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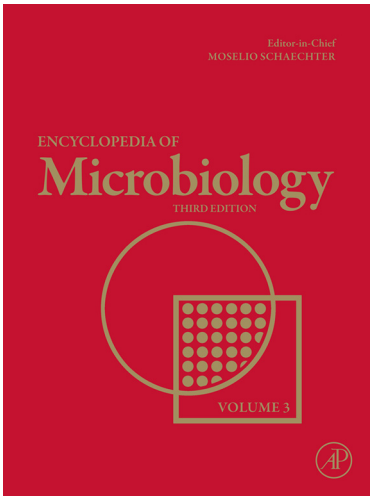

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Phosphorus Cycle

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Glossary

assimilation (transitory immobilization) The process of incorporating nutrients into cellular biomass.
authigenic Formed *in situ* rather than by having been transported or deposited in a location through secondary processes.
chelation The reversible binding (complexation) of a ligand to a metal ion.
diagenesis The process by which sediment undergoes chemical and physical changes during its lithification.
eolian transport Advection of material via the atmosphere or wind.
eutrophication Excessive nutrients in a body of water that cause a dense algal growth, followed by algal decomposition, anoxia, and impairment of the aquatic community.
immobilization The process by which labile phosphorus is sequestered and removed from the environmental reservoir of reactive phosphorus for a period of time.
inorganic phosphorus A class of chemical compounds that comprises those not existing in or derived immediately from living organisms (e.g., orthophosphate).
mineral formation Processes in which anions react with cations in the environment to form insoluble precipitates.
mineralization The conversion of organic matter into simple inorganic compounds, primarily by microbial decomposition.
nutrient limitation The cessation of photosynthetic biomass production in response to low availability of a physiologically important nutrient or nutrients.
organic phosphorus A class of chemical compounds that comprises only those existing in or derived from living organisms.
orthophosphate Form of orthophosphoric acid (H_3PO_4) in which three protons have been lost (i.e., PO_4^{3-}); also called the phosphate anion.
primary production The conversion of radiant or chemical energy into organic matter.
productivity The rate at which radiant energy is used by producers to form organic substances as food for consumers.
solubilization The conversion of insoluble compounds into soluble compounds.
weathering Processes by which rocks, minerals, and soils get broken down through direct contact with the atmosphere; can be physical or chemical.

Abbreviations

ELF	enzyme-labeled fluorescence
PhoA	alkaline phosphomonoesterase
Pit	phosphate transport system
PNP	*para*-nitrophenyl phosphate
Pst	phosphate-specific transport
SRP	soluble reactive phosphorus

Defining Statement

This article includes a discussion of the global phosphorus cycle, including sources, sinks, and transport pathways of phosphorus in the environment, microbially mediated transformations of phosphorus and their genetic regulation, and a discussion of microbial responses to anthropogenic changes to the phosphorus cycle.

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Introduction

Phosphorus is an essential nutrient for all living organisms, and the phosphorus cycle is an important link between Earth's living and nonliving entities. The availability of phosphorus strongly influences primary production, the process by which photosynthetic organisms fix inorganic carbon into cellular biomass. Therefore, knowledge of the phosphorus cycle is critically important for understanding the global carbon budget and hence how biogeochemical cycles impact and are influenced by global climate.

Global Significance of the Phosphorus Cycle

Natural assemblages of microbes have a critical role in the phosphorus cycle because they forge a link between phosphorus reservoirs in the living and nonliving environment. Microbes facilitate the weathering, mineralization, and solubilization of nonbioavailable phosphorus sources, making orthophosphate available to microbial and plant communities and hence to higher trophic levels within the food web. However, microbes also contribute to immobilization of phosphorus, a process that diminishes bioavailable phosphorus by converting soluble reactive forms into insoluble forms. The mechanisms of microbial involvement in these processes vary from passive (e.g., resulting from microbial metabolic byproducts) to highly regulated active contributions (e.g., the regulation of gene expression in response to environmental cues).

Microbially mediated processes also link the phosphorus cycle to the carbon cycle and hence to global climate. During photosynthesis, photoautotrophs incorporate phosphorus and carbon at predictable ratios, with approximately 106 carbon atoms assimilated for every one phosphorus atom for marine photoautotrophs and terrestrial vegetation. The phosphorus cycle therefore plays an important role in regulating primary productivity, the process in which radiant energy is used by primary producers to form organic substances as food for consumers, as in photosynthesis.

Because phosphorus is required for the synthesis of numerous biological compounds, its availability in the environment can limit the productivity of producers when other nutrients are available in excess. This fact carries important implications for the global carbon budget because the rate of incorporation (fixation) of carbon dioxide into photosynthetic biomass can be directly controlled by the availability of phosphorus; if phosphorus is not available, carbon dioxide fixation is halted. The intersection of the phosphorus and carbon cycles is of particular significance for global climate, which is affected by atmospheric carbon dioxide levels. Hence, through the growth of producers, the phosphorus cycle contributes to the regulation of global climate.

In aquatic environments, photosynthetic microbes (i.e., phytoplankton) may comprise a substantial portion of the photosynthetic biomass and hence primary production. Marine and freshwater phytoplankton are characterized by extensive biodiversity, and as a group, inhabit an incredible number of different niches within aquatic environments. Phytoplankton, like other microbes, have strategies that enable them to adapt to changes in the amounts and forms of phosphorus available within their environment. For example, the production of phosphatase enzymes, which hydrolyze organic P compounds to inorganic phosphate, helps to mediate the mineralization of organic phosphorus compounds in surface waters and allows cells to adapt when phosphate levels are low.

Recent estimates suggest that phytoplankton are responsible for as much as half of global carbon fixation, thereby contributing significantly to the regulation of Earth's climate. Phytoplankton productivity is strongly influenced by nutrient availability, and which nutrient ultimately limits production depends on (1) the relative abundance of nutrients and (2) the nutritional requirements of the phytoplankton. With some exceptions, production in most lakes is limited by the availability of phosphorus, whereas limitation of primary production in the ocean has traditionally been attributed to nitrogen, another nutrient required by cells in large quantities. However, phosphorus differs from nitrogen in that the major source of phosphorus to aquatic environments is the weathering of minerals on land that are subsequently introduced into water bodies by fluvial and aeolian sources. In contrast, microbially mediated nitrogen fixation, in which bioavailable forms of nitrogen are generated from nitrogen gas in the atmosphere, is a major pathway by which phytoplankton gain access to nitrogen (in addition to continental weathering). Because there is no phosphorus input process analogous to nitrogen fixation, marine productivity over geological timescales is considered to be a function of the supply rate of phosphorus from continental weathering and the rate at which phosphorus is recycled in the ocean. Accordingly, the phosphorus cycle influences phytoplankton ecology, productivity, and carbon cycling in both marine and freshwater ecosystems.

Characterizing and Measuring Environmental Phosphorus Pools

Occurrence of elemental phosphorus in the environment is rare, given that it reacts readily with oxygen and combusts when exposed to oxygen; thus phosphorus is typically found bound to oxygen in nature. Phosphorus has the chemical ability to transfer a 3s or p-orbital electron to a d-orbital, permitting a relatively large

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number of potential configurations of electrons around the nucleus of the atom. This renders the structures of phosphorous-containing molecules quite variable and relatively reactive. These properties are likely responsible for the ubiquity and versatility of phosphorus-containing compounds in biological systems.

Because phosphorus exists in many different physical and chemical states in the environment, specific definitions are needed to clarify different parts of the phosphorus pool. Chemical names reflect the chemical composition of the phosphorus substance in question, whereas other classifications are based on methodological aspects of how the substance is measured. For example, 'orthophosphate' is a chemical term that refers specifically to a phosphorus atom bound to four oxygen atoms – forming the orthophosphate molecule (PO_4^{3-}, also referred to as phosphate), whereas the term 'soluble reactive phosphorus' (SRP) is a methodological term referring to everything that gets measured when an orthophosphate assay is performed (such as the ascorbic acid method, described below). The majority of measured SRP comprises orthophosphate and other related derivatives (e.g., $H_2PO_4^-$, HPO_4^{2-} depending on pH) but other forms of phosphorus may also be included due to experimental inaccuracy. Therefore, although SRP tends to closely reflect the amount of orthophosphate in a sample, the values may not be identical.

The most common assay for measuring SRP is the ascorbic acid method, which is approved by the US Environmental Protection Agency for monitoring phosphate in environmental samples. In this method, ascorbic acid and ammonium molybdate react with SRP in the sample, forming a blue compound that can be observed visually or determined spectrophotometrically. Assays for measuring total phosphorus are also based on the ascorbic acid method, but begin with a step to transform all of the phosphorus in the sample to orthophosphate (typically through digestion by heating the sample in the presence of acid). After digestion, the sample is analyzed by the ascorbic acid method. A filtration step is typically not included in either of these methods, and accordingly in such cases, all size fractions are measured.

When phosphorus is measured in water samples, distinguishing forms that are part of particulate matter from those that are in solution is often useful. Phosphorus is therefore classified as 'soluble' or 'insoluble', a distinction based on the method used to measure the sample. Soluble phosphorus includes all forms of phosphorus that are distributed in solution and that pass through a filter with a given pore size (typically 0.45 μm), whereas the insoluble, or particulate, fraction is the amount retained on the filter. Measurements of soluble phosphorus include both the 'dissolved' and 'colloidal' fractions. Dissolved phosphorus includes all forms that have entered a solute to form a homogeneous solution. (For example, orthophosphate that is not bound to a cation is considered dissolved because it is associated with water molecules homogeneously in solution rather than being held within a salt crystal.) By contrast, colloidal forms include any tiny particles that are distributed evenly throughout the solution but that are not dissolved in solution. Soluble phosphorus is commonly reported because colloidal phosphorus particles are very small, and differentiating between colloidal and dissolved phosphorus is methodologically difficult.

When living organisms assimilate phosphorus into their cells, the resulting phosphorus-containing compounds are collectively called 'organic phosphorus'. It must be stressed that this definition of the biologically associated phosphorus as 'organic phosphorus' is not identical to the chemical definition of organic compounds (e.g., containing carbon). For example, some intracellular biologically synthesized compounds such as polyphosphate may not contain C bonding. The term organic phosphorus encompasses molecules within living cells as well as molecules that are liberated into the environment after decay of an organism. The major source of terrestrial organic phosphorus is plant material, which is released as vegetation undergoes decay; however, microbial and animal sources also contribute significantly. In the marine environment, organic phosphorus comes from a variety of sources (e.g., plankton, fish excrement, advection from land), the relative contributions of which differ widely depending on location in the ocean. In contrast to organic forms, inorganic phosphorus compounds are not always directly of biogenic origin. Rather, they also encompass phosphorus derived from the weathering of phosphate-containing minerals, including dissolved and particulate orthophosphate.

Phosphorus Sources, Sinks, and Transport Pathways

The phosphorus cycle encompasses numerous living and nonliving environmental reservoirs and various transport pathways. In tracing the movement of phosphorus in the environment, the interplay between physical and biological processes becomes apparent. In addition to acting as reservoirs of phosphorus in the environment (as discussed in this section), microbes contribute to the transformation of phosphorus within other reservoirs such as in soil or aquatic environments (see 'Microbially mediated processes').

Within the Earth's crust, the abundance of phosphorus is 0.10–0.12% (on a weight basis), with the majority of phosphorus existing as inorganic phosphate minerals and phosphorus-containing organic compounds. A phosphate mineral is any mineral in which phosphate anion groups form tetrahedral complexes in association with cations, although arsenate (AsO_4^{3-}) and vanadanate (VO_4^{3-}) may also be substituted in the crystalline

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structure. Apatite is the most abundant group of phosphate minerals, comprising hydroxyapatite, fluorapatite, and chlorapatite (Table 1). These three forms of apatite share nearly identical crystalline structures, but differ in their relative proportions of hydroxide, fluoride, and chloride, each being named for the anion that is most abundant in the mineral. Phosphate minerals generally form in the environment in magmatic processes or through precipitation from solution (which may be microbially mediated), and the chemical composition of the minerals depends on the ion or ions present in solution at the time of precipitation. For this reason, it is not uncommon for natural deposits of phosphate minerals to be heterogeneous, rather than composed of one homogeneous type of phosphate mineral. These natural deposits of phosphate minerals are collectively called 'phosphorites' to reflect variations in their chemical compositions.

Table 1 Phosphate minerals and their chemical compositions. Apatite is the general term for the three minerals hydroxylapatite, fluorapatite, and chlorapatite

Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$
Hydroxylapatite	$Ca_5(PO_4)_3OH$
Fluorapatite	$Ca_5(PO_4)_3F$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Frankolite	$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}(CO_3F)_y(SO4)_zF_2$
Lazulite	$(Mg,Fe)Al_2(PO_4)_2(OH)_2$
Monazite	$(Ce,La,Y,Th)PO_4$
Pyromorphite	$Pb_5(PO_4)_3Cl$
Strengite	$FePO_4{\cdot}2H_2O$
Triphylite	$Li(Fe,Mn)PO_4$
Turquoise	$CuAl_6(PO_4)_4(OH)_8{\cdot}5H_2O$
Variscite	$AlPO_4{\cdot}2H_2O$
Vauxite	$FeAl_2(PO_4)_2(OH)_2{\cdot}6H_2O$
Vivianite	$Fe_3(PO_4)_2{\cdot}8H_2O$
Wavellite	$Al_3(PO_4)_2(OH)_3{\cdot}5H_2O$

Soils and lake sediments are another terrestrial reservoir of phosphorus, comprising primarily inorganic phosphorus from weathered phosphate minerals, along with organic phosphorus from the decomposition, excretion, and lysis of biota (Figure 1). The behavior of phosphorus in soils largely depends on the particular characteristics of each soil, and besides microbial activity, factors such as temperature, pH, and the degree of oxygenation all influence phosphorus mobility. In soils, inorganic phosphorus is typically associated with Al, Ca, or Fe, and each compound has unique solubility

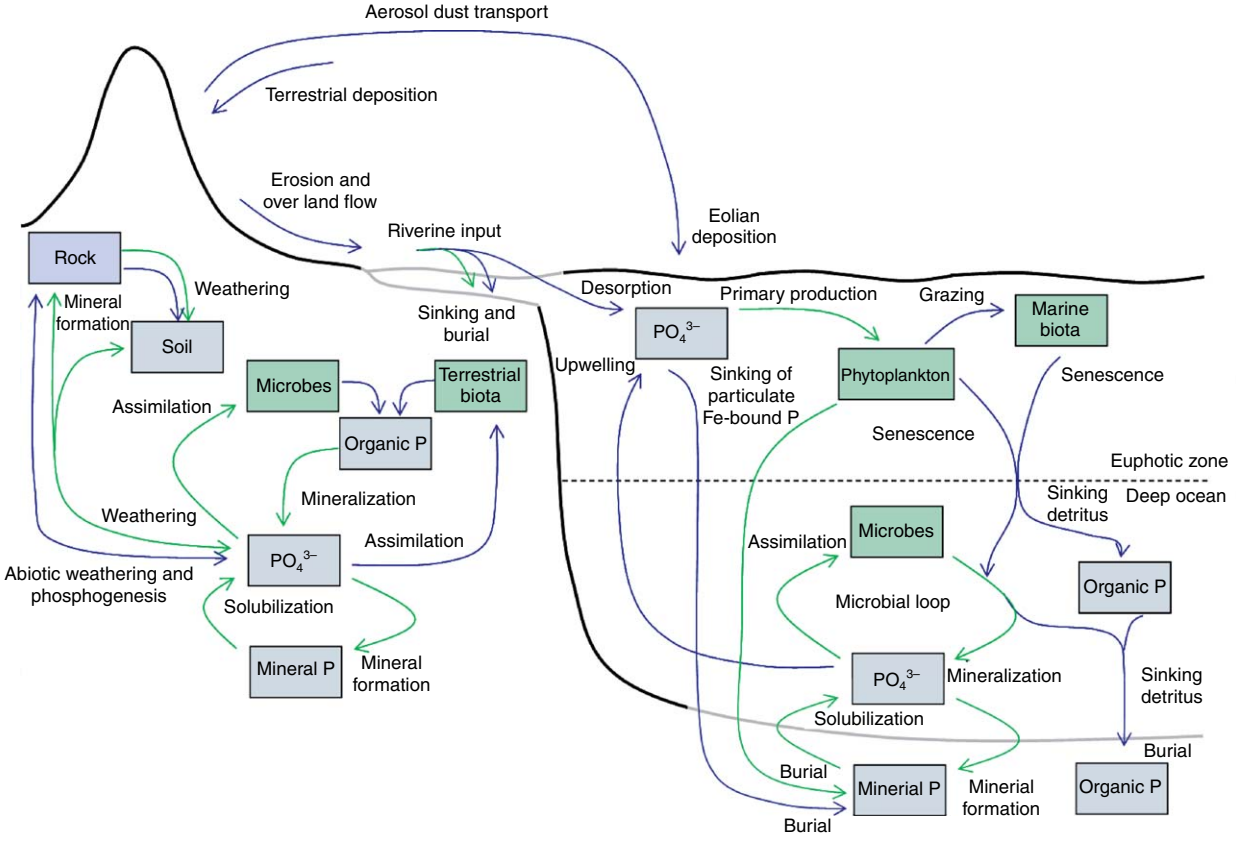

Figure 1 Schematic diagram of the phosphorus cycle showing phosphorus reservoirs (living in green boxes; nonliving in gray boxes), physical transport pathways (blue arrows), and microbially mediated transformations (green arrows).

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characteristics that determine the availability of phosphate to plants. The mobility and bioavailability of phosphate in soils are limited primarily by adsorption (the physical adherence or bonding of phosphate ions onto the surfaces of other molecules), and the rate of microbially mediated mineralization of organic forms of phosphorus. Mineralization is discussed in detail in the section titled 'Microbially mediated processes'.

Marine sediments also represent an important phosphorus reservoir, but because the physical and chemical factors affecting marine sediment differ considerably from those on land, processes controlling phosphorus dynamics in marine sediments are somewhat different from that of soils. In marine sediment, phosphate can be present in insoluble inorganic phosphates minerals (such as phosphorites), which are relatively immobile. Phosphate can also be sorbed onto iron or manganese oxyhydroxides. The sorbed phosphate can regain mobility in response to changes in the redox potential at the sediment–water interface and thus is considered more mobile. As in terrestrial sediments, phosphorus in marine detrital organic matter can also become remobilized as decomposition progresses through microbially mediated processes.

Biota (i.e., microbes, plants, and animals) serve as another reservoir of phosphorus in the environment, as they assimilate phosphorus within their cellular biomass. Biota can contribute significantly to environmental phosphorus levels; for example, microbial communities contribute 0.5–7.5% of total phosphorus in grassland and pasture topsoil, and up to 26% in indigenous forests. Microbes are also responsible for generating the myriad of organic phosphorus compounds found throughout the environment. In particular, microbes and primary producers play an important role in providing nutrition, including phosphorus, to higher trophic levels by making it biologically available (bioavailable). Phosphorus assimilation is a microbially mediated process, which is discussed in the section titled 'Transitory immobilization'.

Phosphorus is transported within the environment through various mass transfer pathways. For example, rivers are important in the phosphorus cycle as both reservoirs and transport pathways. Phosphorus that has weathered from minerals and has leached or eroded from soils enters rivers through a variety of vectors, including dissolved and particulate forms in water from overland flow and in groundwater, and particulates brought by wind. Approximately 95% of phosphorus in rivers is particulate, and approximately 40% of that is bound within organic compounds. Rivers influence the distribution of phosphorus in soils and lakes by contributing or removing phosphorus, and riverine input is the single largest source of phosphorus to the oceans.

A number of outcomes are possible for phosphorus entering the ocean. Much of the riverine phosphorus flux is trapped in near-shore areas of the ocean, such as continental margins and estuaries, through immediate sedimentation and biological assimilation. The remaining phosphorus enters the dynamic surface ocean, also called the euphotic zone, in which nearly all bioavailable phosphorus is sequestered within biota through primary production. Upon death of the organisms, a fraction of the biologically sequestered phosphorus sinks below the euphotic zone and most of it is regenerated into bioavailable forms like orthophosphate by heterotrophic organisms. This recycling is part of the so-called 'microbial loop'. Physical processes such as upwelling and deep convective mixing draw the deep water, which, in most parts of the ocean, is nutrient-rich compared to the surface waters in the euphotic zone, where up to 95% of it is reused in primary production. The remainder is removed from the ocean reservoir through particulate sedimentation, mineral formation (which may be microbially mediated), and scavenging by iron and manganese oxyhydroxides, all of which deposit phosphorus as a component of ocean sediment.

The phosphorus cycle differs from the cycles of other biologically important elements, such as carbon, nitrogen, and sulfur, in that it lacks a significant gaseous component; nearly all phosphorus in the environment resides either in solid or in aqueous forms. The one exception to this rule is the volatile compound phosphine (PH_3, also called phosphane), a colorless, poisonous gas formed in the environment from the breakdown of alkali metal or alkali earth metal phosphides with water. This process is poorly characterized and likely comprises various multistage chemical reactions. Microbially mediated phosphine production can be a major source of the gas in engineered systems (e.g., sewage treatment facilities and constructed wastewater treatment wetlands) where organic phosphorus is abundant and reducing conditions are common, suggesting that microbes could also play a role in phosphine formation in natural systems (although the direct enzymatic production of phosphine has not yet been identified). Although phosphorus can exist as phosphine, the gas does not persist in the environment owing to rapid autoxidation, precluding significant accumulation of phosphine in the atmosphere. Phosphine is therefore a minor component of the environmental phosphorus pool.

The absence of a significant gaseous phase does not eliminate the atmosphere as an important reservoir in the phosphorus cycle. When weathering and erosion of soils generate inorganic and organic particulate phosphorus, wind transports some of the particles from their source to a new location. These particles can include mineral dust, pollen and plant debris, insect fragments, and organic phosphorus bound to larger particles. This distribution of terrestrial particulate phosphorus, termed eolian deposition, plays an important role in delivering nutrients to the oceans. In oligotrophic ocean waters

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where nutrient levels are naturally low, such as in the open ocean gyres where riverine inputs do not extend and significant upwelling does not occur, eolian deposition may comprise a large portion of the nutrient flux that is available for primary production. The eolian phosphorus flux to the oceans is approximately 1×10^{12} g year^{-1}, of which approximately half is organic and the other half is inorganic. The solubility, and therefore bioavailability, of the phosphorus in eolian particulate matter differs significantly depending on its source; however, estimates suggest that approximately 15–50% is typically soluble.

Microbially Mediated Processes

Weathering

Rock material exposed to the atmosphere breaks down, or weathers, as a result of numerous environmental processes. Weathering processes are classified into two categories. In mechanical weathering, physical processes (including thermal expansion, pressure release, hydraulic action, salt crystal formation, freeze–thaw, and frost wedge events) cause deterioration of rock material without changing the chemical composition of the parent material. In contrast, chemical weathering causes deterioration by altering the chemical structure of the minerals that the rock is made of. Chemical weathering processes include dissolution, hydrolysis, hydration, and oxidation–reduction (redox) reactions. Biological organisms can contribute to mechanical weathering by altering the microenvironments at the surface of the parent material (e.g., by increasing local humidity or by forming biofilms on surfaces); however, most biological weathering processes are classified as chemical weathering because they chemically alter the composition of the parent rock material directly or indirectly. These biological weathering processes are also referred to as solubilization.

Solubilization

Inorganic phosphorus can occur in nature in soluble and insoluble forms. The solubility of the most abundant form of inorganic phosphorus, orthophosphate, is determined by the ambient pH and the cation to which it is bound as a mineral (e.g., Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+}). Microbially mediated phosphorus solubilization plays an important role in the conversion of insoluble phosphorus minerals into soluble forms of phosphorus. Solubilization directly benefits the microbes that perform it by providing the bioavailable phosphorus needed for growth. Similarly, the process benefits other organisms (including other cells, fungi, and higher plants) that are able to utilize the surplus of solubilized phosphorus.

Production of organic and inorganic acids is the primary mechanism of microbial phosphorus solubilization. In this process, biogenic acid interacts with phosphorus minerals to form mono- and dibasic phosphates, thereby bringing phosphorus into solution. Chemoautotrophic bacteria (e.g., nitrifying bacteria and *Thiobacillus* spp.) generate nitric and sulfuric acids by oxidizing ammonium and sulfur, respectively, and these acids are able to liberate soluble phosphorus from apatite, the most abundant phosphorus mineral. Production of organic acids occurs in numerous microbial taxa, and contributes to the solubilization of phosphorus minerals.

In addition to acid production, microbially mediated redox reactions contribute to phosphorus solubilization through the reduction of iron oxyhydroxides and associated ferric phosphate (strengite). In this process, dissimilatory iron reduction of ferric phosphates liberates soluble ferrous iron as well as orthophosphate associated with it. This occurs under reducing conditions, such as in flooded, anoxic soils and in some benthic aquatic environments. In another redox process, hydrogen sulfide (H_2S) produced by sulfur-reducing bacteria reduces the ferric iron in iron phosphate ($FePO_4$) to ferrous iron. In this reaction, iron sulfide and elemental sulfur are precipitated, and orthophosphate is generated.

Microbes also produce chelating compounds that contribute to phosphorus mineral solubilization. Chelation is the reversible binding (complexation) of a ligand to a metal ion. Chelators increase the solubility of insoluble phosphate mineral salts by complexing the metal cations, thereby making dissolution of the salt more energetically favorable. Examples of common chelators produced by microbes include citrate, oxalate, lactate, and 2-ketogluconate.

Mineralization

Plant and animal detritus comprises a large reservoir of organic phosphorus in the soil environment. However, because organically bound phosphorus sources are generally unable to cross cell membranes, most of the organic phosphorus from the detrital pool is not directly available to many living organisms. In order to become bioavailable, phosphorus bound to organic material must first be mineralized to phosphate. Mineralization is the process in which organically bound phosphorus is converted to inorganic phosphate, and is accomplished through the activity of a suite of microbial enzymes. Because this process makes available nutrients that would otherwise be sequestered in nonreactive forms, mineralization provides a vital link between the detrital pool and living organisms. It is estimated that approximately 70–80% of soil microbes are able to participate in phosphorus mineralization.

In general, mineralization is optimal and more phosphorus is liberated in uncultivated soils than in soils

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undergoing extensive cultivation, and a higher proportion of the organic phosphorus pool is mineralized in uncultivated soils. Further, mineralization rates tend to be higher in soils where inorganic phosphates are actively taken up and sequestered in plants and where microbial grazers are present, as would be expected in mature, uncultivated soils with fully developed, autochthonous microbial communities and trophic structures. As in many enzyme-catalyzed systems, mineralization is encouraged by higher levels of available substrate; however, high levels of inorganic phosphate (the product) do not impede the reaction, and mineralization will occur even if an abundance of phosphate is present. Other ambient conditions favoring phosphorus mineralization include warm soil temperatures and near-neutral pH values, which are conditions that also favor mineralization of other elements. Accordingly, phosphorus mineralization rates tend to reflect rates of ammonification and carbon mineralization in soils, and together these microbially mediated mineralization processes yield a C:N:P ratio that is similar to the ratio of these elements in humus (i.e., the organic soil fraction consisting of decomposed vegetable or animal matter.)

Enzymes involved in mineralization comprise a diverse group of proteins, called phosphatases, with a broad range of substrates and substrate affinities, and varying conditions for optimal activity. In addition, phosphatases can either be constitutively expressed by an organism, or the expression can be upregulated under conditions of low phosphate (and in some cases, low carbon). Enzyme synthesis allows microbial cells to access organic phosphorus during periods of phosphate limitation, thereby avoiding the growth limitation and physical stress associated with nutrient deprivation. Phosphatases can be classified based on the type of carbon–phosphorus bond they cleave, but any given phosphatase enzyme may catalyze reactions for numerous organic phosphorus compounds. In other words, a phosphatase enzyme has specific substrate requirements for a class of compounds, but lacks specificity in selecting substrates from within that class. The most common categories of microbial phosphatases contributing to phosphorus mineralization include phosphomonoesterases, phosphodiesterases, nucleases, and nucleotidases, as well as phytases.

Phosphomonoesterases catalyze reactions with phosphomonoesters, which are compounds in which one phosphate group is covalently bound to one carbon atom. The reaction involves the hydrolysis of the phosphorus–carbon bond, generating a free phosphate molecule and an alcohol as products. One example of a phosphomonoester is glycerol phosphate, a source of phosphate and carbon for some microbes. Phosphomonoesterases are further classified as 'acid' or 'alkaline' on the basis of their optimal pH ranges for maximum catalytic activity. Probably as a result of their ubiquity and importance in phosphorus mineralization, phosphomonoesterases tend to be referred to simply as phosphatases in the scientific literature, rather than by their full name, and context is often necessary to determine which group is being referenced. Therefore, a phosphomonoesterase with a pH optima near 8 might be referred to as an 'alkaline phosphatase' rather than an 'alkaline phosphomonoesterase' (PhoA) in the scientific literature.

A similar class of enzymes, phosphodiesterases, attack diester bonds in which a phosphate group is bonded to two separate carbon atoms, such as in phospholipids and nucleic acids. For example, the sugar-phosphate backbone in DNA comprises phosphodiester bonds. With water added across the phosphorus–carbon bond, cleaving of a diester proceeds similarly to the monoester reaction, yielding phosphate and an alcohol. Once a diester has undergone hydrolysis, the resulting alcohol phosphomonoester must undergo another hydrolysis step, catalyzed by a phosphomonoesterase, for phosphorus mineralization to be complete.

Nucleic acids represent an important source of organic nutrients and are released from a cell upon lysis. Their rapid degradation and relatively low concentrations in the environment suggest an important role for nucleic acids as microbial nutrient sources. Many heterotrophic microbes are able to use nucleic acids as their only source of phosphorus, nitrogen, and carbon, and numerous others can use nucleic acids to supplement their nutritional requirements. The mineralization of phosphorus from nucleic acids proceeds in a two-step process involving two different enzymes. In the first step, depolymerizing nuclease enzymes such as DNase for DNA and RNase for RNA cleave the nucleic acid molecules into their constituent monomer nucleotides. Complete phosphorus mineralization of the resulting fragments proceeds via the activity of nucleotidase enzymes, which yield a phosphate group and a nucleoside molecule after hydrolysis.

Phytins, which are complex organic molecules containing up to six phosphate groups, are mineralized by a class of enzymes called phytases. Phytases catalyze hydrolysis of the phosphate ester bonds that attach phosphate groups to the inositol ring, yielding reactive phosphate and a series of lower phosphoric esters. The location on the ring of the first hydrolysis reaction catalyzed by a phytase determines its classification; 3-phytases initiate hydrolysis at the phosphate ester bond of the ring's third carbon atom, whereas 6-phytases initiate at the sixth carbon atom. Hydrolysis by 6-phytases always leads to complete dephosphorylation of the inositol ring, whereas the 3-phytases may lead to incomplete dephosphorylation. Phytases are produced broadly by microbes, plants, and animals. In general, plants produce 6-phytases and microbes produce 3-phytases; however, 6-phytase activity has been observed in *Escherichia coli*. Microbial phytase activity is optimal over a broader range of pH values as compared to plant phytases, with pH

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optima spanning from 2 to 6 (plant phytases are optimal near pH 5). In addition to being affected by ambient pH, hydrolysis by phytases is also influenced by the degree of complexation of the phytin substrate with metal cations.

Because many phosphatase enzymes are synthesized in response to low environmental phosphate levels (i.e., when the cells experience phosphate limitation), phosphatase activity has been used extensively as a metric for determining the nutrient status of microbial communities. The activity of phosphatase enzymes has been measured in many terrestrial, limnic, and marine environments using a variety of methods, and numerous laboratory studies have also been conducted. In the environment, the bulk phosphatase activity of an entire microbial community is commonly measured by incubating soil, sediment, or water samples with a phosphate-bound substrate in which the hydrolytic product undergoes a color change that can be observed visually or spectrophotometrically, such as *para*-nitrophenyl phosphate (PNP) (**Figures 2**(**a**) and **2**(**b**)), phenolphthalein phosphate, glycerophosphate, and 5-bromo-4-chloro-3-indolyl-phosphate (**Figure 2**(**c**)). In addition, measurements can be made fluorometrically for the substrates 3-*O*-methylfluoresein phosphate and 4-methylumbellyferyl phosphate. Radiometric analyses can similarly be made using ^{32}P-labeled glycerol phosphate (or an equivalent molecule). Chemical analysis of the hydrolytic products of glycerol phosphate and other bioenergetically important molecules has also been used to estimate phosphatase activity in bulk populations.

A major drawback to measuring bulk phosphatase activity is that it provides limited information, if any, about which members of the microbial community experience phosphate limitation at the time of sampling. This can be addressed to some extent by size-fractionating cells (as on a filter) before incubation with the substrate, thereby allowing phosphatase activity to be assigned to gross taxonomic classes of organisms. However, size fractionation introduces other obstacles for data interpretation, and results must be interpreted with care. For example, activity in different size fractions can be skewed by groups of bacteria that coalesce to form larger particles, although the individual cells are small and would otherwise be grouped with smaller size fractions. Studies with mixed populations of bacteria and green algae showed that 44% of the measured phosphatase activity was attributable to aggregated groups of cells. Moreover, in the marine environment, substantial phosphatase activity has been shown to persist for 3–6 weeks at 50% of initial levels in water samples filtered to remove particles. These observations suggest that phosphatases free in solution or bound to soluble organic material can contribute a significant amount of phosphatase activity,

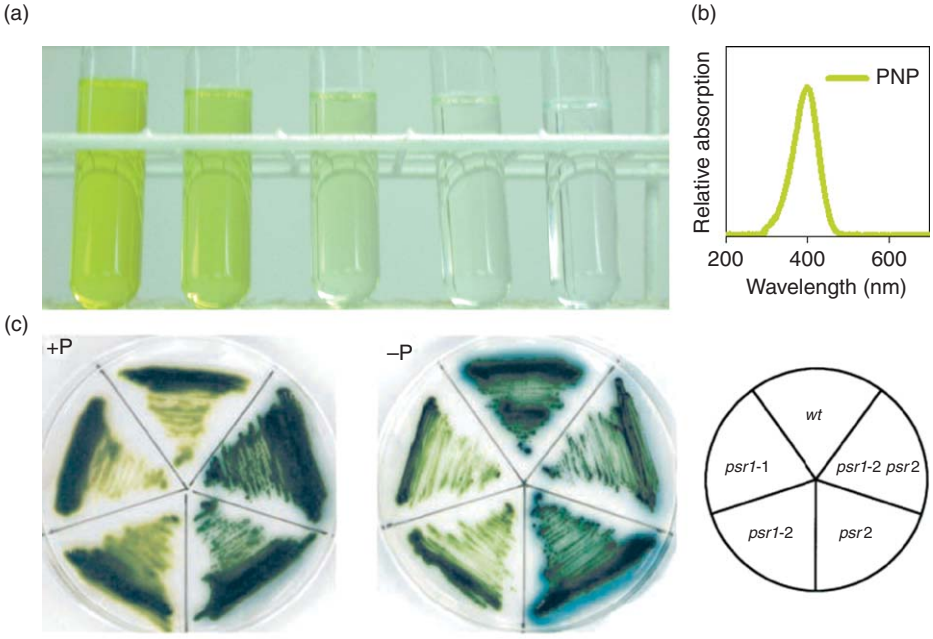

Figure 2 (a) The *para*-nitrophenyl phosphate (PNP) assay for alkaline phosphatase activity produces a yellow color in the presence of the enzyme. (b) The PNP assay quantifies alkaline phosphatase activity based on the absorption of light at 380 nm. (c) The 5 bromo-4-chloro-3-indolyl-phosphate assay with *Chlamydomonas* algae under phosphate-replete (left panel) and phosphate-limited (middle panel) conditions shows phosphatase activity using the blue coloration formed around the cells when they express the enzyme. Key (right panel) identifies mutants used in the study (wt is wild type). The phosphatase of the wild-type cells is induced in phosphate-free medium. Reproduced from Shimogawara K, Wykoff DD, Usuda H, and Grossman AR (1999). *Chlamydomonas reinhardtii* mutants abnormal in their responses to phosphorus deprivation. *Plant Physiology* 120: 685–693, with permission from the American Society of Plant Biologists.

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potentially leading to overestimates of phosphatase activity in the small cell size fraction. A difficulty common to both bulk- and size-fractionated samples is that phosphatases can persist for long periods of time without being bound to a living cell. It is not uncommon for microbial cells to retain phosphatase activity for months or years after being dried or preserved, indicating that cell viability is not critical for maintaining phosphatase enzymes over these time periods, and dead cells may contribute to the overall phosphatase activity in a sample.

Several methods have been developed to overcome the limitations of bulk measurements by directly labeling cells when phosphatases are present. These methods allow phosphatase activity to be attributed to individual cells or taxa, allowing greater resolution of the phosphate status of organisms within a mixed community. Direct cell staining with azo dyes or precipitation of lead phosphate at the site of enzyme-mediated phosphate release has been used together with light microscopy to visualize phosphatase activity on individual cells. Similarly, enzyme-labeled fluorescence (ELF) labels individual cells with a fluorescent precipitate (ELF-97) after hydrolysis of the nonfluorescent substrate molecule (2-(5′-chloro-2′phosphoryloxyphenyl)-6-chloro-4-(3H)-quinazolinone) at the site of the enzyme (**Figures 2**(**c**) and **3**).

Immobilization

Immobilization refers to the process by which labile phosphorus is sequestered and removed from the environmental reservoir of reactive phosphorus for a period of time. Immobilization processes can generally be grouped into two categories. The first category, transitory immobilization or cellular assimilation, includes all processes that sequester phosphorus within living microbial cells and is rapidly reversible upon cell death. The second category, mineral formation, encompasses processes that generate phosphorus-containing minerals.

Transitory immobilization

Transitory immobilization, or assimilation, is an important mechanism of phosphorus sequestration in soil and freshwater environments. Within cells, phosphorus is incorporated in numerous essential biological molecules and is required in larger quantities than many other elements. However, unlike other biologically important nutrients such as nitrogen and sulfur that must first undergo reduction before being incorporated into the cell, phosphorus remains oxidized before and after assimilation. Because mineralization of cellular material occurs rapidly after cell death, cellular assimilation of phosphorus into biological macromolecules leads to

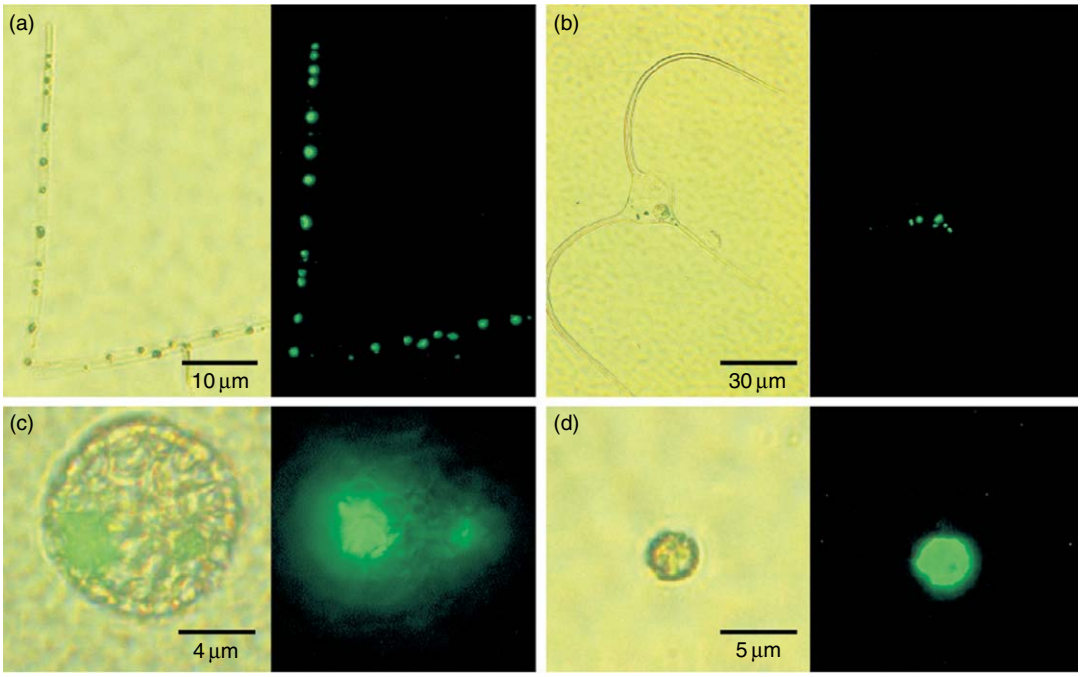

Figure 3 Micrographs of ELF-97-labeled phytoplankton from the euphotic zone in the Gulf of Aqaba (a) *Trichodesmium* sp., (b) *Ceratium* sp., (c) coccolithophore, and (d) *Cyanothece* sp. For each pair, the left panel is a view under visible light and the right panel under UV illumination. ELF-97-labeled areas appear as bright areas under UV illumination and show the location of phosphatase enzymes on the cells. Reproduced from Mackey KRM, Labiosa RG, Calhoun M, Street JH, Post AF, and Paytan A (2007). Phosphorus availability, phytoplankton community dynamics, and taxon-specific phosphorus status in the Gulf of Aqaba, Red Sea. *Limnology and Oceanography* 52: 873–885, with permission from the American Society of Limnology and Oceanography, Inc.

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relatively short-term phosphorus retention in living cells where the duration is related to the characteristics of the microbial community in question. Within the cellular reservoir, phosphorus is present as different compounds and serves various functions.

Phospholipids are lipids in which a phosphate group has replaced one of the fatty acid groups. Lipids are generally hydrophobic; however, phospholipids are amphipathic, meaning that each molecule has a hyrdrophilic portion and a hydrophobic portion. The phosphate group is responsible for giving phospholipids their partially hydrophilic character, hence imparting a wide range of biochemical properties. In the cell, phospholipids are important in the formation of biological membranes and in some signal transduction pathways.

Nucleotides are biological compounds consisting of a pentose sugar, a purine or pyrimidine base, and one or more phosphate groups. Nucleotides are the structural subunits (monomers) of RNA and DNA, and alternating bonds between the sugar and phosphate groups form the backbones of these nucleic acids. Specifically, the phosphate groups form phosphodiester bonds between the third and fifth carbon atoms of adjacent sugar rings, hence imparting directionality to the molecule. In addition, nucleotides are present as several major cofactors in the cell (e.g., flavin adenine dinucleotide, nicotinamide adenine dinucleotide phosphate) that have important functions in cell signaling and metabolism.

Adenosine triphosphate (ATP) is a nucleotide that performs multiple functions of considerable importance to the cell. The primary function of ATP is to aid in intracellular energy transfer by storing energy that is generated during photosynthesis and respiration so that it can be used in other cellular processes that require energy (e.g., cell division and biosynthetic reactions). In the cell, phosphate can be assimilated in ATP through substrate-level phosphorylation, oxidative phosphorylation, photophosphorylation, and via the adenylate kinase reaction. ATP is also active in signal transduction pathways, where it can be used as a substrate for kinase enzymes in reactions that transfer phosphate groups to proteins and lipids, forming phosphoproteins and phospholipids, respectively. Phosphorylation is an important and ubiquitous form of signal transduction in many organisms.

Phytic acid (also called inositol hexaphosphate, IP6, phytate, and myoinositol 1,2,3,4,5,6-hexakis dihydrogen phosphate) is an organic, phosphorylated, cyclic, sugar alcohol produced by plants and found in high concentrations in seeds, and may also be produced by microbes. In its fully phosphorylated form, six phosphate groups attach to the inositol ring; however, various isomers of the less highly substituted inositol phosphate molecules also exist. Phytic acid is a highly reactive compound that forms stable complexes with a variety of mineral cations (e.g., Zn^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}), as well as proteins and starches within mature seeds and when present in the environment. The complexed form of phytic acid, also known as phytin, can be a persistent phosphorus reservoir in the environment because it is less accessible to degradation by hydrolytic enzymes when complexed.

In addition to biological molecules such as nucleic acids and phospholipids, which by weight consist primarily of carbon along with smaller portions of phosphorus, the intracellular accumulation of polyphosphate granules in microbial cells is an important type of transitory phosphorus immobilization. Polyphosphates are chains of 3–1000 phosphate residues connected by anhydride bonds that form by the activity of polyphosphate kinase enzymes, and therefore represent a highly concentrated reservoir of phosphorus in the cell. The energy stored in the anhydride bonds can be used by the microbial cell during periods of starvation. Polyphosphates may also serve as ligands for metal cations such as calcium, aluminum, and manganese in some microbes; however, the extent and the elemental stoichiometry of intracellular polyphosphate cation complexation vary among organisms.

Phosphorus immobilized within cells is considered transitory because it is able to rapidly reenter the reactive phosphate pool after cell death through microbially mediated mineralization processes. The immobilization of phosphorus via cellular assimilation is therefore relatively brief (i.e., within the lifetime of a cell) compared with other processes within the phosphorus cycle, some of which occur over geological timescales.

Phosphate mineral formation

Phosphate mineral formation represents another phosphorus sink that is influenced by microbial activity; however, it encompasses processes other than cellular assimilation and short-term storage of phosphorus as biological molecules. In mineral formation (also called phosphogenesis), phosphate anions react with cations in the environment to form insoluble precipitates. Sediments that comprise significant amounts of phosphorus-containing minerals are called 'phosphorites', and may contain apatite, francolite, and a number of other phosphorus minerals (**Table 1**). Mineral formation is generally an important mechanism of phosphorus sequestration in marine environments where the high seawater calcium levels facilitate microbially mediated formation of insoluble phosphorites. The sequestration of phosphorus by this process retains (immobilizes) phosphorus for longer periods of time than does transitory immobilization.

For an insoluble mineral to form, the concentration of the ions forming the mineral must be high enough such that supersaturation is reached and equilibrium of the precipitation reaction is shifted toward the product. In addition, the physical and chemical characteristics of the environment must be conducive to precipitation of that

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mineral based on its solubility characteristics, and factors such as pH, redox state, and concentrations of co-occurring ions all influence mineral precipitation. The mineral must also be stable in the environment for mineral formation to constitute a long-term sink for phosphorus.

Mineral formation occurs both authigenically and diagenetically in the environment. Authigenic mineral formation is the formation of insoluble precipitates (minerals) *in situ* rather than by having been transported or deposited in a location through secondary processes. In contrast, diagenetic mineral formation is the alteration of existing minerals by chemical changes occurring after the initial deposition of a mineral (i.e., during or after burial and lithification). The primary type of diagenetic phosphorus mineral formation in marine environments is the substitution of phosphate into calcium carbonate minerals such as calcite or aragonite. Microbes contribute to this process by mineralizing organic phosphorus to reactive phosphate, which then substitutes diagenetically into calcium carbonate.

In authigenic mineral formation, microbes may generate reactive phosphate from the mineralization of organic phosphorus sources, and the resulting localized high phosphate concentrations favor precipitation of phosphate minerals. In soils, microbes convert organic phosphorus into phosphate, increasing its concentration in the soil and promoting formation of stable minerals such as apatite. In productive areas of the ocean, microbial mineralization of detrital matter at the sediment–water interface generates reactive phosphate, some of which reacts with seawater calcium to form phosphorite. (Reactive phosphate that does not contribute to mineral formation is available for biological assimilation by benthic microbes, or may be reintroduced to the euphotic zone by diffusion and upwelling for use by phytoplankton.)

The accumulation of phosphorus in microbial cells during transitory immobilization also contributes to mineral formation by increasing the pool of phosphate that could react with cations to form minerals. This is particularly important in anoxic areas of the ocean and soils where reactive phosphorus levels are low. Under oxic conditions where reactive phosphate is more abundant, luxury uptake and storage of phosphate as polyphosphate molecules occur in some microbes (e.g., *Pseudomonas* spp., *Actinobacter* spp.), as discussed above. Cells use the energy stored in polyphosphates to activate an alternative organic electron acceptor when conditions shift toward anoxia, freeing substantial levels of reactive orthophosphate in the process. The sequestration and release of phosphate by the cell under oxic and anoxic conditions, respectively, represent a mechanism by which microbes contribute to mineral formation because it generates locally elevated reactive phosphate concentrations in the vicinity of the cells that are high enough to induce precipitation of minerals. Accumulation of phosphate within cells may also lead to phosphorus immobilization via mineral formation if phosphorus minerals are generated and stored within the cell. Intracellular formation of mineral apatite is an example of phosphorus immobilization that has been observed in some microbes (e.g., *E. coli*, *Bacterionema matruchotii*) after incubation with calcium phosphate at a slightly basic pH. This process occurs in living and dead cells, suggesting that the locally elevated reactive phosphate concentrations within the cell help initiate apatite formation. Similarly, the formation of carbonate fluorapatite after cell death has been observed in Gram-negative rods, possibly pseudomonads, in coastal marine sediment, and is believed to be an important phosphorite formation process in locations where sedimentation rates are low.

Genetic Regulation of Microbially Mediated Processes

Microbially mediated processes, including those involved in the phosphorus cycle, are the outcome of numerous biological pathways occurring in concert across diverse microbial communities. Even cursory observations of natural microbial communities demonstrate that while microbially mediated processes influence and change the environment, the environment likewise shapes the activity of microbes, in many cases by providing feedback that either inhibits or enhances the processes. (An example of this type of feedback is the synthesis of phosphomonoesterase enzymes, many of which are only present during periods of orthophosphate deprivation but not when orthophosphate is abundant in the environment.) Similarly, microbially mediated processes can also be controlled indirectly by secondary factors (other than phosphorus) that influence growth and metabolism, such as the availability of oxidized nitrogen or sulfur in some chemoautotrophic microbes.

These processes, which are manifest in the environment as the combined outcome of activities from a diverse microbial community, are in fact a result of genetic mediation within single cells. The regulation of genes in response to environmental stimuli determines how a cell will respond to its environment, including if and how it will contribute to microbially mediated processes in the phosphorus cycle. To understand gene regulation in greater detail, highly sensitive genetic and molecular methods have been developed. Under laboratory conditions, these methods have elucidated pathways important in the immobilization (i.e., phosphorus assimilation into cell biomass) and mineralization (i.e., phosphatase production) of phosphorus, as well as countless other pathways and processes.

In *E. coli*, two major phosphate assimilation pathways have been identified. The phosphate transport system

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(Pit), which comprises a hydrogen phosphate symport powered by protonmotive force, is expressed constitutively and provides the cell with sufficient phosphorus for growth when phosphate concentrations in the media are not limiting. When media phosphate concentrations decrease below a threshold concentration, the high-affinity phosphate-specific transport (Pst) system becomes engaged. This system has a 100-fold greater affinity for phosphate than Pit, enabling the cell to acquire phosphate from a limited reservoir. Uptake of phosphate through Pst is an ATP-dependent process (e.g., requires energy input from the cell).

Pst is activated as part of the Pho regulon, a group of operons that is expressed when phosphate levels are low. Activation of the Pho regulon is initiated through phosphorylation of the PhoB cytoplasmic protein, which, in its phosphorylated state, is a transcriptional activator of the operons within the Pho regulon. In addition to Pst, the Pho regulon also includes genes encoding PhoA, outer-membrane porin proteins that facilitate diffusion of phosphate into the periplasm (PhoE), and proteins for the uptake and processing of glycerol-3-phosphate (*ugp* operon) and phosphonates (*phn* operon).

Metabolism of glycerol-3-phosphate is an interesting strategy for heterotrophic microbes, such as *E. coli*, because it is a potential source of both phosphate and carbon for the cell. However, when grown under phosphate-deplete conditions and expressing *ugp* genes, cells are only able to use glycerol-3-phosphate as a phosphate source, not as a carbon source. For cells to grow with glycerol-3-phosphate as the only phosphate source, another carbon source must also be provided. The *ugp* system is less efficient when internal cell phosphate levels are high, and is no longer expressed if external phosphate levels increase above a threshold level. Another system that is not part of the Pho regulon, the *glp* transport system, is regulated by external and internal glycerol-3-phosphate levels rather than by phosphate concentrations. Unlike in the *ugp* system, glycerol-3-phosphate acquired by the *glp* system is able to serve as the sole source of carbon and phosphate for the cell. Both *ugp* and *glp* systems facilitate the direct cellular uptake of glycerol-3-phosphate; however, each is regulated by different internal and external cues (i.e., phosphate or glycerol-3-phosphate levels), and has a different nutritional strategy (i.e., supplying phosphate alone vs. phosphate and carbon together).

These two systems are an example of how microbes, by developing multiple interrelated pathways, are able to contribute to microbially mediated processes in the phosphorus cycle under a range of environmental and physiological conditions Experimental evidence shows that the phosphate assimilation pathways in other heterotrophic bacteria are similar to *E. coli*, and many microbes are known to have portions of the Pho regulon. In particular, the alkaline phosphomonoesterase gene (*phoA*) and homologues have been identified in numerous microbial taxa, and although the primary function of the protein remains the same, factors that influence its expression and activity vary from organism to organism. The diversity of organisms and environmental conditions in which this gene exists allow microbially mediated mineralization of phosphorus to occur in nearly every environment where microbes are found. For example, photosynthetic cyanobacteria in the genus *Synechococcus*, which populate freshwater environments, coastal waters, and vast areas of the open ocean, have the *phoA* gene along with many of the other genes encoded in the Pho regulon, highlighting the global ubiquity of microbially mediated processes in the phosphorus cycle.

Anthropogenic Alteration of the P Cycle: Eutrophication in Aquatic Ecosystems

As discussed above, microbes have an important role in nearly every aspect of the phosphorus cycle, and their activities help control the relative rates at which phosphorus is mobilized and immobilized within the environment. However, humans also influence the phosphorus cycle and alter the structure of microbial communities, causing devastating ecological consequences.

Postindustrial human activities, including deforestation, phosphorus mining, and agricultural practices, affect the phosphorus cycle by increasing the mobility of phosphorus in the environment and causing it to accumulate in soils and aquatic environments. Several factors contribute to the mobilization of phosphorus by these activities. Deforestation and mining expose phosphate (and other) minerals in rock and soil to the atmosphere, leading to increased rates of weathering and erosion. Agricultural soils are also highly susceptible to erosion, making the localized elevation of phosphorus levels from application of fertilizers a particularly large source of the anthropogenic phosphorus flux. As a result of these practices, recent estimates suggest that the net storage of phosphorus in terrestrial and freshwater habitats has increased 75% over preindustrial levels, and the total reactive phosphorus flux to the ocean is twofold higher than prehuman levels. Consequently, eutrophication (the excessive growth of phytoplankton in response to over-enrichment of a growth-limiting nutrient) has become a widespread problem in lakes and estuaries throughout the world, carrying serious environmental, economic, esthetic, and human health consequences. Eutrophication has been observed in many ecosystems, including freshwater lakes such as Lake Erie, large estuaries such as the Chesapeake Bay, and coastal areas such as the hypoxic 'dead zone' of the Gulf of Mexico.

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Organic fertilizers (e.g., poultry litter, manure) are typically applied to crops based on the rate of crop nitrogen uptake, resulting in the overapplication of phosphorous and its rapid accumulation in soils. Elevated soil phosphorus levels increase the amount of phosphorus in runoff and ultimately lead to the accumulation of phosphorus in lakes and estuaries. When phosphorus from agriculture application is washed into water bodies where phosphorus limits production, substantial changes in the microbial community occur. Reversal of phosphorus limitation leads to the rapid growth of bloom-forming phytoplankton, some of which are toxic or nuisance species (such as *Pfiesteria* sp.) that are harmful to aquatic organisms and humans. As the bloom exhausts the supply of phosphorus, the phytoplankton senesce, sink to the bottom of the water body, and are decomposed by the heterotrophic microbial community. At depth, where light levels are low, photosynthetic phytoplankton are not able to balance the metabolic oxygen demands of the heterotrophs, and anoxia occurs in the bottom waters. Anoxia damages the benthic environment, leading to fish kills and harming benthic invertebrate communities. Loss of submerged aquatic vegetation, coral reef death, human shellfish poisoning, and a reduction in biodiversity are among the possible outcomes caused by microbial responses to the anthropogenic introduction of excess phosphorus to sensitive aquatic ecosystems.

Conclusion

Microbially mediated processes in the phosphorus cycle forge a critical link between the geosphere and biosphere by assimilating phosphorus within biological molecules and contributing to chemical transformations of phosphorus in the environment. In addition to acting as living reservoirs of phosphorus, microbes also contribute to the transformation of phosphorus within other nonliving reservoirs, such as rock, soils, rivers, lakes, and oceans. Microbially mediated phosphorus transformation includes processes that increase the bioavailability of phosphorus in the environment, such as weathering, solubilization, and mineralization, as well as those that decrease its bioavailability, such as assimilation and mineral formation. These large-scale environmental processes are the outcome of numerous biological pathways occurring in concert across diverse microbial communities. Genetic diversity and finely tuned regulation of gene expression allow microbes to adapt to harsh environments, and to contribute to the phosphorus cycle under numerous and diverse environmental conditions. Human alteration of the natural phosphorus cycle causes unintended consequences in microbial communities, and serious environmental, economic, esthetic, and human health problems are caused by microbial responses to the anthropogenic introduction of excess phosphorus to sensitive aquatic ecosystems.

See also: Algal Blooms; Ecology, Microbial; Freshwater Habitats; Marine Habitats; Sediment Habitats, including Watery

Further Reading

Alexander M (1967) Microbial transformations of phosphorus. In: *Introduction to Soil Microbiology*, 2nd edn. New York, NY: John Wiley and Sons.

Compton J, Mallinson CR, Glenn D, *et al*. (2000) Variations in the global phosphorus cycle. In: Glennal CR, *et al*. (eds.) *Marine Authigenesis: From Global to Microbial* Tulsa: Special Publication 66. SEPM (Society for Sedimentary Geology).

Dyhrman ST, Ammerman JW, and Van Mooy BAS (2007) Microbes and the marine phosphorus cycle. *Oceanography* 20: 110–116.

Ehrlich HL (1999) Microbes as geologic agents: Their role in mineral formation. *Geomicrobiology Journal* 16: 135–153.

Ehrlich HL (2002) Geomicrobial interactions with phosphorus. In: *Geomicrobiology*, 4th edn. New York, NY: CRC Press, Inc.

Follmi KB (1996) The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth-Science Reviews* 40: 55–124.

Heath RT (2005) Microbial turnover of organic phosphorus in aquatic systems. In: Turner BL, Frossard E, and Baldwin DS (eds.) *Organic Phosphorus in the Environment*. Cambridge, MA: CABI Publishing.

Oberson A and Joner EJ (2005) Microbial turnover of phosphorus in soil. In: Turner BL, Frossard E, and Baldwin DS (eds.) *Organic Phosphorus in the Environment*. Cambridge, MA: CABI Publishing.

Paytan A and McLaughlin K (2007) The oceanic phosphorus cycle. *Chemical Reviews* 107: 563–576.

Ruttenberg KC (2003) The global phosphorus cycle. In: William H Schlesinger (ed.), Heinrich D Holland and Karl K. Turekian (Executive eds.) *Treatise on Geochemistry,* vol. 8, pp. 585–643, 682. Elsevier.

Sharpley AN, Daniel T, Sims T, *et al.* (2003) *Agricultural Phosphorus and Eutrophication*, 2nd edn, p. 149. U.S. Department of Agriculture, Agricultural Research Service, ARS.

Stewart JWB and Tiessen H (1987) Dynamics of soil organic phosphorus. *Biogeochemistry* 4: 41–60.

Sundby B, Gobeil C, Silverberg N, *et al.* (1992) The phosphorus cycle in coastal marine sediments. *Limnology and Oceanography* 37: 1129–1145.

USEPA (1983) *Methods for Chemical Analysis of Water and Wastes*. 2nd edn. Washington, DC: Environmental Protection Agency.

USEPA (1996) *Environmental Indicators of Water Quality in the United States*. Washington, DC: Environmental Protection Agency.

Whitton BA, Al-Shehri AM, Ellwood NTW, *et al.* (2005) Ecological aspects of phosphatase activity in cyanobacteria, eukaryotic algae and bryophytes. In: Turner BL, Frossard E, and Baldwin DS (eds.) *Organic Phosphorus in the Environment*, Cambridge, MA: CABI Publishing.