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Phosphate and iron stress control global surface ocean dissolved organic phosphorus concentrations

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Abstract

Dissolved organic phosphorus (DOP) has a dual role in the surface ocean as both a product of primary production and as an organic nutrient fueling primary production and nitrogen fixation, especially in oligotrophic gyres. Though poorly constrained, understanding the geographic distribution and environmental controls of surface ocean DOP concentration is critical to estimating distributions and rates of primary production and nitrogen fixation in the global ocean. Here we pair DOP concentration measurements with a metric of phosphate (PO_4^{3-}) stress (P^*), and satellite-based chlorophyll *a* concentrations and iron stress estimates to explore their relationship with upper 50 m DOP stocks. Our results show that PO_4^{3-} and iron stress work together to control surface DOP concentrations at basin scales. Specifically, upper 50 m DOP stocks decrease with increasing phosphate stress, while alleviated iron stress leads to either surface DOP accumulation or loss depending on PO_4^{3-} availability. Our work suggests an interdependence between DOP concentration, inorganic nutrient ratios, and iron availability, and establishes a predictive framework for DOP distributions in the global surface ocean.

Main

In oligotrophic gyres, dissolved organic phosphorus (DOP) is the dominant form of phosphorus (P) in surface waters¹⁻³ and supports phytoplankton growth when the preferred substrate, phosphate (PO_4^{3-}), is scarce⁴⁻¹⁰. Estimates from the Biogeochemical Elemental Cycling (BEC) model indicate that global marine net primary production (NPP) and di-nitrogen (N_2) fixation rates are ~8% and ~33% higher, respectively, and better match observed rates, when they include DOP as an assimilative P source¹¹. Like dissolved organic carbon and nitrogen (DOC and DON) in the ocean, DOP is a product of primary production¹². However, a clear understanding of both the distribution of DOP in the global surface ocean as well as the controls on those distributions is limited by the relatively small number of DOP concentration measurements in the global ocean¹¹. A mechanistic framework to understand the controls on surface ocean DOP concentrations would thus improve model-based estimates of the rates and distributions of marine NPP and N_2 fixation.

Given that DOP is both produced and consumed by photosynthetic organisms, we explored relationships between DOP distributions and metrics of primary production (i.e., DOP production), PO_4^{3-} stress (i.e., DOP consumption), as well as iron stress, which can limit primary production. Additionally, iron has recently been identified as a co-factor in a version of the enzyme responsible for DOP utilization by phytoplankton, alkaline phosphatase^{10,13,14}, and thus iron availability may also affect DOP consumption. To test these relationships, we paired surface ocean DOP concentration measurements (Fig. 1) with satellite-based measurements of chlorophyll *a* concentration, climatological “excess PO_4^{3-} ” or “ P^* ” values evaluated in surface waters (< 5m), where P^* is defined as $[\text{PO}_4^{3-}] - ([\text{NO}_3^-]/16)$ ¹⁵, and satellite-derived iron stress estimates¹⁶ (Figs. 1, 2). We find that upper 50 m DOP concentrations are significantly positively correlated with

surface P^* values ($R^2 = 0.28$, $p < 0.000001$) (Fig. 1b). Here, higher P^* values correspond to lower PO_4^{3-} stress, consistent with stoichiometric biomass demands for N and P^{17} , as well as PO_4^{3-} concentration thresholds for DOP utilization by phytoplankton². In addition to PO_4^{3-} stress, iron stress also plays a significant but more complicated role regulating surface DOP concentrations and can lead to either surface DOP accumulation under enhanced iron stress or consumption under alleviated iron stress. Based on these relationships, we present a conceptual model of the factors controlling surface ocean DOP concentrations.

Global regions of net DOP production and loss

The ultimate source of dissolved organic matter (DOM) to the ocean is marine primary production, and DOC and DON accumulate in regions with elevated productivity^{18–21}. Similar to DOC and DON, we find that upper 50 m DOP stocks are significantly positively correlated with satellite-based measures of chlorophyll *a* concentration on the P18-2016 GO-SHIP and BIOSOPE cruises²² in the Eastern Pacific as well as in the Gulf of Mexico (Figs. 1, 2, Table 1). Correspondingly, the Eastern North and South Pacific Ocean and Gulf of Mexico have the highest mean surface ocean DOP concentrations in our dataset, averaging $0.34 \pm 0.07 \mu\text{M}$, $0.23 \pm 0.07 \mu\text{M}$, and $0.23 \pm 0.07 \mu\text{M}$ (Fig. S1), respectively, and represent regions of net DOP production. In contrast, North Atlantic and Western North and South Pacific surface ocean DOP and chlorophyll *a* concentrations are significantly negatively correlated (Fig. 2, Table 1). In these samples, when chlorophyll *a* is high, DOP concentrations are low, indicating that these regions are not associated with DOP production, but that instead DOP is used as an assimilative P source sustaining productivity. Thus, the North Atlantic, Western North and South Pacific Oceans appear to be net sinks for DOP, and have the lowest observed basin-mean concentrations, $0.10 \pm 0.07 \mu\text{M}$, $0.12 \pm 0.02 \mu\text{M}$ and $0.14 \pm 0.04 \mu\text{M}$ (Fig.

S1), respectively, all of which are statistically significantly lower than the mean values in the Eastern Pacific and Gulf of Mexico (Fig. S1). Below we explore the interdependence of surface ocean DOP concentrations, primary productivity, PO_4^{3-} stress (P^*), and surface ocean iron availability.

PO_4^{3-} as the primary control on surface ocean DOP concentrations

The primary control on surface ocean DOP concentrations is PO_4^{3-} stress, gauged by P^* , with upper 50 m DOP stocks in all data sets significantly positively correlated with P^* (Fig. 1b) (Table. 1). Global regions of net DOP production in the Eastern Pacific are associated with elevated P^* values, typically $>0.2 \mu\text{M}$ (Fig. 1b), generated by subsurface denitrification and anammox in the oxygen deficient zones (ODZs) in and upstream of these sampling locations²³. Surface waters with high P^* values thus correspond to regions with “excess PO_4^{3-} ”, or low PO_4^{3-} stress, relative to supplies of NO_3^- and “Redfieldian” phytoplankton N and P demands^{15,17}. The upwelling-driven elevated DOP production in regions with low PO_4^{3-} stress allows DOP to accumulate to relatively high concentrations in the Eastern Pacific, as observed in the P18-2016 GO-SHIP and BIOSOPE²² data sets, as well as in the Gulf of Mexico (Figs. 1, 2). While high P^* values, and thus low PO_4^{3-} stress, are correlated with elevated DOP concentrations in surface waters above the Eastern Pacific ODZs, DOP consumption happens elsewhere in the global ocean with low P^* values, and thus higher PO_4^{3-} stress. In particular, samples from the North Atlantic and Western North and South Pacific Oceans show decreasing upper 50 m DOP stocks with increasing chlorophyll *a* concentration (Figs. 1, 2), consistent with previous observations of DOP being an important assimilative P source sustaining autotrophs in the Sargasso Sea^{2,3,5,7,24}. Given the significant correlation of upper 50 m DOP stocks and P^* (Fig. 1), PO_4^{3-} stress is considered the primary control on surface ocean DOP

distributions.

Iron stress modifies surface ocean DOP accumulation and loss

Whereas higher PO_4^{3-} stress leads to enhanced DOP consumption on the global scale, alleviated iron stress can promote either DOP production or consumption. Here, remote sensing products are used to evaluate iron stress experienced by phytoplankton¹⁶. In the P18-2016 GO-SHIP and BIOSOPE²² Eastern Pacific samples, iron stress and upper 50 m DOP stocks are significantly negatively correlated (Table 1), which we interpret to reflect enhanced DOP production when iron stress is alleviated in high-chlorophyll *a* upwelling regions (Fig. 2). A significant negative correlation between upper 50 m DOP stocks and iron stress is also found on the West Florida Shelf in the Gulf of Mexico (Table 1) (Fig. 2). On the global scale, the Eastern Pacific appears unique as a region of net DOP production in upwelling-associated, relatively low-iron stress surface waters, with that DOP subsequently advected west away from regions of net DOP production and accumulating due to low PO_4^{3-} stress in the eastern portion of the Pacific.

In contrast to the Eastern Pacific and Gulf of Mexico, basins with net DOP consumption exhibit significant positive correlations between upper 50 m DOP stocks and iron stress (Table 1) (Fig. 2). Specifically, in samples from the P06-2017 GO-SHIP cruise in the subtropical South Pacific, and the AMT17, AMT14 and 36N cruises² from the Atlantic Ocean, and the KH12-3 cruise²⁵ from the Western North Pacific Ocean, upper 50 m DOP stocks increase with increasing iron stress (Fig. 2). We interpret the higher DOP stocks in these waters with higher iron stress to reflect iron limitation of primary productivity, and thus decreasing demand for DOP as an assimilative P source, and/or iron limitation of alkaline phosphatase activity^{14,13}, thus limiting the ability of

phytoplankton to use DOP. The low DOP concentrations ($<0.15 \mu\text{M}$) in the North Atlantic and Western Pacific are found in regions with relatively high chlorophyll *a* concentrations (i.e., typically $>0.1 \text{ mg chl } a \text{ m}^{-3}$), low P^* values ($<0.1 \mu\text{M}$), and low iron stress (Fig. 2), consistent with DOP use by phytoplankton associated with oligotrophic environments as an assimilative P source when iron is available and PO_4^{3-} is scarce. The North Atlantic Ocean in particular receives high rates of dust deposition²⁶, and the South Western Pacific Ocean may receive significant hydrothermal iron fluxes²⁷, lowering iron stress in these regions. These regions are also associated with high rates of N_2 fixation^{28–31}, which may be due to certain diazotrophs (e.g., *Trichodesmium* spp.) being particularly well-adapted to utilizing DOP when PO_4^{3-} is scarce^{5,24,32,33}.

Finally, we note that DOP appears to accumulate in other specific regions of the ocean due to convergence of surface currents where iron stress is also high and thus limits productivity. Specifically, in the convergence zone of the South Pacific (Fig. 2d and S2), we observed elevated DOP concentrations ($\sim 0.3 \mu\text{M}$) in waters with high iron stress, low P^* , and low chlorophyll *a* concentrations (Fig 2). The same scenario was also found in the surface convergence zone of the South Atlantic, where the DOP concentration is higher than that of the gyre boundary (Fig. 2j and S2). We suggest here that DOP will accumulate in the surface convergence zone of the North Pacific, as well, which is another region with high iron stress, low P^* , and low chlorophyll *a* (Fig. S2). Further sampling would test this hypothesis.

Conceptual model of DOP accumulation and loss in the surface ocean

According to the observed relationships between upper 50 m DOP stocks, surface chlorophyll *a* concentrations, and PO_4^{3-} and iron stress, we propose a simple conceptual model of the factors

influencing DOP distributions in the surface ocean (Fig. 3). On the global scale, DOP loss is enhanced under elevated PO_4^{3-} stress, which increases to the right along the x-axis in Fig. 3, with surface DOP concentrations decreasing to the right and increasing to the left. Additionally, iron stress promotes both DOP production and consumption, depending on PO_4^{3-} stress. In Figure 3, iron stress increases up the y-axis. The four quadrants in Fig. 3 correspond to different PO_4^{3-} and iron stress regimes reflecting the corresponding role of DOP as either a product of or substrate for primary productivity in specific ocean regions.

As discussed above, the Eastern Pacific is a highly productive region with low PO_4^{3-} stress, resulting in net DOP production and accumulation (Figs. 1 and 2), and is represented by the two pink quadrants in the left of Fig. 3. Iron stress further influences the magnitude of DOP accumulation under low PO_4^{3-} stress. When both iron and PO_4^{3-} stress are alleviated, such as in surface waters overlying ODZs, enhanced primary production will lead to significant net DOP accumulation, so that DOP has a “production” signature. In contrast, the upper left light pink quadrant reflects regions in the Eastern Pacific Ocean exhibiting more muted net DOP accumulation due to surface ocean convergence of DOP produced in “upstream” regions and to the lower, iron-limited rates of primary productivity locally. Global surface ocean regions with the lowest DOP concentrations are associated with high PO_4^{3-} and low iron stress, such as the North Atlantic and Western North and South Pacific Oceans (Fig. 1). These regions are represented by the dark blue, lower right quadrant in Figure 3, and correspond to regions of net DOP loss that we interpret to reflect use of DOP as an assimilative P source sustaining productivity, perhaps especially by diazotrophs. Finally, the upper right, light blue quadrant corresponds to regions experiencing elevated PO_4^{3-} and iron stress, potentially including the South Atlantic. The South

Atlantic Ocean receives relatively low atmospheric dust inputs²⁶, and the lack of significant rates of water column denitrification and/or anammox in the eastern portion of the basin leaves low P^* values in the surface waters (Figs. 1, 2). Here, net changes in DOP distributions are small, with the potential co-limitation of primary productivity by PO_4^{3-} and iron.

Interestingly, the linear regression model used to fit the upper 50 m DOP stocks vs. P^* values (Fig. 1) predicts a surface DOP concentration at the BATS site (46 ± 22 nM, 95% confidence level of best fit line) that is similar to observations (~ 60 nM³). However, the predicted surface DOP concentration at Station ALOHA (146 ± 31 nM, 95% confidence level of best fit line) is lower than observations (~ 200 nM³⁴). We suggest the difference between the observed surface ocean DOP concentrations and those predicted by the linear regression at Station ALOHA potentially reflects iron limitation of DOP consumption, which is not accounted for in the simple correlation of surface ocean DOP concentration vs. P^* values. Given the higher atmospheric dust fluxes to the North Atlantic relative to the North Pacific near Hawaii, it is reasonable to expect that iron limitation plays a smaller role controlling DOP distributions at the BATS site. While the simple linear relationship between P^* and surface DOP concentration does not capture all the processes influencing surface ocean DOP concentration in the global ocean ($R^2 = 0.28$), the surface DOP concentrations predicted by the linear regression reflects observed basin-scale differences in surface DOP concentrations (Fig. S3). Meanwhile, the predicted global surface DOP distribution is much improved when including iron stress, P^* , and chlorophyll *a* concentration as predictors by using two machine learning algorithms (Fig S4, $R^2 = 0.44$ for support vector machine model and $R^2 = 0.42$ for boosted tree model), indicating that the influence of iron on DOP accumulation and loss in the surface ocean cannot be ignored.

Implications

Our observations demonstrate significant, basin-scale differences in correlations of upper 50 m DOP stocks with surface ocean chlorophyll *a* concentration, climatological upper 50 m inorganic nutrient concentration ratios, and remote sensing products of iron stress. Based on these observations, we present a predictive conceptual model for the controls on surface ocean DOP concentrations. Net DOP production is observed in regions with elevated P^* values and relatively low iron stress, consistent with elevated rates of productivity and low pressure on the DOP pool as an assimilative P source. Net DOP consumption is apparent in regions with P^* values $<0.1 \mu\text{M}$ and relatively low iron stress, suggesting phytoplankton growth is limited by PO_4^{3-} availability and not iron in these regions. This is consistent with emerging work evaluating the role of N, P, and Fe limitation in different ocean basins³⁵. This mechanistic model of surface DOP concentration distributions in the ocean provides a testable framework for both observational and modeling work, and can help constrain rates of NPP and N_2 fixations in the global ocean. Indeed, the region with the greatest net DOP loss, from the eastern to western end of the P06-2017 GO-SHIP cruise in the South Pacific, (i.e., $0.2 \mu\text{M}$ DOP loss between 130°W and 80°E longitudes), is consistent with where both recent observations and modeling work predicts high rates of N_2 fixation^{30,31,36,37}, indicating that DOP is likely an important P source fueling N_2 fixation in this region where PO_4^{3-} concentrations are low ($<0.1 \mu\text{M}$). Additionally, surface ocean DOP consumption enhances ocean-to-atmosphere methane fluxes³⁸, a potent greenhouse gas, and a predictive understanding of where DOP consumption occurs may improve CH_4 flux estimates. Finally, we note that geochemical measurements from cruises crossing significant biogeochemical gradients and/or basin-scale

transects paired with remote sensing products provide a unique opportunity to evaluate mechanistic controls on nutrient distributions and their role in fertilizing the ocean.

Methods

DOP concentration data

The DOP concentration data and additional cruise and sampling information can be found in the DOPv2021 database (<https://www.bco-dmo.org/dataset/855139>). Briefly, DOP concentrations from the P06-2017 GO-SHIP, P18-2016 GO-SHIP, and GOM2019 cruises were measured via the ash/hydrolysis method, a method recommended for more accurate DOP concentration analysis³⁹. DOP concentrations from the AMT17, AMT14 and 36N cruises were measured by the UV oxidation method^{2,40}. DOP concentrations from the BIOSOPE and KH12-3 cruises were measured by the persulfate oxidation method^{41,22,25}.

Surface P* values

NO₃⁻ concentrations ([NO₃⁻]) and PO₄³⁻ concentrations ([PO₄³⁻]) are taken from the World Ocean Atlas 2013 climatological field (1°x1°)⁴² at 0 m level. P* is calculated by the equation below with surface [NO₃⁻] and [PO₄³⁻]:

$$P^* = [PO_4^{3-}] - \frac{[NO_3^-]}{16}$$

DOP data are then paired to the nearest points of P*.

Satellite data products

Remotely sensed chlorophyll *a* concentration

Surface chlorophyll *a* concentrations were taken from the MODIS-AQUA 9 km resolution product⁴³, evaluated as the mean of the monthly value during the period of each cruise. DOP data are paired to the nearest points for correlation analysis.

Iron stress

Remotely sensed fluorescence quantum yields (φ_{sat}) have been shown to be a good indicator for iron stress experienced by phytoplankton^{14,42}. Following the method given by Behrenfeld et al., 2009, we calculated the global iron stress 9 km field by the equation below:

$$\varphi_{sat} = 0.00043 \frac{nFLH * iPAR}{Chl_{sat}^{0.684}}$$

In which, nFLH is the normalized fluorescence line height ($mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$), iPAR is the instantaneous photosynthetically available radiation ($\mu mol\ photons\ m^{-2}\ s^{-1}$) and Chl_{sat} is satellite derived chlorophyll *a* concentration ($mg\ m^{-3}$) with OC algorithm. φ_{sat} is unitless. nFLH, iPAR and Chl_{sat} 9 km fields are all downloaded from MODIS level 3 products (<https://oceancolor.gsfc.nasa.gov/l3/>). The equation above was used to obtain the climatological φ_{sat} fields between 2003 and 2019. Note that the equation is a simplified expression for φ_{sat} but its global distribution is indistinguishable from the φ_{sat} field with full expression¹⁴.

Statistics

We performed a correlation analysis between upper 50 DOP stocks and P*, chlorophyll *a* concentration, or iron stress by using a Type II linear regression model. The type II linear regression model was calculated in MATLAB (2019a version) with the file ‘gmregress.m’⁴⁵

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Data availability

DOP data used in this study can be found in the DOPv2021 database (<https://www.bco-dmo.org/dataset/855139>)

Code availability

Code used to generate figure 1 and figure 2 and perform the analysis is available upon request from the corresponding author.

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Contributions

Z.L. performed the analysis. Z.L. and A.K. designed the study. Z.L., A.K and R.L. wrote the paper. A.K. and R.L. lead the project.

Ethics declarations

Competing interests

The authors declare no competing financial interests

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Figure 1. (a) The global distribution of mean upper 50 m DOP concentrations [μM]. (b) Correlation between upper 50 m DOP stock and P^* (μM). Black solid line is the best fit line using a Type II linear regression model and blue lines are the 95% confidence level.

Figure 2. Relationships between upper 50 m DOP stock, surface chlorophyll *a* concentration ([Chl-*a*]), and iron stress in different basins, showing regions with DOP accumulation and loss: (a, b and c) the GO-SHIP P18-2016 in the Eastern Pacific; (d, e and f) the BIOSOPE cruise in the Eastern sub-and tropical South Pacific, one sample with $[\text{PO}_4^{3-}] > 1.5 \mu\text{M}$ is excluded from this analysis; (g, h and i) the GOM2019 cruise in the Gulf of Mexico; (j, k and l) the GO-SHIP P06-2017 cruise in the subtropical South Pacific, where red filled circles are samples from the surface convergence zone ($100^\circ\text{W} - 130^\circ\text{W}$), samples from the surface convergence zone are within the red box in the map (j); (m, n and o) the AMT17, AMT 14 and 36N cruises in the Atlantic, where the surface convergence zone is circled with a red box in the map (m); (p, q and r) the KH12-3 cruise in the Western North Pacific. All black lines are lines of best fit determined with a Type II linear regression model. Note the different scales for the x- and y-axes in the panels. Details of correlations and sample sizes from each cruise are listed in Table 1.

Table 1. Correlation analysis between upper 50 m DOP stock with chlorophyll *a* and iron stress for cruises in Figure 2.

Cruise	Location	Year	DOP stock vs. chl <i>a</i> concentration	DOP stock vs. iron stress	n
GO-SHIP P18-2016 ^a	Eastern Pacific	2016	$R^2 = 0.67$, $p < 0.001$	$R^2 = 0.31$, $p < 0.001$	24
BIOSOPE ^b	Eastern South Pacific	2004	$R^2 = 0.52$, $p < 0.001$	$R^2 = 0.41$, $p < 0.001$	24
GOM2019 ^a	Gulf of Mexico	2019	$R^2 = 0.30$, $p < 0.001$	$R^2 = 0.38$, $p < 0.001$	15
AMT 17, AMT14 and 36N ^c	North Atlantic, South Atlantic	2004, 2005	$R^2 = 0.10$, $p < 0.001$	$R^2 = 0.36$, $p < 0.001$	99
KH12-3 ^d	Western North Pacific	2012	$R^2 = 0.12$, $p = 0.02$	$R^2 = 0.82$, $p < 0.001$	9
P06-2016 ^a	Western and Eastern South Pacific	2016	$R^2 = 0.41$, $p < 0.001$	$R^2 = 0.71$, $p < 0.001$	30

^a this study

^b Moutin et al., 2018

^c Mather et al., 2008

^d Hashihama et al., 2020

Figure 1. Conceptual model of factors influencing surface ocean DOP distributions.

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