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Phosphorus as an integral component of global marine biogeochemistry

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Phosphorus (P) is essential for life, but most of the global surface ocean is P depleted, which can limit marine productivity and affect ecosystem structure. Over recent decades, a wealth of new knowledge has revolutionized our understanding of the marine P cycle. With a revised residence time (~10–20 kyr) that is similar to nitrate and a growing awareness that P transformations are under tight and elaborate microbial control, the classic textbook version of a tectonically slow and biogeochemically simple marine P cycle has become outdated. P moves throughout the world's oceans with a higher level of complexity than has ever been appreciated before, including a vast, yet poorly understood, P redox cycle. Here, we illustrate an oceanographically integral view of marine P by reviewing recent advances in the coupled cycles of P with carbon, nitrogen and metals in marine systems. Through this lens, P takes on a more dynamic and connected role in marine biogeochemistry than previously acknowledged, which points to unclear yet profound potential consequences for marine ecosystems, particularly under anthropogenic influence.

Although the indispensable role of phosphorus (P) for life has long been recognized, our understanding of the marine P cycle has changed considerably over recent decades. Early research took place from a geologically dominated viewpoint[1], aiming to balance riverine P sources with sedimentary sinks, while neglecting transformations that occur within the marine water column[2]. This perspective was overturned by the realization that marine plankton use diverse metabolic strategies to cope with variable P availability[3], suggesting that the marine P cycle is more complex than previously recognized. Alongside this microbially driven perspective, taking into account revised estimates of P burial shortened the oceanic residence time of P from ~80 kyr (ref. [1]) to 10–20 kyr (ref. [4]), and evidence for P deficiency and limitation over wide extents of the global surface ocean accumulated[5], confirming the modern view of marine P as a dynamic, scarce and bio-limiting nutrient. The present time marks another chapter in the evolution of marine P research, in which microbial mechanisms of P cycling are being incorporated into a broader oceanographic context (Fig. 1). This oceanographically integral view acknowledges the vast yet poorly understood redox-active nature of the marine P cycle and clarifies the cycle's connectivity to other bioactive elements, including carbon (C), nitrogen (N) and trace metals, while quantifying its influence on large-scale marine ecosystem dynamics and climate-relevant processes. In these ways, our understanding of the marine P cycle continues to evolve along a trajectory of increasing complexity.

Signatures of microbial P physiology across oceanographic scales

The long-standing debate regarding the nature of growth-limiting nutrient(s) in the ocean has been reviewed elsewhere[6]. Modelling and field incubation studies predict P limitation of primary production[5] and N_2 fixation[7] in only a restricted number of geographical areas, while co-limitation with N may be more widespread[6]. Still, surface mixed-layer inorganic phosphate (Pi) concentrations are low (<40 nmol l^{-1}) in oligotrophic biomes[8], particularly in the northwest Atlantic, northwest Pacific and southwest Pacific, as well as in the Mediterranean Sea, where concentrations of less than 10 nmol l^{-1} are typically measured during periods of stratification. Such concentrations are below the theoretical Pi-uptake capacity for many marine phytoplankton, implying that numerous microorganisms inhabiting these regions must be Pi stressed even though microbial communities may not necessarily be P limited for growth[9]. Here, we define P stress as a distinct cellular metabolic state caused by low Pi availability in the environment. For example, a key cellular-level response supporting biomass and ecosystem-level production under low Pi availability is the enhanced uptake and turnover of dissolved and particulate P pools by microbial communities[10,11]. Even in coastal environments, Pi availability can be chronically or transiently low enough to induce P stress and constrain biological productivity[12]. Accordingly, microbial communities throughout diverse regions of the ocean cope with P scarcity on a variety of timescales.

Flexible microbial P demand. At least two major aspects of microbial P physiology are reflected on oceanographic scales. One of these involves the exceptional plasticity of microbial P demand. The cellular requirement for P is defined in relation to other bioactive elements according to the canonical Redfield ratio of 106C:16N:1P. Yet diverse P-starved plankton decouple these ratios by substituting P lipids with P-free alternatives[3,13] and by downregulating P-rich growth machinery while upregulating N-rich nutrient-acquisition proteins[14]. Furthermore, picocyanobacteria that dominate phytoplankton communities in the low-latitude oligotrophic ocean exhibit consistently low P:N and P:C ratios regardless of prevailing nutrient availability[15]. This could be partly explained by the finding that marine prokaryotes secure Pi using a large periplasmic buffer instead of intracellular storage[16]. Short-term acclimation strategies and species-specific evolutionary adaptations to P depletion therefore coalesce to shape microbial P demand at the community level.

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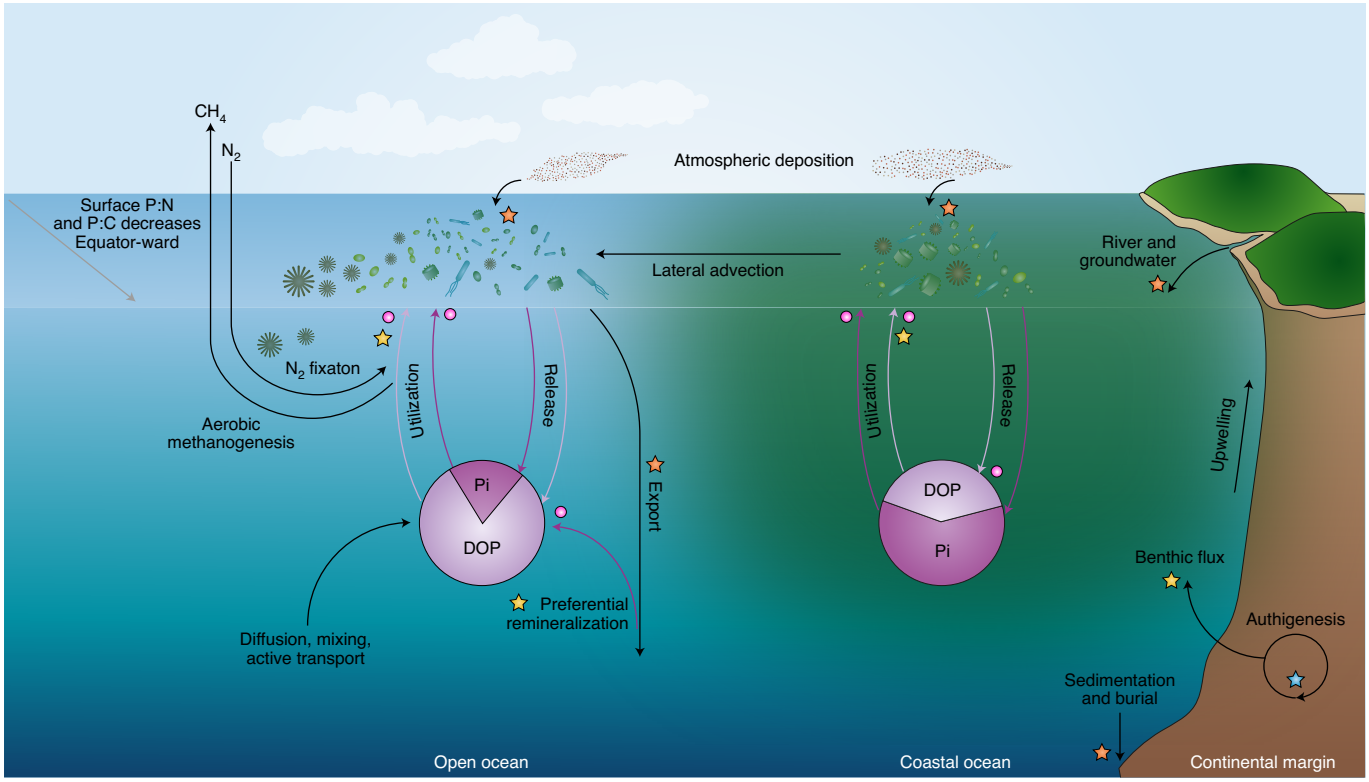

Fig. 1 | The marine P cycle with an emphasis on the North Atlantic. Black arrows represent the movement or chemical transformations of P, unless otherwise noted. Relative DOP and Pi contributions to TDP are represented as pie charts in the low-Pi open ocean and the high-Pi coastal ocean, where both P forms are simultaneously utilized and released by microbial communities (dark purple arrows, Pi; light purple arrows, DOP). Interactions with metals are indicated by stars, including mineral-adsorbed P (orange star), metal-associated P precipitation (blue star) and metal-associated P hydrolysis (yellow star). Processes involving reduced-P compounds are shown as pink circles. In the surface ocean, particulate P:N and P:C ratios decrease with latitude (grey arrow). For quantitative information on these fluxes, the reader is referred to previous reviews[2,4,98].

Consistent with flexible P demand, the P:C composition of marine microbes[17] and bulk particulate organic matter[18] (POM) each correlate positively with overall Pi availability. The P:C composition of both cultures and POM is more flexible than N:C[17,18], suggesting that microbial communities economize P with a specialized degree of versatility. Indeed, the global median N:C composition of POM is consistent with Redfield stoichiometry, but global median particulate P:C and P:N ratios are ~30% lower than Redfield values[19]. These global deviations are driven by strong latitudinal trends, with particulate P:C and P:N ratios showing elevated values in the nutrient-rich high latitudes and relatively diminished values in the low-latitude oligotrophic gyres[18] (Fig. 1), as expected from flexible P physiology. For example, diatoms tend to be more dominant at high latitudes and seem to store more P internally than cyanobacteria[20], contributing to the higher P:C and P:N ratios, as well as to the export and sequestration of P in the seafloor[21]. Using Pi as a predictor of particulate P:C reproduces the observed large-scale stoichiometry of POM in the global surface ocean[22], consistent with the dominant role of P nutritional status in establishing microbial stoichiometry.

Nutritional DOP utilization. A second oceanographically prominent aspect of microbial P physiology involves the nutritional acquisition of dissolved organic P (DOP). In the low-latitude oligotrophic gyres, DOP concentrations greatly exceed Pi (Fig. 2) and could potentially support a large fraction of microbial community P demand. DOP is also rapidly cycled in coastal and high-nutrient systems[11,23], which may be driven by species-level resource partitioning[24,25]. DOP is commonly more labile than dissolved organic C (DOC) and N (DON)[26], consistent with the nutrient-depleted, non-Redfield composition of dissolved organic matter (DOM[27]; Extended Data Fig. 1). Leveraging sparse DOP observations across an interocean dataset of DOM, a previous study[27] determined that DOP is remineralized twice as rapidly as DOC and DON on a global scale, consistent with the wide capacity of microorganisms to use DOP as an exceptionally valuable nutritional commodity. Indeed, non-Redfield DOM production and remineralization is also necessary to reproduce global DOM distributions[28].

As a subset of the larger DOM pool, DOP can be described as a continuum of labile, semi-labile and refractory forms. DOP is poorly characterized at the molecular level, yet operationally includes organic and inorganic polymeric forms of P within three main bond classes[29]: P-esters (including mono (P–O–C) and diesters (C–O–P–O–C)), P-anhydrides or polyphosphates (P–O–P) and phosphonates (P–C). Marine microbial communities have a wide capacity to use DOP sources within each of these main bond classes through the activity of diverse P hydrolase enzymes (Box 1), including alkaline phosphatase (AP; Fig. 3b).

Impacts on the C cycle

The widespread capacity of marine microorganisms to cope with P scarcity by altering cellular P demand and utilizing DOP both lead to non-Redfield patterns within POM and DOM (Extended Data Fig. 1) that drive critical aspects of the marine C cycle, including primary productivity, export production and aerobic methanogenesis.

Flexible stoichiometry facilitates C export. C export, or export production, broadly refers to the amount of organic matter produced by primary production that sinks into the deep ocean, where

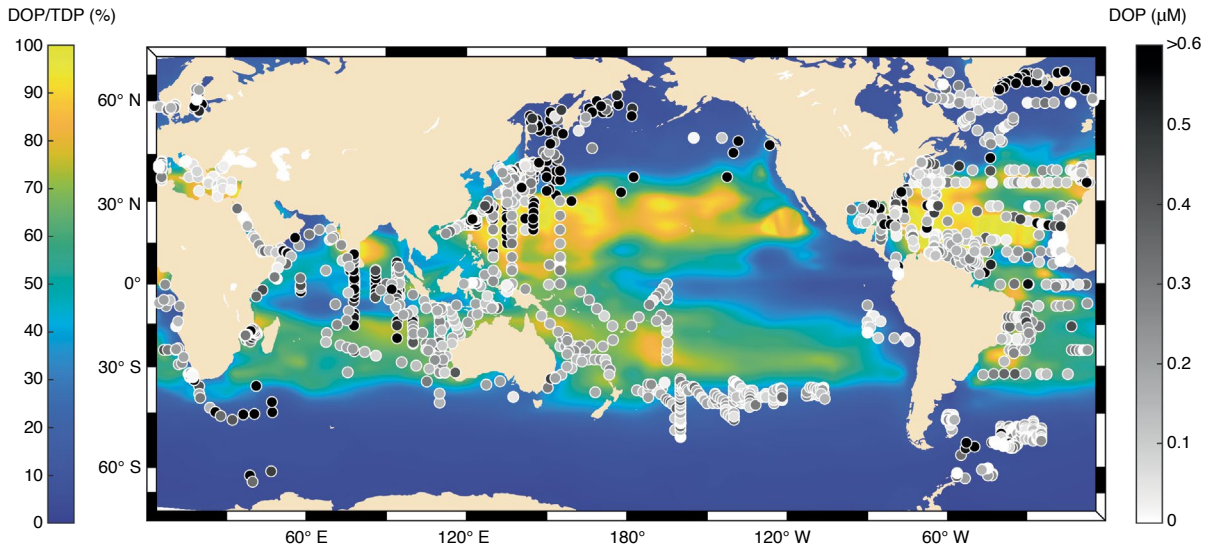

Fig. 2 | Distribution of DOP concentrations and contribution to TDP over the global ocean. Percentage contribution (colour bar) of DOP to TDP and observed DOP concentrations (greyscale circles) at 50 m depth. DOP contributions to TDP were mapped using both modelled DOP data from ref. [28] and soluble reactive P (SRP) from the GLODAPv2_2016 climatology[99]. Note the sparse DOP measurements.

it can no longer readily exchange with the atmosphere. Regional variability in the P:C composition of export production is consistent with broad geographic trends in bulk surface POM[30]. As a result, C export from the low-latitude oligotrophic gyres is more efficient per unit P than commonly assumed based on fixed Redfield stoichiometry[18,30]. On a global scale, one model estimate suggests that flexible stoichiometry accounts for an increase in particulate organic C export of 12%[7], which will probably buffer against predicted decreases in C export due to the climate-related expansion of low-latitude oligotrophic regions. Indeed, by the year 2100, global C export may be 30% more efficient due to flexible P:C stoichiometry than it would otherwise be under fixed Redfield conditions[31]. In this way, the recognition of flexible P physiology in microbial communities has helped to transform the current understanding of biological C flow within the ocean. In turn, recent modelling studies indicate that anthropogenic C uptake by the biological pump will increase in the future by 0.5–5% due to flexible P:C stoichiometry[22,31].

DOP use enhances primary productivity and export production. Taking the preferential remineralization of DOP into account, global net primary production (NPP) and export production estimates increase by ~10% and ~9%, respectively, with bigger effects on regional scales[27]. In models of the North Sea, including DOP utilization increases NPP estimates by 30%[32]. In the subtropical Atlantic, NPP estimates more than double when taking into account the preferential DOP use[27]. C flow in the western subtropical gyres is especially dependent on DOP, which is largely supplied to these regions by lateral advection[27]. Indeed, lateral mixing may supply 44–67% of the P budget in the ocean gyres worldwide[33], with lateral DOP delivery potentially supporting 22–46% of export production across all five subtropical gyres[33] and 70% of export production in the North Atlantic subtropical gyre (NASG) alone[34].

Phosphonate degradation drives aerobic methanogenesis. Nutritional utilization of methylphosphonate, a form of DOP, produces methane, a potent greenhouse gas[35–37]. Dominant pathways of methanogenesis are anaerobic, yet most oxygenated surface waters of the open ocean are supersaturated with respect to methane[37], reflecting an aerobic source whose origins are controversial. Dissolved methylphosphonate and related phosphonate esters have been reported in the North Pacific subtropical gyre (NPSG)[35] and the western NASG[36], where they are dynamically cycled under low Pi conditions, but the quantitative contribution of their degradation to the total marine methane flux is not completely understood.

Linkages to the N cycle

Recent advances in our understanding of the coupled P and N cycles have been made along two main themes: the effects of non-Redfield P cycling on N_2 fixation and anthropogenic impacts on nutrient-limitation patterns.

Non-Redfield P cycling and N_2 fixation. The virtually inexhaustible supply of atmospheric N_2 ensures that other factors limit diazotrophs, such as the availability of Pi. The ability to use DOP would therefore provide N_2 fixers with a substantial ecological advantage. The globally important colonial diazotroph *Trichodesmium* can use a variety of phosphonates as sole P sources, a capacity that is shared with the non-N_2-fixing picocyanobacteria *Synechococcus* and *Prochlorococcus*, as well as many heterotrophic bacterioplankton[3]. The diazotroph *Crocosphaera*, on the other hand, lacks the ability to use phosphonates but achieves equivalent levels of growth on model P-esters compared with Pi[38], reflecting potential resource partitioning. N_2 fixers may be better competitors for DOP than non-diazotrophs, as seen with *Trichodesmium* from the Sargasso Sea, which outcompetes the rest of the microbial community for the model P-ester adenosine 5′-triphosphate[39] (ATP). Furthermore, phosphodiesterase activity correlates positively with N_2 fixation in the central North Pacific, suggesting that diazotrophs are important drivers of DOP cycling in this region and, in turn, that DOP is a key resource supporting N_2 fixation in this environment[40].

DOP use carries an additional N and energy cost[41], in the form of producing N-rich enzymes that can hydrolyse P bonds, which may explain the high N:P requirements of phytoplankton in the oligotrophic ocean[15,42]. This DOP utilization cost probably exacerbates widespread N limitation, giving diazotrophs an ecological advantage that expands their niche, especially in areas such as the NASG, where the relatively elevated supply of N should otherwise preclude substantial N_2 fixation[41]. Indeed, flexible phytoplankton N:P stoichiometries are necessary to explain the global marine N budget[42]. Accounting for variable phytoplankton stoichiometry and

Box 1 | Bioavailability

Bioavailability refers to the relative ease with which a specific DOP source can be biologically degraded and ultimately assimilated into microbial biomass. Rapid and variable turnover rates within dissolved and particulate P pools suggest that a fraction of DOP is bioavailable and supports oceanic production[10,11,100]. Still, much remains unknown about the biologically available P (BAP) pool, but approaches involving radiotracers[23,100,101] and the oxygen isotopic signature of dissolved Pi (δ^{18}OPi)[102,103] provide key insights. The δ^{18}OPi has been used to estimate the minimum fraction of Pi that is generated from DOP by extracellular enzymes[102] and to show that P is rapidly recycled within cells[102,103]. Nonetheless, this approach is limited by a lack of molecular-level information about DOP composition, a poor understanding of P hydrolases involved in DOP utilization and the respective fractionation factors associated with them, resulting in highly variable estimates of BAP[102]. DOP bioavailability has been estimated from ^{32}P–ATP hydrolysis[104] time, and results indicate that the most labile DOP compounds can be degraded very rapidly[23,101] (hours). However, this approach is limited by a lack of compositionally representative DOP radiotracers. Accordingly, an index of the relative microbial metabolic preference for different DOP compounds can be calculated based on changes in the turnover time of the Pi pool, measured using the ^{32}Pi radiotracer, in the absence and presence of selected DOP compounds, relative to controls with Pi[105]. While phosphomonoesters have been traditionally considered the most bioavailable DOP bond class, such experiments reveal that nucleotides, followed by inorganic polyphosphates, are more bioavailable than model phosphomonoesters[100,101,105], although these preferences may vary as a function of community composition[106]. In fact, polyphosphates are preferentially recycled relative to other forms of P in the Sargasso Sea[107] and Indian Ocean[108], which is also reflected in model diatom studies[109]. Furthermore, recent evidence suggests that phosphodiesters and organophosphate triesters are actively degraded as an alternative P source under Pi stress[40,110]. Dissolved phosphonates, once considered to be recalcitrant, are now recognized as bioavailable, but their utilization is more taxonomically restricted than the other DOP compound classes (see main text).

A few microorganisms directly assimilate select low-molecular-weight DOP molecules via cell surface transporters[111] (Fig. 3a). In contrast, cell-surface-associated and cell-free[112,113] P hydrolase enzymes originating from diverse prokaryotic and eukaryotic plankton[104,111,114] provide broader access to the bulk DOP pool. APs are ubiquitous metalloenzymes across the tree of life (Fig. 3b) that can act on many DOP substrates, but their dominant role is assumed to be P-monoester degradation. Although the mechanisms of polyphosphate use are not clear, APs may be involved[80], but apparently not in diatoms of the genus *Thalassiosira*, which utilize polyphosphates using previously unrecognized P hydrolases[109]. Furthermore, mechanisms of P-diester use are also unclear but may involve some AP forms[57].

The enzymatically hydrolysable fraction of DOP can be assessed through the addition of P hydrolase enzymes to natural seawater samples, leading to an estimate of BAP. For example, bioassays with AP from *Escherichia coli* estimate that BAP accounts for 10–50% of total ambient DOP[98]. Similarly, using P-diesterases, phytases, nucleases and mixtures thereof, most of the environmental DOP pool appears enzymatically accessible[98]. However, broad substrate versatilities of these P hydrolases[80] make it difficult to deduce BAP composition. Additionally, commercially available P hydrolases are from terrestrial organisms (typically *E. coli* or calf intestine), and marine BAP measurements could be improved with the application of diverse representative marine enzymes.

As APA is upregulated under P depletion, it has been suggested that DOP bioavailability may vary over space and time as a function of prevailing P status[115]. Community-level APA has therefore been used to track the P nutritional status of aquatic systems for at least 60 years. In a recent compilation of APA observations from the Atlantic and Pacific oceans, APA increases hyperbolically below 30 nmol l^{-1} Pi[62], illustrating APA as a critical response to P depletion. However, certain P hydrolase activities are not inhibited by Pi[104,109]. Indeed, APA may liberate sizable amounts of Pi in Pi-replete open oceans[64,113] and coastal systems[114,116]. Consistent with these findings, cell-free APA is high across different marine environments[112,113] and maintains most of its activity over a period of at least two weeks[111], resulting in potential spatiotemporal uncoupling between APA and Pi availability.

preferential DOP utilization, N_2 fixation estimates increase by ~30–60% globally[7,27,43] and by a factor of three in the North Atlantic[44], consistent with the essential role of microbial P physiology in the N cycle. The flexible N:P composition of primary production leads to local non-Redfield ratios of dissolved inorganic N (DIN) and Pi within surface waters down to the thermocline[45]. The conventional N* tracer, which measures deviations from DIN:Pi relative to Redfield proportions, has been used as an indicator of N cycling processes alone (N_2 fixation and denitrification), but microbial P cycling also clearly plays a role, which should be considered.

Anthropogenic impacts on nutrient-limitation patterns. Anthropogenic activity has not only increased the input of bioavailable nutrients to the environment but has also substantially altered the ratio of N and P delivered, with reactive N pollution exceeding that of P[46]. The ecological and biogeochemical impacts of these perturbations on marine ecosystems are becoming clearer. For example, nutrient pollution is a problem that was once considered to be primarily confined to coastal zones. However, recent studies highlight the potential for large-scale anthropogenic impacts in the open ocean via atmospheric deposition. For example, because of anthropogenic N emissions, the total atmospheric N input to the ocean is now comparable in magnitude to the other external N sources, albeit regionally variable[47]. The NPSG is not P limited, but atmospheric N pollution carried from northeast Asia to the NPSG enriches DIN availability compared with Pi, which may ultimately eliminate the niche of N_2 fixers[48,49], exacerbate P depletion and possibly drive the system to P limitation[49]. Coupled with climate warming and natural variability such as the Pacific decadal oscillation, the enhanced atmospheric delivery of anthropogenic N relative to P may shift microbial communities in the NPSG towards the dominance of DOP-utilizing prokaryotes[49,50] with efficiently buffered Pi-uptake systems[16]. Atmospheric deposition enriched in N (and iron (Fe)) with respect to P may contribute to P stress and limitation in the NASG as well[51]. Although the potential degree of atmospheric nutrient pollution remains unclear in the Atlantic, biomass burning represents a major and previously overlooked seasonal source of aerosol P to the Atlantic[52], which probably carries some degree of direct anthropogenic influence. Because consistent periods of P limitation have direct impacts on ecosystem community structure and functioning, the strength of (de)coupling between P and N cycling in the oligotrophic gyres and other ocean regions influenced by anthropogenic activities has potentially far-reaching implications for marine biogeochemistry and ecology[48,53].

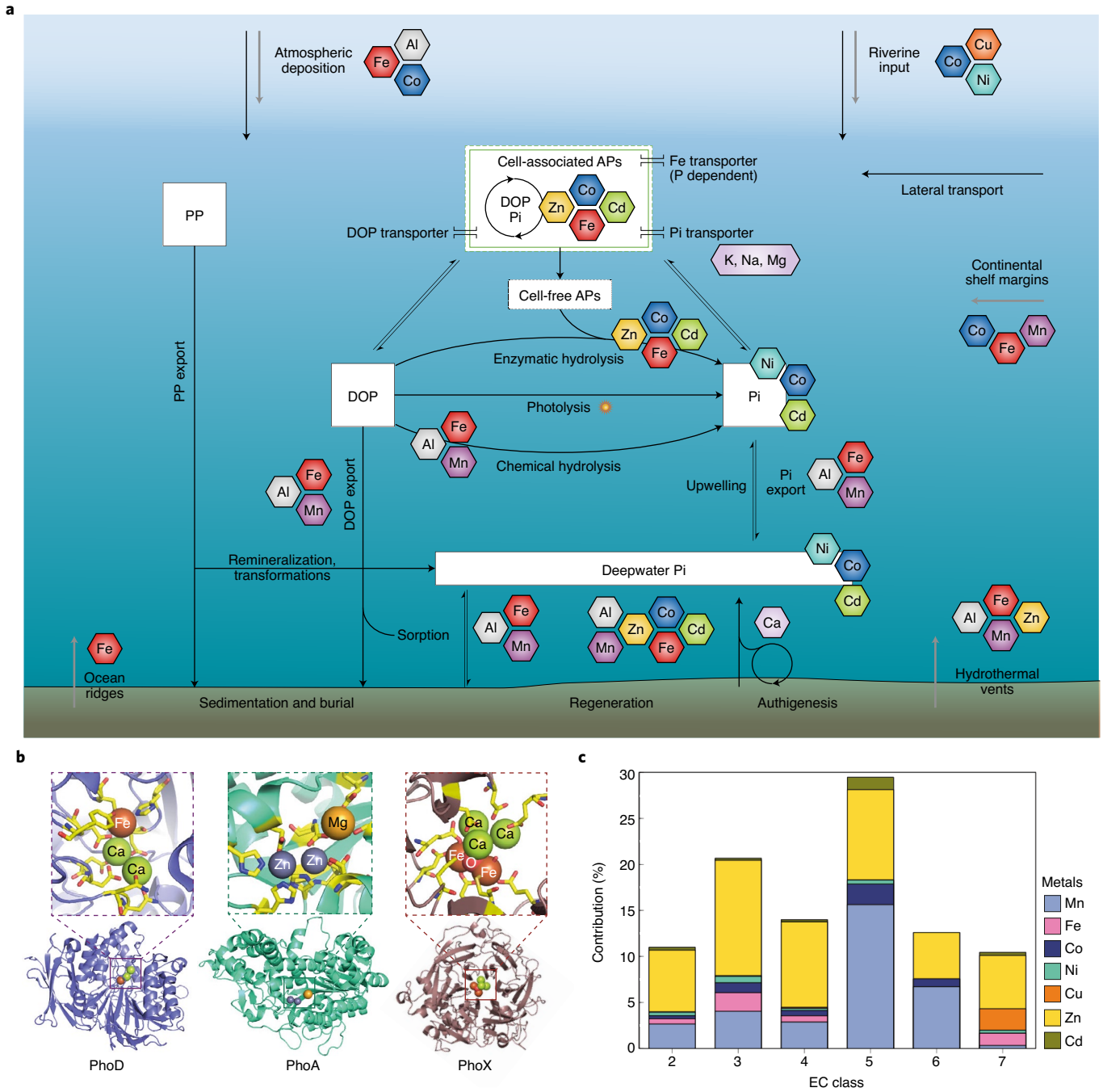

Fig. 3 | Metals and metalloenzymes coupled with P cycling. a, The role of metals in transforming P pools. Black arrows represent sources, sinks and transformations of P, grey arrows represent major sources of metals[55] and white boxes represent P inventories (Pi, phosphate; PP, particulate P). Boxes with dashed lines indicate distribution of APs. **b**, Crystal structures of terrestrial PhoD (*Bacillus subtilis*, PDB: 2YEQ), marine PhoA (*Vibrio* sp. G15-21, PDB: 3E2D) and terrestrial PhoX (*Pseudomonas fluorescens*, PDB: 4ALF). Enlarged panels show the enzyme active site highlighting the respective metal cofactors (sphere models) and coordinating amino acid residues (stick models, yellow). **c**, Percentage of P-metabolizing enzymes that are metal dependent, classified by enzyme commission (EC) number: transferases, 2; hydrolases, 3; lyases, 4; isomerases, 5; ligases, 6; and translocases, 7 (Supplementary Information). Metal-dependent oxidoreductases (1) acting on P were not found.

Coupled cycling with metals

Previously unrecognized interactions between P and metal cycling have come to light in recent years after the major discovery that two dominant forms of the AP enzyme require Fe[54,55]. Recent advances have also been made regarding mineral-associated transformations of P in marine sediments (Fig. 3a), as discussed below.

Metal-dependent DOP acquisition by AP. Bioinformatics analyses confirm that AP gene sequences are ubiquitous throughout the global ocean[56], with a range of divergent and biochemically versatile APs in marine prokaryotes and eukaryotes[57–59]. APs can be classified into three main families with different metal cofactors occupying their active sites (Fig. 3b), and other atypical APs with various metal

contents[57] (Extended Data Fig. 2). Fe-dependent proteins PhoD and PhoX are the most widespread APs among marine microbial communities[56,60]; however, the zinc (Zn)-dependent protein PhoA may play a dominant role in some ecologically prevalent taxa[61].

For several model marine microbes, an enhancement of AP-mediated DOP hydrolysis has been observed with the addition of metals in axenic cultures[62], suggesting potential metal limitation of environmental AP activity (APA). Indeed, APA responded positively to Fe amendments within the Fe-poor western NASG[63]. In the eastern North Atlantic, where the Saharan dust plume can alleviate the shortage of Fe, APA increased following treatment with Zn instead[62]. On interbasin scales, higher Fe concentrations in the North Atlantic could spur APA relative to the South Atlantic and the subtropical Pacific[64,65], where metal scarcity could explain lower observed APA in areas with comparable ambient Pi[62,64]. Supporting this interpretation, *Trichodesmium* expresses Fe-dependent PhoX along with P stress markers in the NASG, whereas the NPSG is enriched in Zn-dependent PhoA transcripts and Fe stress markers[66]. These studies demonstrate widespread linkages between Zn, Fe and microbial nutrition in Pi-depleted, oligotrophic ocean areas (Fig. 3a). Although the cycles of P and Fe are not tightly coupled over ocean-basin scales, these findings, and the environmental prevalence of Fe-dependent AP isoforms[56], suggest that Fe may limit P nutritional acquisition and DOP turnover across wide areas of the surface ocean.

In addition to Fe and Zn, marine APs may interact with other trace elements (Extended Data Fig. 2). For example, dissolved cobalt (Co) is substantially less abundant in the North than in the South Atlantic[65], which is potentially caused by incorporation of Co into PhoA in the North Atlantic, per natural Co requirement[67] and/or substitution for Zn[68,69]. In the Southern Ocean, heavy seasonal manganese (Mn), Fe and Zn depletion enhances microbial cadmium (Cd) uptake[70], which is presumed to substitute for divalent cations in APs[61]. This process could potentially be related to the puzzlingly coupled uptake, export and regeneration of Cd and P at high latitudes[71].

Given the pervasively low concentrations of biologically accessible Co[69], Fe[5] and Zn[68], metal availability may not only limit APA, but AP-associated metal demands may also impact Fe, Zn and Co budgets. However, there is currently a lack of observations to evaluate this hypothesis accurately, in large part owing to the absence of quantitative AP protein-abundance data from marine ecosystems. Furthermore, as APA can be substantial, independent of ambient Pi (Box 1), APs could potentially influence trace metal budgets regardless of prevailing P status.

Linkages between microbial P physiology and metal cycling probably exist beyond DOP utilization by the AP metalloenzyme family. For example, both cellular Fe content and Fe uptake rates in cultures of the diazotrophic cyanobacterium *Halothece* sp. were positively correlated with cellular P levels, indicating P-dependent Fe uptake under N_2-fixing conditions[72]. Although the mechanism(s) remain unclear, P may therefore influence metal acquisition, just as metals influence DOP use via AP[72,73], which suggests a potential two-way metabolic choreography linking these biogeochemical cycles (Fig. 3a). Furthermore, our survey of 25,000 proteins involved in P metabolism, including APs (Supplementary Information), shows widespread metal dependence, illustrating that many potential linkages between the cycles of P and metals remain to be discovered in ocean systems (Fig. 3c).

Mineral-associated transformations of P. Over geologic timescales, P is ultimately removed from the oceans via long-term burial in marine sediments[2]. Sinking organic matter and Pi adsorbed to oxyhydroxides of aluminium (Al), Fe or Mn represent large and well-known sinking fluxes of P to the seabed[74], yet DOP compounds including P-esters, phosphonates[75] and polyphosphates[76] also readily adsorb onto metal oxyhydroxides. During early diagenesis, most of the P delivered to sediments is rereleased to the benthos through reductive dissolution of these mineral phases by metal-oxide-respiring bacteria[74,75] and through the remineralization of organic P. In fact, several marine heterotrophic bacteria promote the dissolution of Fe oxides by secreting metal-chelating ligands/chelators and redox-active antibiotics in order to gain access to the adsorbed Pi pool and/or liberate metallocofactors for AP production under conditions of P scarcity[73,77] (Fig. 3a). Al, Mn and Fe metal oxides also serve as powerful abiotic catalysts for P-ester[78] and polyphosphate[76] hydrolysis through a phosphatase-mimetic reaction mechanism that has implications for AP evolution[76].

A small portion of P that reaches the seafloor is retained in sediments over geologic timescales through the thermodynamically favourable, yet kinetically inhibited, precipitation of authigenic calcium phosphate mineral phases that form in common sedimentary environments worldwide[4]. The formation of enriched calcium phosphate mineral deposits has been linked to polyphosphate hydrolysis by large sulfur bacteria in sediments underlying highly productive upwelling environments[79]. Similarly, AP-driven Pi release from DOP sources, including polyphosphate, is responsible for calcium phosphate mineralization in pure enzyme assays[80] and laboratory cultures of a soil bacterium[58]. Analogously, metal-oxyhydroxide-catalysed polyphosphate hydrolysis can lead to the authigenesis of calcium phosphate minerals in laboratory settings[76] (Fig. 3a). The extracellular Pi buffer of marine bacteria may also have the potential, albeit deleterious, to precipitate insoluble calcium phosphate complexes if free Ca^{2+} concentrations in the periplasm are not minimized[16]. Therefore, several different mechanisms of biologically mediated calcium phosphate precipitation may have potential relevance in the marine environment, depending on the diagenetic setting. In addition to authigenic calcium phosphate, another potentially quantitative P-removal pathway in some sedimentary environments is the formation of the iron phosphate mineral vivianite[81], although the overall role of vivianite formation in the marine P cycle remains uncertain.

The P redox cycle

While it is commonly assumed that P occurs almost exclusively in its fully oxidized (V) state in the environment, organic P(III) compounds, or phosphonates, have been recognized in the ocean for decades[82]. Early research revealed phosphonates in DOM[82] and bulk particulates[83], where they accounted for up to 18–25% of total P[82,83]. In particulates, phosphonates were preferentially removed (either physically released or remineralized) relative to phosphoesters[83], reflecting the active character of the P redox cycle. Yet overall, the distribution and molecular identity of marine phosphonates remain poorly characterized, critically constraining our understanding of their biogeochemical importance. Similarly, natural levels of aquatic phosphite (III) and hypophosphite (I) have been quantified only in Florida rivers, where they accounted for up to 25% of total dissolved P (TDP)[84], but the biogeochemical importance of these reduced-P forms also remains unclear. Indeed, an understanding of the processes linking P redox states has only begun to emerge in marine systems. While most advances have been made in soil and freshwater environments, recent investigations suggest a possibly important role of reduced-P compounds, including inorganic and organic forms, in marine microbial metabolism, revealing an active and extensive oceanic P redox cycle (Fig. 4).

P oxidation. Dissimilatory (DPO) and assimilatory phosphite oxidation (APO) convert both hypophosphite (I) and phosphite (III) to orthophosphate, thereby sustaining cellular growth (Fig. 4). In the DPO pathway, only the energy provided by the phosphite oxidation reaction is used for growth. The respiratory waste product, orthophosphate, is released into the surrounding environment, as seen in

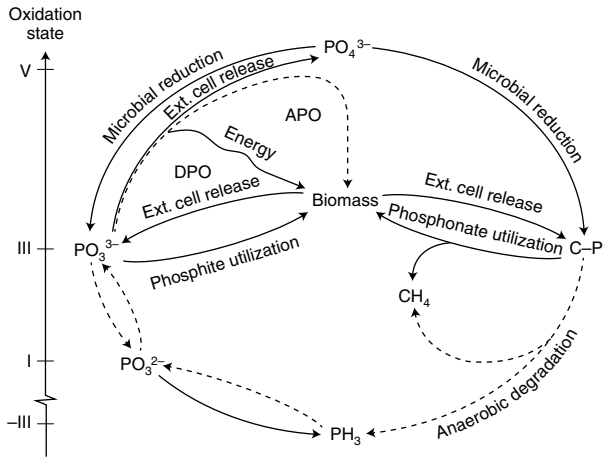

Fig. 4 | Reduced-P compounds and microbial transformations, including APO and DPO in natural environments. The chemical forms of P are represented along with their oxidation state. Solid arrows refer to microbial processes that are known to occur in, but are not necessarily limited to, marine environments. Dashed arrows refer to microbial processes reported from, but not necessarily confined to, anoxic soils.

a sulfate-reducing bacterium purified from marine sediments[85,86]. In contrast, reduced-P sources are incorporated into biomass through a phosphate intermediate in the APO pathway. Marine cyanobacteria, including *Prochloroccocus*[87,88] and *Trichodesmium*[10,89], can use phosphite as a sole source of P, with metagenomic data[87] and laboratory isolates[88,89] suggesting that the *ptxABCD* gene cluster mediates phosphite oxidation. A range of marine bacteria and cyanobacteria can grow on phosphonate as well[3,35,36]. In fact, bacterial C–P lyase genes involved in the nutritional utilization of phosphonates are present in prokaryotic genomes throughout the global ocean, especially in severely P-depleted regions[90]. However, phosphonate bioavailability is not limited to prokaryotes, as phosphonate can sustain low levels of growth by select eukaryotic phytoplankton[91].

P reduction. In surface waters of the western NASG, one study[10] reported that ~1–15% of the bulk community Pi uptake was reduced to P(III), resulting in a flux of P(III) that rivals the global riverine input of new Pi to the ocean. P(V) reduction by *Trichodesmium* exceeded that by the whole community[10], consistent with culture studies indicating that *Trichodesmium* has a specialized capacity for P(III) production[92]. Surprisingly, despite Pi depletion in the western NASG and the energetically expensive production of P(III), most of the Pi reduced by *Trichodesmium* was released to the surrounding environment[10]. Therefore *Trichodesmium*, which is known to host a diverse community of bacterial epibionts, may exchange P(III) symbiotically with its microbiome[10]. The molecular identity and function of P(III) compounds produced in the marine environment still remains unclear, however. For example, previous work[10] did not distinguish between organic and inorganic P(III) forms, both of which occur in seawater[27]. Given that some low-molecular-weight organophosphonates have antibiotic properties, this knowledge gap has potential implications for drug discovery and marine natural products research[93].

Synthesis and future directions

The application of modern tools, particularly molecular-level omics approaches and sensitive geochemical techniques (Boxes 1 and 2), has illuminated a complex, dynamic and microbially driven marine P cycle that is intimately integrated with the cycling of C, N and metals on oceanographic scales. While these developments modernize our understanding of the marine P cycle and invigorate our continued study of it, fundamental gaps in knowledge persist. Many regions remain undersampled (Fig. 2 and Extended Data Fig. 1), and DOP, particulate P and low-level Pi datasets are particularly sparse relative to analogous measurements of C and N, despite the availability of straightforward methods that could close this gap (Box 2). Routinely incorporating these measurements into more large-scale sampling programmes and time series would not only advance understanding of marine P, but also accelerate knowledge of coupled elemental cycles along the lines of established processes reviewed here, and potentially reveal connections that have yet to be discovered.

Additionally, there is much to be learned about the link between microbial community composition, DOP bioavailability and microbial P metabolism (Box 1). For example, the environmental distribution of different AP families and the contribution of distinct microbial community members towards bulk APA are still poorly characterized. Purification and characterization of different APs and other P hydrolases from relevant marine microorganisms would improve our understanding of metal-dependent P nutritional acquisition and advance much-needed approaches to evaluate DOP bioavailability. Furthermore, in situ quantification of metal-dependent P hydrolases would quantify the vague, yet potentially important, impact of microbial P acquisition on trace metal

Box 2 | Analytical techniques

Operationally, the TDP pool (typically <0.2–0.7 µm) is defined as the sum of SRP and DOP (TDP = SRP + DOP). SRP includes Pi and some acid-hydrolysable organics but is often referred to as dissolved inorganic P. TDP and SRP are measured directly, whereas DOP is determined by difference. While SRP is routinely measured, concentrations often fall below the detection limit (20–40 nmol l^{-1} (ref. [117])) of conventional analytical techniques. Moreover, estimates of DOP concentrations are relatively rare, despite the existence of reliable analytical methods[98]. These limitations have yielded a sparse database of DOP (Fig. 2) and SRP, leading to substantial gaps in our understanding of the oceanic P cycle. Recent methodological developments provide low-cost, sensitive analytical approaches that require minimal training, which should help extend the global coverage of paired SRP and DOP data across ocean depths.

The most sensitive routine methods of SRP determination are based on colorimetric detection using the magnesium-induced coprecipitation (MAGIC) method[117] or the liquid waveguide capillary cell[118] (LWCC). The MAGIC method pre-concentrates SRP by adsorption onto magnesium hydroxide, while the LWCC increases the optical path length of detection up to 2.5 m. Each approach achieves detection limits below 1 nM (refs. [119,120]). While MAGIC is not amenable for automation, the LWCC can be coupled with an autoanalyser, allowing high-resolution in situ measurements that require small volumes of seawater[120] (several millilitres). High-sensitivity SRP methods have identified previously overlooked areas of P depletion and biases in Earth system models[8], while their application to TDP measurements would also improve quantification of DOP.

TDP is measured through oxidation of organic molecules, typically based on high-temperature combustion, wet chemical oxidation, or ultraviolet photo-oxidation, and subsequent analysis as SRP[98]. While ultraviolet photo-oxidation has historically been regarded with scepticism[98], modernized methods provide consistent recovery and reproducibility, even in deep-sea samples where DOP is typically a small fraction of TDP[121].

budgets. Although poorly resolved, the discovery of large rates of marine P reduction unambiguously reflects an unprecedented level of complexity in marine microbial P metabolism. Understanding which members of microbial communities are involved and why they partake in such an energetically expensive cycle, especially under extreme Pi scarcity, requires insight on the biological role of reduced-P compounds, including inorganic and organic forms.

Anthropogenic perturbations will likely continue to trigger biogeochemical feedbacks through the marine P cycle. For example, with predictions of increased N_2 fixation[48] and anthropogenic N emissions[49], both leading to enhanced P demand and Pi drawdown, the extent to which microbial communities are able to modulate cellular stoichiometry and access DOP, including reduced-P compounds, would influence the efficiency of the biological C pump. Furthermore, recent simulations predict a 1–7% decline in the global inventory of ocean oxygen by the year 2100, and a dramatic 50% increase in the hypoxic water volume of the global ocean[94]. The decrease of oxygen may enlarge the niche of sulfide-oxidizing bacteria and other prokaryotes that carry out the DPO pathway[85,86] (Fig. 4), possibly resulting in an expansion of P redox cycling. Owing to the role of sulfide-oxidizing bacteria in mediating calcium phosphate mineralization, expanding hypoxic regions might also have consequences for P burial. Expanding hypoxia creates conditions in benthic environments that enhance Pi release via microbially mediated reductive dissolution of metal oxides[79], which will in turn help to stabilize atmospheric oxygen levels over geologic timescales[95].

Many uncertainties remain regarding the future of marine P under anthropogenic change, yet our understanding of the marine P cycle represents only one dimension of humanity's relationship with this important natural resource. Global food security relies on the production of fertilizers from exhaustible P mineral deposits whose formation was mediated by the activity of ancient marine organisms[4]. Estimates of mineable P depletion are uncertain (40–400 years[96]), yet these essential P reserves are controlled by only a small number of countries, which means that P may become increasingly inaccessible to low-income nations[46,96]. At the same time, much could be done to improve P use efficiency in order to secure global P supply[97]. Indeed, agricultural P use has long been wasteful on a global scale, contributing to a pandemic of aquatic nutrient pollution, eutrophication, and marine 'dead zones'[97]. Still, anthropogenic P inputs have not kept up with reactive N emitted by human activities, which could ultimately lead to P limitation of oceanic productivity[46,49]. Marine processes are therefore inextricably linked to P use and sustainability, and in this way continued research on marine P has the broad potential to reveal fundamental knowledge that could help improve human society's interactions with this essential element[96].

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Author contributions

This Review is the result of a team effort with all authors contributing to writing the overall manuscript. J.M.D. and S.D. are co-first authors, and J.C.A., K.D., V.S. and E.M.W. are co-contributing authors on this publication. S.D. and J.M.D. jointly and equally conceived, led, and supervised this paper. S.D. and J.M.D. co-led the introductory material, J.M.D. led the carbon section, J.C.A. led the nitrogen section, V.S. led the metals section, and K.D. and E.M.W. co-led the P redox section. S.D. led the boxes. K.D., V.S. and E.M.W. prepared figures and supplementary materials with input from all authors.

Competing interests

The authors declare no competing interests.

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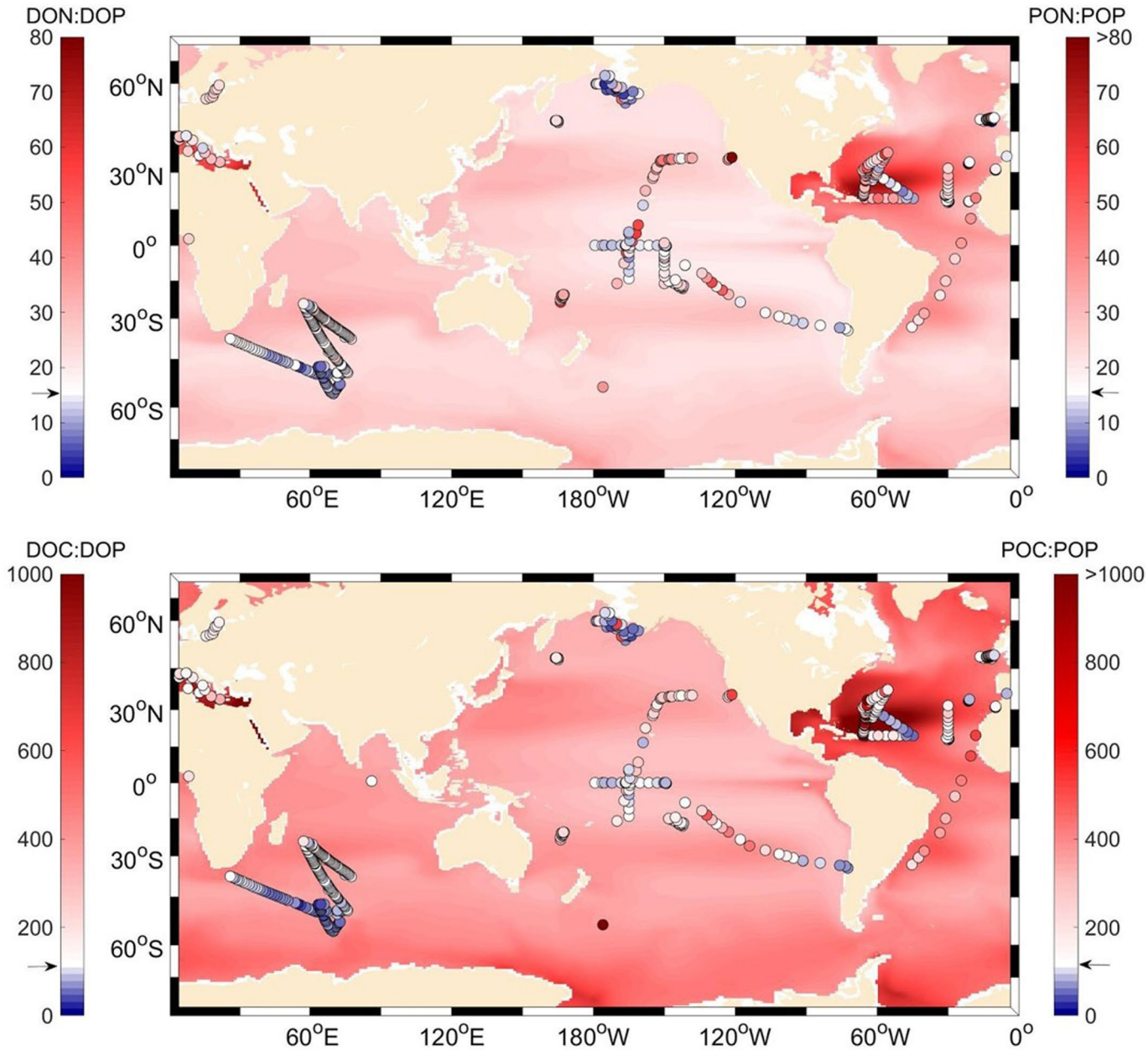
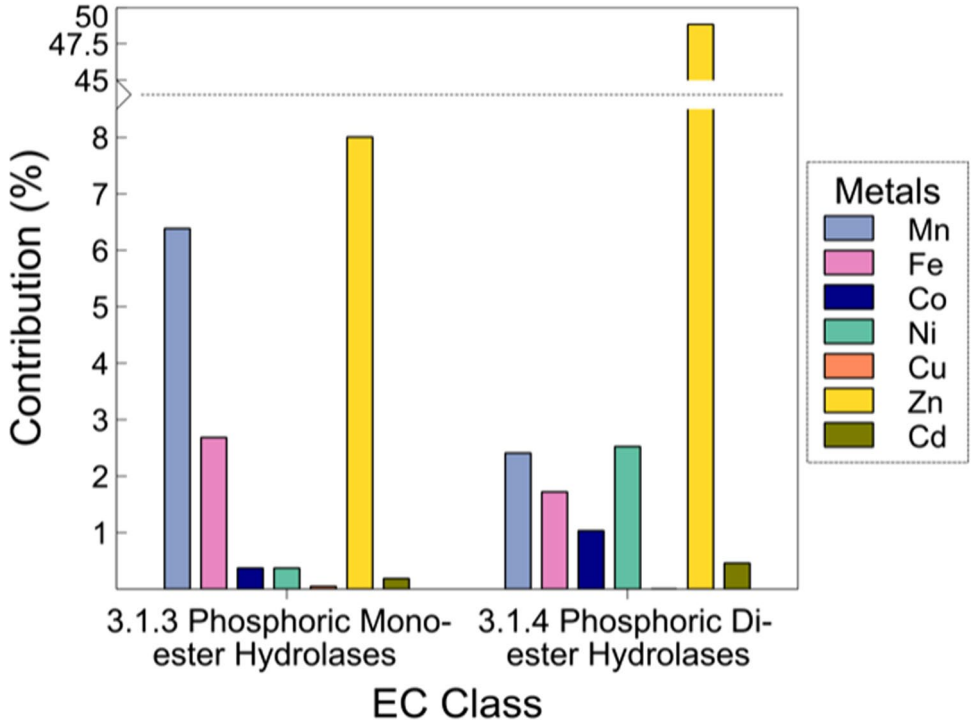


Extended Data Fig. 1 | Distribution of dissolved and particulate organic N:P and C:P ratios over the global ocean. Modeled (colormap) DON to DOP (upper panel) and DOC to DOP ratios (lower panel) at 50 m depth and, observed (coloured circles) PON:POP and POC:POP ratios between the surface and 50 m depth (see Supplementary Information 2). The arrows by the colour scales indicate the Redfield ratios. Note the deviations from the C:N:P Redfield ratio of 106:16:1 (represented in white), with red and blue hues indicating values greater and lower than Redfield, respectively. The sparse particulate data are particularly due to the few POP measurements available.



Extended Data Fig. 2 | Metal content of phosphoric ester hydrolases. Percent of P-monoester (EC 3.1.3) and P-diester hydrolases (EC 3.1.4) that are metal-dependent, illustrating that APs can vary greatly in their metal content. While Mn and Fe occur more often in mono- compared to diesterases, Zn and Co occur more frequently in diesterases over monoesterases.