients or trace elements, such as iron, may be more important for sustaining plankton growth and productivity.

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