At sea, apparent declines are even more difficult to understand. The number of phalaropes staging for fall migration in the western Bay of Fundy declined from estimates of two million to almost nothing in the mid-1990s. This disappearance may represent a true population decline, or simply a shift of currents and prey, and thus of birds, to some as-yet undiscovered area of the Bay or the western Atlantic. Similar declines have been reported in the number of phalaropes seen off coastal Japan in spring. Limited evidence suggests that the numbers of birds passing through the Bay of Fundy during spring migration is unchanged.

Threats

Compared to many oceanic birds, phalaropes probably face relatively few threats. Their breeding populations are widely distributed and thus, unlike those of many colonially nesting seabirds breeding on islands, are resistant to depredations of introduced predators. Their predators on the breeding grounds include raptorial birds such as pomarine and parasitic jaegers, mammals such as arctic and red foxes and short-tailed weasels, and chick and egg predators such as glaucous gulls, sandhill cranes, and arctic ground squirrels. They are safe from most of these when at sea. However, they are not invulnerable even at sea: four red-necked phalaropes were once found in the stomach of a common dolphin taken off Baja California, Mexico. With the exception of minor subsistence hunting by indigenous northerners, phalaropes are not hunted by humans and as surface-swimming planktivores, are not incidentally taken in fishing nets, as so many seabirds are. They are potentially vulnerable to spilled oil, particularly since oil and food particles may be concentrated at the same convergence zone.

As for all oceanic organisms, human-caused disruption and destruction of marine environments is likely the most serious threat facing phalarope populations.

See also

Baleen Whales. Copepods. Plankton and Climate. Seabird Foraging Ecology. Seabird Migration. Seabird Population Dynamics. Seabirds and Fisheries Interactions. Seabirds as Indicators of Ocean Pollution. Upwelling Ecosystems.

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PHOSPHORUS CYCLE

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doi:10.1006/rwos.2001.0277

Introduction

The global phosphorus cycle has four major components: (i) tectonic uplift and exposure of phosphorus-bearing rocks to the forces of weathering; (ii) physical erosion and chemical weathering of rocks producing soils and providing dissolved and particulate phosphorus to rivers; (iii) riverine transport of phosphorus to lakes and the ocean; and (iv) sedimentation of phosphorus associated with organic and mineral matter and burial in sediments (**Figure 1**). The cycle begins anew with uplift of sediments into the weathering regime.

Phosphorus is an essential nutrient for all life forms. It is a key player in fundamental biochemical reactions involving genetic material (DNA, RNA) and energy transfer (adenosine triphosphate, ATP),

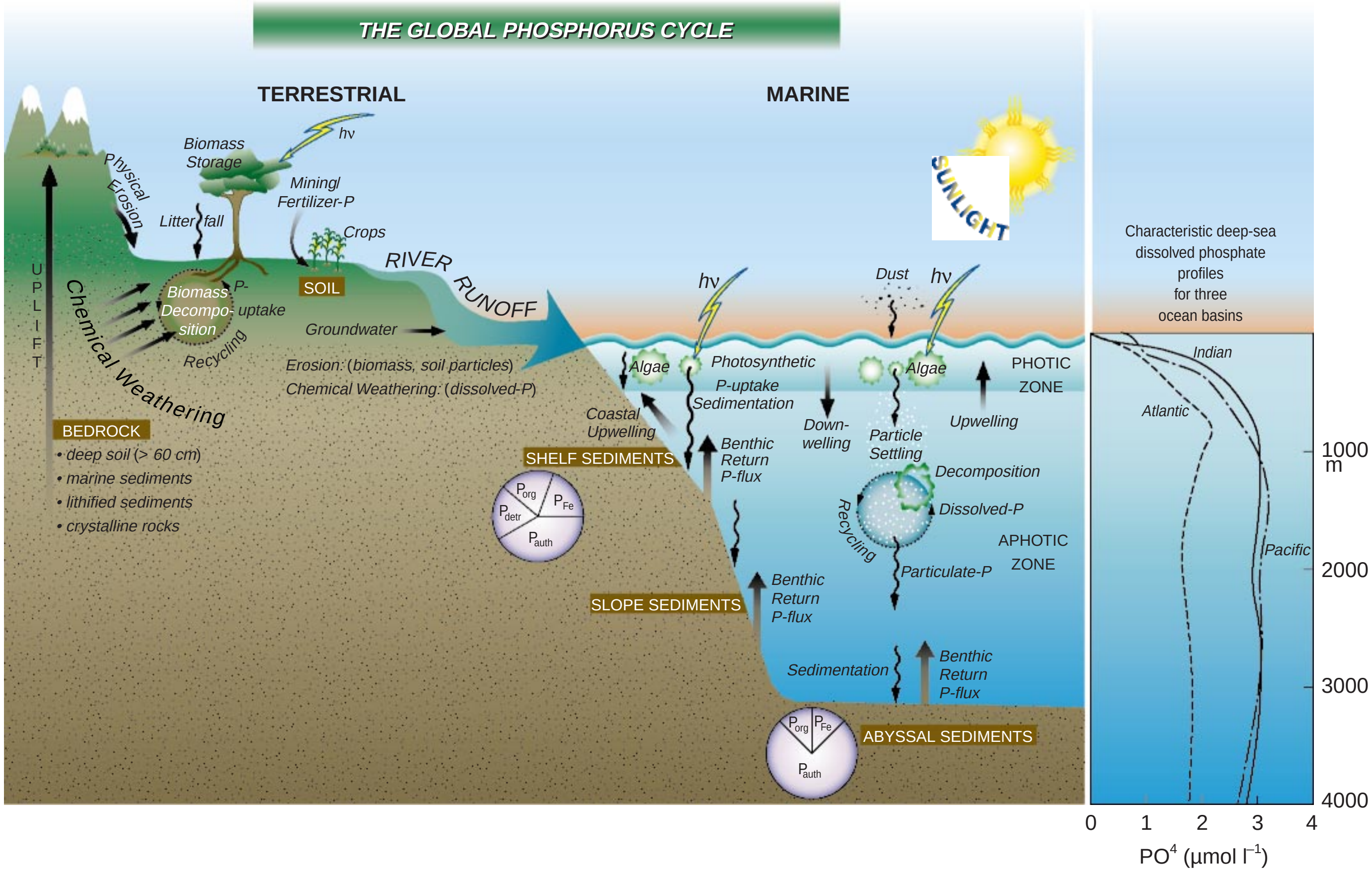

Figure 1 Cartoon illustrating the major reservoirs and fluxes of phosphorus described in the text and summarized in **Tables 1** and **2**. The oceanic photic zone, idealized in the cartoon, is typically thinner in coastal environments owing to turbidity from continental terrigenous input, and deepens as the water column clarifies with distance away from the continental margins. The distribution of phosphorus among different chemical/mineral forms in marine sediments is given in the pie diagrams, where the abbreviations used are: P_{org}, organic phosphorus; P_{Fe}, iron-bound phosphorus; P_{detr}, detrital apatite; P_{auth}, authigenic/biogenic apatite. The P_{org}, P_{Fe}, and P_{auth} reservoirs represent potentially reactive phosphorus pools (see text and **Tables 2** and **5** for discussion), whereas the P_{detr} pool reflects mainly detrital apatite weathered off the continents and passively deposited in marine sediments (note that P_{detr} is not an important sedimentary phosphorus component in abyssal sediments, far from continents).

Continental margin phosphorus speciation data were compiled from Louchouarn P, Lucotte M, Duchemin E and de Vernal A (1997) Early diagenetic processes in recent sediments of the Gulf of St-Lawrence: Phosphorus, carbon and iron burial rates. *Marine Geology* 139(1/4): 181–200, and Ruttenberg KC and Berner RA (1993) Authigenic apatite formation and burial in sediments from non-upwelling continental margin environments. *Geochimica et Cosmochimica Acta* 57: 991–1007. Abyssal sediment phosphorus speciation data were compiled from Filippelli GM and Delaney ML (1996) Phosphorus geochemistry of equatorial Pacific sediments. *Geochimica et Cosmochimica Acta* 60: 1479–1495, and Ruttenberg KC (1990) *Diagenesis and burial of phosphorus in marine sediments: implications for the marine phosphorus budget*. PhD thesis, Yale University. The global phosphorus cycle cartoon is from Ruttenberg (2000). The global phosphorus cycle. In: *The Encyclopedia of Global Change*, Oxford University Press. (in Press), with permission. The vertical water column distributions of phosphate typically observed in the three ocean basins are shown in the panel to the right of the global phosphorus cycle cartoon, and are from Sverdrup HV, Johnson MW and Fleming RH (1942) *The Oceans, Their Physics, Chemistry and General Biology*. New York: Prentice Hall, ©1942 Prentice Hall; used with permission.

and in structural support of organisms provided by membranes (phospholipids) and bone (the biomineral hydroxyapatite). Photosynthetic organisms utilize dissolved phosphorus, carbon, and other essential nutrients to build their tissues using energy from the sun. Biological productivity is contingent upon the availability of phosphorus to these organisms, which constitute the base of the food chain in both terrestrial and aquatic systems.

Phosphorus locked up in bedrock, soils, and sediments is not directly available to organisms. Conversion of unavailable forms to dissolved orthophosphate, which can be directly assimilated, occurs through geochemical and biochemical reactions at various stages in the global phosphorus cycle. Production of biomass fueled by phosphorus bioavailability results in the deposition of organic matter in soil and sediments, where it acts as a source of fuel and nutrients to microbial communities. Microbial activity in soils and sediments, in turn, strongly influences the concentration and chemical form of phosphorus incorporated into the geological record.

This article begins with a brief overview of the various components of the global phosphorus cycle. Estimates of the mass of important phosphorus reservoirs, transport rates (fluxes) between reservoirs, and residence times are given in **Tables 1** and **2**. As is clear from the large uncertainties associated with

Table 1 Major reservoirs active in the global phosphorus cycle and associated residence times[a]

Reservoir no.	*Reservoir description*	*Reservoir size (10^{12} mol P)*	*Reference*	*Residence time τ (years)*
R1	Sediments (crustal rocks and soil >60 cm deep and marine sediments)	0.27×10^8–1.3×10^8	b, a = c = d	42–201×10^6
R2	Land ($\approx$ total soil <60 cm deep: organic + inorganic)	3100–6450	b, a = c = d	425–2311
R3	Land biota	83.9–96.8	b, a = c = d	13–48
R4	Surface ocean, 0–300 m (total dissolved P)	87.4	a = c	2.46–4.39
R5	Deep sea, 300–3300 m (total dissolved P)	2810	a = c & d	1502
R6	Oceanic biota	1.61–4.45	b & d, a = c & d	0.044–0.217 (16–78 d)
R7	Minable P	323–645	a = c, b & d	718–1654
R8	Atmospheric P	0.0009	b = c = d	0.009 (80 h)

[a] *Notes*

(1) Ranges are reported for those reservoirs for which a consensus on a single best estimated reservoir size does not exist. Maximum and minimum estimates found in a survey of the literature are reported. References cited before the comma refer to the first (lowest) estimate, those after the comma refer to the second (higher) estimate. References that give identical values are designated by an equality sign, references giving similar values are indicated by an ampersand. As indicated by the wide ranges reported for some reservoirs, all calculations of reservoir size have associated with them a large degree of uncertainty. Methods of calculation, underlying assumptions, and sources of error are given in the references cited.

(2) Residence times are calculated by dividing the concentration of phosphorus contained in a given reservoir by the sum of fluxes out of the reservoir. Where ranges are reported for reservoir size and flux, maximum and minimum residence time values are given; these ranges reflect the uncertainties inherent in reservoir size and flux estimates. Fluxes used to calculate residence times for each reservoir are as follows: R1 (F_{12}), R2 ($F_{23}+F_{28}+F_{24(d)}+F_{24(p)}$), R3 ($F_{32}$), R4 ($F_{45}+F_{46}$), R5 ($F_{54}$), R6 ($F_{64}+F_{65}$), R7 ($F_{72}$), R8 ($F_{82}+F_{84}$). Flux estimates are given in **Table 2**. The residence time of R5 is decreased to 1492 y by inclusion of the scavenged flux of deep-sea phosphate at hydrothermal mid-ocean ridge systems, mostly onto ferric oxide and oxyhydroxide phases (Wheat CG, Feely RA and Mottl MJ (1996). Phosphate removal by oceanic hydrothermal processes: an update of the phosphorus budget in the oceans. *Geochimica et Cosmochimica Acta* 60(19): 3593–3608).

(3) Estimates for the partitioning of the oceanic reservoir between dissolved inorganic phosphorus and particulate phosphorus are given in references b and d as follows: 2581–2600×10^{12} mol dissolved inorganic phosphorus (b, d) and 20–21×10^{12} mol particulate phosphorus (d, b).

(4) The residence times estimated for the minable phosphorus reservoir reflect estimates of current mining rates; if mining activity increases or diminishes the residence time will change accordingly.

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Table 2 Fluxes between the major phosphorus reservoirs[a]

Flux no.	*Description of flux*	*Flux (10^{12} mol P y^{-1})*	*References and comments*
Reservoir fluxes			
F_{12}	Rocks/sediments → soils (erosion/weathering, soil accumulation)	0.645	a = c & d
F_{21}	Soils → rocks/sediments (deep burial, lithification)	0.301–0.603	d, a = c
F_{23}	Soils → land biota	2.03–6.45	a = c, b & d
F_{32}	Land biota → soils	2.03–6.45	a = c, b & d
$F_{24(d)}$	Soil → surface ocean (river total dissolved P flux)	0.032–0.058	e, a = c; ∼ > 50% of TDP is DOP (e)
$F_{24(p)}$	Soil → surface ocean (river particulate P flux)	0.59–0.65	d, e; ∼40% of RSPM-P (Riverine Suspended Particulate Matter-Phosphorus) is organic P (e); it is estimated that between 25–45% is reactive once it enters the ocean (f).
F_{46}	Surface ocean → oceanic biota	19.35–35	b, d; a = c = 33.5, b reports upper limit of 32.3; d reports lower limit of 28.2
F_{64}	Oceanic biota → surface ocean	19.35–35	b, d; a & c = 32.2, b reports upper limit of 32.3, d reports lower limit of 28.2
F_{65}	Oceanic biota → deep sea (particulate rain)	1.13–1.35	d, a = c
F_{45}	Surface ocean → deep sea (downwelling)	0.581	a = c
F_{54}	Deep sea → surface ocean (upwelling)	1.87	a = c
F_{42}	Surface ocean → land (fisheries)	0.01	d
F_{72}	Minable P → land (soil)	0.39–0.45	a = c = d, b
F_{28}	Land (soil) → atmosphere	0.14	b = c = d
F_{82}	Atmosphere → land (soil)	0.1	b = c = d
F_{48}	Surface ocean → atmosphere	0.01	b = c = d
F_{84}	Atmosphere → surface ocean	0.02–0.05	c, b; d gives 0.04; ∼30% of atmospheric aerosol P is soluble (g)
Subreservoir fluxes: marine sediments			
sF_{ms}	Marine sediment accumulation (total)	0.265–0.280	i, j; for higher estimate (j), use of sediment P concentration below the diagenesis zone implicitly accounts for P loss via benthic remineralization flux and yields pre-anthropogenic net burial flux. For estimates of reactive P burial see note (j).
sF_{cs}	Continental margin ocean sediments → burial	0.150–0.223	j, i; values reported reflect total P, reactive P burial constitutes from 40–75% of total P (h). These values reflect pre-agricultural fluxes, modern value estimated as 0.33 (d).
sF_{as}	Abyssal (deep sea) sediments → burial	0.042–0.130	i, j; a = c gives a value of 0.055. It is estimated that 90–100% of this flux is reactive P (h). These values reflect pre-agricultural fluxes, modern value estimates range from 0.32 (d) to 0.419 (b).

(Continued)

Table 2 *Continued*

Flux no.	*Description of flux*	*Flux (10^{12} mol P y^{-1})*	*References and comments*
sF_{cbf}	Coastal sediments → coastal waters (remineralization, benthic flux)	0.51–0.84	d, k; these values reflect pre-agricultural fluxes, modern value estimated as 1.21 with uncertainties ±40% (k)
sF_{abf}	Abyssal sediments → deep sea (remineralization, benthic flux)	0.41	k; this value reflects pre-agricultural fluxes, modern value estimated as 0.52, uncertainty ±30% (k)

[a] *Notes*

(1) Reservoir fluxes (*F*) represent the P-flux between reservoirs #R1–R8 defined in **Table 1**. The subreservoir fluxes (s*F*) refer to the flux of phosphorus into the marine sediment portion of reservoir #1 via sediment burial, and the flux of diagenetically mobilized phosphorus out of marine sediments via benthic return flux. These subfluxes have been calculated as described in references h–k. Note that the large magnitude of these sub-fluxes relative to those into and out of reservoir #1 as a whole, and the short oceanic-phosphorus residence time they imply (**Tables 1** and **5**), highlight the dynamic nature of the marine phosphorus cycle.

(2) Ranges are reported where consensus on a single best estimate does not exist. References cited before the comma refer to the first (lowest) estimate, those after the comma refer to the second (higher) estimate. References that give identical values are designated by an equality sign, references giving similar values are indicated by an ampersand. Maximum and minimum estimates found in a survey of the literature are reported. In some cases this range subsumes ranges reported in the primary references. As indicated by the wide ranges reported, all flux calculations have associated with them a large degree of uncertainty. Methods of calculation, underlying assumptions, and sources of error are given in the references cited.

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(e) Meybeck M. (1982). *American Journal of Science* 282(4): 401.

(f) The range of riverine suspended particulate matter that may be solubilized once it enters the marine realm (e.g. so-called 'reactive phosphorus') is derived from three sources. Colman AS and Holland HD ((2000). In: Glenn, C.R., Prévôt-Lucas L and Lucas J (eds) *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication No. 66. pp. 53–75) estimate that 45% may be reactive, based on RSPM-P compositional data from a number of rivers and estimated burial efficiency of this material in marine sediments. Berner RA and Rao J-L ((1994) *Geochimica et Cosmochimica Acta* 58: 2333) and Ruttenberg KC and Canfield DE ((1994) *EOS, Transactions of the American Geophysical Union* 75: 110) estimate that 35% and 31% of RSPM-P is released upon entering the ocean, based on comparison of RSPM-P and adjacent deltaic surface sediment phosphorus in the Amazon and Mississippi systems, respectively. Lower estimates have been published: 8% (Ramirez AJ and Rose AW (1992) *American Journal of Science* 292: 421); 18% (Froelich PN (1988) *Limnology and Oceanography* 33: 649); 18%: (Compton J, Mallinson D, Glenn CR *et al.* (2000) In: Glenn CR, Prévôt-Lucas L and Lucas J (eds) *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication No. 66, pp. 21–33). Higher estimates have also been published: 69% (Howarth RW, Jensen HS, Marine R and Postma H (1995) In: Tiessen H (ed) *Phosphorus in the Global Environment*, SCOPE 54, pp. 323–345. Chichester: Wiley). Howarth *et al.* (1995) also estimate the total flux of riverine particulate P to the oceans at 0.23×10^{12} moles P y^{-1}, an estimate likely too low because it uses the suspended sediment flux from Milliman JD and Meade RH ((1983) Journal of Geology 91: 1), which does not include the high sediment flux rivers from tropical mountainous terranes (Milliman JD and Syvitski JPM (1992) *Journal of Geology* 100: 525).

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(h) Ruttenberg KC (1993) *Chemical Geology* 107: 405.

(i) Howarth RW, Jensen HS, Marino R and Postma H (1995) In: Tiessen H (ed.) *Phosphorus in the Global Environment*, SCOPE 54, pp. 323–345, Chichester: Wiley.

(j) Phosphorus-burial flux estimates as reported in Ruttenberg ((1993) *Chemical Geology* 107: 405) modified using pre-agricultural sediment fluxes updated by Colman AS and Holland HD ((2000) In: Glenn CR, Prévôt-Lucas L and Lucas J (eds) *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication No. 66, pp. 53–75). Using these total phosphorus burial fluxes and the ranges of likely reactive phosphorus given in the table, the best estimate for reactive phosphorus burial flux in the oceans lies between 0.177 and 0.242×10^{12} moles P y^{-1}. Other estimates of whole-ocean reactive phosphorus burial fluxes range from, at the low end, $0.032–0.081 \times 10^{12}$ moles P y^{-1} (Compton J, Mallinson D, Glenn CR *et al.* (2000) In: Glenn CR, Prévôt-Lucas L and Lucas J (eds) *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication No. 66, pp. 21–33), and 0.09×10^{12} moles P y^{-1} (Wheat CG, Feely RA and Mottl MJ (1996) *Geochimica et Cosmochimica Acta* 60: 3593); to values more comparable to those derived from the table above (0.21×10^{12} moles P y^{-1}: Filippelli GM and Delaney ML (1996) *Geochimica Cosmochimica Acta* 60: 1479)

(k) Colman AS and Holland HD (2000) In: Glenn CR, Prévôt-Lucas L and Lucas J (eds) *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication No. 66, pp. 53–75.

these estimates of reservoir size and flux, there remain many aspects of the global phosphorus cycle that are poorly understood. The second half of the article describes current efforts underway to advance our understanding of the global phosphorus cycle. These include (i) the use of phosphate oxygen isotopes (δ^{18}O-PO_4) as a tool for identifying the role of microbes in the transformer of phosphate from one reservoir to another; (ii) the use of naturally occurring cosmogenic isotopes of phosphorus (^{32}P and ^{33}P) to provide insight into phosphorus-cycling pathways in the surface ocean; (iii) critical evaluation of the potential role of phosphate limitation in coastal and open ocean ecosystems; (iv) reevaluation of the oceanic residence time of phosphorus; and (v) rethinking the global phosphorus-cycle on geological timescales, with implications for atmospheric oxygen and phosphorus limitation primary productivity in the ocean.

The Global Phosphorus Cycle: Overview

The Terrestrial Phosphorus Cycle

In terrestrial systems, phosphorus resides in three pools: bedrock, soil, and living organisms (biomass) (**Table 1**). Weathering of continental bedrock is the principal source of phosphorus to the soils that support continental vegetation (F_{12}); atmospheric deposition is relatively unimportant (F_{82}). Phosphorus is weathered from bedrock by dissolution of phosphorus-bearing minerals such as apatite ($Ca_{10}(PO_4)_6(OH, F, Cl)_2$), the most abundant primary phosphorus mineral in crustal rocks. Weathering reactions are driven by exposure of minerals to naturally occurring acids derived mainly from microbial activity. Phosphate solubilized during weathering is available for uptake by terrestrial plants, and is returned to the soil by decay of litterfall (**Figure 1**).

Soil solution phosphate concentrations are maintained at low levels as a result of absorption of phosphorus by various soil constituents, particularly ferric iron and aluminum oxyhydroxides. Sorption is considered the most important process controlling terrestrial phosphorus bioavailability. Plants have different physiological strategies for obtaining phosphorus despite low soil solution concentrations. For example, some plants can increase root volume and surface area to optimize uptake potential. Alternatively, plant roots and/or associated fungi can produce chelating compounds that solubilize ferric iron and calcium-bound phosphorus, enzymes and/or acids that solubilize phosphate in the root vicinity. Plants also minimize phosphorus loss by resorbing much of their phosphorus prior to litterfall, and by efficient recycling from fallen litter. In extremely unfertile soils (e.g., in tropical rain forests) phosphorus recycling is so efficient that topsoil contains virtually no phosphorus; it is all tied up in biomass.

Systematic changes in the total amount and chemical form of phosphorus occur during soil development. In initial stages, phosphorus is present mainly as primary minerals such as apatite. In mid-stage soils, the reservoir of primary apatite is diminished; less-soluble secondary minerals and organic phosphorus make up an increasing fraction of soil phosphorus. Late in soil development, phosphorus is partitioned mainly between refractory minerals and organic phosphorus (**Figure 2**).

Transport of Phosphorus from Continents to the Ocean

Phosphorus is transferred from the continental to the oceanic reservoir primarily by rivers (F_{24}). Deposition of atmospheric aerosols (F_{84}) is a minor flux. Groundwater seepage to the coastal ocean is a potentially important but undocumented flux.

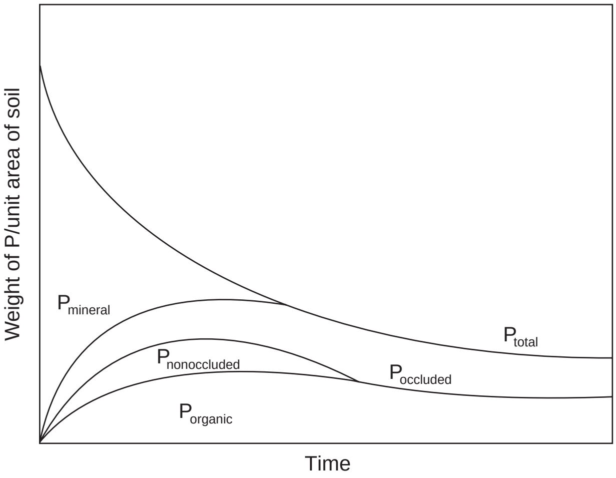

Figure 2 The fate of phosphorus during soil formation can be viewed as the progressive dissolution of primary mineral P (dominantly apatite), some of which is lost from the system by leaching (decrease in P_{total}), and some of which is reincorporated into nonoccluded, occluded and organic fractions within the soil. Nonoccluded P is defined as phosphate sorbed to surface of hydrous oxides of iron and aluminum, and calcium carbonate. Occluded P refers to P present within the mineral matrix of discrete mineral phases. The initial build-up in organic P results from organic matter return to soil from vegetation supported by the soil. The subsequent decline in $P_{organic}$ is due to progressive mineralization and soil leaching. The timescale over which these transformations occur depends upon the initial soil composition, topographic, and climatic factors. Figure is after Walker and Syers (1976) The fate of phosphorus during pedogenesis. *Geoderma* 15: 1–19, with permission.

Riverine phosphorus derives from weathered continental rocks and soils. Because phosphorus is particle-reactive, most riverine phosphorus is associated with particulate matter. By most estimates, over 90% of the phosphorus delivered by rivers to the ocean is as particulate phosphorus ($F_{24(p)}$). Dissolved phosphorus in rivers occurs in both inorganic and organic forms. The scant data on dissolved organic phosphorus suggest that it may account for 50% or more of dissolved riverine phosphorus. The chemical form of phosphorus associated with riverine particles is variable and depends upon the drainage basin geology, on the extent of weathering of the substrate, and on the nature of the river itself. Available data suggest that approximately 20–40% of phosphorus in suspended particulate matter is organic. Inorganic forms are partitioned mainly between ferric oxyhydroxides and apatite. Aluminum oxyhydroxides and clays may also be significant carriers of phosphorus.

The fate of phosphorus entering the ocean via rivers is variable. Dissolved phosphorus in estuaries at the continent–ocean interface typically displays nonconservative behavior. Both negative and positive deviations from conservative mixing can occur, sometimes changing seasonally within the same estuary. Net removal of phosphorus in estuaries is typically driven by flocculation of humic-iron complexes and biological uptake. Net phosphorus release is due to a combination of desorption from fresh water particles entering high-ionic-strength marine waters, and flux of diagenetically mobilized phosphorus from benthic sediments. Accurate estimates of bioavailable riverine phosphorus flux to the ocean must take into account, in addition to dissolved forms, the fraction of riverine particulate phosphorus released to solution upon entering the ocean.

Human impacts on the global phosphorus cycle

The mining of phosphate rock (mostly from marine phosphorite deposits) for use as agricultural fertilizer (F_{72}) increased dramatically in the latter half of the twentieth century. In addition to fertilizer use, deforestation, increased cultivation, and urban and industrial waste disposal all have enhanced phosphorus transport from terrestrial to aquatic systems, often with deleterious results. For example, elevated phosphorus concentrations in rivers resulting from these activities have resulted in eutrophication in some lakes and coastal areas, stimulating nuisance algal blooms and promoting hypoxic or anoxic conditions that are harmful or lethal to natural populations.

Increased erosion due to forest clear-cutting and widespread cultivation has increased riverine suspended matter concentrations, and thus increased the riverine particulate phosphorus flux. Dams, in contrast, decrease sediment loads in rivers and therefore diminish phosphorus-flux to the oceans. However, increased erosion below dams and diagenetic mobilization of phosphorus in sediments trapped behind dams moderates this effect. The overall effect has been a 50–300% increase in riverine phosphorus flux to the oceans above pre-agricultural levels.

The Marine Phosphorus Cycle

Phosphorus in its simplest form, dissolved orthophosphate, is taken up by photosynthetic organisms at the base of the marine food web. When phosphate is exhausted, organisms may utilize more complex forms by converting them to orthophosphate via enzymatic and microbiological reactions. In the open ocean most phosphorus associated with biogenic particles is recycled within the upper water column. Efficient stripping of phosphate from surface waters by photosynthesis combined with build-up at depth due to respiration of biogenic particles results in the classic oceanic dissolved nutrient profile. The progressive accumulation of respiration-derived phosphate at depth along the deep-water circulation trajectory results in higher phosphate concentrations in Pacific Ocean deep waters at the end of the trajectory than in the North Atlantic where deep water originates (**Figure 1**).

The sole means of phosphorus removal from the oceans is burial with marine sediments. The phosphorus flux to shelf and slope sediments is larger than the phosphorus flux to the deep sea (**Table 2**) for several reasons. Coastal waters receive continentally derived nutrients via rivers (including phosphorus, nitrogen, silicon, and iron), which stimulate high rates of primary productivity relative to the deep sea and result in a higher flux of organic matter to continental margin sediments. Organic matter is an important, perhaps primary, carrier of phosphorus to marine sediments. Owing to the shorter water column in coastal waters, less respiration occurs prior to deposition. The larger flux of marine organic phosphorus to margin sediments is accompanied by a larger direct terrigenous flux of particulate phosphorus (organic and inorganic), and higher sedimentation rates overall. These factors combine to enhance retention of sedimentary phosphorus. During high sea level stands, the sedimentary phosphorus reservoir on continental margins expands, increasing the phosphorus removal flux and therefore shortening the oceanic phosphorus residence time.

Terrigenous-dominated shelf and slope (hemipelagic) sediments and abyssal (pelagic) sediments have distinct phosphorus distributions. While both are dominated by authigenic Ca-P (mostly carbonate fluorapatite), this reservoir is more important in pelagic sediments. The remaining phosphorus in hemipelagic sediments is partitioned between ferric iron-bound phosphorus (mostly oxyhydroxides), detrital apatite, and organic phosphorus; in pelagic sediments detrital apatite is unimportant. Certain coastal environments characterized by extremely high, upwelling-driven biological productivity and low terrigenous input are enriched in authigenic apatite; these are proto-phosphorite deposits. A unique process contributing to the pelagic sedimentary Fe-P reservoir is sorptive removal of phosphate onto ferric oxyhydroxides in mid-ocean ridge hydrothermal systems.

Mobilization of sedimentary phosphorus by microbial activity during diagenesis causes dissolved phosphate build-up in sediment pore waters, promoting benthic efflux of phosphate to bottom waters or incorporation in secondary authigenic minerals. The combined benthic flux from coastal (sF_{cbf}) and abyssal (sF_{abf}) sediments is estimated to exceed the total riverine phosphorus flux ($F_{24(\mathrm{d+p})}$) to the ocean. Reprecipitation of diagenetically mobilized phosphorus in secondary phases significantly enhances phosphorus burial efficiency, impeding return of phosphate to the water column. Both processes impact the marine phosphorus cycle by affecting the primary productivity potential of surface waters.

Topics of Special Interest in Marine Phosphorus Research

Phosphate Oxygen Isotopes (δ^{18}O-PO$_4$)

Use of the oxygen isotopic composition of phosphate in biogenic hydroxyapatite (bones, teeth) as a paleotemperature and climate indicator was pioneered by Longinelli in the late 1960s–early 1970s, and has since been fairly widely and successfully applied. A novel application of the oxygen isotope system in phosphates is its use as a tracer of biological turnover of phosphorus during metabolic processes. Phosphorus has only one stable isotope (^{31}P) and occurs almost exclusively as orthophosphate (PO_4^{3-}) under Earth surface conditions. The phosphorus–oxygen bond in phosphate is highly resistant to nonenzymatic oxygen isotope exchange reactions, but when phosphate is metabolized by living organisms, oxygen isotopic exchange is rapid and extensive. Such exchange results in temperature-dependent fractionations between phosphate and ambient water. This property renders phosphate oxygen isotopes useful as indicators of present or past metabolic activity of organisms, and allows distinction of biotic from abiotic processes operating in the cycling of phosphorus through the environment.

Currently, the δ^{18}O-PO$_4$ system is being applied in a number of studies of marine phosphorus cycling, including (i) application to dissolved sea water inorganic phosphate as a tracer of phosphate source, water mass mixing, and biological productivity; (ii) use in phosphates associated with ferric iron oxyhydroxide precipitates in submarine ocean ridge sediments, where the δ^{18}O-PO$_4$ indicates microbial phosphate turnover at elevated temperatures. This latter observation suggests that phosphate oxygen isotopes may be useful biomarkers for fossil hydrothermal vent systems.

Reevaluating the Role of Phosphorus as a Limiting Nutrient in the Ocean

In terrestrial soils and in the euphotic zone of lakes and the ocean, the concentration of dissolved orthophosphate is typically low. When bioavailable phosphorus is exhausted prior to more abundant nutrients, it limits the amount of sustainable biological productivity. Phosphorus limitation in lakes is widely accepted, and terrestrial soils are often phosphorus-limited. In the oceans, however, phosphorus limitation is the subject of controversy and debate.

The prevailing wisdom has favored nitrogen as the limiting macronutrient in the oceans. However, a growing body of literature convincingly demonstrates that phosphate limitation of marine primary productivity can and does occur in some marine systems. In the oligotrophic gyres of both the western North Atlantic and subtropical North Pacific, evidence in the form of dissolved nitrogen : phosphorus (N:P) ratios has been used to argue convincingly that these systems are currently phosphate-limited. The N:P ratio of phytoplankton during nutrient-sufficient conditions is 16N:1P (the Redfield ratio) (*see* **Redfield Ratio**). A positive deviation from this ratio indicates probable phosphate limitation, while a negative deviation indicates probable nitrogen limitation. In the North Pacific at the Hawaiian Ocean Time Series (HOT) site, there has been a shift since the 1988 inception of the time series to N:P ratios exceeding the Redfield ratio in both particulate and surface ocean dissolved nitrogen and phosphorus (**Figure 3**). Coincident with this shift has been an increase in the prevalence of the nitrogen-fixing cyanobacterium *Trichodesmium* (**Table 3**). Currently, it appears as though the supply of new nitrogen has shifted from a limiting flux of upwelled nitrate from below the euphotic zone to an unlimited pool of atmospheric N_2 rendered bioavail-

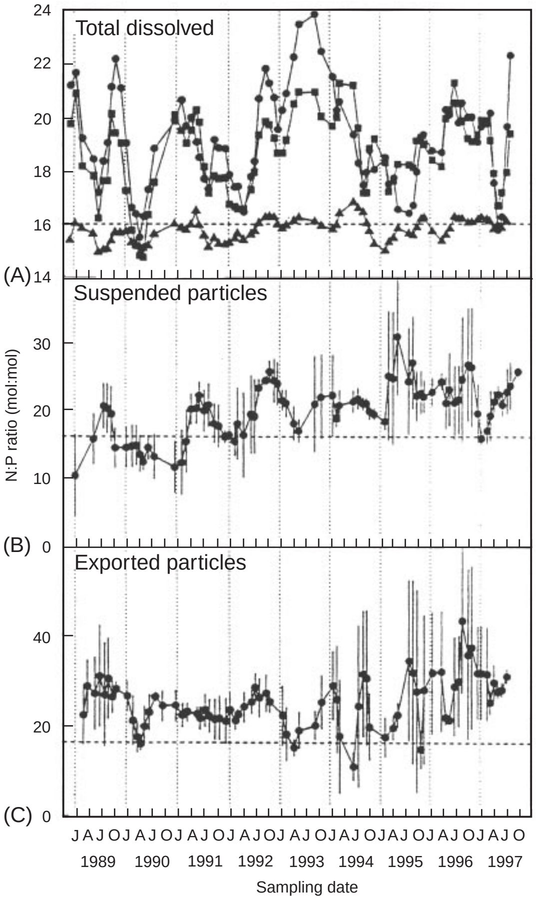

Figure 3 Time-series molar N:P ratios in (A) the dissolved pool, (B) suspended particulate matter, and (C) exported particulate matter from the HOT time series site at station ALOHA in the subtropical North Pacific near Hawaii. (A) The 3-point running mean N:P ratios for 0–100 m (circles), 100–200 m (squares), and 200–500 m (triangles). (B) The 3-point running mean (± 1 SD) for the average suspended particulate matter in the upper water column (0–100 m). (C) The 3-point running mean (± 1 SD) for the average N:P ratio of sediment trap-collected particulate matter at 150 m. The Redfield ratio (N:P = 16) is represented by a dashed line in all three panels. Particulate and upper water column dissolved pools show an increasing N:P ratio throughout the time-series, with a preponderance of values in excess of the Redfield ratio. (After Karl DM, Letelier R, Tupas L *et al.* (1997) The role of nitrogen fixation in the biogeochemical cycling in the subtropical North Pacific Ocean. *Nature* 388: 533–538, with permission.)

able by the action of nitrogen fixers. This shift is believed to result from climatic changes that promote water column stratification, a condition that selects for N_2-fixing microorganisms, thus driving the system to phosphate limitation. A similar situation exists in the subtropical Sargasso Sea at the Bermuda Ocean Time Series (BATS) site, where currently the dissolved phosphorus concentrations (especially dissolved inorganic phosphorus (DIP)) are significantly lower than at the HOT site, indicating even more severe phosphate limitation (**Table 3**).

Table 3 Parameters affecting nutrient limitation: comparison between North Atlantic and North Pacific Gyres

Parameter	*Sargasso Sea*	*Pacific HOT site*
DIP	0.48 ± 0.27^{a}	$9–40^{b}$
TDN (n mol l^{-1})	4512 ± 430	5680 ± 620^{b}
TDP (n mol l^{-1})	75 ± 42	222 ± 14^{b}
TDN : TDP	60 ± 7	26 ± 3^{b}
N_2-fixation rate (mmol N m^{-2} y^{-1})	72^{c}	$31–51^{c}$

After Wu J, Sunda W, Boyle EA and Karl DM (2000) *Science* 289: 759, with permission.

[a] Average DIP between 26° and 31°N in Sargasso Sea surface waters in March 1998.

[b] North Pacific near Hawaii at station ALOHA (the HOT site) during 1991–1997.

[c] See Wu *et al.* (2000) for method of calculation or measurement.

A number of coastal systems also display evidence of phosphate limitation, sometimes shifting seasonally from nitrogen to phosphate limitation in concert with changes in environmental features such as upwelling and river runoff. On the Louisiana Shelf in the Gulf of Mexico, the Eel River Shelf of northern California (USA), the upper Chesapeake Bay (USA), and portions of the Baltic Sea, surface water column dissolved inorganic N:P ratios indicate seasonal phosphate limitation. The suggestion of phosphate limitation is reinforced in the Louisiana Shelf and Eel River Shelf studies by the occurrence, or presence of alkaline phosphatase activity, an enzyme induced only under phosphate-limiting conditions. Alkaline phosphatase has also been observed seasonally in Narragansett Bay. Although these coastal sites are recipients of anthropogenically derived nutrients (nitrogen and phosphate) that stimulate primary productivity above 'natural' levels, the processes that result in shifts in the limiting nutrient are not necessarily related to anthropogenic effects. Other oceanic sites where phosphorus limitation of primary productivity has been documented include the Mediterranean Sea and Florida Bay (USA).

One key question that studies of nitrogen and phosphorus limitation must address before meaningful conclusions may be drawn about phosphorus versus nitrogen limitation of marine primary productivity is the extent to which the dissolved organic nutrient pools are accessible to phytoplankton. In brief, this is the question of bioavailability. Many studies of nutrient cycling and nutrient limitation do not include measurement of these quantitatively important nutrient pools, even though there is indisputable evidence that at least some portion of the dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) pools is bioavailable. An important direction for future research is to characterize the DON and DOP pools at the molecular level, and to evaluate what fraction of these are bioavailable. The analytical challenge of identifying the molecular composition of the DOP pool is significant. Recent advances in ^{31}P-nuclear magnetic resonance (NMR) spectroscopy have permitted a look at the high molecular weight ($>1\,$nm) fraction of the DOP pool. However, this fraction represents only one-third of the total DOP pool; the other two-thirds of this pool, made up of smaller-molecular-weight DOP compounds, remains outside our current window of analytical accessibility.

Debate continues among oceanographers about the most probable limiting nutrient on recent and on long, geological timescales. While there is an abundant reservoir of nitrogen (gaseous N_2) in the atmosphere that can be rendered bioavailable by nitrogen-fixing photosynthetic organisms, phosphorus supply to the ocean is limited to that weathered off the continents and delivered by rivers, with some minor atmospheric input. As a consequence of continental weathering control on phosphorus supply to the oceans, phosphorus limitation has been considered more likely than nitrogen limitation on geological timescales. As the recent studies reviewed in this section suggest, phosphorus limitation may be an important phenomenon in the modern ocean as well. Overall, current literature indicates that there is a growing appreciation of the complexities of nutrient limitation in general, and the role of phosphorus limitation in particular, in both fresh water and marine systems.

Cosmogenic ^{32}P and ^{33}P as Tracers of Phosphorus Cycling in Surface Waters

There are two radioactive isotopes of phosphorus, ^{32}P (half-life = 14.3 days) and ^{33}P (half-life = 25.3 days). Both have been widely used in the study of biologically mediated phosphorus cycling in aquatic systems. Until very recently, these experiments have been conducted by artificially introducing radiophosphorus into laboratory incubations or, far more rarely, by direct introduction into natural waters under controlled circumstances. Such experiments necessarily involve significant perturbation of the system, which can complicate interpretation of results. Recent advances in phosphorus sampling and radioisotope measurement have made it possible to use naturally produced ^{32}P and ^{33}P as *in situ* tracers of phosphorus recycling in surface waters. This advance has permitted studies of net phosphorus recycling in the absence of experimental perturbation caused by addition of artificially introduced radiophosphorus.

^{32}P and ^{33}P are produced naturally in the atmosphere by interaction of cosmic rays with atmospheric argon nuclei. They are then quickly scavenged onto aerosol particles and delivered to the ocean surface predominantly in rain. The ratio of ^{33}P/^{32}P introduced to the oceans by rainfall remains relatively constant, despite the fact that absolute concentrations can vary from one precipitation event to another. Once the dissolved phosphorus is incorporated into a given surface water phosphorus pool (e.g., by uptake by phytoplankton or bacteria, grazing of phytoplankton or bacteria by zooplankton, or abiotic sorption), the ^{33}P/^{32}P ratio will increase in a systematic way as a given pool ages. This increase in the ^{33}P/^{32}P ratio with time results from the different half-lives of the two phosphorus radioisotopes. By measuring the ^{33}P/^{32}P ratio in rain and in different marine phosphorus pools – e.g., DIP, DOP (sometimes called soluble nonreactive phosphorus, or SNP), and particulate phosphorus of various size classes corresponding to different levels in the food chain – the net age of phosphorus in any of these reservoirs can be determined (**Table 4**). New insights into phosphorus cycling in oceanic surface waters derived from recent work using the cosmogenically produced ^{33}P/^{32}P ratio include the following. (1) Turnover rates of dissolved inorganic phosphorus in coastal and oligotrophic oceanic surface waters ranges from 1 to 20 days. (2) Variable turnover rates in the DOP pool range from <1 week to >100 days, suggesting differences in either the demand for DOP, or the lability of DOP toward enzymatic breakdown. (3) In the Gulf of Maine, DOP turnover times vary seasonally, increasing from 28 days in July to >100 days in August, suggesting that the DOP pool may evolve compositionally during the growing seasons. (4) Comparison of the ^{33}P/^{32}P ratio in different particulate size classes indicates that the age of phosphorus generally increases at successive levels in the food chain. (5) Under some circumstances, the ^{33}P/^{32}P ratio can reveal which dissolved pool is being ingested by a particular size class of organisms. Utilization of this new tool highlights the dynamic nature of phosphorus cycling in surface waters by revealing the rapid rates and temporal variability of phosphorus turnover. It further stands to provide new insights into ecosystem nutrient dynamics by revealing, for example, that low phosphorus concentrations can support high primary productivity through rapid turnover rates, and

Table 4 Turnover rates of dissolved inorganic phosphorus (DIP)[a] and dissolved organic phosphorus (DOP)[b] in surface sea water

	Phosphorus turnover rate		
Phosphorus pool	*Coastal*	*Open Ocean*	*References*
DIP	<1 h to 10 d (>1000 d in Bedford Basin)	Weeks to months	c, d, e, f, g, h, i, j, k, l, m
Total DOP	3 to >90 d	50 to 300 d	l, m, n, o, p, q, r
Bioavailable DOP (model compounds)	2 to 30 d	1 to 4 d	k, s, t, u
Microplankton ($<1\,\mu$m)	>1 to 3 d	NA	m
Phytoplankton ($>1\,\mu$m)	<1 to 8 d	<1 week	m, v
Macrozooplankton ($>280\,\mu$m)	14 to 40 d	30 to 80 d	m, p, q, v, w

After Benitez-Nelson CR (2000) *Earth-Science Reviews* 51: 109, with permission.

[a] DIP is equivalent to the soluble reactive phosphorus (SRP) pool, which may include some phosphate derived from hydrolysis of DOP (e.g., see Monaghan EJ and Ruttenberg KC (1998) *Limnology and Oceanography* 44(7): 1702).

[b] DOP is equivalent to the soluble nonreactive phosphorus (SNP) pool which may include dissolved inorganic polyphosphates (e.g., see Karl DM and Yanagi K (1997) *Limnology and Oceanography* 42: 1398).

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that there is preferential utilization of particular dissolved phosphorus pools by certain classes of organisms.

The Oceanic Residence Time of Phosphorus

As phosphorus is the most likely limiting nutrient on geological timescales, an accurate determination of its oceanic residence time is crucial to understanding how levels of primary productivity may have varied in the Earth's past. Residence time provides a means of evaluating how rapidly the oceanic phosphorus inventory may have changed in response to variations in either input (e.g., continental weathering, dust flux) or output (e.g., burial with sediments). In its role as limiting nutrient, phosphorus will dictate the amount of surface-ocean net primary productivity, and hence atmospheric CO_2 drawdown that will occur by photosynthetic biomass production. It has been suggested that this so-called 'nutrient–CO_2' connection might link the oceanic phosphorus cycle to climate change due to reductions or increases in the atmospheric greenhouse gas inventory. Oceanic phosphorus residence time and response time (the inverse of residence time) will dictate the timescales over which such a phosphorus-induced climate effect may operate.

Over the past decade there have been several reevaluations of the marine phosphorus cycle in the literature, reflecting changes in our understanding of the identities and magnitudes of important phosphorus sources and sinks. One quantitatively important newly identified marine phosphorus sink is precipitation of disseminated authigenic carbonate fluoroapatite (CFA) in sediments in nonupwelling environments. CFA is the dominant phosphorus mineral in economic phosphorite deposits. Its presence in terrigenous-dominated continental margin environments is detectable only by indirect methods (coupled pore water/solid-phase chemical analyses), because dilution by terrigenous debris renders it below detection limits of direct methods (e.g. X-ray diffraction). Disseminated CFA has now been found in numerous continental margin environments, bearing out early proposals that this is an important marine phosphorus sink. A second class of authigenic phosphorus minerals identified as a quantitatively significant phosphorus sink in sandy continental margin sediments are aluminophosphates. Continental margins in general are quantitatively important sinks for organic and ferric iron-bound phosphorus, as well. When newly calculated phosphorus burial fluxes in continental margins, including the newly identified CFA and aluminophosphate (dominantly aluminum rare-earth phosphate) sinks are combined with older estimates of phosphorus burial fluxes in the deep sea, the overall burial flux results in a much shorter residence time than the canonical value of 100 000 years found in most text books (**Table 5**). This reduced residence time suggests that the oceanic phosphorus-cycle is subject to perturbations on shorter timescales than has previously been believed.

The revised, larger burial flux cannot be balanced by the dissolved riverine input alone. However, when the fraction of riverine particulate phosphorus that is believed to be released upon entering the marine realm is taken into account, the possibility of a balance between inputs and outputs becomes more feasible. Residence times estimated on the basis of phosphorus inputs that include this 'releasable' riverine particulate phosphorus fall within the range of residence time estimates derived from phosphorus burial fluxes (**Table 5**). Despite the large uncertainties associated with these numbers, as evidenced by the maximum and minimum values derived from both input and removal fluxes, these updated residence times are all significantly shorter than the canonical value of 100 000 years. Revised residence times on the order of 10 000–17 000 y make phosphorus-perturbations of the ocean–atmosphere CO_2 reservoir on the timescale of glacial–interglacial climate change feasible.

Table 5 Revised oceanic phosphorus input fluxes, removal fluxes, and estimated oceanic residence time

	Flux description[a]	*Flux* (10^{12} *mol P* y^{-1})	*Residence time* (*y*)[e]
Input fluxes			
F_{84}	atmosphere → surface ocean	0.02–0.05	
$F_{24(d)}$	soil → surface ocean (river dissolved P flux)[b]	0.032–0.058	
$F_{24(p)}$	soil → surface ocean (river particulate P flux)[b]	0.59–0.65	
	Minimum reactive-P input flux	0.245	12 000
	Maximum reactive-P input flux	0.301	10 000
Removal fluxes			
sF_{cs}	Best estimate of total-P burial in continental margin marine sediments (**Table 2**, note j)[c]	0.150	
sF_{as}	Best estimate of total-P burial in abyssal marine sediments (**Table 2**, note j)[c]	0.130	
	Minimum estimate of reactive-P burial in marine sediments[d]	0.177	17 000
	Maximum estimate of reactive-P burial in marine sediments[d]	0.242	12 000

[a] All fluxes are from **Table 2**.

[b] As noted in **Table 2**, 30% of atmospheric aerosol phosphorus (Duce *et al.* (1991) *Global Biogeochemical Cycles* 5: 193) and 25–45% of the river particulate flux (see note (f) in **Table 2**) is believed to be mobilized upon entering the ocean. The reactive phosphorus input flux was calculated as the sum of $0.3(F_{84}) + F_{24(d)} + 0.35(F_{24(p)})$, where the mean value of the fraction of riverine particulate phosphorus flux estimated as reactive phosphorus (35%) was used. Reactive phosphorus is defined as that which passes through the dissolved oceanic phosphorus reservoir, and thus is available for biological uptake.

[c] These estimates are favored by the author, and reflect the minimum sF_{cs} and maximum sF_{as} fluxes given in **Table 2**. Because the reactive phosphorus contents of continental margin and abyssal sediments differ (see **Table 2** and note d, below), these fluxes must be listed separately in order to calculate the whole-ocean reactive phosphorus burial flux. See note (j) in **Table 2** for other published estimates of reactive-phosphorus burial flux.

[d] As noted in **Table 2**, between 40% and 75% of phosphorus buried in continental margin sediments is potentially reactive, and 90% to 100% of phosphorus buried in abyssal sediments is potentially reactive. The reactive phosphorus fraction of the total sedimentary phosphorus reservoir represents that which may have passed through the dissolved state in oceanic waters, and thus represents a true phosphorus sink from the ocean. The minimum reactive phosphorus burial flux was calculated as the sum of $0.4(sF_{cs}) + 0.9\,(sF_{as})$; the maximum reactive phosphorus burial flux was calculated as the sum of $0.75(sF_{cs}) + 1(sF_{as})$. Both the flux estimates and the % reactive phosphorus estimates have large uncertainties associated with them.

[e] Residence time estimates are calculated as the oceanic phosphorus inventory (reservoirs #4 and 5 (**Table 1**) $= 3 \times 10^{15}$ mol P) divided by the minimum and maximum input and removal fluxes.

Long Time-Scale Phosphorus Cycling, and Links to Other Biogeochemical Cycles

The biogeochemical cycles of phosphorus and carbon are linked through photosynthetic uptake and release during respiration. During times of elevated marine biological productivity, enhanced uptake of surface water CO_2 by photosynthetic organisms results in increased CO_2 evasion from the atmosphere, which persists until the supply of the least abundant nutrient is exhausted. On geological timescales, phosphorus is likely to function as the limiting nutrient and thus play a role in atmospheric CO_2 regulation by limiting CO_2 drawdown by oceanic photosynthetic activity. This connection between nutrients and atmospheric CO_2 could have played a role in triggering or enhancing the global cooling that resulted in glacial episodes in the geological past. It has recently been proposed that tectonics may play the ultimate role in controlling the exogenic phosphorus mass, resulting in long-term phosphorus-limited productivity in the ocean. In this formulation, the balance between subduction of phosphorus bound up in marine sediments and underlying crust and creation of new crystalline rock sets the mass of exogenic phosphorus.

Phosphorus and oxygen cycles are linked through the redox chemistry of iron. Ferrous iron is unstable at the Earth's surface in the presence of oxygen, and oxidizes to form ferric iron oxyhydroxide precipitates, which are extremely efficient scavengers of dissolved phosphate. Resupply of phosphate to surface waters where it can fertilize biological productivity is reduced when oceanic bottom waters are well oxygenated owing to scavenging of phosphate by ferric oxyhydroxides. In contrast, during times in Earth's history when oxygen was not abundant in the atmosphere (Precambrian), and when expanses of the deep ocean were anoxic (e.g., Cretaceous), the potential for a larger oceanic dissolved phosphate inventory could have been realized due to the reduced importance of sequestering with ferric oxyhydroxides. This iron–phosphorus–oxygen coupling produces a negative feedback, which may have kept atmospheric O_2 within equable levels throughout the Phanerozoic. Thus, it is in the oceans that the role of phosphorus as limiting nutrient has the greatest repercussions for the global carbon and oxygen cycles.

Summary

The global cycle of phosphorus is truly a biogeochemical cycle, owing to the involvement of phosphorus in both biochemical and geochemical reactions and pathways. There have been marked advances in the last decade on numerous fronts of phosphorus research, resulting from application of new methods as well as rethinking of old assumptions and paradigms. An oceanic phosphorus residence time on the order of 10 000–20 000 y, a factor of 5–10 shorter than previously cited values, casts phosphorus in the role of a potential player in climate change through the nutrient–CO_2 connection. This possibility is bolstered by findings in a number of recent studies that phosphorus does function as the limiting nutrient in some modern oceanic settings. Both oxygen isotopes in phosphate ($\delta^{18}O\text{-}PO_4$) and *in situ*-produced radiophosphorus isotopes (^{33}P and ^{32}P) are providing new insights into how phosphorus is cycled through metabolic pathways in the marine environment. Finally, new ideas about global phosphorus cycling on long, geological timescales include a possible role for phosphorus in regulating atmospheric oxygen levels via the coupled iron–phosphorus–oxygen cycles, and the potential role of tectonics in setting the exogenic mass of phosphorus. The interplay of new findings in each of these areas is providing us with a fresh look at the marine phosphorus cycle, one that is sure to evolve further as these new areas are explored in more depth by future studies.

See also

Carbon Cycle. Eutrophication. Nitrogen Cycle. Phytoplankton Blooms. Redfield Ratio.

Further Reading

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PHOTOCHEMICAL PROCESSES

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doi:10.1006/rwos.2001.0072

Introduction

Life on Earth is critically dependent on the spectral quality and quantity of radiation received from the sun. The absorption of visible light (wavelengths from 400 to 700 nm) by pigments within terrestrial and marine plants initiates a series of reactions that ultimately transforms the light energy to chemical energy, which is stored as reduced forms of carbon. This complex photochemical process, known as photosynthesis, not only provides all of the chemical energy required for life on Earth's surface, but also acts to decrease the level of a major greenhouse gas, CO_2, in the atmosphere. By contrast, the absorption of ultraviolet light in the UV-B (wavelengths from 280 to 320 nm) and UV-A (wavelengths from 320 to 400 nm) by plants (as well as other organisms) can produce seriously deleterious effects (e.g. photoinhibition), leading to a decrease in the efficiency of photosynthesis and direct DNA damage (UV-B), as well as impairing or destroying other important physiological processes. The level of UV-B radiation received at the Earth's surface depends on the concentration of ozone (O_3) in the stratosphere where it is formed photochemically. The destruction of O_3 in polar regions, leading to increased levels of surface UV-B radiation in these locales, has been enhanced by the release of man-made chlorofluorocarbons (CFCs), but may also be influenced in part by the natural production of halogenated compounds by biota.

These biotic photoprocesses have long been recognized as critical components of marine ecosystems and air–sea gas exchange, and have been studied extensively. However, only within the last decade or so has the impact of abiotic photoreactions on the chemistry and biology of marine waters and their possible coupling with atmospheric processes been fully appreciated. Light is absorbed in the oceans not only by phytoplankton and water, but also by colored dissolved organic matter (CDOM), particulate detrital matter (PDM), and other numerous trace light-absorbing species. Light absorption by these constituents, primarily the CDOM, can have a number of important chemical and biological consequences including: (1) reduction of potentially harmful UV-B and UV-A radiation within the water column; (2) photo-oxidative degradation of organic matter through the photochemical production of reactive oxygen species (ROS) such as superoxide (O_2^-), hydrogen peroxide (H_2O_2), the hydroxyl radical (OH) and peroxy radicals (RO_2); (3) changes in metal ion speciation through reactions with the ROS or through direct photochemistry, resulting in the altered biological availability of some metals; (4) photochemical production of a number of trace gases of importance in the atmosphere such as CO_2, CO, and carbonyl sulfide (COS), and the destruction