

The Oceanic Phosphorus Cycle

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Received October 25, 2006

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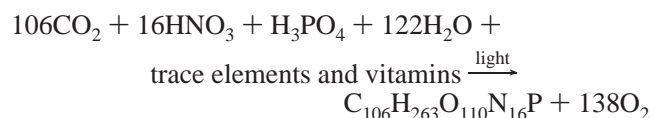
1. Introduction

Phosphorus (P) is an essential element to all life, being a structural and functional component of all organisms.^{1–4} P provides the phosphate-ester backbone of DNA and RNA, and it is crucial in the transmission of chemical energy through the ATP molecule (Figure 1). P is also a structural constituent in many cell components such as phosphoproteins, and phospholipids in cell membranes, teeth, and bones (Figure 1). In some organisms it can also be present as intracellular polyphosphate storage granules (Figure 1).

Phosphorus availability can impact primary production rates in the ocean as well as species distribution and ecosystem structure.^{5–8} In some marine and estuarine environments, P availability is considered the proximal macronutrient that limits primary production.^{8,9} Specifically, in recent years it has been recognized that phosphorus limitation in the ocean may be more prevalent than previously thought.

For example, it is generally accepted that orthophosphate (PO_4^{3-}) is the limiting nutrient in the eastern Mediterranean Sea.^{10–12} In addition, phosphate is suspected to play an important role in limiting production in the Sargasso Sea¹³ and may also be limiting in bodies of water receiving large freshwater inputs or fertilizer runoff from agriculture, as in the Chesapeake Bay.^{14,15} Furthermore, research in the Pacific Ocean gyres indicates that biological P uptake rates far surpass the combined input from atmospheric and deep water sources, suggesting that P is efficiently recycled within oligotrophic euphotic zones.¹⁶ It has also been suggested that transitions over the last two decades from nitrogen (N) limitation to P limitation have taken place in the North Pacific subtropical gyre and that this may be responsible for the observed succession of prokaryotic picophytoplankton such as *Prochlorococcus* and *Synechococcus* in oligotrophic waters.⁶ In other marine environments, P may only be limiting a subset of organisms within the ecosystem.^{17–19}

Phosphorus, in the form of orthophosphate, plays a key role in photosynthesis (i.e., primary productivity). The chemical equation representing average ocean photosynthesis can be written as



Thus, the availability of P in marine systems can strongly influence the marine carbon cycle and the sequestration of atmospheric carbon dioxide. The “biological pump”, a process by which carbon is “pumped” from the euphotic zone to the deep ocean, exports organic carbon to depth primarily as sinking particulate material (e.g., dead organisms or fecal pellets). However, some carbon also reaches the deep ocean as dissolved organic matter (DOM) by physical transport processes such as mixing, eddy diffusion, and downwelling, and as calcium carbonate minerals.²⁰ Remineralization (or decomposition) processes return some of the organic carbon to dissolved carbon dioxide and regenerate nutrients within the water column. The amount of new carbon fixed during photosynthesis that is subsequently exported from the euphotic zone is known as export production. This export production can influence global climate through the sequestration of atmospheric carbon dioxide to the deep ocean.²⁰ Unlike nitrogen, P cannot be fixed from the atmosphere. Thus, over geologic time scales, P is often considered to be the ultimate limiting macronutrient in marine ecosystems^{21,22} and therefore influences primary production and the sequestration of atmospheric carbon dioxide in organic matter.^{23–25}

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Adina Paytan's principal research interests lie in the fields of chemical oceanography, paleoceanography, and marine biogeochemistry. The goal of her research is to use the chemical and isotopic record enclosed in seawater and marine sediments to study present and past biogeochemical processes. This research spans a wide range of temporal (seasons to millions of years) and spatial (molecular to global) scales. An overarching goal of this research is to link changing ocean composition to global changes in climate and tectonics. In addition, Dr. Paytan is interested in natural and anthropogenically induced perturbations that affect biogeochemical processes in the ocean such as methane emission from wetlands, trace metal recycling in sediments, aerosol impact on marine biota, and coastal water pollution. Dr. Paytan is the author of over 65 scientific publications. She has received numerous awards including the AGU—Oceanography Early Career Award, the NSF Early CAREER Award, and the NASA New Investigator Award. She is currently an assistant professor in the Department of Geological and Environmental Sciences at Stanford University.



Karen McLaughlin received her B.S. from Pennsylvania State University in Geosciences in 1999 and her Ph.D. from Stanford University in Geological and Environmental Sciences in 2005. For her dissertation, she developed an extraction protocol to analyze low concentrations of phosphate for its oxygen isotopic composition and utilized this technique to understand P sources and cycling in several oceanic and estuarine environments. She is currently a postdoctoral researcher at the University of California, Irvine, investigating sources and loading of fecal indicator bacteria to a southern California estuary.

2. Phosphorus Occurrence in the Earth's Crust

P is the eleventh most abundant element in the Earth's crust, comprising approximately 0.1% by mass.^{26,27} It occurs in the form of inorganic phosphate minerals and organic phosphate derivatives in rocks and soil. Apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$] is the most common naturally occurring P containing mineral in the Earth's crust (over 95% of P); however, approximately 300 additional minerals that contain phosphate (PO_4^{3-}) have been described.²⁸

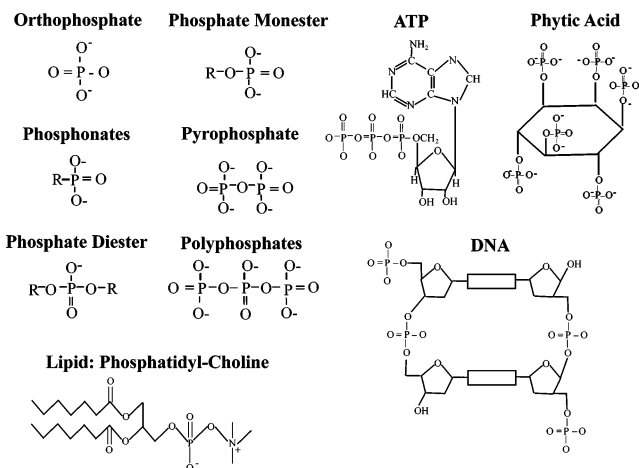


Figure 1. Biologically important compounds.

The organic phosphorus derivatives in soils and sediments include orthophosphate monoesters, orthophosphate diesters, phosphonates, and phosphorus anhydrides (specifically ATP). Of these, orthophosphate monoesters predominate, and in soils particularly, inositol phosphates such as phytic acid are abundant²⁹ (see Figure 1 for chemical structures). In marine sediments and sedimentary rocks, organic P constitutes a minor fraction of the bulk sediment weight, and in most cases, it is also much less abundant than inorganic P forms. Orthophosphate monoesters, orthophosphate diesters, and phosphonates have been detected in sediment samples; however, published data on organic P forms in sediments is relatively sparse.^{30,31}

3. Phosphorus Sources and Sinks in the Ocean

Phosphorus is primarily delivered to the ocean via continental weathering (Figure 2). This P is transported to the ocean primarily in the dissolved and particulate phases via riverine influx.⁵ However, atmospheric deposition through aerosols, volcanic ash, and mineral dust is also important, particularly in remote oceanic locations⁵ (Figure 2). Much of the riverine particulate phosphorus is retained within continental shelves and is thus not important for open ocean processes.^{32,33} The dominant sink for oceanic P is deposition and burial in marine sediment (after transformation from dissolved to particulate forms). A minor sink for P is uptake through seawater—oceanic crust interactions associated with hydrothermal activity on the ocean's floor. The P inventory in the open ocean is dominated by the dissolved forms and consists of a total of about 3×10^{15} mol of P; 2.9×10^{15} mol of which are in the deep water and $\sim 0.1 \times 10^{15}$ mol of which are in surface water.²³ The oceanic residence time of dissolved P (oceanic inventory of P divided by the input or output fluxes assuming steady state) is estimated to be between 20 and 100 kiloyears, although P is extensively cycled within the ocean on much shorter time scales.²³ Specifically, the deep water P turnover time is similar to the oceanic mixing time of 1500 years while in the surface ocean the turnover time is in the range of 1–3 years or less. Although a number of global P budgets have been proposed,^{25,34–37} the rapid exchange of P among the different reservoirs combined with the large anthropogenic influence on the budget and difficulties of quantifying the widely dispersed P output into ocean sediment make it challenging to precisely quantify and balance this budget. A simple representation of the oceanic P cycle is given in Figure 2.

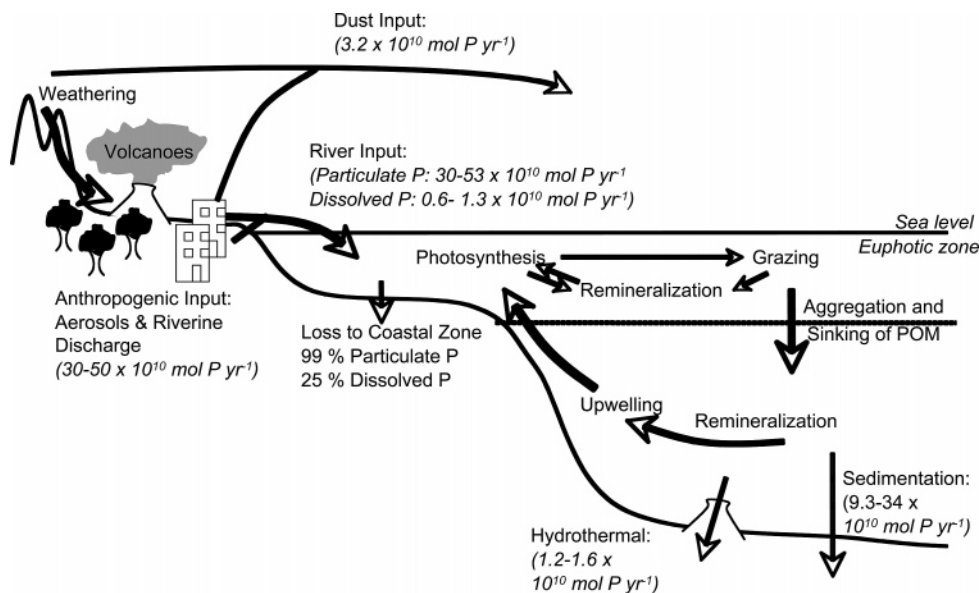


Figure 2. The marine phosphorus cycle. Fluxes are given in italics. Flux data are from Benitez-Nelson⁵ and Follmi.¹⁸¹ Continental weathering is the primary source of phosphorus to the oceanic phosphorus cycle. Most of this phosphorus is delivered via rivers with a smaller portion delivered via dust deposition. In recent times, anthropogenic sources of phosphorus have become a large fraction of the phosphorus delivered to the marine environment, effectively doubling the preanthropogenic flux. The primary sink for phosphorus in the marine environment is loss to the sediments. Much of the particulate flux from rivers is lost to sediments on the continental shelves, and a smaller portion is lost to deep-sea sediments.

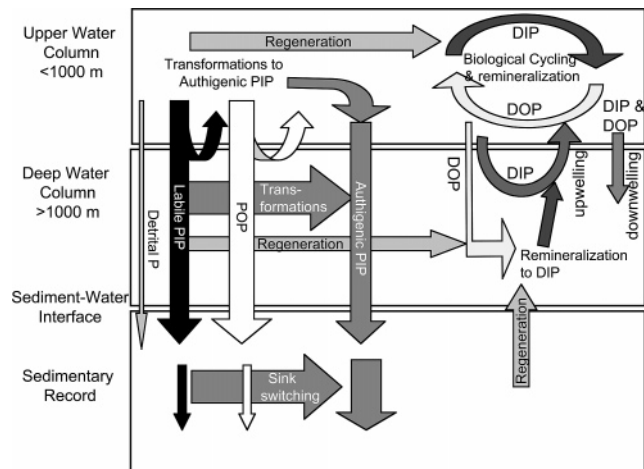


Figure 3. Transformations between P pools in the water column and sediments. Abbreviations are as follows: PIP, particulate inorganic phosphorus; POP, particulate organic phosphorus; DIP, dissolved inorganic phosphorus; DOP, dissolved organic phosphorus. Particulate phosphorus forms can undergo transformations throughout the water column and within the sedimentary record. Particulate phosphorus forms may also undergo regeneration into dissolved forms. Particulate phosphorus is lost from surface waters via sinking. Biological cycling and remineralization are the primary mechanisms of transformations of the dissolved phases and are dominant in surface waters, though microbial remineralization continues at depth. Dissolved phosphorus forms are lost from surface waters via downwelling and biological uptake (into POP) and are returned to surface waters via upwelling.

Transformations between different oceanic P pools are shown in Figure 3.

3.1. Continental Weathering

Continental weathering represents the most significant source of P to marine environments.^{24,25,38} This P is transported to the ocean in particulate and dissolved phases via

riverine influx.^{5,24} Riverine particulate phosphorus exists as particulate inorganic (PIP) and particulate organic (POP) components. Flux estimates using average riverine discharges range between 27 and 49×10^{10} mol/year for PIP and 2.9×10^{10} mol/year for POP.³⁸ Using average river discharge fluxes and preanthropogenic DIP river concentrations of 0.23 – $0.32 \mu\text{M}$, Compton et al.³⁸ estimate the river flux to be $(0.8$ – $1.5) \times 10^{10}$ mol/year for dissolved inorganic P (DIP) and a flux of 0.6×10^{10} mol/year for dissolved organic P (DOP) (See Table 1 in ref 38 for details).

Much of the P in rivers is associated with particulate inorganic matter, specifically P occurring in grains of apatite and other minerals and P adsorbed to iron-manganese oxide/oxyhydroxides. This particulate load is deposited quickly in estuarine and coastal shelf environments and does not contribute directly to the P pool available to marine biota.³⁹ However, clay particles with iron and aluminum oxyhydroxides on their surface have a high capacity to adsorb phosphate from freshwater solutions. This phosphate is then transported into estuaries and can subsequently be released into the sea once salinity increases. It has been estimated that the total load of P which desorbs from clay particles is 2–5 times more than the dissolved phosphate load which enters the ocean via rivers.^{40,41} As for the fate of riverine DOP, some of it may be trapped in the estuaries via flocculation⁴² or it may be photohydrolyzed and recycled within the estuaries.⁴³ It has been estimated that only about 10–30% of the total riverine P flux is potentially “reactive” (e.g., available for biological uptake) and one-quarter of that reactive P may be trapped in estuaries and never reaches the open ocean³⁸ (Figure 2). The “nonreactive” P is primarily deposited on continental shelves and removed from the oceanic phosphorus cycle; however, there is some evidence that this P pool may be released into sediment pore waters during diagenesis and the subsequent flux into bottom waters may significantly contribute to the oceanic P cycle.⁴⁴

3.2. Anthropogenic Sources

Phosphorus, more than any other element, can become the limiting factor for agricultural plant growth. Many tons of phosphate rock are mined each year in the production of fertilizers to replace some of the phosphates lost from farmland through erosion and crop production. Much of this fertilizer P and P from other human activities (sewage, soil erosion, livestock, paper pulp manufacturing) is washed into rivers, groundwater, and estuaries and adds a substantial amount of anthropogenic P to the ocean.^{45,46} Estimates for the present-day total river P flux range from 57×10^{10} to 100×10^{10} mol/year; a doubling of the preanthropogenic flux. It is not clear what fraction of this anthropogenically added P is reactive and available for the biomass. Calculations suggest that the present-day, potentially reactive anthropogenic P flux may be similar to the prehuman flux (0.1×10^{10} mol/year) or up to twice that of the pre-human-impact value (Figure 2). Anthropogenic phosphates in aerosols, which are primarily derived from eolian soil erosion of cleared land and biomass burning, can also contribute to phosphorus loading into the global ocean.^{47,48} Nutrient enrichment in aquatic systems can cause diverse problems such as toxic algal blooms, anoxia, fish kills, loss of biodiversity, and a host of other problems.^{45,49}

When nutrient enrichment of a water body results in algal growth that exceeds the normal uptake capacity of organisms higher in the food web, a state of eutrophication (e.g., Gulf of Mexico Dead Zone) might be induced. Eutrophication occurs when the input of excess nutrients into a water body stimulates excessive growth (algal bloom), which then reduces the dissolved oxygen in the water when the organic material decomposes. This reduction in oxygen levels (hypoxia) can result in the death of other organisms in the ecosystem. Indeed, it has been documented that nutrient loads entering the coastal ocean can stimulate large scale phytoplankton blooms.^{50,51} In some systems, such as the Florida Everglades which is an extremely oligotrophic system, small increases in P concentrations and P-enrichment have been indicated as one of the dominant anthropogenic impacts on this ecosystem.⁵² Agricultural expansion is expected to be accompanied by a 2.4- to 2.7-fold increase in nitrogen (N)- and phosphorus (P)-driven cultural-eutrophication of terrestrial, freshwater, and near-shore marine environments.⁴⁹

Submarine groundwater may also play an important role in coastal nutrient cycling.^{53–55} Nutrient inputs from submarine groundwater discharge in some systems can rival nutrient inputs via rivers.^{55,56} In many coastal groundwater systems, N/P ratios exceed those of rivers and are higher than the Redfield Ratio.⁵⁴ Consequently, increased nutrient input via submarine groundwater discharge, from anthropogenic activity, can drive a N-limited coastal system toward P-limitation.⁵⁴

3.3. Atmospheric Deposition

Aerosols associated with eolian dust particles are another source of P to the ocean, comprising approximately 5% of the total preanthropogenic P input to the ocean or about 3.2×10^{10} mol/year^{57,58} (Figure 2). This influx is increasingly important farther from shore, where other P inputs are small.⁵ The P content of mineral dust is similar to the crustal abundance; for example, Saharan dust contains on average 0.09% of particulate P.⁵⁹ This atmospheric P exists both as organic and inorganic compounds in the aerosols at roughly

equal proportions.^{59–61} Inorganic P in mineral aerosols is predominantly bound to Fe oxides or associated with Ca, Mg, Al, and Fe, which are known to be weakly soluble^{59,62} while the organic P fraction has not been well characterized. Anthropogenic P sources may be associated with more soluble components.⁶³ The atmospheric P flux over the ocean is quite variable in space and time, ranging from $0.9 \mu\text{mol m}^{-2} \text{day}^{-1}$ in the Mediterranean⁶³ to $0.1–0.3 \mu\text{mol m}^{-2} \text{day}^{-1}$ in the Atlantic Ocean and to $0.08–0.4 \mu\text{mol m}^{-2} \text{day}^{-1}$ in the Pacific Ocean.^{60,61} This atmospheric P deposition over oligotrophic, P-limited regions has been shown to increase the level of primary productivity.^{19,64,65}

Volcanic sources of P can also have important influence in localized areas and over short time scales.^{66,67} P in volcanic ash can reach concentrations of up to 1%, and it has been shown that P is released from volcanic ash into seawater at relatively high rates of $1.7 \mu\text{mol g}^{-1} \text{h}^{-1}$.⁶⁸ High phosphorus concentrations, between 22 and $36 \mu\text{mol L}^{-1}$ have been measured in the steam plumes from the Pu'u O'o volcano.^{66,69} Similarly, Kilauea volcano plume P concentrations are estimated to be >50 times background levels.⁷⁰ Despite these high concentrations, it is unlikely that shallow ocean volcanism can significantly impact the global ecosystem, even during massive lava emplacements, because the effect is local in scale.⁷⁰

3.4. Marine Sediments

Sediments are the main repository in the oceanic phosphorus cycle. P is delivered to marine sediments primarily as sinking particulate matter, although other components have been detected, specifically P associated with metal oxides and hydroxides (see sections 4 and 5). Estimates of total P burial in open ocean marine sediments range from 9.3×10^{10} mol/year⁷¹ to 34×10^{10} mol/year^{5,72} (Figure 2). The major component of this burial flux is reactive P, with most of the nonreactive P having been deposited in the continental shelves. The reactive P is calculated from sequential extraction of marine sediments and consists of P in organic matter, associated with iron oxides, loosely sorbed, and present in authigenic minerals such as carbonate fluorapatite and rare earth element phosphate minerals.^{37,73} This reactive P is considered to have been either biologically available or associated with biologically related P components in the water column at some point before burial. The nonreactive P component in sediments is associated with terrigenous detrital material. Berner and Berner⁷¹ estimate that the sedimentary P sink is comprised of about 3.2×10^{10} mol/year of finely dispersed carbonate fluorapatite and a similar flux of organic P. Other estimates for the carbonate fluorapatite burial flux are somewhat higher, reaching between $8–9 \times 10^{10}$ mol/year.^{24,37} The iron-bound/adsorbed P sedimentary flux may be as high as 5×10^{10} mol/year^{24,37} while authigenic phosphate minerals precipitated after burial as rare earth element phosphate minerals formation may also account for a substantial fraction of P burial.⁷³

Phosphorite deposits are authigenic formations derived from the microbial hydrolysis and release of organic P.^{74,75} The soluble phosphate released reacts with calcium ions to form insoluble calcium phosphate compounds, specifically carbonate fluorapatite. Models of phosphorite genesis link the authigenic mineralization to biologically productive waters such as upwelling areas.^{76,77} Mineralization can occur at the sediment/water interface or in interstitial pore waters. At present, formation of phosphorite is not widespread and

is reported at the continental margin of Peru and Mexico^{77–79} and on the continental shelves of southwest Africa.⁸⁰ Phosphorite deposits are found in the geological record and are interpreted to represent periods and locations of intense biological productivity and low oxygen availability at the sediment/water interface. The conditions for the formation of phosphorite deposits in the geologic record are thought to be similar to those of modern day deposits.⁸¹

The relative contribution of specific sinks to P burial in the sediments depends on sedimentary redox conditions (abundance of oxidizing and reducing chemicals). Oxygen-bearing (oxic) surface sediments are often rich in ferric iron and manganese phases which take up large amounts of phosphate by adsorption and mineral formation, while anoxic (oxygen-free) sediments are depleted in these phases so that phosphate is predominantly bound to calcium minerals.^{82–84} Burial of organic P associated with the remains of marine plankton also depends on sedimentary redox conditions. Under reducing conditions, the C/P ratio of sedimentary organic matter may be as high as 5000 while the composition of particulate organic matter in oxic deposits is considerably lower.^{82,83} Hence, P is buried very efficiently in oxic sediments while anoxic deposits have a diminished retaining capacity (when compared to organic C burial). Despite the effect of redox conditions on some sedimentary P pools, Anderson et al.⁸⁵ found that labile forms of P (organic and oxide-associated) were transformed to authigenic P throughout the sediment column at all redox states and sedimentation rates. They also found that C/P ratios are always greater than or equal to the Redfield Ratio of 106:1 and that C/P ratios increase linearly with organic carbon concentration, which is consistent with degradation of organic carbon with age and specifically the preferential degradation of P-rich organic matter.

The P dynamics within marine sediments after burial are quite complex and involve diagenetic redistribution of P between phases (sink switching)^{24,37,72} (Figure 3). Phosphorus in sediments can be remobilized during degradation of organic matter and reduction of iron oxides. Indeed, pore-water phosphate ion concentrations in many marine settings increase with depth.^{83,84} Most of the remobilized phosphate is precipitated authigenically in the sediment as carbonate fluorapatite or is adsorbed onto iron oxide particles.^{72,82,86} However, when sediment is resuspended in coastal areas, significant amounts of DIP may be released into the water column.⁸⁴ In areas of low oxygen bottom water concentrations, some of the pore water P may diffuse from the sediment into seawater.^{82,87} Benthic incubation chambers deployed in a variety of geochemical environments along the California Continental Margin have shown that where bottom water oxygen is low (<50 μM) and the rate of organic matter oxidation is also low (<1 $\text{mmol m}^{-2} \text{day}^{-1}$), phosphate may be released at a rate exceeding the production expected from the oxidation of organic matter.⁸⁸ In contrast, where bottom water oxygen concentrations were high, with rates of organic matter decomposition of $\sim 7 \text{ mmol m}^{-2} \text{day}^{-1}$, and where benthic irrigation is not significant, P regeneration is consistent with that expected from the decomposition of organic debris.^{88,89} Where there is a decoupling of phosphate regeneration and organic decomposition, high benthic iron fluxes were observed, whereas low to zero iron fluxes were observed in regions where P regeneration is either consistent with or less than that expected from the decomposition of organic material, sug-

gesting a coupling between iron cycling and phosphate cycling in suboxic environments, where P is regenerated at high rates by the reduction of iron-oxyhydroxides and the release of scavenged P from these phases.^{88,89} This coupling may result in either preferential phosphate burial or release relative to organic C burial in suboxic environments.⁸⁸ More data are needed to better quantify the P flux from sediment resuspension and from diffusion at the sediment/water interface.

3.5. Seawater–Ocean Crust Interactions

Wheat et al. estimate that the total amount of P removed by hydrothermal processes associated with midocean ridges is between 1.2×10^{10} and 1.6×10^{10} mol/year, about 10% of the sedimentary burial flux.⁹⁰ Most of this P burial is in the form of DIP removed by iron oxides entrained in nonbuoyant plumes.^{91,92} An additional small amount of P is removed in the process of convective seawater flow and interaction with basalt on ridge flanks. While once thought to play a significant role in phosphorus delivery into the ocean, the phosphorus contents of volcanic–hydrothermal sources from different parts of the ocean are similar to or lower than seawater concentrations, suggesting that hydrothermal processes at the ocean floor do not constitute an important source of P to the ocean.⁹³

4. Phosphorus Forms and Transformations in the Water Column

Phosphorus in the ocean exists in both dissolved and particulate forms throughout the water column (Figure 3). These fractions are operationally defined and determined by filtration through 0.2 or 0.45 μm filters. The dissolved fraction (which passes through the filter) includes inorganic phosphorus (generally in the soluble orthophosphate form), organic phosphorus compounds, and macromolecular colloidal phosphorus. Particulate P (retained on the filter) includes living and dead plankton, precipitates of phosphorus minerals, phosphorus adsorbed to particulates, and amorphous phosphorus phases.

Within each fraction (dissolved and particulate), P can be in the form of inorganic (orthophosphate, pyrophosphate, polyphosphate, and phosphate containing minerals) or organic (P-esters, P-diesters, phosphonates) compounds (see Figure 1 for compound structures). The organic and inorganic particulate and dissolved forms of phosphorus undergo continuous transformations. The dissolved inorganic phosphorus (usually as orthophosphate) is assimilated by phytoplankton and altered to organic phosphorus compounds.⁹⁴ The phytoplankton are then ingested by detritivores or zooplankton. A large fraction of the organic phosphorus taken up by zooplankton is excreted as dissolved inorganic and organic P.⁹⁵ Phytoplankton cell lysis also releases cellular dissolved inorganic and organic P to seawater.⁹⁶ Continuing the cycle, the inorganic P is rapidly assimilated by phytoplankton while some of the organic P compounds can be hydrolyzed by enzymes synthesized by bacteria and phytoplankton and subsequently assimilated^{95,97} (Figure 2, euphotic zone transformations). Dissolved inorganic and organic P is also adsorbed onto and desorbed from particulate matter sinking in the water column moving between the dissolved and the particulate fractions.^{24,98} Much of this cycling and these transformations occur in the upper water column, although all of these processes, with the exception

of phytoplankton assimilation, also occur at depth, throughout the water column⁹⁸ (Figure 3).

4.1. Dissolved Phosphorus in the Ocean

The largest dissolved phosphorus pool in the ocean is soluble reactive phosphorus (SRP), which is defined as the dissolved P fraction that reacts in an acid solution containing molybdate ions to form a phosphomolybdate complex which when reduced with ascorbic acid forms a colored molybdenum blue complex. This fraction in seawater is comprised primarily (~87%) of dissolved inorganic phosphate (DIP) as HPO_4^{2-} and a small percentage of PO_4^{3-} (the relative abundance of these forms is pH dependent), but it may also include some easily hydrolyzable inorganic and organic forms of P.⁵

Soluble nonreactive phosphorus (SNP), the dissolved fraction that does not react with molybdate ions and is determined by difference between total dissolved P (that measured following acid digestion) and SRP, is comprised primarily of dissolved organic phosphorus (DOP) compounds (proteins, carbohydrates, lipids, and a molecularly uncharacterized fraction) but also contains inorganic polyphosphates. Of the SNP pool, the low-molecular-weight fraction (LMW, <10 kDa) comprises the majority, 50–80%, while the high-molecular-weight portion (HMW, >50 kDa) is typically a smaller fraction, 15–30% of the pool.⁵ P esters and phosphonates are the major components of high-molecular-weight DOP (as determined by solid-state P NMR) and are present in relatively constant proportions throughout the ocean, suggesting that the processes which lead to this chemical composition are ubiquitous.⁹⁹

Marine phytoplankton and autotrophic bacteria take up P from solution for their metabolic needs, mostly as orthophosphate (HPO_4^{2-} , PO_4^{3-}). Heterotrophic bacteria are responsible for much of the DOP hydrolysis and conversion back to DIP; however, phytoplankton and autotrophic bacteria can also hydrolyze organic P compounds when their P demand is not satisfied by inorganic orthophosphate.^{94,95,97} Much of the DIP uptake takes place in the sunlit upper zone of the water column (euphotic zone), where marine photosynthesis takes place; hydrolysis of organic P (both particulate and dissolved) to DIP occurs throughout the water column (Figure 3). Accordingly, DIP (measured as SRP) depth profiles in the oceans exhibit a “nutrient trend” such that surface waters are depleted due to intense biological uptake in the euphotic zone and concentrations increase with depth as a result of conversion of organic P forms to DIP (also called regeneration) (Figure 4). Within deep waters, an increase in DIP concentrations is also observed with increasing deep water age due to continuous accumulation of sinking particulate matter and its regeneration (e.g., the cumulative accumulation during deep water mass aging and transit). At present, deep water that forms in the North Atlantic flows through the deep ocean basins to the North Pacific: a process that takes about 1500 years. Thus, waters in the deep Pacific are older than waters in the deep Atlantic.²³ As a result, at present, the DIP concentration in the deep Pacific water is higher than that in the deep Atlantic (e.g., increased concentration along the deep ocean circulation path).^{5,23} Figure 4a shows typical depth profiles of SRP in the Atlantic and Pacific Oceans.

The DOP depth distribution in the ocean, in contrast, is characterized by high concentration in the surface ocean, where most of the marine life which synthesizes these organic

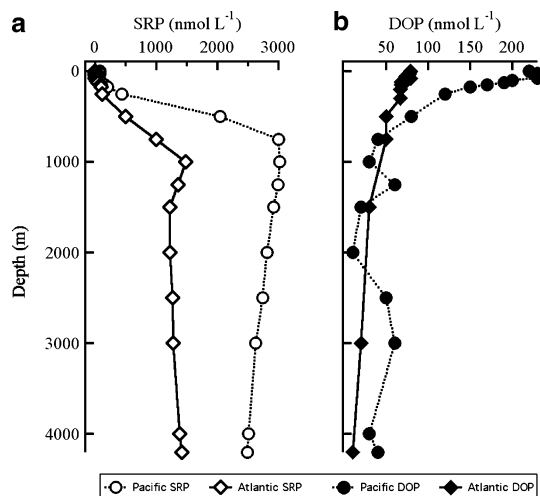


Figure 4. Soluble reactive phosphorus concentration and dissolved organic phosphorus concentration profiles for the Atlantic (BATS) and the Pacific (HOT). BATS data were provided by M. Lomas and the Bermuda Atlantic Time-series Study website (<http://bats.bbsr.edu/firstpage.html>), and HOT data are available on the web at <http://hahana.soest.hawaii.edu/hot/hot-dogs/>. Soluble reactive phosphorus (SRP) is depleted in surface waters due to intense biological uptake. Dissolved organic phosphorus (DOP) is generated in surface waters and is remineralized to SRP at depth.

compounds resides^{100–102} (Figure 4b). Much of this DOP is hydrolyzed by bacteria to DIP (which is rapidly taken up and utilized by organisms) within the surface layer, and only a small fraction is transferred to the deep ocean; thus, the concentration of DOP is typically lower at depth. Interestingly, the DOP concentrations at depth in all oceanic basins are quite similar, suggesting a relatively long residence time for the majority of components of the DOP pool in the deep ocean.⁹⁹ Indeed, radiocarbon dating of dissolved organic matter (DOM) in deep water suggests that this fraction is on average 6000 years old.^{103,104} However, different components of DOM may have substantially different ages and distributions.^{103,105–107} Specifically, while the dissolved forms of all three major organic fractions (lipids, proteins, and carbohydrates) are older in DOM than in their particulate counterparts,^{108,109} the differences are higher for the dissolved lipid fraction compared to the other fractions, suggesting that dissolved and particulate lipids (including phospholipids) cycle on dramatically different time scales or arise from different sources.¹⁰⁷ Even within a given organic fraction, individual molecules may have unique cycling times.^{110,111}

Although the absolute concentration of high-molecular-weight DOP decreases from 90 nM in surface waters to 15 nM in deep waters, ³¹P NMR spectra of DOP show phosphorus esters and phosphonates in unchanging proportions throughout the water column, indicating that phosphorus esters and phosphonates are used (regenerated) at equivalent rates throughout the deep water column.¹¹² Reactive phosphorus esters are used rapidly in surface waters, resulting in enrichment of deep waters in less reactive DOP compounds. The persistence of phosphorus esters and phosphonates from surface to deep waters suggests that the less reactive fractions of DOP consist of common biochemical structures that are probably produced in surface waters.¹¹²

The regeneration of nutrients in seawater is often compared to the Redfield ratio, which approximates the average composition of marine planktonic organisms (C/N/P = 106/16/1).¹¹³ Dissolved organic matter (DOM) is depleted in phosphorus throughout the entire water column relative to

Redfield values. This increase in C/P and N/P ratios with depth indicates that phosphorus is preferentially regenerated from DOM, which implies that DOP must ultimately cycle more efficiently than either dissolved organic carbon (DOC) or dissolved organic nitrogen (DON).^{100,112} DOM is divided into labile and refractory pools, which differ in C/N/P composition.¹¹⁴ Refractory DOM consists of old DOM (~4 kiloyear average age) that is carbon-rich and nutrient-poor. Most of the refractory DOM completes the mixing loop between surface and deep water several times, regenerating few inorganic nutrients.¹¹⁴ Labile DOM consists of young DOM (0–1 kiloyear), which has a C/N ratio similar to that of the particulate organic matter (POM) pool, but is relatively C-rich compared to living plankton. Labile DOM does not complete a mixing cycle and is essentially completely regenerated. Labile DOM is replenished by autotrophic and heterotrophic activities in surface waters. Replenishment of refractory DOM is less clear and probably includes inputs from continental runoff as well as some abiotic and biotic conversion of labile DOM.¹¹⁴

4.2. Particulate Phosphorus in the Ocean

The sinking particulate P pool (e.g., collected in sediment traps) has been found to be composed of particulate organic P (POP) (~40%), authigenic particulate inorganic P (PIP) (~25%), which is formed when organic P is remineralized and reprecipitated as calcium fluorapatite, and labile PIP (21%), with lesser amounts of nonreactive detrital P (~13%)⁹⁸ (Figure 3). Compared to DOM, sinking POM has C/N/P ratios much closer to the Redfield ratio, pointing to the origin of sinking POM (e.g., organisms in the surface ocean) and the relatively short time (weeks to months) since this material has been part of the living matter. Despite the greater similarity in bulk composition (molar C/N/P ratios) of POM to that of the average living plankton, there are indications that P is generally preferentially remineralized from particulate organic matter in the water column.^{31,105} More specifically, certain organic P compounds are preferentially remineralized in sinking particulate matter and the hydrolysis of organic P occurs throughout the water column, though more prevalently in shallow depths.^{31,98}

³¹P NMR (nuclear magnetic resonance) and sequential extractions (SEDEX)¹¹⁵ of phytoplankton, sinking and suspended particulate matter, and sediments have been used to determine the makeup, associations, and transformations of the particulate P pool, and the spatial and temporal variability in these parameters.^{31,98,116} Significant spatial and temporal variability has been detected in the total flux and relative distribution of the various P pools in particulate matter. There is more POP at shallow depths (80% in the euphotic zone), whereas at depth the continued hydrolysis of POP results in a relative increase in the PIP pool (POP <25% of total particulate P at depth). Organisms synthesize various P compounds at different ratios, and specific compounds are more susceptible to regeneration. For example, analyses of the sinking POP pool collected using sediment traps suggest that phosphate-diester are preferentially remineralized in the open ocean.³¹ Fluxes of total particulate P, particulate inorganic P, and particulate organic P to depth vary seasonally and decrease significantly with depth at all seasons.⁹⁸ Furthermore, phosphonates were observed to be selectively removed relative to more bioavailable P esters under anoxic conditions, suggesting that phosphates may be an unrecognized source of DIP under anoxic conditions.¹¹⁶ The above

observations collectively point to the complex and highly variable (spatially and temporally) nature of P cycling and transformation within the oceanic water column and imply that when studying the oceanic P cycle the specific time scale of operation of the relevant processes studied (e.g., burial on geological time scales versus uptake and regeneration in the euphotic zone) should be considered.

4.3. Turnover Rates of Phosphorus in the Water Column

The concentrations of DIP and DOP in coastal waters reveal a high level of both spatial and temporal variability. These fluctuations in surface water DIP and DOP are controlled by the interplay of physical (upwelling/relaxation events) and biological (DIP uptake, DOP production, and regeneration) factors.¹¹⁷ The detection of alkaline phosphatase activity in coastal waters also suggests the potential for enzymatic DOP hydrolysis and production of bioavailable DIP from an initially unavailable substrate.¹¹⁷ Furthermore, enzyme-labeled fluorescence (ELF) analysis of alkaline phosphatase in single cells within coastal waters revealed substantial variability in the degree of expression of this enzyme both among genera as well as within genera, suggestive of microscale differences in the nutrient status and the nutritional history of cells.^{18,117} In these cases, some species utilize enzymes to obtain P from the organic pool, while others do not display such an adaptation. Measurements of the turnover times of dissolved and particulate nucleotide triphosphate pools in comparison to the bulk DOP pools in the Pacific oligotrophic gyre region near station ALOHA suggest that P-flux through the nucleotide pools can be up to 5-times as fast as that through the bulk DOP pool, indicating that P derived from the nucleotide pool is an important source to the marine P-cycle in this region.¹¹⁸

Efforts to understand P turnover rates in the ocean utilized the cosmogenic isotopes of P (³³P and ³²P).^{119,120} ³²P (half-life 14.28 days) and ³³P (half-life 25.3 days) are primarily produced via cosmic ray interactions with atmospheric argon and enter the ocean predominantly with rain.¹¹⁹ If the production (input) ratio of ³³P/³²P is known, then the age of the cosmogenic phosphorus in ocean waters can be assessed by measuring the ³³P/³²P ratio in different P pools, where higher ³³P/³²P ratios indicated older pools.¹¹⁹ However, because the inventories of ³³P and ³²P in the ocean are quite small, large volumes of seawater (thousands of liters) and extensive purification of seawater samples to eliminate interference from other ions are required. This hampers the widespread use of this powerful method for P turnover studies. Nevertheless, several researchers have successfully implemented this methodology and have found that P recycling rates in the dissolved and particulate pools in surface waters are very rapid (less than a day to two weeks), suggesting that low phosphorus concentrations can support relatively high primary production.^{119–123} Furthermore, using this method it has been shown that P recycling rates vary seasonally and picoplankton seem to preferentially utilize certain dissolved organic phosphorus compounds to obtain P and other associated nutrients.¹¹⁹ This method was also utilized to estimate the P residence times at Station ALOHA. Results of this study suggest that the soluble nonreactive P pool (which is thought to be mostly DOP) is a potentially important source of P to organisms and that its utilization can vary significantly on scales of weeks to months.¹²⁴

5. Phosphorus Forms and Transformations in the Sediment

P is primarily lost from surface waters in the form of sinking particulate organic matter (POM). The vast majority of P is remineralized within the water column, and approximately 1% of P carried to the deep sea by falling particles is removed from the ocean reservoir into the sediments²³ (Figures 2 and 3). Three primary sedimentary sinks have been identified for P burial in marine sediments: P associated with organic matter, P adsorbed on particles or oxide associated, and P in authigenic apatite.²⁴ The above fractions are defined as reactive P, based on the understanding that the majority of P in these phases originated from organisms (biological) or at least at some stage were available for uptake by organisms. Nonreactive P from riverine sources is primarily lost from the oceanic P cycle via deposition in coastal areas. Reactive P is primarily, although not exclusively, delivered to the sediment/water interface in the form of POM.^{24,98} The initial burial of P occurs with organic carbon or as P associated with iron oxyhydroxides.²⁴ Once in the sediments, labile forms of P are transformed to authigenic forms of P throughout the sediment column in a variety of redox states and sedimentation rates until a substantial portion of the reactive P is in the authigenic form.⁸⁵ Indeed, it has been shown that with time (burial depth), formation of authigenic P phases takes place at the expense of the organic and iron associated P (sink switching) and that this phase becomes a substantial portion of the sedimentary P pool in open ocean marine sediments^{24,37,72} (Figure 3). Organic P forms that are less susceptible to degradation, such as phosphonates, are also prevalent in marine sediments (~25% of total organic P), compared to their abundance in living organisms (much <1%) and in sinking particulate matter (typically less than 3%), suggesting they could also be an important sink for P in the ocean. However, more work needs to be done on the distribution of phosphonates at various ocean basins to evaluate changes in their abundance with depth/age in the sediment.^{30,31}

In an oxidizing sedimentary environment, a major portion of the flux of organic phosphorus from the water column is mineralized within the sediments, and the released phosphate is partitioned between the pore water and surface adsorption sites.⁸⁴ Surface adsorbed phosphate is released into the pore water as needed to replace the dissolved phosphate that escapes the sediment/water interface and into the water column. Deeper in the sediment column, if conditions become more reducing, phosphate is released to pore waters from the reduction of iron oxides.^{84,125} In all settings, however, the phosphorus that is ultimately retained in the sedimentary record is predominantly in the form of stable minerals such as apatite.⁹⁸ As a result of the above reactions, the concentration of dissolved phosphate in pore waters increases sharply across the sediment/water interface while deeper in the sedimentary column the phosphate concentration in the pore waters is controlled by the buffering capacity of the sediment, and the thickness of the diffusive boundary layer at the sediment/water interface.⁸⁴ Figure 5 shows profiles of dissolved phosphate concentrations in coastal oxic sediment pore waters and deep-sea sediment pore waters. Analysis of sediments from anoxic marine environments indicates that the desorption/release of phosphate from the sediment exceeds the adsorption capacity, which is in contrast to the case for oxic sediments where desorbed phosphate is rapidly reabsorbed by iron oxyhydroxides or precipitated as

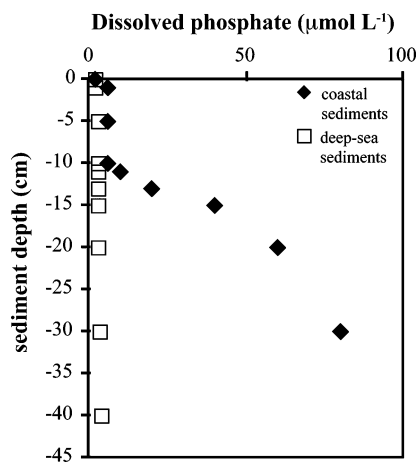


Figure 5. Dissolved phosphate profiles in a coastal sediment core overlain by oxic waters⁸⁴ and a deep-sea sediment core.¹⁸² Near the sediment/water interface, phosphate concentration is buffered by adsorption–desorption equilibria with the sediments. At depth, dissolved phosphate is released from sediments during the reduction of iron oxides and microbial regeneration.

apatite.⁸³ Indeed, there are some suggestions that in anoxic settings P regenerated from the sediment diffuses back into the water column.^{83,84}

6. Phosphorus and Ocean Biota

Phosphate historically has been considerably less studied compared to nitrogen in nutrient studies of marine systems because it is typically considered to not be the proximal limiting nutrient. Most marine systems are often nitrate or iron-limited,¹²⁶ although an increasing number of systems have been identified as P-limited.^{10,127–129} Recent studies have shown that while an ecosystem on a whole may be nitrate-limited, certain species within the system are actually phosphate-limited.^{17–19} In addition, with increased anthropogenic input of nutrients with higher than Redfield N/P ratios, P may progressively become more limiting in many systems.

6.1. Phosphorus and Primary Production

In 1934, researchers noticed a striking similarity between the C/N/P elemental composition of bulk marine organic matter and dissolved nutrient concentrations in the deep ocean water. This led them to hypothesize that plankton have a relatively constrained C/N/P elemental ratio of 106:16:1^{113,130,131} (Table 1). This C/N/P ratio is known as the Redfield Ratio, after its chief discoverer, Alfred Redfield. This ratio has withstood the test of time and has been repeatedly found in all ocean basins.¹³² The ubiquity of this ratio led to the premise that autotrophic organisms utilize nitrogen and phosphorus in the proportion in which they are found in seawater and return these elements back to seawater upon their death and decomposition.^{132–134} Redfield noted the similarity between the average nitrogen-to-phosphorus ratio in plankton (N/P = 16 by atoms) and that in deep oceanic waters (N/P = 15). He argued that this was neither a coincidence nor the result of the plankton adapting to the oceanic stoichiometry, but rather that phytoplankton adjust the N/P stoichiometry of the ocean to meet their requirements through nitrogen fixation,^{113,130,131} an idea supported by recent modeling studies.¹³⁵ Specifically, he stated that the concentration of phosphorus in the oceans is set by the ratio of

Table 1. Ratios of C/N/P (by Atoms) in Plankton and Seawater

source	by atoms		
	C	N	P
Redfield (1943), plankton ¹³²	137	18	1
Redfield (1934), seawater ¹³²		20	1
Fleming (1940), phytoplankton ¹³²	108	15.5	1
Fleming (1940), zooplankton ¹³²	103	16.5	1
Fleming (1940), average ^a ¹³²	106	16	1
Copin-Montegut and Copin-Montegut, ¹⁸³ plankton and particulate matter	103	16.1	1
GEOSECS (nitrate/phosphate ratio > 500 m), seawater		14.7	1
Takahashi et al., ¹⁸⁴ organic material	103	16	1
Anderson and Sarmiento, ¹³³ organic material between 400 and 4000 m depth	117 ± 14	16 ± 1	1
Geider and La Roche, ¹³⁹ marine particulate matter	114 ± 45	16 ± 6	1

^a This average of phytoplankton and zooplankton is the Redfield Ratio (Redfield 1958).

riverine inputs from continental sources and outputs via sediment burial but that the concentration of inorganic nitrogen is governed not only by terrestrial inputs but also by fixation by cyanobacteria, thus regulating the N/P ratio.¹³⁶ Thus, when nitrogen becomes limiting, nitrogen fixers can provide a source of inorganic nitrogen to the ecosystem and, thus, phosphorus limits marine ecosystem productivity over geologic time scales.^{22,23} However, nitrogen fixation by cyanobacteria can be limited by iron, because the process of nitrogen fixation has a relatively high iron demand, and iron inputs to oligotrophic regions are relatively small; thus, many regions of the world's oceans remain nitrogen-limited.^{137,138} Nitrogen-fixing organisms may be limited by P, in addition to iron; therefore, at some oceanic locations P availability may limit N fixation.

The Redfield N/P ratio of 16 is, however, not a universal biochemical optimum, but it rather represents an average of diverse species-specific N/P ratios which can vary from 8.2 to 45.0 depending on ecological conditions.^{135,139} Furthermore, the Redfield ratio varies substantially in response to changes in algal nutrient status and taxonomic affiliation and whether the P is adsorbed to the cell's surface or is intracellular.¹⁴⁰ N/P ratios of the dissolved inorganic N and P in the water column (e.g., nitrate to SRP) measured over 9 years at station ALOHA in the North Pacific subtropical gyre reveal complex interactions between N and P pools, suggesting that currently the gyre is in a period of net fixed N sequestration and P control of plankton growth rate.⁶ On longer time scales and over large areas, the nitrogen versus phosphorus limitation in open ocean environments is determined by the balance between nitrogen fixation and denitrification such that areas that are currently P-limited could switch to nitrogen limitation in the absence of nitrogen fixation.^{141,142} Recent research suggests that climate warming over the last few decades has resulted in stratification of the subtropical Pacific gyre, which favors nitrogen-fixing diazotrophs, thus increasing the nitrogen pool and pushing the system toward P limitation.¹⁰¹

Similarly, higher than Redfield N/P ratios, high alkaline phosphatase activities, and high rates of nitrogen fixation in the Atlantic point to phosphorus limitation or colimitation in that basin as well.^{129,141} Oceanic N/P ratios in seawater in the northern hemisphere show substantial temporal fluctuations over the past five decades, suggesting that the biological part of the marine carbon cycle is not at steady state.¹⁴³ However, one must keep in mind that the N/P ratios

measured in bulk particulate matter or in algal cells are strongly affected by the partitioning into surface-adsorbed and intracellular phosphorus pools. Total C/N/P ratios of algae may reflect Redfield values, while in contrast the intracellular ratios consistently exceed the Redfield ratio, suggesting P deficiency, unless the surface bound P is readily available.¹⁴⁰ In addition, certain organisms such as the picophytoplankton *Prochlorococcus* and *Synechococcus* may have relatively low P requirements and thus the particulate organic matter they produce could differ from the Redfield Ratio.¹⁴⁴ The implication of the above observations is that, to properly assess phytoplankton nutrient status, knowledge of the specific phytoplankton nutritional needs and measurements of the distinct phytoplankton phosphorus pools should be assessed.¹⁴⁰ Ideally, this should be combined with genetic and physiological measures of limitation.¹⁹

6.2. Utilization of Organic Phosphorus Forms

Organically bound P is for the most part not directly available to living organisms because it cannot be taken into the cell in this form. To be taken up, organic P must first be converted (hydrolyzed) to orthophosphate.⁹⁴ In response to P limitation, some species of phytoplankton produce enzymes that can catalyze the hydrolytic cleavage of phosphate from organic matter. Notably, alkaline phosphatases have been shown to be expressed in response to phosphate limitation in many species.¹⁴⁵ In addition, cell lysis releases enzymes (phosphomono- and phosphodiesterases, nucleases, nucleotidases, kinases) with greater or lesser substrate specificity that act to liberate orthophosphate from organic P compounds.¹⁴⁶

In large regions of the ocean, particularly in surface waters, much of the dissolved P is in the form of dissolved organic phosphorus (DOP), and oceanic productivity in these regions may be dependent on regeneration of bioavailable forms of P from dissolved organic matter (DOM).¹⁰⁰ For example, in oligotrophic surface waters, dissolved organic P (DOP) often comprises a significant portion of the dissolved P pool.^{147–149} Consequently, regeneration of DOP is a potentially important source of bioavailable P in these regions.

The biologically available pool of phosphorus can be measured using a ³²P-labeling technique developed by Karl and Bossard,¹⁵⁰ in which samples are incubated with ³²P-labeled phosphate at various light levels and the incorporation of labeled ³²P into organic matter is measured. This methodology gives a measure of the P pool that is available as DIP and does not reflect processes operating on longer time scales than the incubation period of the sample (typically 24 h or less). A study at station ALOHA in the Pacific oligotrophic gyre indicated that the bioavailable P exceeds the SRP pool, suggesting that the community utilizes DOP compounds for their P nutrition.¹⁵¹ It has been estimated that DOP utilization can be of the same magnitude as SRP utilization in the upper water column at station ALOHA.¹⁵¹

Phosphorus needs and sources may differ by species. There are systematic phylogenetic differences in C/N/P ratios of marine phytoplankton.¹⁵² Accordingly, species-specific differences in the response to nutrient enrichment can be explained by differences in the species physiology and resource competition.¹⁵³ *Emiliania huxleyi* blooms, for example, occur under low NO₃/PO₄ ratios, suggesting that, for a bloom to occur, *E. huxleyi* requires high phosphate concentrations relative to nitrate¹⁵⁴ although, considering the low level of nutrients in surface water (close to detection

limits), the measured nutrient ratios may incorporate a large error.^{19,155} These results may also be explained by the relatively large surface area to volume of this relatively small phytoplankton.¹⁵⁶ Phosphorus stress could also be assessed by the production of the enzyme alkaline phosphatase, which is induced at low phosphate concentrations, and measured in bulk or via an enzyme-labeled fluorescence (ELF) assay.^{157,158} Alkaline phosphatase expression was found to be seasonally variable in the Sargasso Sea and in the Gulf of Aqaba.^{19,159} At these sites, in the summer period, when waters are highly stratified but dominated by small cell picoplankton (*Synechococcus* and *Prochlorococcus*), a smaller percentage of the bulk autotrophic community in the surface waters exhibit enzyme-labeled fluorescence, relative to the case of the well-mixed fall period, which is dominated by larger cells with higher P needs.¹⁵⁹ At both sites and in all seasons, the ELF-labeled community is dominated by larger autotrophic groups, and even within these groups, the ELF labeling varied significantly.^{19,159} In Monterey Bay, California, a coastal ocean upwelling environment, alkaline phosphatase enzyme-labeled fluorescence (ELF) assays indicate that dinoflagellates utilize organic phosphorus to fulfill P requirements while coexisting diatoms do not.¹⁸ Conversely, in another upwelling nutrient-rich system, the northwestern African coast, alkaline phosphatase activity and turnover rates of P suggested that bacteria utilize alkaline phosphatase not necessarily to sustain their P needs but rather to supply themselves with easily assimilated organic carbon.^{160,161} Clearly, organic P compounds have an important role in the P cycle; however, more work is needed to fully understand the extent of the biological availability of this pool and its contribution to ocean productivity.

6.3. Phosphorus Constraints on Nitrogen Fixation

Some marine phytoplankton (like *Trichodesmium* spp. and other diazotrophs) have the physiological capacity to fix atmospheric nitrogen; however, the ability to fix N₂ is constrained by phosphate (and trace metal) bioavailability.¹⁶² Unicellular N₂-fixing cyanobacteria in tropical marine oligotrophic environments could be better adapted to low phosphate concentrations as a result of their smaller size and high surface area to volume ratios.¹⁶³ It would be advantageous for diazotrophs to have the capacity to utilize the more prevalent DOP pool. Indeed, Dyhrman et al.¹⁶⁴ found that *Trichodesmium* spp. are uniquely adapted for scavenging phosphorus from organic sources such as phosphonates, a DOP source previously thought to be unavailable to organisms. The *Trichodesmium erythraeum* IMS101 genome has genes that are thought to encode proteins associated with the high-affinity transport and hydrolysis of phosphate compounds, which other phytoplankton species do not possess. This indicates that some *Trichodesmium* species may be uniquely adapted to low-phosphorus conditions by their ability to utilize phosphonates as a P source.¹⁶⁴ However, field-based research in the Gulf of Aqaba suggests that, even with these potential adaptations to low P, *Trichodesmium* spp. abundance may be controlled by P availability while smaller diazotrophs could fair better in very-low-nutrient settings.¹⁹

While oceanic phosphorus pools set the upper limit for total amount of organic matter produced in the ocean over geologic time scales, at any instant in geologic time, ocean primary production may fall below this limit because of iron, light, nutrient, or some other limiting factor.¹²⁷ The primary

external source (e.g., not advection or upwelling sources) of both iron and P to open ocean oligotrophic gyres is in the form of dust deposition.^{59,165} Concentrations and forms of P in aerosols vary with the origin of the dust in the sample and are seasonally variable at any given location. While iron enhances phytoplankton productivity in high-nutrient, low-chlorophyll ocean regions, recent studies show that at some locations community primary productivity was generally nitrogen-limited and that nitrogen fixation was colimited by iron and phosphorus.^{166,167} Saharan dust addition to cultures stimulated nitrogen fixation by supplying both iron and phosphorus, indicating that eolian mineral dust deposition promotes nitrogen fixation in the eastern tropical North Atlantic¹⁶⁶ and biomass growth in the Gulf of Aqaba, Red Sea.^{19,61}

7. Microbial Role in the Phosphorus Cycle

In most regions of the ocean, microbes play an important role in the remineralization of organic phosphorus compounds.¹⁰² Bacterial biomass in the sea is related to the concentration of phytoplankton, and furthermore, bacteria utilize 10–50% of the carbon fixed by photosynthesis.⁹⁷ With the development of tools capable of identifying specific microbial populations and associated biochemical pathways, we are gaining a deeper understanding of the role of microbes in the marine environment. Several studies have focused on specific microbially mediated processes and their relationship to the marine P-cycle.

Phosphonates are among the more recalcitrant of organophosphorus compounds; they are extremely resistant to chemical hydrolysis, thermal decomposition, and photolysis.^{99,168,169} Phosphonates characterized by a stable C–P bond widely occur as xenobiotics which pollute the environment.¹⁶⁸ Thus, there has been great interest in understanding the pathways and mechanisms of their degradation. Only prokaryotic microorganisms and the lower eukaryotes (e.g., *E. Coli*, *Pseudomonas* sp., and *Candida maltosa*, a yeast) have been recognized as being capable of phosphonate remineralization, and they can do so via a wide range of pathways, which are determined by the diversity of the phosphonate structures.¹⁶⁸ However, only the degradation of the more simple phosphonate structures has been observed so far.¹⁶⁸ Benitez-Nelson et al.¹¹⁶ found preferential removal of phosphonate compounds in the anoxic Cariaco Basin during periods of low-particle-flux events, which implies that phosphonates may be an active source of bioavailable P in the water column under anoxic conditions. The specific microbial community responsible for this degradation has yet to be characterized.

Microbes in the marine environment can also create new pathways for the uptake of phosphorus by zooplankton. Phosphate addition experiments to surface waters obtained from the oligotrophic, low-phosphorus eastern Mediterranean Sea resulted in a decrease in chlorophyll concentration, while at the same time exhibiting an increase in bacterial production and copepod egg abundance.¹¹ Thus, while phytoplankton growth was inhibited simultaneously by nitrogen and phosphorus such that P additions alone did not enhance their growth (chlorophyll increased only with combined N and P addition), phosphorus may have been transferred through the microbial food web to copepods, thus increasing the copepod population while not necessarily increasing the phytoplankton community.¹¹

Phosphorus transformations at the sediment/water interface are generally considered to be governed by abiotic processes

(see section 5), and bacteria were assumed to play only an indirect role. However, recent findings by Gachter and Meyer¹⁷⁰ suggest that not only bacteria in sediments regenerate phosphate but that they also do contribute to the production of refractory organic P compounds. Thus, such bacteria may regulate the flux of P across the sediment/water interface and contribute to its terminal burial by the production of refractory organic P compounds and biogenic apatite.

8. Phosphate Oxygen Isotopic Ratios: A Tracer for Phosphate Sources and Cycling

Recently, the oxygen isotope ratio in phosphate has become a more widely used tool for identifying distinct phosphate sources and understanding phosphate cycling in marine and estuarine systems. Because P has only one stable isotope, P stable isotope ratios cannot be used for studies of nutrient sources, cycling, and utilization (as is the case for nitrogen and carbon). However, most of the P found in nature is strongly bound to oxygen (O), which has three stable isotopes; hence, phosphate (PO_4) can be analyzed for its oxygen isotopic composition ($\delta^{18}\text{O}_p$). The P–O bond in phosphate is resistant to inorganic hydrolysis, and at the temperature and pH of most natural systems, phosphate does not exchange oxygen with water without biological mediation.^{171–173} Thus, any observed variability in the oxygen isotopic composition of phosphate will either reflect mixing of isotopically distinct sources of phosphate or the alteration of the phosphate $\delta^{18}\text{O}$ signature as a result of the exchange of oxygen during the cycling of phosphate through living cells. In the latter case, each time a phosphate molecule is cycled (taken up by organisms and processed by enzymes), phosphate oxygen will be exchanged with cellular water, resulting in isotopic equilibrium with the surrounding water at the temperature of reaction.

Results of several laboratory studies characterizing the exchange and fractionation of phosphate oxygen isotopes suggest that the $\delta^{18}\text{O}_p$ of DIP could be used to evaluate the degree of recycling of the DIP pool.^{171,174–176} Enzyme-mediated turnover of phosphate and the microbially mediated degradation of organic matter demonstrated that significant exchange of oxygen isotopes between phosphate and water accompanies the hydrolytic cleavage and metabolism of both organically bound phosphate and inorganic orthophosphate.¹⁷¹ Bacterial metabolic processes have also been found to significantly alter the $\delta^{18}\text{O}_p$ of DIP in laboratory culture experiments, even when phosphate concentrations were high.¹⁷⁴ Furthermore, results of an algae culture experiment indicate that intracellular oxygen isotope exchange between phosphorus compounds and water is very rapid (hours to days).¹⁷⁶

Observations, both in microbial culture experiments and in cell-free systems where specific enzymes were used,¹⁷⁵ indicate that intracellular phosphate cycling by pyrophosphatase results in a temperature-dependent equilibrium oxygen isotope fractionation, which imparts the equilibrium $\delta^{18}\text{O}_p$ on phosphate recycled within cells. In contrast, extracellular phosphate regeneration by alkaline phosphatase is accompanied by disequilibrium isotope effects (both kinetic effects and inheritance of phosphate oxygen from hydrolyzed phosphomonoesters) in the inorganic phosphate released into the system.¹⁷⁵ However, the equilibrium isotope effects associated with intracellular phosphate cycling are expected to dominate in most natural systems.¹⁷⁵

To date, there are relatively few studies assessing the oxygen isotopic composition of DIP in natural aquatic systems. Pioneering work by Longinelli et al.¹⁷² found no variation in the $\delta^{18}\text{O}_p$ of DIP in seawater or of marine organism soft tissue with either depth or latitude in the Atlantic and Pacific Oceans, although there was a significant difference between the two ocean basins. The $\delta^{18}\text{O}_p$ values were thought to reflect kinetic-biological isotopic fractionation. However, Longinelli et al.¹⁷² extracted P from seawater without prefiltration and used Fe-coated fibers which absorb both inorganic and organic P, and such complications may confound interpretation of their results. More recently, Colman¹⁷⁷ concluded that the large deviations in $\delta^{18}\text{O}_p$ between riverine and coastal waters in the Long Island Sound reflected equilibration with local water and indicated that rapid microbial cycling overprints source $\delta^{18}\text{O}_p$ values on a time scale of weeks. In contrast, phosphate in the San Francisco Bay estuary is typically not equilibrated with environmental water and reflects two end-member mixing between oceanic phosphate and riverine phosphate with seasonally important additional riverine inputs along this flow path.¹⁷⁸ In California coastal waters (Monterey Bay), phosphate oxygen isotope ratios tracked seasonal changes in phosphate cycling through the biomass (e.g., phosphate utilization rates) with the greatest phosphate oxygen isotope exchange occurring during the upwelling season.¹⁷⁹ The $\delta^{18}\text{O}_p$ in open ocean waters is a function of DIP transport and biological turnover in both the Atlantic and the Pacific Oceans and highlights the importance of cell lysis in the regeneration of DIP in the euphotic zone. Furthermore, at depth, the $\delta^{18}\text{O}_p$ values are near the temperature-dependent equilibrium, suggestive of bacterial turnover of DIP in seawater.¹⁸⁰ These data suggest that the $\delta^{18}\text{O}_p$ can be used as a powerful tool for identifying and quantifying the contribution of non-point sources of phosphate pollution into some aquatic systems and has the potential to be used to determine relative rates of P cycling and utilization in marine systems.

9. Summary

Phosphorus is undeniably an important element in the marine environment. Its role as a limiting macronutrient for primary productivity inextricably links it to the global carbon cycle and thus the climate system over geologic time scales. However, there remain many unanswered questions or ambiguous answers to the global phosphorus cycle. Pinpointing the sources and sinks of this globally important element remain elusive, and changes of either one could greatly alter the residence time of P in the ocean and, thus, estimates of its contribution to carbon export through ocean productivity. Furthermore, anthropogenic inputs of P to the marine environment are greatly altering the source contribution of P, and the ultimate effects of these additions and how they will interact with anthropogenic inputs of nitrogen and other elements and, more importantly, how they will affect marine ecosystems are still largely unknown.

With the advent of new techniques, we have gained a greater understanding of the forms of phosphorus in the marine environment and how specific organisms utilize each of these phosphorus pools. Major advances have been made not only in identifying the microorganisms which are active in the turnover of organic phosphorus compounds but also in identifying the genes which are involved in creating the enzymes that make this turnover possible. Furthermore, specific species have been identified which can utilize

specific enzymes to access forms of P that were previously thought to be too recalcitrant to be biologically available. However, the time scales and the quantity of P turnover in this manner remain undefined. Consequently, despite the advancements in both knowledge and techniques available to understand the marine phosphorus cycle, we still have a long way to go before the cycle can be fully characterized. However, with the increased realization that the marine P cycle is more dynamic than previously thought, it is likely that more studies will focus on this element in the future.

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CR0503613