Dissolved organic phosphorus concentrations in the surface ocean controlled by both phosphate and iron stress

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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, the geographic distribution and environmental controls of surface ocean DOP concentration influence the distributions and rates of primary production and nitrogen fixation in the global ocean. Here we pair DOP concentration measurements with a metric of phosphate stress, satellite-based chlorophyll *a* concentrations, and a satellite-based iron stress proxy to explore their relationship with upper 50 m DOP stocks. Our results suggest that phosphate 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

phosphate availability. Our work extends the relationship between DOP concentrations and phosphate availability to the global ocean, suggests a linkage between marine phosphorus cycling and iron availability, and establishes a predictive framework for DOP distributions and its use as an organic nutrient source supporting global ocean fertility.

Main

In oligotrophic gyres, dissolved organic phosphorus (DOP) is the dominant form of phosphorus (P) in surface waters[1–3] and supports phytoplankton growth when the preferred substrate, phosphate (PO_4^{3-}), is scarce[4–10]. Estimates from the marine ecosystem component of the Community Earth System 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 DOP is included as an assimilative P source[11], which was also necessary to match the large scale gradients in surface ocean bulk DOP concentrations. Like dissolved organic carbon and nitrogen (DOC and DON), DOP is a product of primary production[12]. However, a clear understanding of both the distribution of DOP in surface waters as well as the controls on those distributions is limited by the relatively small number of DOP concentration measurements in the global ocean[11]. 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, N_2 fixation, and ultimately the biological pump.

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 monthly satellite-based measurements of chlorophyll *a* concentration, climatological "excess PO_4^{3-}" or "P*" values[15] evaluated in surface waters (< 5m), and a climatological, satellite-based iron stress proxy (NPQ-corrected φ_{sat}, see below)[16] (Figs. 1, 2). Although small but significant seasonal changes in DOP concentrations have been found at the ALOHA and BATS stations[3,17] we assume these DOP concentrations (Fig. 1) represent steady state conditions and perform a basin scale analysis of their distributions. We find that upper 50 m DOP stocks, which include multiple mixed-layer DOP concentration measurements, 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[18], as well as PO_4^{3-} concentration thresholds for DOP utilization by phytoplankton[2]. 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 (Fig. 2). Based on these relationships, we present a conceptual model of the factors controlling surface ocean DOP concentrations.

Global regions of net DOP accumulation and loss

The primary source of dissolved organic matter to the open ocean is marine primary production, and DOC and DON accumulate in regions with elevated productivity[12,19–22]. Similarly, we find that upper 50 m DOP stocks are significantly positively correlated with satellite-based measures of chlorophyll *a* concentration on the GO-SHIP P18-2016 and BIOSOPE cruises[23] in the Eastern

Pacific as well as the Gulf of Mexico (GOM2019 cruise) (Figs. 1, 2, Table 1). Correspondingly, the Eastern North Pacific, Eastern South Pacific, and Gulf of Mexico have the highest mean surface ocean DOP concentrations in our dataset, averaging 0.34±0.07 μM, 0.23±0.07 μM, and 0.23±0.07 μM (Extended Data Fig. 1), respectively, and represent regions of net DOP production. In contrast, North Atlantic, Western North Pacific, and Western 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 net DOP production, but that instead DOP is used as an assimilative P source sustaining productivity. Thus, the North Atlantic, Western North Pacific, and Western South Pacific appear to be net sinks for DOP, and have the lowest observed basin-mean concentrations, 0.10±0.07 μM, 0.12±0.02 μM and 0.14±0.04 μM, respectively (Extended Data Fig. 1). Below we explore the interdependence of surface ocean DOP concentrations, primary productivity, PO_4^{3-} stress (P*), and iron stress.

Surface ocean DOP primarily controlled by PO_4^{3-}

The primary control on surface ocean DOP concentrations is PO_4^{3-} stress, as gauged by P*, with upper 50 m DOP stocks in all data sets significantly positively correlated with P* (Fig. 1b) (Table 1). This positive relationship is robust whether calculating P* using upper 50 m *in situ* nutrients or climatological nutrients between 100 m and 250 m from World Ocean Atlas 2013[24] (Extended Data Figs. 2, 3). Regions of net DOP production in the Eastern Pacific are associated with elevated P* values, typically >0.2 μM (Fig. 1b), generated by subsurface denitrification and anammox in the oxygen deficient zones (ODZs) in and upstream of these sampling locations[25]. Surface waters with high P* values thus correspond to regions with "excess PO_4^{3-}", or low PO_4^{3-} stress, relative

93 to supplies of NO_3^- and "Redfieldian" phytoplankton N and P demands[15,18]. The upwelling-driven
94 elevated DOP production in regions with low PO_4^{3-} stress allows DOP to accumulate to relatively
95 high concentrations in the Eastern Pacific, as observed in the GO-SHIP P18-2016, BIOSOPE[23]
96 data (Figs. 1, 2). While high P* values are correlated with elevated DOP concentrations in surface
97 waters above the Eastern Pacific ODZs, DOP consumption happens elsewhere in the global ocean
98 with low P* values, and thus higher PO_4^{3-} stress. In particular, samples from the North Atlantic,
99 Western North Pacific, and Western South Pacific show decreasing upper 50 m DOP stocks with
100 increasing chlorophyll *a* concentration (Figs. 1, 2), consistent with previous observations of DOP
101 being an important assimilative P source sustaining autotrophs in the Sargasso Sea[2,3,6,8,26] and
102 subtropical North Pacific[1]. Given the significant correlation of upper 50 m DOP stocks and P*
103 (Fig. 1), PO_4^{3-} stress is considered the primary control on surface ocean DOP distributions.
104
105 **Iron stress modifies DOP accumulation and loss**
106 Whereas higher PO_4^{3-} stress leads to enhanced DOP consumption on the global scale, alleviated
107 iron stress can promote either DOP production or consumption regionally. Remotely sensed
108 fluorescence quantum yields (φ_{sat}) have been used as a proxy for iron stress experienced by
109 phytoplankton after correcting for non-photochemical quenching (NPQ)[16,27–30]. Here, we use
110 climatological, NPQ-corrected φ_{sat} as a relative measure of the iron stress experienced by
111 phytoplankton[16], with higher NPQ-corrected φ_{sat} corresponding to higher iron stress. In the GO-
112 SHIP P18-2016 and BIOSOPE[23] Eastern Pacific samples, NPQ-corrected φ_{sat} and upper 50 m
113 DOP stocks are significantly negatively correlated (Table 1) (Fig. 2), which we interpret to reflect
114 enhanced DOP production when iron stress is alleviated in high-chlorophyll *a* upwelling regions
115 (Table 1) (Fig. 2). A significant negative correlation between upper 50 m DOP stocks and NPQ-

corrected φ_{sat} is also found on the West Florida Shelf in the Gulf of Mexico (GOM2019 cruise) (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 PO_4^{3-} and iron stress surface waters, with that DOP subsequently advected west towards oligotrophic gyres experiencing higher PO_4^{3-} and iron stress, ultimately contributing to DOP loss within the Western 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 NPQ-corrected φ_{sat} (Table 1) (Fig. 2). Specifically, in samples from the GO-SHIP P06-2017 cruise in the subtropical South Pacific, and the AMT17, AMT14 and 36N cruises[2] from the Atlantic Ocean, and the KH12-3 cruise[31] from the Western North Pacific, 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[13,14], thus limiting the ability of phytoplankton to use DOP. The low DOP concentrations (<0.15 μM) in the North Atlantic and Western Pacific are found in regions with modest chlorophyll *a* concentrations (i.e., typically >0.1 mg chl *a* m^{-3}), low P* values (<0.1 μM), and low NPQ-corrected φ_{sat} (Fig. 2), consistent with DOP use by phytoplankton as an assimilative P source when iron is available and PO_4^{3-} is scarce. The North Atlantic in particular receives high rates of dust deposition[32], and the South Western Pacific may receive significant hydrothermal iron fluxes[33], lowering iron stress in these regions. These regions are also associated with high rates of N_2 fixation[34–37], which may be due to certain diazotrophs (e.g., *Trichodesmium* spp.) being particularly well-adapted to utilizing DOP when PO_4^{3-} is scarce[4,6,26,38].

Additionally, DOP appears to accumulate in regions where surface currents converge and iron stress is relatively high, thus limiting productivity. Specifically, in the convergence zone of the Eastern South Pacific (Fig. 2j and Extended Data Fig. 4), we observed elevated DOP concentrations (~0.3 μM) in waters with high NPQ-corrected φ_{sat}, low P*, and low chlorophyll *a* concentrations (Figs. 2j, k and l). The same scenario was found in the surface convergence zone of the South Atlantic, where the DOP concentration was higher than at the gyre boundary (Fig. 2m and Extended Data Fig. 4). We suggest that DOP will accumulate in the surface convergence zone of the Eastern North Pacific (Extended Data Fig. S4) as well, which is another region with high iron stress, low P*, and low chlorophyll *a.* Further sampling would test this hypothesis.

NPQ-corrected φ_{sat} as a measure of iron stress has been evaluated in NO_3^--replete surface waters[39,40] with one recent study finding evidence of elevated NPQ-corrected φ_{sat} in low-NO_3^- surface waters that corresponded with molecular markers of iron stress[30]. Since we evaluate φ_{sat} in environments with a range of NO_3^- concentrations, we underscore the novel nature of our correlations of NPQ-corrected φ_{sat} with DOP stocks within low nutrient surface waters, which will best be further investigated by future field studies characterizing phytoplankton community composition, their photo-physiology, and molecular markers of iron and light stress[30,41,42]. However, we also note that evaluation of NPQ-corrected φ_{sat} using a range of NPQ correction schemes yields the same sense and statistical significance of correlation with DOP stocks (Figs. S1, S2), although the absolute value of NPQ-corrected φ_{sat} should be used with caution. Photoacclimation adds uncertainty to φ_{sat} [28], however using a 16-year climatological NPQ-corrected φ_{sat} temporally averages some of this variability, and most observations investigated

here come from the low to mid-latitudes, where photoacclimation has a smaller effect[28]. We also acknowledge the reduced signal to noise ratio of φ_{sat} in low nFLH waters (typically <0.003 mW cm^{-2} μm^{-1} sr^{-1}) [43–45] which are marked with triangle symbols in Fig. 2. We find no significant changes in the relationships between DOP stock and NPQ-corrected φ_{sat} when these samples are excluded. Regardless, we emphasize the evolving nature of remote sensing-based ocean color metrics[16,27–30] that are best validated by direct observations with multiple tools, in this case phytoplankton community composition, photo-physiology, and molecular markers of iron and light stress.

Conceptual model of controls on surface ocean DOP

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). 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. 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, along the y-axis, promotes both DOP production and consumption, depending on PO_4^{3-} stress.

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 left pink quadrants of Fig. 3. Iron stress further influences the magnitude of DOP accumulation under

185 low PO_4^{3-} stress. When both iron and PO_4^{3-} stress are alleviated, such as in surface waters overlying
186 ODZs, enhanced primary production will lead to significant net DOP accumulation, so that DOP
187 has a "production" signature. In contrast, the upper left light pink quadrant reflects regions in the
188 Eastern Pacific exhibiting more muted net DOP accumulation due to surface ocean convergence
189 of DOP produced in "upstream" regions and to the lower, iron-limited rates of primary productivity
190 locally. Global surface ocean regions with the lowest DOP concentrations are associated with high
191 PO_4^{3-} stress and low iron stress, such as the North Atlantic, Western North Pacific, and Western
192 South Pacific (Fig. 1). These regions are represented by the dark blue, lower right quadrant in Fig.
193 3, and correspond to regions of net DOP loss that we interpret to reflect use of DOP as an
194 assimilative P source sustaining productivity, perhaps especially by diazotrophs. Finally, the upper
195 right, light blue quadrant corresponds to regions experiencing relatively balanced degrees of
196 enhanced PO_4^{3-} and iron stress, potentially including the South Atlantic, although observation gaps
197 exist. The South Atlantic receives relatively low atmospheric dust inputs[32], and the lack of
198 significant rates of water column denitrification and/or anammox in the eastern portion of the basin
199 leaves low P* values in the surface waters (Figs. 1, 2). Here, net changes in DOP distributions are
200 small, suggesting the potential for co-limitation of primary productivity by PO_4^{3-} and iron in the
201 region.
202
203 The linear regression model fitting the upper 50 m DOP stocks vs. P* values (Fig. 1) predicts a
204 surface DOP concentration at the BATS site (46 ± 22 nM) similar to observations (~60 nM[3]).
205 However, the predicted surface DOP concentration at Station ALOHA (146±31 nM) is lower than
206 observations (~200 nM[46]), with the difference potentially reflecting iron limitation of DOP
207 consumption, which is not accounted for in this correlation (Fig. 1). 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 does not capture all the processes influencing surface ocean DOP concentration ($R^2 = 0.28$), the predictions reflect observed, basin-scale differences in surface DOP concentrations (Extended Data Fig. 5). Meanwhile, the modeled global surface ocean DOP distribution is improved when including P* and NPQ-corrected φ_{sat} with or without chlorophyll *a* concentration as predictors by using three machine learning algorithms (Extended Data Table 1).

Implications

Our observations demonstrate significant, basin-scale differences in correlations of upper 50 m DOP stocks with climatological inorganic nutrient concentration ratios and remote sensing products of surface ocean chlorophyll *a* concentration and 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 (lower PO_4^{3-} stress) 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 μM 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 basins[47]. While a link between PO_4^{3-} stress and DOP use as an organic nutrient by phytoplankton has been established in the Atlantic[2,14], our analysis identifies for the first time a potential role for iron availability in modulating DOP accumulation versus consumption in global ocean surface waters. The enhanced role for DOP use as an organic nutrient within oligotrophic waters requires that DOP accumulate elsewhere, with iron availability

potentially serving in a similar role as in the regulation of intrabasin N_2 fixation rates[48]. Such a predictive framework for the distribution of surface ocean DON concentrations is lacking, suggesting a decoupling between these two organic nutrients. This mechanistic model of surface DOP concentration distributions in the ocean provides a testable framework for both observational and modeling work, and can help identify conditions where DOP acts as an organic nutrient source augmenting rates of NPP and N_2 fixation. Indeed, the region with the greatest net DOP loss, i.e., 0.2 μM between 130˚W and 80˚E in the South Pacific, is consistent with high rates of N_2 fixation[36,37,48,49] 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 μM) and iron stress is reduced. Additionally, surface ocean DOP consumption enhances ocean-to-atmosphere methane fluxes[50], a potent greenhouse gas, and a predictive understanding of where DOP consumption occurs may improve methane flux estimates. Finally, our observations linking marine DOP cycling with iron availability extend the previously described coupling of the marine iron, carbon, and nitrogen cycles to also include phosphorus.

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Author contributions

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

Competing interests

The authors declare no competing financial interests.

Tables

Table 1. **Correlation analysis between upper 50 m DOP stock with chlorophyll *a* and NPQ-corrected φ_{sat} for cruises in Figure 2.**

Cruise	Location	Year	DOP stock vs. chl *a* concentration	DOP stock vs. NPQ-corrected φ_{sat}	n
GO-SHIP P18-2016[a]	Eastern Pacific	2016	R = 0.82, p<0.001	R = -0.56, p<0.001	24
BIOSOPE[b]	Eastern South Pacific	2004	R = 0.72, p<0.001	R = -0.64, p<0.001	24
GOM2019[a]	Gulf of Mexico	2019	R = 0.55, p<0.001	R = -0.62, p<0.001	15
GO-SHIP P06-2017[a]	Western and Eastern South Pacific	2016	R = -0.64, p<0.001	R = 0.84, p<0.001	30
AMT17, AMT14 and 36N[c]	North Atlantic, South Atlantic	2004, 2005	R = -0.31, p<0.001	R = 0.60, p<0.001	99
KH12-3[d]	Western North Pacific	2012	R = -0.35, p=0.02	R = 0.90, p<0.001	9

[a] this study

[b] Raimbault et al., 2008

[c] Mather et al., 2008

[d] Hashihama et al., 2020

Figure legends

Figure 1. **Distribution of DOP concentrations and the relationship between upper 50 m DOP stock and P* over the global ocean.** (a) Observations of mean upper 50 m DOP concentrations (μM) (colored circles) overlain upon the 2˚x 2˚ mean DOP concentrations from the average of three machine learning algorithms, with predictors of P*, Chl *a* concentration, and NPQ-corrected φ_{sat}, see Methods. (b) Correlation between observed upper 50 m DOP stock and surface ocean P* (μM) computed from the World Ocean Atlas 2013[24] with Type II linear regression model best fit line (black) and 95% confidence level (blue lines). Annual mean upper 50 m DOP stock from the BATS site (open blue circle) and ALOHA station (open red circle) shown for reference.

Figure 2. **Relationships between upper 50 m DOP stock, surface chlorophyll *a* concentration, and NPQ-corrected $\boldsymbol{\varphi_{sat}}$, corresponding to net DOP accumulation/loss.** (a, b and c) the GO-SHIP P18-2016 cruise in the Eastern Pacific; (d, e and f) the BIOSOPE cruise in the Eastern South Pacific[23], one sample with $[PO_4^{3-}]$ > 1.5 μM 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 South Pacific; (m, n and o) the AMT17, AMT14 and 36N cruises in the Atlantic[2], where open circles/triangles represent samples from the North Atlantic and solid circles/triangles represent samples from the South Atlantic; and (p, q and r) the KH12-3 cruise in the Western North Pacific[31]. The surface convergence zones in the Eastern South Pacific and South Atlantic are denoted by the red boxes (j and m) and samples from these regions are represented by red circles/triangles in plots k, l, n, and o. Samples with climatological nFLH <0.003 mW cm^{-2} μm^{-1} sr^{-1} are represented by

triangles. All black lines are lines of best fit determined with a Type II linear regression model. Details of correlations and sample sizes from each cruise are listed in Table 1.

Figure 3. **Conceptual model of factors influencing surface ocean DOP distributions with representative ocean regions.**

References

1. Björkman, K. M. & Karl, D. M. Bioavailability of dissolved organic phosphorus in the euphotic zone at Station ALOHA, North Pacific Subtropical Gyre. *Limnol. Oceanogr.* **48**, 1049–1057 (2003).
2. Mather, R. L. *et al.* Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres. *Nat. Geosci.* **1**, 439–443 (2008).
3. Lomas, M. W. *et al.* Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). *Biogeosciences* **7**, 695–710 (2010).
4. Dyhrman, S. T. *et al.* Phosphonate utilization by the globally important marine diazotroph Trichodesmium. *Nature* **439**, 68–71 (2006).
5. Dyhrman, S. T. & Ruttenberg, K. C. Presence and regulation of alkaline phosphatase activity in eukaryotic phytoplankton from the coastal ocean: Implications for dissolved organic phosphorus remineralization. *Limnol. Oceanogr.* **51**, 1381–1390 (2006).

6. Orchard, E. D., Ammerman, J. W., Lomas, M. W. & Dyhrman, S. T. Dissolved inorganic and organic phosphorus uptake in Trichodesmium and the microbial community: The importance of phosphorus ester in the Sargasso Sea. *Limnol. Oceanogr.* **55**, 1390–1399 (2010).
7. Sato, M., Sakuraba, R. & Hashihama, F. Phosphate monoesterase and diesterase activities in the North and South Pacific Ocean. *Biogeosciences* **10**, 7677–7688 (2013).
8. Reynolds, S., Mahaffey, C., Roussenov, V. & Williams, R. G. Evidence for production and lateral transport of dissolved organic phosphorus in the eastern subtropical North Atlantic. *Glob. Biogeochem. Cycles* **28**, 805–824 (2014).
9. Diaz, J. M. *et al.* Dissolved Organic Phosphorus Utilization by Phytoplankton Reveals Preferential Degradation of Polyphosphates Over Phosphomonoesters. *Front. Mar. Sci.* **5**, (2018).
10. Duhamel, S. *et al.* Phosphorus as an integral component of global marine biogeochemistry. *Nat. Geosci.* **14**, 359–368 (2021).
11. Letscher, R. T. & Moore, J. K. Preferential remineralization of dissolved organic phosphorus and non-Redfield DOM dynamics in the global ocean: Impacts on marine productivity, nitrogen fixation, and carbon export. *Glob. Biogeochem. Cycles* **29**, 325–340 (2015).
12. Carlson, C. A. & Hansell, D. A. Chapter 3 - DOM Sources, Sinks, Reactivity, and Budgets. in *Biogeochemistry of Marine Dissolved Organic Matter (Second Edition)* (eds. Hansell, D. A. & Carlson, C. A.) 65–126 (Academic Press, 2015). doi:10.1016/B978-0-12-405940-5.00003-0.
13. Browning, T. J. *et al.* Iron limitation of microbial phosphorus acquisition in the tropical North Atlantic. *Nat. Commun.* **8**, 15465 (2017).

14. Mahaffey, C., Reynolds, S., Davis, C. E. & Lohan, M. C. Alkaline phosphatase activity in the subtropical ocean: insights from nutrient, dust and trace metal addition experiments. *Front. Mar. Sci.* **1**, (2014).

15. Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N. & Dunne, J. P. Spatial coupling of nitrogen inputs and losses in the ocean. *Nature* **445**, 163–167 (2007).

16. Behrenfeld, M. J. *et al.* Satellite-detected fluorescence reveals global physiology of ocean phytoplankton. *Biogeosciences* **6**, 779–794 (2009).

17. Church, M. J., Ducklow, H. W. & Karl, D. M. Multiyear increases in dissolved organic matter inventories at Station ALOHA in the North Pacific Subtropical Gyre. *Limnol. Oceanogr.* **47**, 1–10 (2002).

18. Quigg, A. *et al.* The evolutionary inheritance of elemental stoichiometry in marine phytoplankton. *Nature* **425**, 291–294 (2003).

19. Bronk, D. A. & Ward, B. B. Gross and net nitrogen uptake and DON release in the euphotic zone of Monterey Bay, California. *Limnol. Oceanogr.* **44**, 573–585 (1999).

20. Hansell, D. A. & Carlson, C. A. Biogeochemistry of total organic carbon and nitrogen in the Sargasso Sea: control by convective overturn. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **48**, 1649–1667 (2001).

21. Letscher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R. & Knapp, A. N. Dissolved organic nitrogen in the global surface ocean: Distribution and fate. *Glob. Biogeochem. Cycles* **27**, 141–153 (2013).

22. Knapp, A. N., Casciotti, K. L. & Prokopenko, M. G. Dissolved Organic Nitrogen Production and Consumption in Eastern Tropical South Pacific Surface Waters. *Glob. Biogeochem. Cycles* **32**, 769–783 (2018).

23. Raimbault, P., Garcia, N. & Cerutti, F. Distribution of inorganic and organic nutrients in the South Pacific Ocean − evidence for long-term accumulation of organic matter in nitrogen-depleted waters. *Biogeosciences* **5**, 281–298 (2008).

24. Garcia, H. E. *et al.* World Ocean Atlas 2013, Volume 4: Dissolved Inorganic Nutrients (phosphate, nitrate, silicate). S. Levitus, Ed., A. Mishonov Technical Ed.; NOAA Atlas NESDIS 76, 25 pp. (2013).

25. DeVries, T., Deutsch, C., Primeau, F., Chang, B. & Devol, A. Global rates of water-column denitrification derived from nitrogen gas measurements. *Nat. Geosci.* **5**, 547–550 (2012).

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

27. Browning, T. J., Bouman, H. A. & Moore, C. M. Satellite-detected fluorescence: Decoupling nonphotochemical quenching from iron stress signals in the South Atlantic and Southern Ocean. *Glob. Biogeochem. Cycles* **28**, 510–524 (2014).

28. Westberry, T. K. *et al.* Annual cycles of phytoplankton biomass in the subarctic Atlantic and Pacific Ocean. *Glob. Biogeochem. Cycles* **30**, 175–190 (2016).

29. Hopwood, M. J. *et al.* Non-linear response of summertime marine productivity to increased meltwater discharge around Greenland. *Nat. Commun.* **9**, 3256 (2018).

30. Larkin, A. A. *et al.* Subtle biogeochemical regimes in the Indian Ocean revealed by spatial and diel frequency of Prochlorococcus haplotypes. *Limnol. Oceanogr.* **65**, S220–S232 (2020).

31. Hashihama, F. *et al.* Biogeochemical Controls of Particulate Phosphorus Distribution Across the Oligotrophic Subtropical Pacific Ocean. *Glob. Biogeochem. Cycles* **34**, e2020GB006669 (2020).

32. Mahowald, N. M. *et al.* Atmospheric global dust cycle and iron inputs to the ocean. *Glob. Biogeochem. Cycles* **19**, (2005).

33. Guieu, C. *et al.* Iron from a submarine source impacts the productive layer of the Western Tropical South Pacific (WTSP). *Sci. Rep.* **8**, 9075 (2018).

34. Carpenter, E. J., Subramaniam, A. & Capone, D. G. Biomass and primary productivity of the cyanobacterium Trichodesmium spp. in the tropical N Atlantic ocean. *Deep Sea Res. Part Oceanogr. Res. Pap.* **51**, 173–203 (2004).

35. Capone, D. G. *et al.* Nitrogen fixation by Trichodesmium spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean. *Glob. Biogeochem. Cycles* **19**, (2005).

36. Knapp, A. N. *et al.* Distribution and rates of nitrogen fixation in the western tropical South Pacific Ocean constrained by nitrogen isotope budgets. *Biogeosciences* **15**, 2619–2628 (2018).

37. Caffin, M. *et al.* N_2 fixation as a dominant new N source in the western tropical South Pacific Ocean (OUTPACE cruise). *Biogeosciences* **15**, 2565–2585 (2018).

38. Van Mooy, B. A. S. *et al.* Quorum sensing control of phosphorus acquisition in Trichodesmium consortia. *ISME J.* **6**, 422–429 (2012).

367 39. Behrenfeld, M. J. *et al.* Controls on tropical Pacific Ocean productivity revealed through
368 nutrient stress diagnostics. *Nature* **442**, 1025–1028 (2006).
369 40. Schrader, P. S., Milligan, A. J. & Behrenfeld, M. J. Surplus Photosynthetic Antennae
370 Complexes Underlie Diagnostics of Iron Limitation in a Cyanobacterium. *PLOS ONE* **6**, e18753
371 (2011).
372 41. Chappell, P. D., Moffett, J. W., Hynes, A. M. & Webb, E. A. Molecular evidence of iron
373 limitation and availability in the global diazotroph Trichodesmium. *ISME J.* **6**, 1728–1739
374 (2012).
375 42. Moreno, C. M., Gong, W., Cohen, N. R., DeLong, K. & Marchetti, A. Interactive effects of iron
376 and light limitation on the molecular physiology of the Southern Ocean diatom Fragilariopsis
377 kerguelensis. *Limnol. Oceanogr.* **65**, 1511–1531 (2020).
378 43. Hu, C. *et al.* Dynamic range and sensitivity requirements of satellite ocean color sensors:
379 learning from the past. *Appl. Opt.* **51**, 6045–6062 (2012).
380 44. Huot, Y., Franz, B. A. & Fradette, M. Estimating variability in the quantum yield of Sun-
381 induced chlorophyll fluorescence: A global analysis of oceanic waters. *Remote Sens. Environ.*
382 **132**, 238–253 (2013).
383 45. Lin, H. *et al.* The fate of photons absorbed by phytoplankton in the global ocean. *Science*
384 **351**, 264–267 (2016).
385 46. Foreman, R. K., Björkman, K. M., Carlson, C. A., Opalk, K. & Karl, D. M. Improved ultraviolet
386 photo-oxidation system yields estimates for deep-sea dissolved organic nitrogen and
387 phosphorus. *Limnol. Oceanogr. Methods* **17**, 277–291 (2019).

47. Ustick, L. J. *et al.* Metagenomic analysis reveals global-scale patterns of ocean nutrient limitation. *Science* **372**, 287–291 (2021).

48. Weber, T. & Deutsch, C. Local versus basin-scale limitation of marine nitrogen fixation. *Proc. Natl. Acad. Sci.* **111**, 8741–8746 (2014).

49. Wang, W.-L., Moore, J. K., Martiny, A. C. & Primeau, F. W. Convergent estimates of marine nitrogen fixation. *Nature* **566**, 205–211 (2019).

50. Repeta, D. J. *et al.* Marine methane paradox explained by bacterial degradation of dissolved organic matter. *Nat. Geosci.* **9**, 884–887 (2016).

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)[51]. Briefly, DOP concentrations were calculated from the difference between total dissolved phosphorus ([TDP]) and PO_4^{3-} concentration ($[PO_4^{3-}]$) measurements. DOP concentrations from the GO-SHIP P06-2017, GO-SHIP P18-2016, and GOM2019 cruises were measured via the ash/hydrolysis method in this study, a method recommended for more accurate DOP concentration analysis[52]. DOP concentrations from the AMT17, AMT14 and 36N cruises were measured by the UV oxidation method[2,53]. DOP concentrations from the BIOSOPE and KH12-3 cruises were measured by the persulfate oxidation method[23,31,54]. No correction or normalization of the TDP or DOP concentration data was applied based on the different analytical methods used in this study.

411

412 **Surface P* values**

413 NO_3^- concentrations ($[NO_3^-]$) and PO_4^{3-} concentrations ($[PO_4^{3-}]$) were taken from the World Ocean
414 Atlas 2013 climatological field (1˚x1˚)[24] at 0 m level. P* was calculated by the equation below
415 with surface $[NO_3^-]$ and $[PO_4^{3-}]$:

416 $$P^* = [PO_4^{3-}] - \frac{[NO_3^-]}{16} \quad (1)$$

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

418

419 **Satellite data products**

420 **Remotely sensed chlorophyll *a* concentration**

421 Surface chlorophyll *a* concentrations were taken from the MODIS-AQUA 9 km resolution
422 product[55], evaluated as the mean of the monthly value during the period of each cruise. DOP data
423 are paired to the nearest points for correlation analysis.

424

425 **NPQ-corrected φ_{sat}**

426 Following the method given by Behrenfeld et al., 2009, we calculated the global φ_{sat} 9 km field
427 and applied a correction for non-photochemical quenching by the equation below:

428 $$\varphi_{\mathrm{sat}} = 0.01 \frac{nFLH}{<a_{ph}>} \quad (2)$$

429

430 $$< a_{ph} > = 0.0147 \mathrm{Chl}_{\mathrm{sat}}^{0.684} \quad (3)$$

431

432 $$\mathrm{NPQ-corrected}\ \varphi_{\mathrm{sat}} = \varphi_{\mathrm{sat}} \frac{iPAR}{1590} \quad (4)$$

In which nFLH is the normalized fluorescence line height (mW cm^{-2} μm^{-1} sr^{-1}), iPAR is the instantaneous photosynthetically available radiation (μmol photons m^{-2} s^{-1}), Chl_{sat} is satellite derived chlorophyll *a* concentration (mg m^{-3}) with the OC algorithm, and $< a_{ph} >$ is an average spectrally-weighted phytoplankton absorption coefficient, which is calculated as a power-law function of Chl_{sat}. φ_{sat} is unitless. 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 NPQ-corrected φ_{sat} fields between 2003 and 2019. Note that the equation used here to calculate NPQ-corrected φ_{sat} is a simplified expression for φ_{sat} but its global distribution is indistinguishable from the φ_{sat} field with full expression[16] (Fig. S1).

Machine learning algorithms

The results of three machine learning algorithms were averaged to generate a map of global surface DOP concentrations (Fig. 1): support vector machine (SVM)[56], boosted tree[57], and Gaussian process regression[58]. For the SVM training model, data were standardized to their z scores and a Gaussian kernel was used. For the boosted tree training model, we built 30 decision trees and set the minimum leaf size to 8. For the Gaussian process regression training model, data were standardized to their z scores and an Exponential kernel was used. Three predictors have been fed to train the model: climatological, satellite-derived, NPQ-corrected φ_{sat}, climatological P*, and remote sensing derived chlorophyll *a* concentration. The three machine learning models were used to predict the global DOP concentration distribution with 2˚x2˚ resolution. All the machine learning algorithms used the Machine Learning Toolbox in MATLAB (2019a version).

Statistics

We performed a correlation analysis between the upper 50 m DOP stocks and P*, chlorophyll *a* concentration, or NPQ-corrected φ_{sat} by using a Type II linear regression model. The type II linear regression model was evaluated in MATLAB (2019a version) with the file 'gmregress.m'[59].

Data availability

Original DOP data used in this study can be found and freely accessed in the DOPv2021 database archived on the BCO DMO website (https://www.bco-dmo.org/dataset/855139) or in the Woods Hole Open Access Server (https://doi.org/10.26008/1912/bco-dmo.855139.2)[51]. Level 3 satellite product can be downloaded from the NASA Ocean Color website (https://oceancolor.gsfc.nasa.gov/l3/).

Code availability

Code and data used to reproduce figure 1 and figure 2 are archived in the GitHub (https://github.com/zliangocean/DOP).

Extend Data

Extended Data Figure 1. **Boxplots of mean DOP concentrations in the surface ocean (0 – 50 m) in different ocean basins.** Asterisks denote confidence levels when testing for unique mean concentrations between basins with ****: p<0.0001, ***: p<0.001, *: p<0.05, using Dunn test (pairwise Kruskal-Wallis test) with Bonferroni correction. Black dots above the Eastern North Pacific and Gulf of Mexico are outliers. Center line is median and box limits are upper and lower quartiles. Whiskers show 1.5x interquartile range.

Extended Data Figure 2. **Correlation between observed upper 50 m DOP stock (mmol m^{-2}) and mean upper 50 m P* (μM) computed from the same samples.** Black solid line is the best fit line using a Type II linear regression model and dashed blue lines are the 95% confidence level. Three stations from the BIOSOPE cruise had only phosphate but no nitrate concentration measurements and they are not included in this figure.

Extended Data Figure 3. **Correlation between observed upper 50 m DOP stock (mmol m^{-2}) and climatological mean P* (µM) between 100 m and 250 m computed from the World Ocean Atlas 2013[24].** Black solid line is the best fit line using a Type II linear regression model and dashed blue lines are the 95% confidence level. There are 12 stations containing DOP data with a bottom depth <100 m which have not been included in this figure.

Extended Data Figure 4. **Annual mean surface geostrophic currents (0.25˚x 0.25˚) and identified surface current convergence zones (SCZ).** Annual mean geostrophic currents (0.25˚x 0.25˚) are obtained from the Copernicus Marine Environmental Monitoring Service (marine.copernicus.eu). Three surface current convergence zones (SCZ) are identified in the North Pacific, South Pacific, and South Atlantic by red circle.

Figure Data Figure 5. **Predicted surface ocean DOP concentrations (µM) based on the linear relationship between DOP concentrations and P* (Figure 1; see main text).**

Extended Data Table 1**. R^2 of observed DOP concentration vs. predicted surface ocean DOP concentration based on different machine learning models (SVM, boosted tree and Gaussian process regression) with different predictors**.

	SVM	Boosted tree	Gaussian process regression
P^* + NPQ- corrected φ_{sat}	$R^2 = 0.43$	$R^2 = 0.40$	$R^2 = 0.45$
P^* + Chl a	$R^2 = 0.28$	$R^2 = 0.31$	$R^2 = 0.35$
P^* + NPQ- corrected φ_{sat} + Chl a	$R^2 = 0.41$	$R^2 = 0.42$	$R^2 = 0.52$

Method references

51. Knapp, A. N., Liang, Z. & Letscher, R. T. DOP concentration observations from the global ocean between 1990 and 2021 (DOP N2 fixation and export production project) (Version 2).

Biol. Chem. Oceanogr. Data Manag. Off. (BCO-DMO) (2022) doi: 10.26008/1912/bco-dmo.855139.2.

52. Monaghan, E. J. & Ruttenberg, K. C. Dissolved organic phosphorus in the coastal ocean: Reassessment of available methods and seasonal phosphorus profiles from the Eel River Shelf. *Limnol. Oceanogr.* **44**, 1702–1714 (1999).

53. Armstrong, F. a. J., Williams, P. M. & Strickland, J. D. H. Photo-oxidation of Organic Matter in Sea Water by Ultra-violet Radiation, Analytical and Other Applications. *Nature* **211**, 481–483 (1966).

54. Pujo-Pay, M. & Raimbault, P. Improvement of the wet-oxidation procedure for simultaneous determination of particulate organic nitrogen and phosphorus collected on filters. *Mar. Ecol. Prog. Ser.* **105**, 203–207 (1994).

55. NASA Goddard Space Flight Center, Ocean Ecology Laboratory, & Ocean Biology Processing Group. Moderate-resolution Imaging Spectroradiometer (MODIS) Aqua Chlorophyll a 9 km Data. NASA OB.DAAC, Greenbelt, MD, USA. https://oceancolor.gsfc.nasa.gov/l3/. Accessed 20 Jan 2021.

56. Vapnik, V. *The Nature of Statistical Learning Theory*. (Springer Science & Business Media, 2013).

57. Breiman, L. Random Forests. *Mach. Learn.* **45**, 5–32 (2001).

58. Rasmussen, C. E. & Williams, C. K. I. *Gaussian Processes for Machine Learning*. (MIT Press, 2005).

59. Trujillo-Ortiz, A. & Hernandez-Walls, R. gmregress: Geometric Mean Regression (Reduced Major Axis Regression. A MATLAB file. http://www. mathworks. com/matlabcentral/fileexchange/27918-gmregress.