

# PHOSPHORUS IN THE ENVIRONMENT: Natural Flows and Human Interferences

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■ **Abstract** Phosphorus has a number of indispensable biochemical roles, but it does not have a rapid global cycle akin to the circulations of C or N. Natural mobilization of the element, a part of the grand geotectonic denudation-uplift cycle, is slow, and low solubility of phosphates and their rapid transformation to insoluble forms make the element commonly the growth-limiting nutrient, particularly in aquatic ecosystems. Human activities have intensified releases of P. By the year 2000 the global mobilization of the nutrient has roughly tripled compared to its natural flows: Increased soil erosion and runoff from fields, recycling of crop residues and manures, discharges of urban and industrial wastes, and above all, applications of inorganic fertilizers (15 million tonnes P/year) are the major causes of this increase. Global food production is now highly dependent on the continuing use of phosphates, which account for 50–60% of all P supply; although crops use the nutrient with relatively high efficiency, lost P that reaches water is commonly the main cause of eutrophication. This undesirable process affects fresh and ocean waters in many parts of the world. More efficient fertilization can lower nonpoint P losses. Although P in sewage can be effectively controlled, such measures are often not taken, and elevated P is common in treated wastewater whose N was lowered by denitrification. Long-term prospects of inorganic P supply and its environmental consequences remain a matter of concern.

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## 1. AN ESSENTIAL ELEMENT OF LIFE

Life's dependence on phosphorus is, even more so than in the case of nitrogen, a matter of quality rather than quantity. The element is rather scarce in the biosphere: In mass terms it does not rank among the first 10 either on land or in water. Its eleventh place in the lithosphere (at 1180 ppm) puts it behind Al and just ahead of Cl, and its thirteenth place in seawater (at a mere 70 ppb) places it between N and I (1). The bulk of the Earth's biomass is stored in forest phytomass, which contains only small amounts of P. The element is entirely absent in cellulose and hemicellulose, as well as in lignin, the three polymers that make up most of the woody phytomass. Whereas C accounts for about 45% of all forest phytomass, and N contributes 0.2–0.3%, P accumulated in tree trunks of coniferous trees may be just 0.005% of that biomass, and above-ground forest phytomass averages no more than 0.025% P (2).

The element is also absent in the N-rich amino acids that make up proteins of all living organisms. However, neither proteins nor carbohydrate polymers can be made without P (3). Phosphodiester bonds link mononucleotide units forming long chains of DNA and RNA, the nucleic acids that store and replicate all genetic information; the synthesis of all complex molecules of life is powered by energy released by the phosphate bond reversibly moving between adenosine diphosphate (ADP) and adenosine triphosphate (ATP). ATP is thus the biospheric currency of metabolism. In Deevey's memorable phrasing (4), the photosynthetic fixation of carbon "would be a fruitless tour de force if it were not followed by the phosphorylation of the sugar produced" (p. 156). Thus, although neither ADP nor ATP contains much phosphorus, one phosphorus atom per molecule of adenosine is absolutely essential. No life (including microbial life) is possible without it (4).

Compared with its general biospheric scarcity, P is relatively abundant in vertebrate bodies because bones and teeth are composite materials comprised mostly of the P-rich ceramic constituent—hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , containing 18.5% P and making up almost 60% of bone and 70% of teeth—and fibrous collagen, a biopolymer (5). An adult weighing 70 kg with 5 kg of bones (dry weight) will thus store about 550 g P in the mineral. In order to get the whole body P content, this total must be extended by about 15% in order to account for P stored in soft tissues in soluble phosphate, nucleic acids, and enzymes.

Lower average body mass and a higher share of children in the total population of low-income countries mean the weighted global mean of human body mass is

only about 45 kg/capita and the average total body P content is around 400 g/capita. Consequently, the global anthropomass contains approximately 2.5 million tonnes (Mt) P, the reservoir less than half as massive as that of the anthropomass N (6). Phosphorus is, obviously, an essential human nutrient, but unlike other micronutrients (Ca, Fe, I, Mg, Zn), whose dietary intakes are often inadequate, it is almost never in short supply. Its typical daily consumption is about 1.5 g/capita for adults, well above the recommended daily allowances, which are 800 mg/capita for adults over 24 years of age and children, and 1.2 g for young adults (7). Dairy foods, meat, and cereals are the largest dietary sources of the element.

Rising production of food—be it in order to meet the growing demand of larger populations or to satisfy the nearly universal human preference for more meat—has been the main cause of the intensifying mobilization of P. Commercial production of inorganic fertilizers began just before the middle of the nineteenth century, and their applications have been essential for the unprecedented rise of food production during the twentieth century. However, this rewarding process has undesirable environmental consequences once some of the fertilizer P leaves the fields and reaches rivers, freshwater bodies, and coastal seas. Dissolved and particulate P from point sources—above all in untreated, or inadequately treated, urban sewage—is an equally unwelcome input into aquatic ecosystems.

Before I concentrate on these anthropogenic interferences in general, and on P in agriculture in particular, I first offer a concise look at the element's natural terrestrial and marine reservoirs, and at its global cycling. I conclude—after a closer look at P requirements in cropping, the element's fate in soils, and its role in eutrophication of waters—by reviewing ways to reduce the anthropogenic mobilization of P and to moderate its losses to the environment, and by outlining some long-term concerns regarding P use.

## 2. BIOGEOCHEMICAL CYCLING OF PHOSPHORUS

The global P cycle has received a small fraction of the attention that has been devoted to the cycles of C, N, and S, the three doubly mobile elements. Although there is no shortage of comprehensive books on global C, N, and S cycles (8–12), there is only one recent volume solely devoted to various aspects of P in the global environment (13); another book focuses on P in subtropical ecosystems (14). Because C, N, and S compounds are transported not only in water but also by the atmosphere, human interference in these cycles has become rather rapidly discernible on the global level (as is demonstrated by rising concentrations of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) or, as in the case of atmospheric deposition of sulfates and nitrates, it has had notable impacts on large regional or continental scales. Problems arising from these interferences—potentially rapid global warming, widespread acidification of soils and waters, and growing N enrichment of ecosystems—are among the most intractable environmental challenges facing humanity. Biological and agricultural databases indicate that more than 1000 papers were published

on all aspects of the biospheric N cycle between 1970 and 1999, but fewer than 100 were devoted to the P cycle. Fewer intricate interactions with biota, and simpler environmental transfers help to explain why the cycle has been so much less studied.

Living organisms are important to the P cycle: Decomposition of dead biomass, solubilization of otherwise unavailable soil phosphates by several species of bacteria, and enhanced release of P from soil apatites by oxalic acid-producing mycorrhizal fungi are especially critical during later stages of soil development when primary minerals have weathered away (15, 16). However, unlike C and N cycles, which are driven by microorganisms and plants, the P cycle is not dominated by biota, and the element's physical transfers are greatly curtailed because it does not form any long-lived gaseous compounds. Consequently, the atmospheric reservoir of P is minuscule, biospheric P flows have no atmospheric link from ocean to land, and increased anthropogenic mobilization of the element has no direct atmospheric consequences.

On the civilizational timescale ( $10^3$  years), the grand natural global P cycle appears to be just a one-way flow, with minor interruptions owing to temporary absorption of a small fraction of the transiting element by biota: Mineralization, weathering, erosion, and runoff transfer soluble and particulate P to the ocean where it eventually sinks into sediments. Recycling of these sediments depends on the slow reshaping of the Earth's surface as the primary, inorganic, P cycle piggybacks on the tectonic uplift, and the circle closes after  $10^7$  to  $10^8$  years as the P-containing rocks are re-exposed to denudation.

In contrast, the secondary, land- and water-based, cycling of organic P has rapid turnover times of just  $10^{-2}$  to  $10^0$  years. Myriads of small-scale, land-based cycles move phosphates present in soils to plants and then return a large share of the assimilated nutrient back to soils when plant litter, dead microorganisms, and other biomass are mineralized and their elements become available once again for autotrophic production. This cycling must be highly efficient. As there is neither any biotic mobilization of the element (akin to nitrogen fixation) nor any substantial input from atmospheric deposition (which provides relatively large amounts of both nitrogen and sulfur to some ecosystems), the nutrient inevitably lost from the rapid soil-plant cycling can be naturally replaced only by slow weathering of P-bearing rocks.

However, P in rocks is present in poorly soluble forms, above all in calcium phosphate minerals of which apatite— $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  (X being F in fluorapatite, OH in hydroxyapatite, or Cl in chlorapatite)—is the most common, containing some 95% of all P in the Earth's crust. Moreover, soluble phosphates released by weathering are usually rapidly immobilized (fixed) into insoluble forms (17). Precipitation with Al determines the upper limit of dissolved phosphate at low pH, whereas reactions with Ca set the maxima in alkaline soils. As a result, only a minuscule fraction of P present in soils is available to plants as a dissolved oxy-anion ( $\text{PO}_3^{-4}$ ), and the element is commonly the growth-limiting nutrient in terrestrial ecosystems in general and in Oxisols and Ultisols in particular (18).

The nutrient's scarcity is usually even greater in aquatic ecosystems. Only in shallow waters can phosphates circulate easily between sediments (which, too, contain P mostly in poorly soluble calcium minerals) and aquatic biota; in deep oceans P is relatively abundant only in the regions of vigorous upwelling. Again, efficient small-scale recycling of organic P is a must, but even so, the scarcity of the nutrient is pervasive and its availability is the most widespread factor limiting photosynthesis in many freshwater bodies, and external P inputs control longer-term primary production in the global ocean (19).

Comprehensive quantifications of the global P cycle, and particularly those accounting for both of its continental and marine segments, have been infrequent (20–29). Perhaps nothing illustrates the relative paucity of such exercises better than the fact that so many estimates of P stores and flows used during the 1990s have been either straight citations or minor adjustments of figures published for the first time during the 1970s (22, 30). This is in contrast with major revisions and frequent updating of many estimates concerning reservoirs and fluxes of global cycles of C, N, and S. My new estimates for biotic reservoirs and fluxes of P should be helpful in assessing the extent of human interventions in the cycle. All major biospheric reservoirs and fluxes of P are charted in Figure 1 and summarized in Tables 1 and 2.

## 2.1 Natural Reservoirs of Phosphorus

Lithospheric stores of P are dominated by marine and freshwater sediments; metamorphic and volcanic rocks contain a much smaller mass of the element. All but a minuscule fraction of this immense reservoir, containing some  $4 \times 10^{15}$  t P, lies beyond the reach of plants, as well as beyond our extractive capabilities. Since

**TABLE 1** Major biospheric reservoirs of phosphorus

<b>P Reservoirs</b>	<b>Total Storage (Mt P)</b>
Ocean	93000
Surface	8000
Deep	85000
Soils	40–50
Inorganic P	35–40
Organic P	5–10
Phytomass	570–625
Terrestrial	500–550
Marine	70–75
Zoomass	30–50
Anthropomass	3

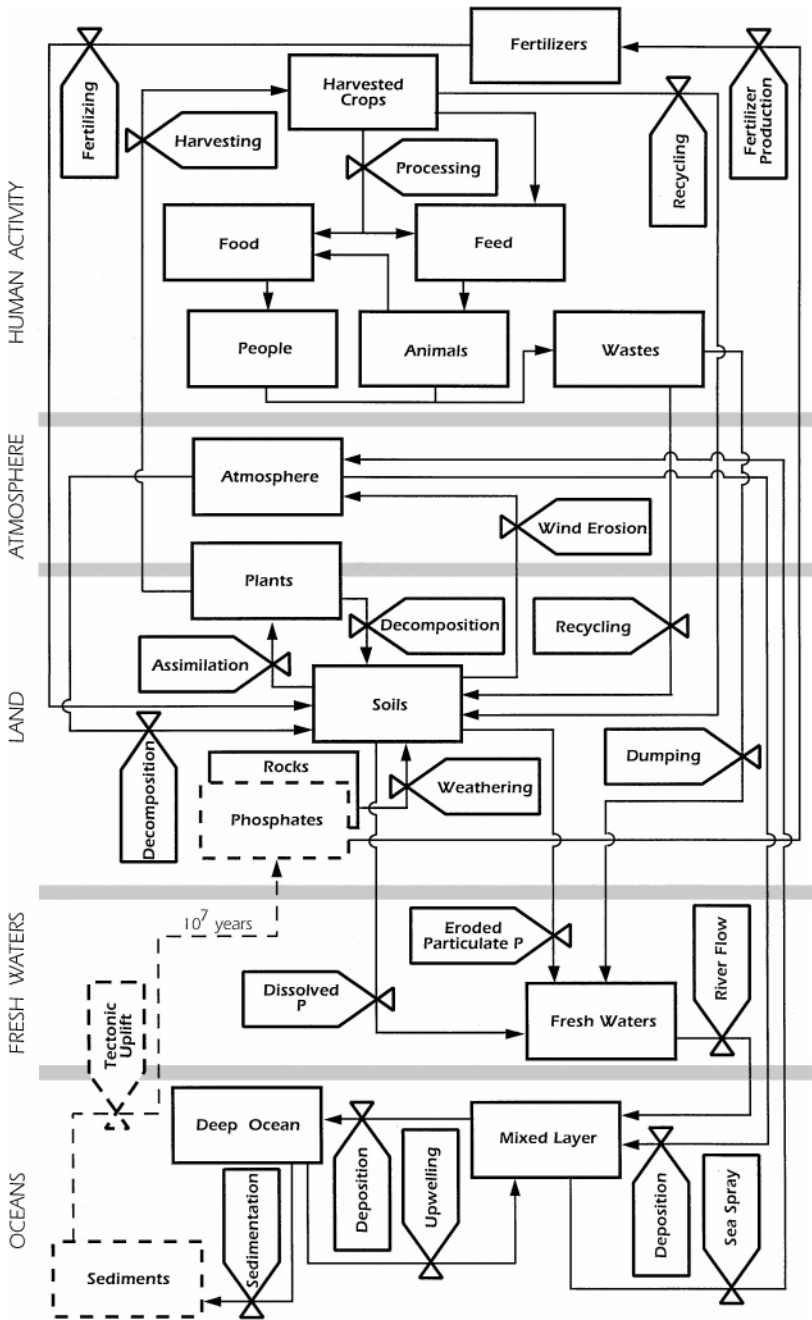


Figure 1 Global phosphorus cycle. (Based on a graph in Reference 26.)

**TABLE 2** Major biospheric fluxes of phosphorus (all rates are in Mt P/year)

<b>P Fluxes</b>	<b>Annual Rate (Mt P/year)</b>
Atmospheric deposition	3–4
Erosion and runoff	25–30
Particulate P	18–22
Dissolved P	2–3
Plant uptake	
Terrestrial	70–100
Marine	900–1200
Burial in marine sediments	20–35
Tectonic uplift	15–25

the middle of the nineteenth century, however, we have been mining some of the richest and most accessible deposits of phosphate rock in order to secure P for fertilizers and industrial uses (for details see section 3.4). By far the largest reservoir of P potentially accessible by plants is in soils.

Assuming an average of 0.05% of total P in the top 50 cm of soil (31) yields about 50 gigatonnes (Gt) P, or roughly 3.75 t P/hectare (ha). Organically bound P, primarily in phytates and in nucleic acids, can make up anywhere between 5 and 95% of the element present in soils, and its presence is, naturally, well correlated with that of organic nitrogen. Assuming at least 5 t of organic N/ha and average soil N:P mass ratio of 12:1, the global reservoir of organic soil P would be about 5.5 Gt (roughly 400 kg P/ha). These totals are in excellent agreement with the latest figures used by Mackenzie et al (29), 36 Gt for inorganic and 5 Gt for organic soil P; in contrast, the earlier estimates of 96–200 Gt of soil P are clear exaggerations (22, 25). Phosphorus in 1.5 Gha (1 Gha = 1 billion hectares) of arable soils most likely amounts to 5–6 Gt.

Estimates of P in biota have generally relied on global averages of elemental ratios in phytomass. In 1934, Redfield set the average C:N:S:P ratio for marine phytoplankton at 106:16:1.7:1 (32). This ratio has been confirmed, with small variations, by many subsequent analyses. Applying it to the best recent estimate of standing marine phytoplankton [about 3 Gt C (33)] results in some 70–75 Mt P stored in the ocean's phytoplankton (with an average turnover of just weeks) and, to a much lesser extent, in marine macrophyta.

Estimates of P stored in land plants have relied on atomic C:P ratios set by Stumm [550:1 (21)], Deevey [882:1 (4)], and Delwiche & Likens [510:1 (24)]; their published totals range from 1.95 to 3 Gt P. C:P ratios between 500:1 and 900:1 are representative of P content in new leaves, but they greatly exaggerate the nutrient's presence in wood, which stores most of the world's phytomass. Detailed analysis of 27 sites studied by the International Biological Programme

resulted in average C:P mass ratio of the above-ground phytomass ranging from about 1450:1 in boreal conifers to 2030:1 in temperate coniferous forests (2). A global C:P mass ratio of 1800:1 for extratropical forest phytomass is perhaps most representative.

This translates to about 0.025% P in dry above-ground phytomass, and analyses from three continents show a very similar average for tropical forests (34). As expected, grassland phytomass has considerably higher average P content, as do crops, with shares around 0.2% P being common (35, 36). A liberal weighted mean of 0.05% P (forests store some 90% of all standing phytomass) results in global storage of some 500 Mt P in the above-ground phytomass. Adding P in global land zoomass (maximum of 10 Gt of dry weight containing less than 50 Mt P) and anthropomass (about 3 Mt P) makes little difference to the global biomass P total, which is definitely below 1 Gt P. Estimates of total P stores in terrestrial biota ranging between 1.8–3 Gt P (22, 25, 27, 29) appear exaggerated.

The surface ocean (the top 300 m) contains less than a tenth of all P in the sea, about 8 out of 93 Gt P (29). Other published estimates of marine P range from totals of 80 to 128 Gt P (23, 25). Less than 0.2% of all oceanic P is in coastal waters where P levels can reach as much as 0.3 mg/L, whereas dissolved P is often nearly undetectable in surface waters of the open ocean.

## 2.2 Annual fluxes

Phosphine ( $\text{PH}_3$ ), a colorless and extremely poisonous gas with a garlic-like odor, is the only gaseous P compound that can be produced in minute amounts by some microorganisms, but its tropospheric presence is usually undetectable. This means that, unlike C, N, or S whose stable gaseous compounds are generated in relatively large quantities by biota, P enters the atmosphere mostly due to wind erosion. However, even such strong dust-bearing surface winds as the Saharan *harmattan* may not deposit more than 0.1 kg P/ha on downwind areas (37). Combustion of fossil fuels, burning of the biomass, and ocean spray are minor contributions of P to the atmosphere.

Biomass consumed annually in fires—almost 9 Gt of woody matter and grasses (38), with average mass C:P ratio at 1500—contains about 2.5 Mt P; combustion of fossil fuels—about 6 Gt C/year, with C:P mass ratio at 9000—contributes 0.7 Mt P. In both cases, however, only a small fraction of P-containing particles becomes airborne, and the atmospheric deposition of P amounts only to 3–3.5 Mt/year, with more than 90% attributable to wind-eroded particles.

Rainfall contains usually between 0.01 and 0.06 mg P/L, which means that most places in the temperate zone would not receive annually more than 0.5–0.7 kg P/ha; actual reported values for P inputs in precipitation range from 0.05 to just over 1 kg P/ha (39–41). Meybeck put the annual dry and wet deposition on land at just 1 Mt P, or a mere 75 g P/ha (41). Given the low solubility of phosphates, it is not surprising that annual losses of the element owing to leaching and runoff have been just 0.01–0.6 kg P/ha in forests and grasslands (2, 42–44). Assuming



that P dissolved in pristine rivers averaged no more than  $40 \mu\text{g P/L}$ , the natural riverborne transfer to the ocean was about 1 Mt P/year (11).

With no volatilization and with usually very low leaching losses, erosion and runoff are by far the most important sources of the nutrient carried in inorganic and organic particulates by streams to the ocean. Mean lithospheric content of 0.1% P and an average global denudation rate of around 750 kg/ha (45) would release about 10 Mt P annually from P-bearing rocks. I estimate the anthropogenic intensification of this flow in the next section.

International Biological Programme forest studies found the average mass ratio of C:P uptake at about 700:1 in boreal and temperate biomes (2). Similar ratios apply to growing tropical forests and grasslands. As the best recent estimates of terrestrial primary productivity range between 48 and 68 Gt C (46–48), the C:P mass ratio of around 700:1 implies annual assimilation of 70 and 100 Mt P. Using Redfield's atomic C:P ratio of 106:1 and oceanic productivity of 36 and 46 Gt C/year (49) results in an annual uptake, and a rapid remineralization, of roughly 900 and 1200 Mt P, the flux an order of magnitude higher than in the terrestrial photosynthesis with its much slower cycling. Surface P eventually ends up at the sea bottom: The rate of P burial in ocean sediments may add up to over 30 Mt P/year (29, 50). Although it is unclear what drives the fluctuations, analyses of deep sea sedimentary cores indicate that the burial rate of P has a statistically significant periodicity of 33 million years (51).

### 3. HUMAN INTENSIFICATION OF PHOSPHORUS FLOWS

Human interferences in the P cycle belong to four major categories. (a) Accelerated erosion and runoff owing to the conversion of forests and grasslands have been going on for millennia, but the process has intensified since the mid-nineteenth century with the expansion of cropping and with advancing urbanization. (b) Recycling of organic wastes was quite intensive in many traditional agricultural systems, and the practice remains a desirable component of modern farming. (c) Untreated human wastes became a major source of P only with the emergence of large cities, and today urban sewage, also containing phosphate detergents, represents the largest point source of the nutrient. (d) Finally, applications of inorganic fertilizers—prepared by the treatment of phosphate rock that began in the middle of the nineteenth century—were substantially expanded after 1950 and now amount to 13–16 Mt P/year.

#### 3.1 Accelerated Erosion, Runoff, and Leaching

Grasslands and forests have negligible soil erosion rates compared to the land planted to annual crops: Consequently, 75–80%, and often more than 90%, of all soil erosion from crop fields is the consequence of losing the canopies, litter layer,

and dense roots of the natural vegetation whose protective effect minimizes the soil loss. Quantifying nutrient losses in eroding agricultural soils is a particularly uncertain task as the erosion rates vary widely even within a single field, and as only a few nations have comprehensive, periodical inventories of their soil loss.

US national surveys showed combined totals of water (sheet and rill) and wind erosion ranging mostly between 10 and 25 t/ha, and the recent mean just below 15 t/ha (52, 53). The global average is higher, at least 20 t/ha (6), implying an annual loss of 10 kg P/ha and 15 Mt P/year from the world's crop fields. Erosion has also been greatly increased by overgrazing, which now affects more than half (that is, at least 1.7 Gha) of the world's permanent pastures; an erosion rate of at least 15 t/ha would release about 13 Mt P annually from overgrazed land. Adding more than 2 Mt P eroded annually from undisturbed land brings the global total to some 30 Mt P/year.

Subtracting about 3 Mt P/year carried away by wind would leave 27 Mt of waterborne P; not all of this nutrient reaches the ocean, as at least 25% of it is redeposited on adjacent cropland and grassland or on more distant alluvia (6). Consequently, riverborne input of particulate organic and inorganic P into the ocean is most likely about 20 Mt/year. Howarth et al used a different reasoning to arrive at the same result (54). To this must be added the losses of dissolved P.

Conversion of roughly 1.5 Gha of forests and grasslands to cropfields and settlements, accompanied by an increase of 0.2 kg P/ha in solution (from 0.1 to 0.3 kg P/ha) would have added about 0.3 Mt P/year; a similar loss from 1.7 Gha of overgrazed pastures would have doubled that loss. Even if inorganic fertilizers were to lose 2% of their P owing to leaching, the additional burden would be less than 0.4 Mt P/year. Enhanced urban loss owing to the leaching of lawn and garden fertilizers, would bring up the total to just over 1 Mt P/year, doubling the preagricultural rate to over 2 Mt P/year. The grand total of particulate and dissolved P transfer to the ocean would then be 22 Mt/year.

### 3.2 Production and Recycling of Organic Wastes

With average daily excretion of 98% of the ingested P (i.e. mostly between 1.2 and 1.4 g P/capita), the world's preindustrial population of one billion people generated about 0.5 Mt P/year at the beginning of the nineteenth century. Given the relatively low population densities in overwhelmingly rural societies, this flux prorated typically to just 1–3 kg P/ha, and it surpassed 5 kg P/ha only in the most intensively cultivated parts of Asia where most of these wastes—as well as all crop residues not used for fuel or in manufacturing and nearly all animal wastes produced in confinement—were recycled.

Fresh manure applications of 5–10 t/ha (with solids amounting to about 15%) were common both in Europe and in Asia, which means that such fields received 5–10 kg P/ha annually. The highest applications—30 to 40 t/ha in the Netherlands (55) and in excess of 100 t/ha in the dike-and-pond region of the Pearl River Delta in Guangdong (56)—transferred, respectively, up to 40 kg P/ha and over 100 kg

P/ha. Animal wastes remain a relatively large source of recyclable P in modern agriculture. Their total annual worldwide output is now about 2 Gt of dry matter, of which about 40% is produced in confinement and recycled to fields (6, 57).

Dairy manures generally have the lowest, and poultry wastes have the highest P content; shares between 1–1.5% P in dry matter are common for well-fed animals (58). With a conservative range of 0.8–1% of P, animal wastes contain at least 16–20 Mt P/year, and field applications of 6–8 Mt P are equivalent to roughly 40–50% of the P now distributed in inorganic fertilizers. With an even distribution, every hectare of arable land would receive only around 4.5 kg P/ha, but manures contribute much more in some regions with high concentrations of domestic animals.

Animal manures contain almost half of all P available for the agricultural use in Western Europe, and a quarter of all P available in the United States (59), but because of their bulkiness, uneven distribution, and prohibitive cost of application beyond a limited radius, they supply much smaller fractions of the overall need. The Netherlands is perhaps the most obvious exception: Because of the country's large animal husbandry supported by imports of concentrate feeds, P in Dutch manure surpasses crop requirements even on the national average, and the nutrient voided in confinement is about twice the mass applied annually in phosphatic fertilizers; consequently, the Dutch manuring should be more accurately called land disposal of enormous volumes of waste (60).

Some fields thus receive applications in excess of 200 kg P/ha every year, and even with washout rates of no more than 1–2% several kg P/ha can be lost every year. Similarly, P recycled in manures during low-density grazing amounts to just 1–2 kg P/ha, but with high cattle densities (up to three heads/ha of pasture) the annual deposition may be up to 12 kg P/ha, and the runoff on compacted soils may carry away more than 0.5 kg P/ha. Much higher losses of the nutrient are associated with huge feedlots holding thousands of animals: These lots generate the nutrient with densities of hundreds of kg P/ha, and the runoff losses under unfavorable conditions may amount to several kg P/ha.

Recycling of crop residues is a much smaller input of P into the world's cropping than is the application of manures. Roughly half of the annual output of 3.75 Gt of dry biomass of crop residues (mostly cereal straws) is not removed from fields (6), and with P content ranging mostly between 0.05 and 0.1% they recycle between 1–2 Mt P. Also, an organic source of P that was actually the first widely used commercial fertilizer is now entirely negligible in the global balance of the nutrient: Guano, solidified bird excrements accumulated on arid tropical and subtropical islands, has relatively high (typically 4–5%) P content, and it was used most intensively (largely for its relatively high N content) between 1840 and 1870 (61).

### 3.3 Sewage and Detergents

Centralized wastewater treatment, an innovation that began in large cities of the late nineteenth-century Europe and North America, shifted the disposal of human

waste from land to water. As a result, a multitude of previously small and diffuse sources of water pollution was replaced by a smaller number of large waste outlets to the nearest stream or a water body. The same process has been going on during the past two generations in growing urban areas of Asia, Latin America, and Africa. In 2000 the global population of just over 6 billion people released almost 3 Mt P in its wastes. Nationwide generation rates are as high as 9 kg P/ha of cultivated and settled land in such densely inhabited countries as Egypt and Japan. The mean in the US is only 0.7 kg, and the global average is about 2 kg P/ha. With the exception of Africa, most of this waste now comes from cities rather from rural areas.

Sewering of urban wastes is still far from universal. Although it has been the norm in European and North American cities for more than a century, large shares of the poorest urban inhabitants in low-income countries, particularly those living in makeshift periurban settlements, have no sewage connections. Less appreciated is the fact that in Japan, one of the world's most urbanized countries (about 80% of Japanese live in cities), the share of all households connected to sewers surpassed 50% only in 1993 (62).

To 1.2 g P/capita discharged daily from food must be added 1.3–1.8 g P/capita from other urban sources, above all from industrial and household detergents. The recent decline in the P content of clothes-washing detergents has been partially offset by the increased use of dishwashing compounds, and so it is unlikely that per capita discharges in affluent countries will fall below 2 g P/day (63). Annual output—at least 0.75 kg P/capita—then translates to 100–150 kg P/ha in most large Western urban areas where virtually all wastes are sewered; in such extremely crowded urban areas as Shanghai's core or Hong Kong's Mongkok, the annual waste generation goes up to 200 kg P/ha (26).

Primary sedimentation of urban sewage removes only 5–10% of all P and it retains much of the element in organic form, and return of the sludge to crop fields is generally limited owing to the common presence of heavy metals (64, 65). Use of trickling filters captures 10–20% of all P, but aeration used during the secondary water treatment transforms nearly all of the organic P into soluble phosphate, and the waste stream can thus contain 10–25 mg P/L. Phosphates in solution can be precipitated in insoluble salts by adding flocculating compounds, usually salts of Fe ( $\text{FeCl}_3$  or  $\text{FeCl}_2$ ) to produce  $\text{FePO}_4$ , Al ( $\text{Al}_2(\text{SO}_4)_3$ ) to produce  $\text{AlPO}_4$ , or lime (CaO) to generate  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (66). Addition of the reagents before the primary sedimentation removes 70–90% of all P, and 80–95% removal is possible with repeated dispensation.

This treatment is expensive, however, and it increases sludge mass by 50% and volume by up to 150%, and even if there were no heavy metals in the sludge it is not a suitable fertilizer, as the excess Fe or Al can remove dissolved phosphates (67). That is why bacterial P removal is now the preferred way of treatment: Standard activated sludge treatment removes 15–40% of all P, and when the activated sewage sludge is subjected to vigorous aeration it can sequester more phosphate than is required for its microbial activity (68).

If half of all human wastes were eventually released to waters (the rest being incorporated into soils and removed in sludges) the annual waterborne burden would be around 1.5 Mt P. To this must be added P releases from the use of synthetic detergents. Sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) and potassium pyrophosphate ( $\text{K}_4\text{P}_2\text{O}_7$ ) are low-cost compounds that have been widely used in production of, respectively, solid and liquid detergents. They were commercially introduced in 1933, but their use grew rapidly only after World War II: By 1953 they accounted for more than 50% of the US sales of cleaners; a decade later they reached 75% of the market, and during the 1960s, they contributed about 33% of all P released into sewage water in large US cities (69). Since the early 1970s their use has been banned or restricted in many countries, but there are indications that the alternatives are hardly more acceptable from the environmental point of view (70).

### 3.4 Inorganic Fertilizers

The modern fertilizer industry actually began with the production of phosphatic compounds based on Liebig's idea that P would be more soluble in water if bones were treated with  $\text{H}_2\text{SO}_4$  (71). James Murray became the first commercial vendor to use this process in 1841 (72). Two years later John Bennett Lawes's factory at Deptford on Thames started producing the calcium phosphate— $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , now commonly known as ordinary superphosphate (OSP)—by treating P-containing rocks with dilute sulfuric acid. Coprolites from Gloucestershire and, later, from East Anglia, were the first raw material and were used until the end of the century.

Expansion of the OSP industry stimulated search for phosphate deposits. They are found either as igneous or sedimentary rocks: The first category is made up of the three primary species of apatite, whereas varieties of carbonate-fluorapatite (francolite) dominate both marine and freshwater sediments (73). Extraction of high-quality apatite started in 1851 in Norway; phosphate mining in the United States began in North Carolina in the late-1860s, but Florida extraction became dominant in 1888, and the United States has been by far the world's largest producer of phosphate rock ever since (74, 75).

Depending on the treated mineral, the OSP contained between 7–10% (8.7% was the standard) of available P, an order of magnitude more than the commonly recycled P-rich manures. (Agricultural literature almost always uses the phosphoric oxide,  $\text{P}_2\text{O}_5$ , rather than P as the common denominator when comparing P fertilizers: In order to convert  $\text{P}_2\text{O}_5$  to P, multiply by 0.4364. Table 3 lists major P fertilizers with their P content.) OSP was also a richer source of the nutrient than the basic slag, available as a by-product of smelting phosphatic iron ores, which was commercially introduced during the 1870s and contained 2–6.5% P. Treating the phosphate rock with phosphoric acid, a process that began in Europe during the 1870s, increased the share of soluble P two to three times above the level in OSP, and the compound generally known as triple superphosphate (TSP) contains 20% P.

**TABLE 3** Major phosphate fertilizers

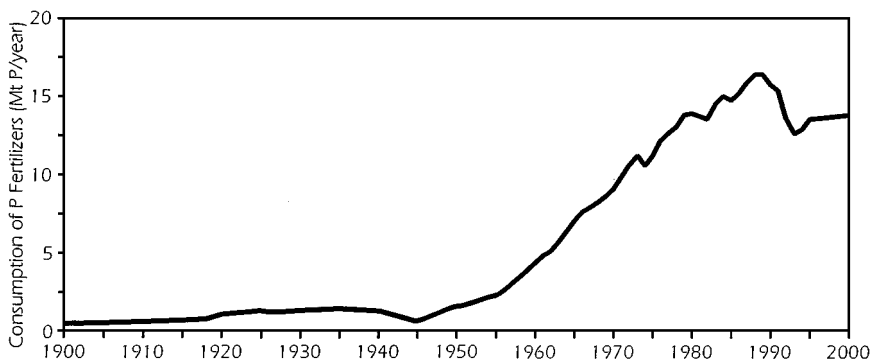
Compound	Acronyms	Formulas	Nutrient content (% P)
Monocalcium phosphate or ordinary superphosphate	MCP OSP	Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	8–9
Dicalcium phosphate	DCP	CaHPO <sub>4</sub> · H <sub>2</sub> O	17
Triple superphosphate	TSP	Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	19–20
Monoammonium phosphate	MAP	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	21–24
Diammonium phosphate	DAP	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	20–23
Monopotassium phosphate	MKP	KH <sub>2</sub> PO <sub>4</sub>	17

Two of the world's three largest producers of phosphate rock were added between the world wars. Huge Moroccan deposits were discovered in 1914 and their extraction started in 1921. They are the prime example of marine phosphorites—formed either in areas of upwelling ocean currents along the western coasts of continents (besides Morocco, most notably in Namibia, California, and Peru) or along the eastern coasts where poleward-moving warm currents meet cool coastal countercurrents (Florida, Nauru)—which contain the bulk of the world's phosphate. The former USSR opened its high-grade apatite mines in the Khibini tundra of the Kola Peninsula in 1930. Such deposits, associated with alkaline igneous rocks, are much less abundant. Palabora, South African is another major location.

The only sizeable discoveries after World War II occurred in China and Jordan. More than 30 countries are now extracting phosphate rock, but the global output is highly skewed: The top 12 producers account for 95% of the total, the top 3 (United States, China, and Morocco) for 66%, and the United States alone for 33%. Florida extraction has also the lowest production cost among the major producers. Between 1880 and 1988 extraction of phosphate rock grew exponentially, passing the 1 Mt/year mark in 1890, 10 Mt/year in the early 1920s, 100 Mt/year by the mid-1970s, and 150 Mt/year in 1985; during the late 1990s, the annual output averaged about 140 Mt P, but capacity was over 190 Mt P (76). The mined rock (80% of it come from sedimentary deposits, and more than 75% from surface mines) contains anywhere between more than 40% to less than 5% of phosphate, and after beneficiation the rock concentrate has 11–15% P.

As with many other mineral resources, the average richness of mined phosphate rock has been slowly declining, from just above 15% P in the early 1970s to just below 13% P in 1996 (59). Less than 2% of the extracted rock is applied directly to acidic soils as a fertilizer (77). Preparation of enriched fertilizers claims about 80% of the beneficiated rock, and the rest is used mostly to produce detergents (12%) and as additives to animal feeds (about 5%).

Global consumption of all P fertilizers surpassed 1 Mt P/year during the late-1930s, reached 5 Mt P/year by 1960 and over 14 Mt P/year in 1980 (26). The



**Figure 2** Consumption of inorganic phosphatic fertilizers, 1900–2000. (Based on data from References 76, 79.)

peak consumption of about 16.5 Mt P/year in 1988 was followed by a nearly 25% decline to 12.6 Mt P/year by 1993 (Figure 2), (78, 79). This was due to a combination of declining fertilization rates in the European Union, Japan, and North America, and sharply lower fertilizer use in post-communist economies of the former Soviet Union and Europe. Slow growth of the global extraction resumed in 1994, but the peak level of 1988 may not be reached before the year 2005. Low-income countries now consume just over 60% of all P fertilizers, and they also use about 50% more P per average hectare of farmland than do affluent nations—but still less than half than the amount in per capita terms.

Cumulative anthropogenic transfer of P from rocks to the biosphere can be quantified fairly accurately because relatively reliable global statistics on the production of P fertilizers have been available since the very beginning of the industry. Between 1850 and 2000, the Earth's agricultural soils received about 550 Mt P, an equivalent of almost 10% of arable soils' total P content.

### 3.5 Summarizing the Human Impact

At the beginning of the nineteenth century, crop harvests assimilated about 1 Mt P/year, and anthropogenic erosion and runoff were at least 5 Mt P/year in excess of the natural denudation rate. In contrast, in 2000 the global crop harvest incorporated about 12 Mt P, and increased soil erosion from crop fields and degraded pastures mobilized about twice as much P as did the natural denudation (Table 4).

In 1800 the preindustrial population of 1 billion people generated about 0.5 Mt P in human wastes; domestic animals voided over 1 Mt P, and recycled organic matter returned less than 0.5 Mt P to agricultural soils. In 2000, 6 billion people generate about 3 Mt P/year in human waste, and more than 4 billion domesticated mammals and more than 10 billion domesticated birds void more than 16 Mt P in their urine and feces. At least 7, and up to 10, Mt P/year are returned to soils

**TABLE 4** Human intensification of the global phosphorus cycle (all values are in Mt P/year)

<b>Fluxes</b>	<b>Natural</b>	<b>Preindustrial (1800)</b>	<b>Recent (2000)</b>
Natural fluxes intensified by human actions			
Erosion	>10	>15	>30
Wind	<2	<3	>3
Water	>8	>12	>27
River transport	>7	>9	>22
Particulate P	>6	>8	>20
Dissolved P	>1	<2	>2
Biomass combustion	<0.1	<0.2	<0.3
Anthropogenic fluxes			
Crop uptake	—	1	12
Animal wastes	—	>1	>15
Human wastes	—	0.5	3
Organic recycling	—	<0.5	>6
Inorganic fertilizers	—	—	15

in recycled organic matter, and around 15 Mt P are applied annually in inorganic fertilizers.

The past two centuries have thus seen a roughly 12-fold expansion of the amount of nutrient assimilated by crops, of the total mass of animal wastes, and of the amount of recycled organic matter. In 1800, anthropogenic mobilization of P owing to increased erosion was equal to about 33% of the total continental flux of the nutrient. At the beginning of the twenty-first century, erosion and runoff in excess of the natural rate and applications of inorganic fertilizers account for at least 75% of the continental flows of the nutrient (Table 4).

Natural losses of P from soils to air and waters amounted to about 10 Mt/year. In contrast, in 2000 intensified erosion introduces on the order of 30 Mt P into the global environment, mainly because human actions have roughly tripled the rate at which the nutrient reaches the streams (Table 4). A variable part of this input is deposited before it enters the sea, but the total annual riverborne transfer of P into the ocean has at least doubled; its regional rate is now approaching 1.5 kg/ha in the Northeastern United States, and it is over 1 kg P/ha both in Northwestern Europe and in the part of the Iberian peninsula draining to the Atlantic Ocean (80).

However, the study of the riverine N and P budgets in the North Atlantic Ocean that determined these rates also concluded that almost 70% of the region's P flux comes from the Amazon and Tocantins basins, largely particulate P resulting from high erosion rates in the Andes. In contrast, old, denuded landscapes of Eastern North America contribute relatively little P—the Hudson's Bay watershed discharges a mere 45 g P/ha/year (80)—and most of the region's riverborne P



must be attributed to conversion of natural ecosystems to cropland, to still advancing urbanization, and to now stabilized, but relatively high, applications of P fertilizers.

## 4. PHOSPHORUS IN AGRICULTURE

Besides its irreplaceable role in fundamental biochemical reactions, adequate amounts of P in plants also increase the response to applications of N and K. The nutrient is especially important for young tissues in order to promote root growth, flowering, fruiting, and seed formation. Good P supply also improves the rate of nitrogen biofixation and maintenance of soil organic matter, whose presence enhances the soil's water-holding capacity and reduces erosion (81). Phosphorus deficiencies are not usually marked by specific signs but rather by overall stunting.

Predictably, both the P uptakes and average applications of P fertilizers vary fairly widely with species, cultivars, and yields. Although the average applications of inorganic P have stabilized, or declined, in nearly all high-income countries they remain very inadequate throughout most of the poor world. The fate of P in agricultural soils has been among the key concerns of soil science, and a new consensus that has emerged during the last generation has overturned the traditional paradigm that saw inorganic P applications as extraordinarily inefficient. However, given the sensitive response of aquatic autotrophs to P enrichment, even relatively small losses of agricultural P to waters may contribute to undesirable eutrophication.

### 4.1 Phosphorus Uptake and Applications

Large post-1950 increases in yields mean that today's best cultivars remove 2–3 times as much P as they did two generations ago: For example, English wheat removed about 7 kg P/ha in 1950, 13 kg P/ha in 1975, and 20 kg P/ha in 1995 (82). Typical harvests now take up (in grains and straws) between 15–35 kg P/ha of cereals, 15–25 kg P/ha in leguminous and root crops, and 5–15 kg P/ha in vegetables and fruits (83). The highest rates can top 45 kg P/ha for corn, sugar beets, and sugar cane. The total based on separate calculations for all major field crops shows that the global crop harvest (including forages grown on arable land but not the phytomass produced on permanent pastures) assimilates annually about 12 Mt P in crops and their residues (Table 5). Cereals and legumes account for most of the flux, containing 0.25–0.45% P in their grains (only soybeans have 0.6% P), and mostly only 0.05–0.1% P in their straws (81).

In contrast, weathering and atmospheric deposition most likely supplied no more than 4 Mt P to the world's croplands (Table 6). Consequently, organic recycling and applications of P fertilizers are essential for producing today's harvests—and as the use of manures and crop residues is limited by the number of animals, size of the harvest, and cost of recycling, dependence on inorganic fertilizers will

**TABLE 5** Annual assimilation of phosphorus by the world's crop harvest during the mid-1990s

<b>Crops</b>	<b>Harvest (Mt)</b>	<b>P (%)</b>	<b>Crop residues (Mt)</b>	<b>P (%)</b>	<b>P uptake (Mt P)</b>
Cereals	1670	0.3	2500	0.1	7.5
Sugar crops	450	0.1	350	0.2	1.2
Roots, tubers	130	0.1	200	0.1	0.3
Vegetables	60	0.1	100	0.1	0.2
Fruits	60	0.1	100	0.1	0.2
Legumes	190	0.5	200	0.1	1.1
Oil crops	110	0.1	100	0.1	0.2
Other crops	80	0.1	200	0.1	0.3
Forages	500	0.2			1.0
<b>Total</b>	<b>3250</b>		<b>3750</b>		<b>12.0</b>

**TABLE 6** Phosphorus budget for the world's cropland during the mid-1990s

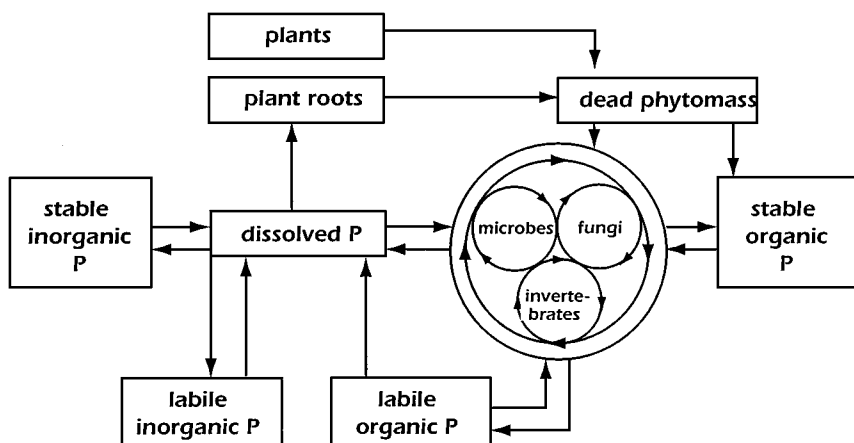
<b>Flows</b>	<b>Annual flows (Mt P)</b>
<b>Inputs</b>	24–29
Weathering	2
Atmospheric deposition	1–2
Organic recycling	7–10
Crop residues	1–2
Animal manures	6–8
Synthetic fertilizers	14–15
<b>Removals</b>	11–12
Crops	8–9
Crop residues	3
<b>Losses</b>	
Erosion	13–15
<b>Balance</b>	0–2
<b>Input shares (%)</b>	
Organic recycling (7/24–10/29)	29–34
Inorganic fertilizers (14/24–15/29)	52–58
<b>Uptake efficiency (%) (11/24–12/29)</b>	41–45

rise even in the case of an early stabilization of the global population. Global applications of fertilizer compounds average just over 10 kg P/ha of arable land; continental means range from about 3 kg P/ha in Africa to over 25 kg P/ha in Europe (78, 79). National averages hide enormous intranational variation: For example, North Dakota spring wheat receives just around 10 kg P/ha, while applications to Iowa corn surpass 60 kg P/ha (84).

The latest international survey of fertilizer use (85) shows that nearly two thirds of the nutrient were used on cereals (20% on wheat, 14% on rice, 13% on corn), oilseeds (about 10%), roots and tubers (6%), and vegetables (about 5%). The highest national applications to wheat are now in China (about 35 kg P/ha), Italy, France, and the United Kingdom, and to rice in Japan (just over 40 kg P/ha) and South Korea (85). Data acquired worldwide at about 60,000 sites over a period of 25 years (86) show, as expected, a wide range of responses to P fertilization. These trials are usually done in combination with the other two macronutrients, but responses to individual nutrients show that high phosphate applications (above 20 kg P/ha) result in additional yields of between 10–25 kg/ha per kg of applied P for both wheat and rice, and up to 30 kg/ha for corn.

## 4.2 Phosphorus in Soils

Phosphorus applied to soils is involved in a multitude of complex reactions that remove it from the solution and incorporate it into a large variety of much less soluble, or insoluble, labile and stabile compounds (Figure 3). Dissolution of a superphosphate granule reduces the acidity of soil water in its immediate surroundings to pH of only 1–1.5 and releases Al, Fe, Ca, K, and Mg compounds in soil particles; they react with fertilizer P and produce relatively insoluble, and hence immobile, compounds (17, 87).



**Figure 3** Phosphorus cycle in soil. (Simplified from a drawing in Reference 153.)

This process of fixation (also referred to as immobilization or retention) of P was first described in 1850, and ever since it has been one of the most researched subjects in soil science (17, 87, 88). The most intriguing question has been to find out how much of the nutrient is irreversibly fixed in the soil soon after application and how much becomes eventually available to subsequent crops. The long-prevailing view saw a rapid P fixation of the applied nutrient as dominant—and the use of fertilizers was then inevitably seen as an overwhelmingly irreversible but laborious, costly, and energy-intensive transfer of the element from extracted and treated rocks to insoluble soil phosphates. As Tinker concluded in 1977, “The central problem in the world phosphate economy...consists largely of digging out phosphorus at one place and storing it in the soil at another” (89:103).

Reality is more complex and more encouraging (90). Sandy soils and soils with nearly neutral pH have relatively little fixation, whereas acidic, clayey soils with high Fe and Al content have the highest fixation capacity. Crop response to water-soluble phosphates is thus strongly dependent on the overall P fixation capacity of fertilized soils. Once this fixation capacity is satisfied, additional P applications will be needed just to replenish the nutrient removed by the crop and to make up for waterborne and erosional losses.

Continuing additions of P in manures and fertilizers may result in considerable annual surpluses of the nutrient in a variety of agroecosystems. Frissel & Kolenbrander's (91) comprehensive reviews found P gains in about three quarters of all studied agroecosystems, with the mean annual gain of over 7 kg P/ha. Recent national surpluses average as much as 40 kg P/ha in the Netherlands, close to 30 kg P/ha in France, about 25 kg P/ha in Germany, and 10 kg P/ha in England (83, 92). At the same time, the formation of P compounds with limited solubility restricts the immediate losses and allows the crops to use the applied P in succeeding years.

Although the crops may recover no more than 15–25% of fertilizer P during the year of the application, more stable accumulated P can be released gradually into the soil solution once the reserves of less strongly held nutrient are exhausted (93). A great deal of evidence confirms that the eventual efficiency with which they utilize the applied P is at least as high as is their uptake of N. Recovery rates of between 50–60% are not uncommon, and some agroecosystems use the applied P with efficiencies as high 70–90% (91–93). My conservatively calculated global P budget in cropping implies average P utilization efficiency of about 45% and an annual gain averaging up to 1.5 kg P/ha (Table 6).

Gradual acceptance of this reality has done away with the traditionally excessive use of phosphates: Worldwide N/P ratio in applied fertilizers was as low as 1.6 until the late-1940s, it passed 2 in 1955, 4 by 1975, and 5 a decade later; during the 1990s it ranged between 5.6–6.1 (78, 79). In countries with the most intensive fertilization it has recently been even higher, as high 7.2 in China. Not surprisingly, recent recommendations are for reduced P inputs, but without synthetic fertilizers many agroecosystems would have a net P loss.

## 5. PHOSPHORUS IN WATERS

Thermal stratification of water bodies—with the warmer, and relatively shallow, surface layer (epilimnion) overlying cooler deeper layers (hypolimnion)—severely restricts the upward flow of nutrients (94). As phytoplankton die and sink, epilimnion P can be rapidly depleted, and only prompt bacterial decomposition in the water column can recycle the nutrient whose turnover may be measured in just weeks, or even days, during the peak photosynthetic season. Turnover of scarce P is similarly rapid in pelagic marine ecosystems (95).

In spite of this rapid recycling, P is commonly the growth-limiting nutrient, and the inadvertent fertilization of streams, and even more so of freshwater bodies, estuaries, and shallow coastal waters, can change them first from oligotrophic (poor in nutrients) to mesotrophic (moderately rich in nutrients) and eventually even to hypereutrophic (extremely well nourished). Excessive growth and eventual decay of algae and aquatic macrophytes have a number of undesirable ecosystemic and economic consequences.

### 5.1 Losses of Dissolved Phosphorus

Substantial retention of P as it moves deeper in soils means that subsurface drainage of the nutrient is, unlike in the case of often serious leaching of N fertilizers, fairly small; the only exceptions arise from heavy applications of animal slurries, on acid organic, peaty soils, and in tiled-drainage fields (88, 96). Consequently, the two globally most important ways of introducing excessive P into water are the releases of untreated or inadequately treated wastewater into streams or lakes from cities and industries (considered to be point sources), and discharges in the runoff from crop fields and pastures (diffuse sources).

As already noted (section 3.1), the worldwide anthropogenic loss of dissolved P from land is on the order of one Mt P/year, roughly equal to the natural rate. The overall loss of just over 2 Mt P/year divided into the annual global stream flow of 27,000 km<sup>3</sup> (97) prorates to about 80  $\mu\text{g/L}$  of river water. With the continental precipitation mean of about 0.8 m/year, this would translate to an average discharge of about 0.6 kg P/ha of land. Undisturbed watersheds covered by climax forests or grasslands discharge up to an order of magnitude less, whereas the flux from densely inhabited and intensively fertilized watersheds may be several times higher.

Dissolved P amounts to anywhere between less than 0.1% and almost 5% of the nutrient applied in inorganic fertilizers, and the annual loss rates may vary by as much as fourfold (98, 99). Rates between 1–2% are common, which means that watersheds heavily fertilized by a combination of manures and phosphates may be discharging several kg P/ha every year. Indeed, concentrations as high as 30 mg P/L were recorded soon after the application of pig and cattle slurry, and annual measured losses of soluble P from fertilized fields go up to about 3 kg P/ha (100).

Contributions of point and diffuse sources to a watershed's P discharge cannot be quantified with high accuracy, but there have been numerous reconstructions of nutrient budgets assigning approximate load shares to these P releases. During the 1970s, urban and industrial wastes accounted almost always for at least 60%, and up to 75%, of all P inputs in populated watersheds of Europe, North America, and Japan (42). Subsequent restrictions on the use of P-containing detergents and better ways of wastewater treatment have generally reduced the contributions of point sources and made agricultural discharges more prominent, or even dominant: P discharges from croplands, pastures, and rangelands now account for more than 80% of the nutrient's release to surface waters in the United States (101).

However, even relatively low diffuse discharges may be of concern. Iowa cornfields receiving 40–65 kg P/ha annually and losing less than 0.2 kg/ha (or no more than 0.5%) as soluble P will be releasing water with concentrations of just 0.2–0.5 mg P/L (100), but because of extremely low threshold of algal response to P enrichment, particularly in shallow lakes with long hydraulic residence times, such levels are high enough to precipitate eutrophication. This means that even the best agronomic practices may not be able to prevent P losses producing eutrophication of sensitive waters: Cropping without fertilization, or return of the land to permanent pasture or forest would be the only ways to lower the P loss.

## 5.2 Eutrophication

Phosphorus-induced eutrophication is due above all to the element's high "leveraging" effect on phytomass production and to its trigger effect on the cycling of C and N. According to Redfield's ratio, a single atom of P supports the production of as much phytomass as 16 atoms of N and 106 atoms of C; although there is no mechanism in freshwater ecosystems that allows for adjustments in the rapid P cycle in order to maintain Redfield's ratio, N and C cycling will respond promptly once P is added (102). Because aquatic photosynthesis cannot be readily toxified, even wastes with a relatively high content of heavy metals can be an effective source of P.

As total P in water increases, the standing phytomass goes up linearly. This relationship breaks at P concentrations around 0.1 mg/L; above that level other factors (especially light availability) become more important. In a formerly clear-water lake, a mere 10  $\mu\text{g}$  P/L can make the water cloudy, reducing its clarity from 9 to 3 m (39). Expressing this in terms of actual mass input makes the sensitivity to P-induced eutrophication even clearer; a concentration of 10  $\mu\text{g}$  P/L is equivalent to just 5 kg P in a 10-hectare lake with average depth of 5 m, and such an amount of dissolved P can be discharged from just 5–10 ha of intensively fertilized farmland in that lake's catchment! Higher P concentrations will further reduce water clarity; those above 50  $\mu\text{g}$  P/L will result in the deoxygenation of bottom waters and will have costly effects on using the water for drinking and recreation.

During the late-1960s, concerns about eutrophication helped to launch, together with worries about persistent pesticides and nitrates in drinking water, the era of

public environmental awareness. Vollenweider's pioneering work (103) was followed during the next two decades by a large number of general appraisals as well as by many local or regional studies (42, 104–113). The interest has been somewhat less intensive during the 1990s (114–121). Basic conclusions have remained unchanged during the past generation. Concentrations above 0.01 mg/L of dissolved P are likely to cause eutrophication, but it is the nutrient supply (loading), rather than the P or N concentration in water, that is the key anthropogenic factor in the process. Comparisons of polluted lakes and estuaries have shown that excessive eutrophication can be generally prevented if annual loadings are lower than 1 g P/m<sup>2</sup> (10 kg P/ha) of water surface (122).

However, the same comparisons also confirmed that much higher loadings may not cause serious problems as long as the average retention time of imported nutrients is short. For example, during the 1970s neither the Tyne nor the Thames estuaries—receiving, respectively, 1900 and 1100 kg P/ha, perhaps the highest P loadings recorded worldwide—were eutrophic because the average retention time of their waters was just 2 and 5 weeks, respectively, compared with one year for the hypereutrophic Potomac estuary, whose average loading was only 43 kg P/ha (122). In his now classical treatment, Vollenweider (106) took care of these realities as he expressed the proneness to eutrophication by relating total P loading (g P/m<sup>2</sup>/year) to the quotient of mean depth and hydraulic residence time.

As already noted, transparency and color are the most obvious indicators of the nutrient condition of a water body: Transparent oligotrophic waters support low plant productivity and appear either blue or brown (when stained in peaty regions); eutrophic waters have high primary productivity as large amounts of phytoplankton make them turbid and limit their transparency to less than 50 cm. Advanced eutrophication is marked by blooms of cyanobacteria (commonly *Anabaena*, *Aphanizomenon*, *Oscillatoria*) and siliceous algae (*Asterionella*, *Melosira*), scum-forming algae (such as *Phaeocystis pichetii*), and potentially toxic algae such as *Dinophysis* and *Gonyaulax*. Eventual decomposition of this phytomass creates hypoxic or anoxic conditions near the bottom, or throughout a shallow water column.

The most worrisome problems arising from these changes range from offensive taste and odor of drinking water (requiring expensive treatment before consumption) and formation of trihalomethanes during chlorination (123) to serious health hazards to livestock and people ingesting soluble neuro- and hepatotoxins released by decomposing algal blooms (124). Fortunately, phosphates themselves are toxic to people or animals only in very high concentrations. Reduced fish yields, extensive summer fish kills, and changed composition of fish species in affected water bodies are common as species adapted to turbid waters become dominant (114).

Submersed rooted macrophytes are reduced or eliminated owing to excessive shading. At the same time, such submersed but weakly rooted species as Eurasian milfoil (*Myriophyllum spicatum*) that absorb most of their nutrients from water, may grow excessively, entangling swimmers as well as boat propellers. Another particularly offensive consequence of eutrophication includes the growth of thick

coats of algae on any submerged substrates, be they aquatic plants, stones, docks, or boats. Because of decades of heavy P applications and high densities of population and animal husbandry, Dutch water bodies are particularly affected (125). Although total P inputs were cut by about 50% by 1995 compared with 1985, P-saturated soils remain a large source of excessive runoff, and many surface waters have P concentrations an order of magnitude above the natural levels.

Eutrophication also seriously disrupts coastal ecosystems in regions receiving high P inputs. Perhaps no other instance is as worrisome as the effects of P discharges from Queensland's growing population and agriculture, which now release about four times as much P as was the natural rate along the coast. Resulting eutrophication threatens the Great Barrier Reef, the world's largest coral formation, by smothering coral with algae as well as by promoting the survival and growth of the larvae of *Acanthaster planci*, the crown-of-thorns starfish, which has recently destroyed large areas of the reef (126). Experiments with artificial N and P enrichment of microatolls have shown that although both N and P stimulate the growth of algae, which block sunlight from reaching deeper waters and make the coral brittle and stunted, only P inhibits the calcification of corals (127).

As the Baltic Sea unfortunately demonstrates, in the absence of vigorous water exchange with the open ocean, even a whole sea can become eutrophic. In 1990, the Baltic Sea received about 80,000 t P, eight times the rate in 1900, and the nutrient's concentrations in its water were, on the average, about four times higher than in 1950; nitrogen enrichment, though not as large in relative terms, was also substantial (128). As a result, a third of the sea bottom of the Baltic proper (the southern part of the sea) is now intermittently deprived of oxygen, a condition that also results in formation of toxic H<sub>2</sub>S by S-reducing bacteria and precludes the survival of previously very common mussels and bottom fish. On the other hand, increased phytoplanktonic production on shallow bottoms with well-oxygenated water has provided more food for herring and sprat.

## 6. REDUCING ANTHROPOGENIC IMPACTS

As with all anthropogenic burdens, the best way to reduce the impact of P on the biosphere is to minimize the initial inputs; controlling the escaping element or compound is the usual strategy in modern high-consumption societies, but it is only the second-best choice. The most fundamental opportunity to minimize the inputs is to reduce the intake of animal foods whose production requires first high P inputs in growing the requisite feed and then entails unavoidably large P losses in animal wastes. The nutritional status of people in affluent countries would not be compromised in the slightest if people were to consume 25% less meat and dairy products than the current average (this would still leave the annual per capita mean at more than 50 kg of meat and above 100 kg of dairy foods); because 66% of all phosphatic fertilizers are used on cereals and 60% of all grains in rich countries are used as animal feed, the need for phosphatic fertilizers would



decline by 10% without any investment. This shift would lower P applications in high-income countries by about 15%.

Given the fact that more than 40% of the global cereal harvest is used for feeding domestic animals (and the share is over 60% in many affluent countries), fertilizer applications can also be reduced by more efficient feeding. The bulk (60–70%) of P in most cereal and leguminous grains is organically bound in phytic acid and hence almost indigestible for monogastric (nonruminant) mammals that lack the requisite enzyme (phytase) to free the phosphate from the molecule (129). This necessitates addition of inorganic P to animal diets and results in large losses of P in excreted manure. Addition of phytase and enhanced utilization of phytate could thus substantially reduce P excretion by pigs.

Legislated limits have already been used to restrict the release of P from point sources and applications of P in both organic and inorganic fertilizers. Restrictions, or outright local bans, on the use of P-containing detergents enacted during the 1970s lowered the P concentrations in urban sewage. In North America, the US Federal Water Pollution Control Act Amendments and US-Canadian Water Quality Agreement restricted all point sources discharging more than 3800 m<sup>3</sup>/day to concentrations of less than 1 mg P/L beginning in 1972 in the Lake Erie and Lake Ontario basins, and since 1978 in the entire Great Lakes basin. Since 1995 sugar cane farmers in Florida have cut their P discharges into the Everglades Agricultural Area by nearly 70% compared with the levels prevailing during 1979–1988, rather than just by the mandated 25% (130).

Gradual Dutch restrictions on P applications may be copied in the future by many other countries. Limits on the number of animals in problem areas were introduced in 1984; three years later came the limits on the amount of manure produced, and in 1998 all farms had to adopt mineral accounting that restricted allowable P losses to 40 kg of P<sub>2</sub>O<sub>5</sub> (about 17.5 kg P/ha); this rate will be halved by 2008 (60, 63). Farmers exceeding this standard will have to pay a proportional levy.

Inputs of P fertilizers can be lowered by relying on a variety of well-tested best management practices (6, 118, 121). Direct measures should always include fertilizer applications based on recommendations derived from repeated soil tests; P applications may also be omitted for several years on soils with high P content without affecting yield. Maintenance of a proper soil pH and the incorporation, rather than broadcasting, of fertilizers and manures are no less important. The last practice is particularly effective for manuring; broadcast dairy manure may release five times as much P as the waste incorporated into soil. Timing of applications is also important; those immediately preceding intensive rains will be associated with much larger losses. And because phosphate diffuses horizontally only about 3 mm from the applied particle, fine distribution of P fertilizers allows for lower applications producing higher yields (67).

Variable rate fertilizing, a principal ingredient of precision farming, is another input-saving technique based on the recognition of spatial variability of nutrient distribution in a field. Instead of managing fields as homogeneous units fertilized

with a single rate, computer-controlled applications guided by a global positioning system make it possible to vary the dose over short distances as predetermined by detailed soil sampling (131).

Indirect measures aimed at reducing initial inputs and moderating postapplication losses should include above all an appropriate land use for the site, practices to limit erosion (cultivation of cover crops, contour plowing, reduced tillage or no-till farming, terracing), and a balanced application of all macro- and micronutrients. Where possible, treed buffer zones around heavily fertilized fields or along streams and water bodies can reduce the runoff into streams. Preventing uncontrolled runoff of barnyard and feedlot waste is still one of the most cost-effective measures to reduce the P loading of nearby waters.

Future possibilities of managing environmental P may include the use of acid-producing bacteria that can increase the solubility of phosphates (commercial success of their applications will depend on developing suitable distribution methods and assuring the survival of the bacteria in soils) and, even more remotely, inoculation with suitable mycorrhizal fungi, currently just an intriguing promise (67).

Removal of P from sewage and industrial waste is now a mature commercial endeavor (66, 132). Primary sedimentation retains organic P in the resulting sludge, which can be used as a fertilizer. Secondary sedimentation with aeration transforms nearly all organic P into inorganic phosphates, and its typical effluent contains 10–25 mg P/L, far in excess of maxima permissible to prevent eutrophication of sensitive waters. Single addition of flocculating agents prior to primary sedimentation removes 70–90% of all P, whereas repeated treatments bind 80–95% of the nutrient initially present. The high cost of the reagents and increased production of sludge (up to 50% by mass and 150% by volume) make chemical precipitation less acceptable than the controls aided by bacteria. Moreover, the sludge from chemical precipitation is neither a good fertilizer nor a suitable raw material (ash from its incineration has too much Al or Fe).

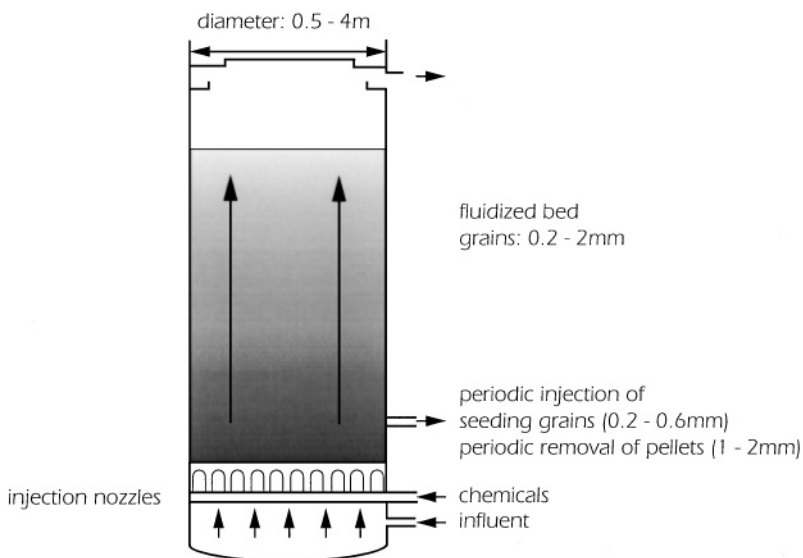
Bacterial removal takes advantage of the so-called luxury uptake and storage of P beyond the amount normally found in microorganisms in activated sludge biomass, which contains just 1.5–3% P (132, 133). Initial anaerobic conditions induce the release of P from the mixture of influent wastewater and recycled sludge. This approach arose from the experience at conventional activated sludge plants during the late-1960s and the early 1970s where a high P removal occurred under anaerobic conditions caused inadvertently by heavy organic loadings and poor aeration (134, 135). In less than six days the soluble P is rapidly taken up by phosphate-accumulating bacteria in the aerated aerobic basin, and the effluent contains less 1 mg P/L. Resulting sludge, with up to 7% P, can be recycled or it can be dried and incinerated and P recovered in the incinerator ash.

Bacteria are not the only organisms that can be employed in controlling P. Combinations of algae and fish may be an effective alternative to conventional P removal (136). Algae assimilate the nutrients from polluted water flowing through a series of vessels; algal-grazing fish feed on the periphyton and the fish and their

feces are convenient P sinks. Experiments show that the sequestered P is roughly equal to P removed in microbial sludge.

Controls of anthropogenic P can go a step further. Although there is no practical way of recovering and reusing P lost from fields, it is possible to recover and reuse the nutrient present in relatively high concentrations in urban and industrial sewage or in animal wastes produced in large feeding facilities. A growing number of P recovery processes, developed first in the Netherlands during the late-1970s, are now either commercially available or are in advanced research or pilot plant stages (66, 137, 138). Some of these processes (Dutch DHV Crystalactor<sup>TM</sup> and the process developed at the Geochem Research/Delft University and Japanese Unitika) recover P in magnesium ammonium phosphate [struvite,  $\text{Mg}(\text{NH}_4)(\text{PO})_4$ ], but this compound cannot be used for the traditional wet acid route of superphosphate production.

Recovery as calcium phosphate (hydroxyapatite) is greatly preferable inasmuch as the compound is indistinguishable from phosphate rock, and hence it is ready for any subsequent processing. Operating plants include DHV Crystalactor designs at three wastewater plants in the Netherlands (Figure 4), three Kurita wastewater plants in Japan; Essex and Norfolk Water in the United Kingdom, Karlsruhe University at Darmstadt, and Water Board in Sidney have built experimental plants. All of these processes use fluid bed crystalization producing pellet-like solids with



**Figure 4** Cross-section through the DHV Crystalactor<sup>TM</sup>. (Based on a cross-section in Reference 66.)

5–15% P. Effluent from these processes has less than 0.5 mg P/L. The economics of these operations will be much improved only when P removal becomes mandatory; reduced sludge production and savings on precipitation reagents matter more than the value of recovered P. Reusing phosphates recovered from wastes with high P content in detergents or as food additives may not find an easy public acceptance.

The combination of legislated limits on inputs and releases and increasingly effective P removal techniques from point sources has reduced P loadings. Encouraging results have been documented within less than a decade of reduced P loadings. By 1980, Lake Ontario showed a substantial improvement and Lake Huron's Saginaw Bay, where total P loading declined by 55% between 1974–1980, had a large drop in chlorophyll concentrations and a substantial decrease in threshold odor in the municipal water supply (139). On the other hand, internal recycling of P from lake sediments may continue to support excessive algal growth even after P inputs have been reduced. Also, reducing P loadings of estuaries may not be enough, as many of them—including Long Island Sound, San Francisco Bay, and the mid-Chesapeake Bay—have their primary productivity limited by nitrogen, rather than by P (140).

Although the most preferable means of managing P in a water body is managing the P flows from the whole catchment, remedial actions can be taken even after excessive amounts of P have reached the water. Increased P export can be achieved by the diversion of hypolimnic water with its high P-levels, and by prolonging P retention through higher sedimentation or lowered redissolution (114, 141). Artificial mixing to destroy stratification and hypolimnic oxygenation are other possibilities.

## 7. LONG-TERM PERSPECTIVES

No other element used in large quantities by modern civilization has such a peculiar fate as P: Millions of tonnes of P are taken every year from just a score of places in the Earth's crust in order to be processed and distributed thinly over an area exceeding one billion hectares of the world's cultivated land. Roughly half of the applied nutrient is assimilated by crops and most of the rest is fixed in soils and stored in sediments; although only a small amount of the lost nutrient is dissolved in water, it is the dominant cause of undesirable eutrophication.

There is no natural process akin to denitrification, the incessantly working enzymatically mediated reduction that closes the biospheric N cycle by returning the element to its nonreactive atmospheric molecule: Applied P cannot be naturally recycled, and although we can now recover it from concentrated urban and industrial wastes, there is nothing we can do to salvage the losses from diffuse applications that keep accumulating in soils and in sediments. Even an early stabilization of the global population at well below 10 billion people will not prevent higher demand for P fertilizers and hence further nonrecyclable applications of P.

Besides the expected increase of roughly another 3 billion people by 2050 (142), the factors tending to boost the use of fertilizers include the elimination of

undernutrition and rapid dietary transitions (higher consumption of animal foods as well as of fruits and vegetables) in low-income countries. On the other hand, further likely declines in fertilizer use in many affluent countries, more efficient applications, and improvements in animal feeding will moderate future demand. Still, the net outcome is for fertilizer P to surpass the growth rate of the world's population during the next two generations. Steen (76) forecast the most likely overall use of 26–30 Mt P by 2050—but I would not exclude a total as low as 21–22 Mt P/year.

In any case, the long-term trend of P applications cannot be a mere intensification of past practices; these are unsustainable not only on a civilizational time scale ( $10^3$  years), but even for another 150 years, or for as long a period as has already elapsed since the beginning of P fertilization by Lawes. Running out of phosphates to mine is actually the least cause for concern. Reserve estimates depend on the criteria used for the economic recoverability of the minerals. Recently published totals range between 1.5–3.5 Gt P for reserves, 4.7–9.5 Gt P for potential reserves, and about 13 Gt P for resources (76, 143).

At the current rate of extraction, global reserves would last about 80 years, and the estimated resources could support the recent rate of applications for nearly 250 years. Analogical figures for Morocco are 280 and 1000 years, whereas for the rest of the world they are just 45 and 100 years (144). This last reserve/production ratio is very similar to the recent value for crude oil, but the distribution of phosphates is even more uneven than that of giant oil fields: Ten of the world's most populous low-income countries, with more than 50% of global population and with enormous potential need for P fertilizers, have a mere 5% of all high-quality reserves. Clearly, higher reliance on Moroccan deposits, which now supply just 15% of the global demand, is inevitable. With it will come environmental and logistic problems, but there is little reason to fear an extortionist monopoly.

The world has enormous phosphate deposits on land and in the ocean, and higher prices would open up economic opportunities for extracting lower quality land ores as well as tapping sediments on continental shelves and seamounts in the Atlantic (off Morocco, the Congo River delta, Namibia, Florida, North Carolina) and the Pacific (Chatham Rise off New Zealand, off Baja California, Peru, and Chile) Oceans, which contain enough P to last for millennia.

Rather than the quantity, it is the quality of extracted phosphates that is already a matter of increasing concern. This is due largely to the contamination with heavy metals. Sedimentary phosphates contain low levels of more than a dozen elements—including As, Cd, Cr, Hg, Pb, U, and V—whose excessive concentrations pose hazards to health. Cadmium is the most enriched element in phosphate rocks, occurring in concentrations almost 70 times higher than in average shale (145). The global average of Cd levels in phosphates is about 21 mg Cd/kg of rock, but some Moroccan rocks have up to 40 mg, and phosphates from Togo and Tunisia contain up to 50–55 mg Cd/kg (146).

Igneous phosphates contain much lower levels of Cd than do the sedimentary rocks, but their production accounts for less than 15% of total extraction and

possibilities of expanding their exports from Russia and South Africa are limited. As Florida phosphates, which have some of the lowest Cd concentrations (average just around 9 ppm Cd for central and 6 ppm Cd for north Florida deposits), become depleted, the average content of Cd and other potentially hazardous trace elements in the global output of phosphate rock will increase. This may lead to banning some ores from countries regulating the introduction of Cd into the environment.

The World Health Organization suggests that the maximum daily intake of Cd should not exceed 1  $\mu\text{g}/\text{kg}$  of body weight, or between 50–70  $\mu\text{g}/\text{day}$  for most adults, although recent European intakes are already as high as 40  $\mu\text{g Cd}/\text{day}$  (146). Consequently, about a dozen countries (including Australia, Denmark, Germany, Japan, and The Netherlands) have already enacted Cd limits for P fertilizers. However, a universal ban on high-Cd ores would eliminate a substantial share of potential extraction from the world market: Deposits in North Carolina, Senegal, Togo, Tunisia, and above all, in Morocco would be entirely or largely affected (147). Removing the trace metals is possible but costly, and different processes require high energy inputs and generate hazardous wastes.

Removal of Cd would also increase the energy cost of P fertilizers. Depending on the final product, their recent energy cost has been 18–32 MJ/kg P; the upper end of this range is almost exactly as high as today's most efficient synthesis of ammonia, which requires as little as 32–33 MJ/kg N (73, 148). The Cd problem goes beyond inorganic fertilizers, as the disposal of sewage sludge can cause heavy loadings of Cd in soils where they are very persistent; Cd in animal manures (particularly where animals are given P supplements) can also add considerably to Cd field burden.

In comparison to the widespread Cd problem, the waste generated by phosphate mining is a highly localized environmental degradation. Phosphate mining in Florida creates an enormous amount of waste, almost 12 tonnes of phosphogypsum for every tonne of P in the processed ore (149). The material accumulated in nearly 30 phosphogypsum piles amounts to more than 800 million tons and is increasing by about 30 Mt/year. Although these wastes could be used in the manufacturing of sulfuric acid and as road aggregates, the Environmental Protection Agency banned any use of phosphogypsum because it contains radium (above 10 pCi Ra/g, whose decomposition releases radon) and heavy metals.

Concerns about eutrophication have already led to legal limits on P applications and P discharges from wastewater treatment. This trend will almost certainly continue, and so it is not audacious to forecast that a maximum practicable removal of P from all significant point sources of the nutrient (sewage plants, industries, and large animal feedlots) will be required within a generation, and that limits on P applications in both manures and inorganic fertilizers will be commonplace in all intensively cultivated regions. The extent of reusing the recovered P is much less certain.

Even more uncertain would be to quantify the role of P in the likely increase of the Earth's phytomass. Although it is generally accepted that the stimulating effect of higher atmospheric  $\text{CO}_2$  concentrations and enrichment of many ecosystems by

substantial nitrogen deposition have already boosted the global photosynthesis during the second half of the twentieth century, the extent of further CO<sub>2</sub>- and nutrient-induced stimulation remains highly uncertain, particularly in the case of natural terrestrial ecosystems (29, 112). Using P to fertilize ocean waters in order to boost the marine catch is a speculative proposal akin to enriching the nutrient-poor surface waters with iron (151).

Whereas it is unlikely that P flows will ever receive as much attention as the cycles of carbon and nitrogen, continuing human intervention in the nutrient's terrestrial and aquatic stores and transfers guarantees that the concerns about the element's role in global environmental change will be with us for generations to come. A realistic hope is for an adoption of effective strategies that would limit these impacts to tolerable levels.

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