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

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Dissolved organic phosphorus (DOP) has a dual role in the surface ocean as both a product of primary production and as an organic nutrient that fuels primary production and nitrogen fixation, especially in oligotrophic gyres. Although poorly constrained, the geographic distribution and environmental controls of surface ocean DOP concentrations 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 ocean 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 their use as an organic nutrient source that supports global ocean fertility.

In oligotrophic gyres, DOP is the dominant form of phosphorus in surface waters 1–3 and supports phytoplankton growth when the preferred substrate, phosphate (PO4−), 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 dinitrogen (N2) fixation rates are ~8% and ~33% higher, respectively, and better match the observed rates when DOP is included as an assimilative phosphorus source 11, which was also necessary to match the large-scale gradients in surface ocean bulk DOP concentrations. Like dissolved organic carbon (DOC) and dissolved organic nitrogen (DON), DOP is a product of primary production. 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, N2 fixation and ultimately the biological pump.

Given that DOP is both produced and consumed by photosynthetic organisms, we explored the relationships between DOP distributions and metrics of primary production (that is, DOP production), PO4− stress (that is, DOP consumption) and iron stress, which can limit primary production. In addition, iron has recently been identified as a co-factor in a version of the enzyme that is responsible for DOP utilization by phytoplankton, that is, alkaline phosphatase 12,13,14, 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 concentrations, climatological ‘excess PO4−’ or ‘P*’ values 15 evaluated in surface waters (<5 m) and a climatological, satellite-based iron stress proxy (NPQ-corrected qFe values, see below) 16 (Figs. 1 and 2). Although small but notable seasonal changes in DOP concentrations have been found at the ALOHA and BATS stations 17,18, we assume that these DOP concentrations (Fig. 1) represent steady-state conditions and perform a basin-scale analysis of their distributions. We find that the upper 50 m DOP stocks, which include multiple mixed-layer DOP concentration measurements, are significantly positively correlated with surface P* values (R2 = 0.28, P < 0.00000001) (Fig. 1b). Here, higher P* values correspond to lower PO4− stress, consistent with stoichiometric biomass demands for nitrogen and phosphorus 19, as well as PO4− concentration thresholds for DOP utilization by phytoplankton 20. In addition to PO4− stress, iron stress also plays a significant but more complicated role in regulating surface DOP concentrations and can lead to either surface DOP accumulation under enhanced iron stress or consumption under alleviated iron stress (Fig. 2). On the basis of these relationships, we present a conceptual model of the factors that control 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 12,15–22. Similarly, we find that upper 50 m DOP stocks are significantly positively correlated with satellite-based measurements of chlorophyll a concentration on the GO-SHIP P18-2016 and BIOSOPE cruises 23 in the eastern Pacific Ocean as well as the Gulf of Mexico (GOM2019 cruise) (Figs. 1 and 2 and Table 1). Correspondingly, the eastern North Pacific, eastern South Pacific and the 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, respectively (Extended Data Fig. 1), and represent regions of net DOP production. By contrast, the North Atlantic, western North Pacific and western South Pacific surface ocean DOP and chlorophyll a concentrations are significantly negatively correlated (Fig. 2 and 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 phosphorus 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 of 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). 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* (ref. 24) (Extended Data Figs. 2 and 3). Regions of net DOP production in the eastern Pacific Ocean are associated with elevated $P^*$ values, typically >0.2 µM (Fig. 1b), generated by subsurface denitrification and anammox (anaerobic ammonium oxidation) in the oxygen-deficient zones (ODZs) in and upstream of these sampling locations. 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 nitrate (NO$_3^-$) and ‘Redfieldian’ phytoplankton nitrogen and phosphorus demands. 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 Ocean, as observed in the GO-SHIP P18-2016 and BIOSOPE$^b$ data (Figs. 1 and 2). Whereas high $P^*$ values are correlated with elevated DOP concentrations in surface waters above the eastern Pacific Ocean 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, western North Pacific and western South Pacific show decreasing upper 50 m DOP stocks with increasing chlorophyll $a$ concentration (Figs. 1 and 2), consistent with previous observations of DOP being an important assimilative phosphorus source that sustains autotrophs in the Sargasso Sea$^{23,24}$ and subtropical North Pacific$^c$. Given the significant correlation of upper 50 m DOP stocks and $P^*$ (Fig. 1), PO$_4^{3-}$ stress is considered to be the primary control on surface ocean DOP distributions.

Iron stress modifies DOP accumulation and loss

Whereas higher PO$_4^{3-}$ stress leads to enhanced DOP consumption on the global scale, elevated iron stress can promote either DOP production or consumption regionally. Remotely sensed fluorescence quantum yield ($\varphi_{sat}$) data have been used as a proxy for iron stress experienced by phytoplankton after correcting for non-photochemical quenching (NPQ)$^{27-28}$. Here we use climatological, NPQ-corrected $\varphi_{sat}$ data as a relative measure of the iron stress experienced by phytoplankton$^{29}$, with higher NPQ-corrected $\varphi_{sat}$ values corresponding to higher iron stress. In the GO-SHIP P18-2016 and BIOSOPE$^b$ eastern Pacific Ocean samples, NPQ-corrected $\varphi_{sat}$ and upper 50 m DOP stocks are significantly negatively correlated (Table 1 and Fig. 2), which we interpret as reflecting enhanced DOP production when iron stress is alleviated in high-chlorophyll $a$ upwelling regions (Table 1 and Fig. 2). A significant negative correlation between upper 50 m DOP stocks and NPQ-corrected $\varphi_{sat}$ is also found on the West Florida Shelf in the Gulf of Mexico (GOM2019 cruise) (Table 1 and Fig. 2). On the global scale, the eastern Pacific Ocean appears unique as a region of net DOP production in upwelling-associated, relatively low PO$_4^{3-}$ and iron stress surface waters, with DOP subsequently advected west towards oligotrophic gyres experiencing relatively high PO$_4^{3-}$ and iron stress, ultimately contributing to DOP loss within the western Pacific Ocean.

In contrast to the eastern Pacific Ocean and Gulf of Mexico, basins with net DOP consumption exhibit significant positive correlations between upper 50 m DOP stocks and NPQ-corrected $\varphi_{sat}$ (Table 1 and Fig. 2). Specifically, in samples from the GO-SHIP P06-2017 cruise in the subtropical South Pacific, the AMT17, AMT14 and 36N$^c$ cruises from the Atlantic Ocean, and the KH12-3 cruise$^c$ 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 as reflecting the iron limitation of primary productivity, and thus decreasing demand for DOP as an assimilative phosphorus source, and/or iron limitation of alkaline phosphatase activity$^{12,14}$, thus limiting the ability of phytoplankton to use DOP. The low DOP concentrations ($<0.15$ $\mu$M) in the North Atlantic and western Pacific Ocean are found in regions with modest chlorophyll $a$ concentrations (that is, typically $>1.5$ $g$ $m^{-2}$), low $P^*$ values ($<0.1$ $\mu$M) and low NPQ-corrected $\varphi_{sat}$ values (Fig. 2), which is consistent with DOP use by phytoplankton as an assimilative phosphorus source when iron is available and PO$_4^{3-}$ is scarce. The North Atlantic in particular receives high rates of dust deposition$^{30}$, and the western South Pacific may receive significant hydrothermal iron fluxes$^{31}$, lowering the 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 (for example, *Trichodesmium* spp.) being particularly well adapted to utilizing DOP when PO$_4^{3-}$ is scarce$^{30,32,34}$.

In addition, 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. 2) and Extended Data Fig. 4), we observed elevated DOP concentrations ($>0.3$ $\mu$M) in waters with high NPQ-corrected $\varphi_{sat}$, low $P^*$ and low chlorophyll $a$ concentrations (Fig. 2c–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. 4) as well, which is

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2** | Relationships between upper 50 m DOP stocks, surface chlorophyll $a$ concentration and NPQ-corrected $\varphi_{sat}$. a–c, Upper 50 m DOP stocks (a), surface chlorophyll $a$ concentration (b) and NPQ-corrected $\varphi_{sat}$ values (c) for the GO-SHIP P18-2016 cruise in the eastern Pacific. d–f, Corresponding plots for the BIOSOPE cruise in the eastern South Pacific$^b$, where one sample with [PO$_4^{3-}$] $>1.5$ $\mu$M was excluded from this analysis. g–i, Corresponding plots for the GOM2019 cruise in the Gulf of Mexico. j–l, Corresponding plots for the GO-SHIP P06-2017 cruise in the South Pacific. m–o, Corresponding plots for the AMT17, AMT14 and 36N cruises in the Atlantic Ocean$^c$, where open circles/triangles represent samples from the North Atlantic and solid circles/triangles represent samples from the South Atlantic. p–r, Corresponding plots for the KH12-3 cruise in the western North Pacific$^c$. Panels a, d, g, j, m and p created in Ocean Data View$^{31}$. 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 $n$FLH $<0.003$ $mW$ $cm^{-2}$ $\mu$M$^{-1}$ $sr^{-1}$ are represented by triangles. All black lines are lines of best fit determined using a Type II linear regression model. Details of correlations and sample sizes from each cruise are listed in Table 1. [Chlorophyll $a$], chlorophyll $a$ concentration.

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**Table 1** | Correlation analysis between upper 50 m DOP stocks and chlorophyll $a$ and NPQ-corrected $\varphi_{sat}$ data for cruises in Fig. 2

| Cruise | Location | Year | DOP stock vs chlorophyll $a$ concentration | DOP stock vs NPQ-corrected $\varphi_{sat}$ | $n$ |
|--------|----------|------|------------------------------------------|-----------------------------------------|-----|
| 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$^c$ | Gulf of Mexico | 2019 | $R=0.55, P<0.001$ | $R=-0.62, P<0.001$ | 15 |
| GO-SHIP P06-2017$^c$ | Western and eastern South Pacific | 2017 | $R=-0.64, P<0.001$ | $R=0.84, P<0.001$ | 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$^c$ | Western North Pacific | 2012 | $R=-0.35, P=0.02$ | $R=0.90, P<0.001$ | 9 |

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$^a$This study. $^b$Raimbault et al.$^{23}$. $^c$Mather et al.$^2$. $^d$Hashihama et al.$^{31}$. 

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**Notes:** 

1. 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 $n$FLH $<0.003$ $mW$ $cm^{-2}$ $\mu$M$^{-1}$ $sr^{-1}$ are represented by triangles. All black lines are lines of best fit determined using a Type II linear regression model. Details of correlations and sample sizes from each cruise are listed in Table 1. [Chlorophyll $a$], chlorophyll $a$ concentration.
Enhanced iron stress

Alleviated PO₄³⁻ stress

DOP accumulation > DOP loss
Increase in DOP concentration
For example, eastern South Pacific surface convergence zone

DOP accumulation < DOP loss
Decrease in DOP concentration
For example, South Atlantic

DOP accumulation >> DOP loss
Increase in DOP concentration
For example, eastern South Pacific, eastern North Pacific and West Florida Shelf of the Gulf of Mexico

DOP accumulation << DOP loss
Decrease in DOP concentration
For example, western South Pacific, western North Pacific and North Atlantic

Alleviated iron stress

DOP as organic nutrient

DOP as product of primary production

Fig. 3 | Conceptual model of factors influencing surface ocean DOP distributions with representative ocean regions. PO₄³⁻ stress increases along the x axis, while iron stress increases along the y axis. Regions explored in this study are classified into four quadrants according to their conditions of PO₄³⁻ stress and iron stress to show whether DOP accumulation or loss occurs. See texts for details. ‘>’ and ‘>>’ in the quadrants mean ‘greater than’ and ‘much greater than’, respectively.

Another region with high iron stress, low P* and low chlorophyll a. Further sampling would test this hypothesis.

NPQ-corrected φsat data as a measure of iron stress have been evaluated in NO₃⁻-replete surface waters⁵⁹,⁶⁰, with one recent study finding evidence of elevated NPQ-corrected φsat in low-NO₃⁻ surface waters that corresponded with molecular markers of iron stress⁶⁰. Since we evaluate φsat in environments with a range of NO₃⁻ concentrations, we underscore the novel nature of our correlations of NPQ-corrected φsat with DOP stocks in low nutrient surface waters, which will best be further investigated via future field studies characterizing the phytoplankton community composition, their photo-physiology, and molecular markers of iron and light stress⁵⁹,⁶¹,⁶². However, we also note that evaluation of NPQ-corrected φsat data using a range of NPQ correction schemes yields the same sense and statistical significance of correlation with DOP stocks (Supplementary Figs. 1 and 2), although the absolute value of NPQ-corrected φsat should be used with caution. Photoacclimation adds uncertainty to φsat data⁴⁶; however, using 16 year climatological NPQ-corrected φsat data temporally averages some of this variability, and most observations investigated here come from low to middle latitudes, where photoacclimation has a smaller effect⁴⁹. We also acknowledge the reduced signal-to-noise ratio of φsat in waters with a low normalized fluorescence line height (nFLH) (typically <0.003 mW cm⁻² µm⁻¹ sr⁻¹)⁴³,⁴⁴, which are marked with triangle symbols in Fig. 2. We find no significant changes in the relationships between DOP stock and NPQ-corrected φsat when these samples are excluded. Nevertheless, we emphasize the evolving nature of remote-sensing-based ocean colour metrics⁴⁶,⁴⁷,⁴⁸ that are best validated through direct observations using multiple tools, in this case the composition of the phytoplankton community, 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 PO₄³⁻ and iron stress, we propose a simple conceptual model of the factors that influence DOP distributions in the surface ocean (Fig. 3). The four quadrants in Fig. 3 correspond to different PO₄³⁻ and iron stress regimes that reflect 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 PO₄³⁻ 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. In addition, iron stress, increasing along the y axis, promotes both DOP production and consumption, depending on PO₄³⁻ stress.

As discussed above, the eastern Pacific Ocean is a highly productive region with low PO₄³⁻ stress, resulting in net DOP production and accumulation (Figs. 1 and 2), and is represented by the left pink-coloured quadrants of Fig. 3. Iron stress further influences the magnitude of DOP accumulation under low PO₄³⁻ stress. When both iron and PO₄³⁻ 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. By contrast, the upper-left light-pink quadrant reflects regions in the eastern Pacific Ocean that exhibit 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 PO₄³⁻ stress and low iron stress, such as the North Atlantic, western North Pacific and western South Pacific (Fig. 1). These regions are represented by the dark-blue, lower-right quadrant in Fig. 3 and correspond to regions of net DOP loss that we interpret as reflecting the use of DOP as an assimilative phosphorus source that sustains productivity, perhaps particularly by diazotrophs. Finally, the upper-right, light-blue quadrant corresponds to regions experiencing relatively balanced degrees of enhanced PO₄³⁻ and iron stress, potentially including the South Atlantic, although observation gaps exist. The South Atlantic receives relatively low atmospheric dust inputs⁵⁸, 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 and 2). Here, net changes in DOP distributions are small, suggesting the potential for co-limitation of primary productivity by PO₄³⁻ and iron in the region.

The linear regression model fitting the upper 50 m DOP stocks versus P* values (Fig. 1b) predicts a surface DOP concentration at the BATS site (46 ± 22 nM) that is similar to observations (~60 nM (ref. 4)). However, the predicted surface DOP concentration at Station ALOHA (146 ± 31 nM) is lower than observations (~200 nM (ref. 46)), with the difference potentially reflecting iron limitation of DOP 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 in controlling DOP distributions at the BATS site. Although the simple linear relationship does not capture all the processes that influence surface ocean DOP concentration ($R^2 = 0.28$), the predictions reflect the observed, basin-scale differences in surface DOP concentrations (Extended Data Fig. 5). Meanwhile, the modelled global surface ocean DOP distribution is improved when including P* and NPQ-corrected $q_{*\text{sat}}$ data with or without the chlorophyll $a$ concentration as predictors 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. On the basis of 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 PO₄³⁻ stress) and relatively low iron stress, consistent with elevated rates of productivity and low pressure on the DOP pool as an assimilative phosphate source. Net DOP consumption is apparent in regions with $P^*$ values of <0.1 μM and relatively low iron stress, suggesting that phytoplankton growth is limited by PO₄³⁻ availability and not iron in these regions. This is consistent with emerging work evaluating the role of nitrogen, phosphorus and iron limitation in different ocean basins 39. Although a link between PO₄³⁻ stress and DOP use as an organic nutrient by phytoplankton has been established in the Atlantic Ocean 40, our analysis identifies 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 in oligotrophic waters requires that DOP accumulates elsewhere, with iron availability potentially serving in a role similar to that in the regulation of intrabasin N₂ fixation rates 41. 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 modelling work, and can help to identify conditions where DOP acts as an organic nutrient source augmenting rates of NPP and N₂ fixation. Indeed, the region with the greatest net DOP loss, that is, 0.2 μM between 130°W and 80°E in the South Pacific, is consistent with high rates of N₂ fixation 37,48,49, indicating that DOP is probably an important phosphate source that fuels N₂ fixation in this region where PO₄³⁻ concentrations are low (<0.1 μM) and iron stress is reduced. In addition, surface ocean DOP consumption enhances ocean-atmosphere fluxes of methane 40, 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 include phosphorus as well.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41561-022-00988-1.

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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 were calculated from the difference between total dissolved phosphorus concentration (TDP) and PO₄⁻³ concentration ([PO₄⁻³] - [NO₃⁻⁵]) 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. DOP concentrations from the AMT17, AMT14 and 36N cruises were measured via the UV oxidation method. DOP concentrations from the BIOSEPO and KH12-3 cruises were measured using the persulfate oxidation method. No correction or normalization of the TDP or DOP concentration data was applied based on the different analytical methods used in this study.

Surface P* values. Nitrate concentration ([NO₃⁻⁵]) and [PO₄⁻³] data were taken from the World Ocean Atlas 2013 climatological field (1° × 1°) at the 0 m level. P* values were calculated using equation (1) with surface [NO₃⁻⁵] and [PO₄⁻³] data:

\[ P^* = \frac{[\text{PO}_{4}^-] \times [\text{NO}_3^-]}{16} \]  

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

Satellite data products. Remotely sensed chlorophyll a concentrations. Surface chlorophyll a concentrations were taken from the MODIS-AQUA 9 km resolution product, 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.

NPQ-corrected \( \varphi_a \) values. Following the method given by Behrenfeld et al., we calculated the global \( \varphi_a \) 9 km field and applied a correction for NPQ using the equations below:

\[ \varphi_a = 0.10 \langle i \bar{P}_{\text{FLH}} \rangle \]  

\[ \langle i \bar{P}_{\text{FLH}} \rangle = 0.0147 \text{Chl}_{a}^{1,004} \]  

\[ \text{NPQ-corrected } \varphi_a = \varphi_a \times \text{iPAR}^{1,590} \]

in which iPAR is the instantaneous photosynthetically available radiation (umol photons m⁻² s⁻¹), Chlₐ is the satellite-derived chlorophyll a concentration (mg m⁻³) using the OceanColor (OC) algorithm and \( \langle i \bar{P}_{\text{FLH}} \rangle \) is an average spectrally weighted phytoplankton absorption coefficient, which is calculated as a power-law function of Chlₐ. The parameter \( \varphi_a \) is unitless. The iPAR and Chlₐ 9 km fields are all downloaded from the MODIS Level-3 product (https://oceancolor.gsfc.nasa.gov/l3/). The equations above were used to obtain the climatological NPQ-corrected \( \varphi_a \) fields between 2003 and 2019. Note that the equation used here to calculate NPQ-corrected \( \varphi_a \) is a simplified expression for \( \varphi_a \) but its global distribution is indistinguishable from the \( \varphi_a \) field with full expression (Supplementary Fig. 1).

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), boosted tree and Gaussian process regression. 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, we built 30 decision trees and set the minimum leaf size to 8. For the boosted-tree 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 \( \varphi_a \); 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° × 2° 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 \( \varphi_a \) using a Type II linear regression model. The Type II linear regression model was evaluated in MATLAB (2019a version) using the file ‘gmrgress.m’.

Plotting. We used Ocean Data View software (MathWorks, 2022) to plot Fig. 2a,d,g,l,m,p, and ‘M_Map’ software (https://github.com/zhanglei/DOOR) to plot Fig. 1a and Extended Data Figs. 4 and 5. The base maps used in these figures are from the software themselves.

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/10.26088/1912/bco-dmo.855139.2). The Level-3 satellite product can be downloaded from the NASA OceanColor website (https://oceancolor.gsfc.nasa.gov/13/).

Code availability

Code and data used to reproduce Figs. 1 and 2 are archived at https://github.com/zliangcean/DOOR.

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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 interests.

Additional information

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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

| Predictor                  | SVM   | Boosted tree | Gaussian process regression |
|----------------------------|-------|--------------|----------------------------|
| $P^*$ + NPQ-corrected $\varphi_{sat}$ | $R^2 = 0.43$ | $R^2 = 0.40$ | $R^2 = 0.45$ |
| $P^*$ + Chl $a$             | $R^2 = 0.28$ | $R^2 = 0.31$ | $R^2 = 0.35$ |
| $P^*$ + NPQ-corrected $\varphi_{sat}$ + Chl $a$ | $R^2 = 0.41$ | $R^2 = 0.42$ | $R^2 = 0.52$ |
Extended Data Fig. 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 ****: $P < 0.0001$, **: $P < 0.01$, *: $P < 0.05$, 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 Fig. 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 Fig. 3 | Correlation between observed upper 50 m DOP stock (mmol m$^{-2}$) and climatological mean $P^*$ ($\mu$M) between 100 m and 250 m computed from the World Ocean Atlas 2013 (ref. 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 Fig. 4 | Annual mean surface geostrophic currents (0.25° × 0.25°) and identified surface current convergence zones (SCZ). Annual mean geostrophic currents (0.25° × 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.
Extended Data Fig. 5 | Predicted surface ocean DOP concentrations (µM) based on the linear relationship between DOP concentrations and P*(Fig. 1; see main text).