Phosphorus: Global Transfers

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Although relatively rare in the biosphere, phosphorus (P) plays several key roles in the chemistry of life, above all due to its presence in nucleic acids (deoxyribonucleic acid, DNA and ribonucleic acid, RNA) and in adenosine triphosphate, the life's carrier of energy. Phosphorus – unlike carbon, C, nitrogen, N and sulfur, S – does not form any long-lived atmospheric compounds and hence its global cycle is just a part of the grand, and slow, process of denudation and geotectonic uplift. But on a small scale the element is rapidly recycled between organic and inorganic forms in soils and water bodies. Human activities now annually move more than four times as much phosphorus as did the natural processes during the preagricultural era.

Together with nitrogen and potassium, phosphorus is one of the three macronutrients needed by all plants, and its applications in inorganic fertilizers have been essential for raising crop yields during the 20th century. The nutrient is also frequently the limiting factor of aquatic productivity, and even its relatively low concentrations present in the runoff from fertilized fields can cause eutrophication (excessive nutritional enrichment) of both fresh and ocean waters, an environmental change with numerous undesirable consequences. Fortunately, appropriate agronomic practices and wastewater treatment can moderate the environmental impact of anthropogenic phosphorus.

IMPORTANCE OF THE ELEMENT

Phosphorus is one of the three macronutrients required by plants. It is particularly important for the growth of young tissues, flowering and seed formation (cereal grains contain 0.25–0.45% phosphorus (P), more than is contained in any other plant tissues). The element is also an essential micronutrient in humans: its daily intakes are usually around 1.5 mg capita^{-1}, well above the recommended daily minima of about 1.2 mg (National Research Council, 1989).

P is absent in cellulose, hemicellulose and lignin, the three polymers that make up the bulk of the plant mass, as well as in proteins that compose the metabolic tissues of heterotrophs. However, the element is abundant in bones and teeth: hydroxyapatite, a calcium phosphate, makes up 60–70% of their mass. The element is indispensable in phosphodiester bonds linking mononucleotide units of RNA and DNA, and all life processes are energized by transformations of adenosine triphosphate.

NATURAL STORES AND FLOWS OF PHOSPHORUS

Comprehensive assessments of the global P cycle have been much rarer than the studies of carbon or nitrogen flows (Smil, 1990; Jahnke, 1992; Mackenzie *et al.*, 1993; Tiessen, 1995; Smil, 2000; Figure 1; Table 1). The Earth's crust is the largest reservoir of the element, nearly all of it bound in apatites, calcium phosphates containing also iron, chlorine or the OH group. Soluble phosphates are released by weathering, but they are rapidly transformed to insoluble compounds in soils. Consequently, plants must be able to absorb P from very dilute solutions and concentrate it 100–1000 fold in order to meet their needs, and P released by decomposition of biomass is rapidly reused.

The element is even less available in fresh waters and in the oceans where its particulate forms sink into sediments and where soluble phosphates are rapidly recycled in order to support phytoplanktonic photosynthesis in surface waters. Only in the areas of upwelling are surface layers enriched by the influx from deeper waters. Phosphorus in marine sediments can become available to terrestrial biota only after the tectonic uplift re-exposes the minerals to denudation. The element's global cycle thus closes only after tens to hundreds of millions of years. However, the temporary interruptions of the element's oceanward journey are indispensable for the Earth's life.

The terrestrial phytomass stores about 500 Mt of the element, plant growth assimilating up to 100 Mt P year^{-1}. Phosphates dissolved in rain and dry-deposited in particles amount to only about 3 Mt a year. Soils store about 40 Gt P, with no more than 15% of this total bound in organic matter. Natural denudation and precipitation transfer annually about 10 Mt of particulate and dissolved phosphorus from land to the ocean. The marine phytomass stores only some 75 Mt phosphorus but because of its rapid turnover, it absorbs annually about 1 Gt P from surface water. Mixing between sediments and the surface layer is effective only in very shallow waters, and high near-surface concentrations of the nutrient only occur in coastal areas receiving phosphorus-rich runoff. Coastal seas contain only some 0.2% phosphorus in the ocean but they support a disproportionately large share of marine productivity, and the top 300 m of the open ocean contain less than one tenth of all marine phosphorus.

ANTHROPOGENIC MOBILIZATION OF PHOSPHORUS

Human activity intensifies biospheric phosphorus flows in five main ways:

1. accelerated erosion and runoff caused by large-scale conversion of natural ecosystems (mainly forests and grasslands) to arable land;
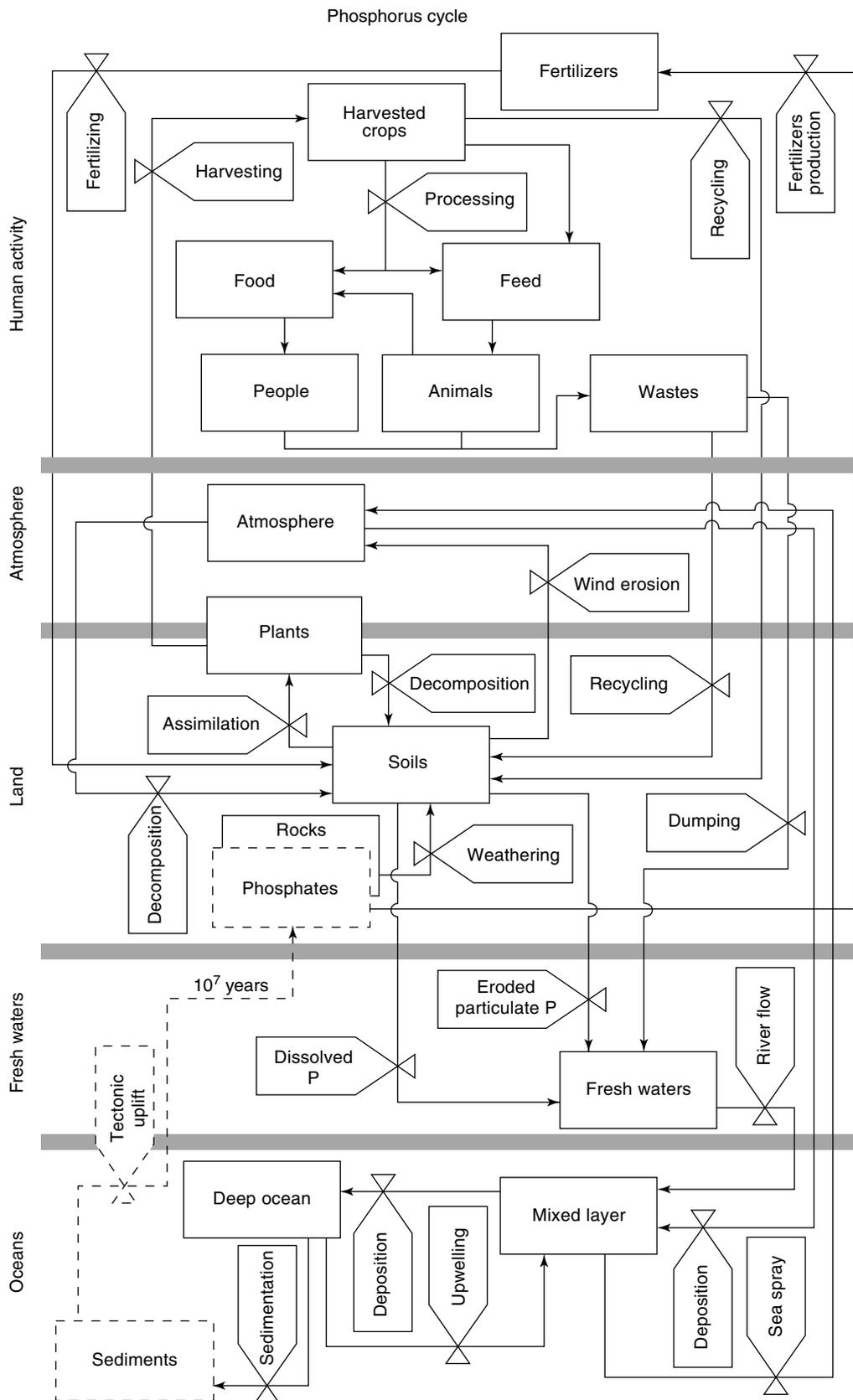
Phosphorus cycle

Figure 1 Global phosphorus cycle

Table 1 Major biospheric reservoirs and fluxes of phosphorus

Phosphorus reservoirs	Total storage (Mt P)
Ocean	93 000
Surface	8000
Deep	85 000
Soils	40–50
Inorganic phosphorus	35–40
Organic phosphorus	5–10
Phytomass	570–625
Terrestrial	500–550
Marine	70–75
Zoomass	30–50
Anthropomass	3
Phosphorus fluxes	Annual rate (Mt P year^{-1})
Atmospheric deposition	3–4
Erosion and runoff	25–30
Particulate phosphorus	18–22
Dissolved phosphorus	2–3
Plant uptake	970–1300
Terrestrial	70–100
Marine	900–1200
Burial in marine sediments	20–35
Tectonic uplift	15–25

Table 2 Human intensification of the global phosphorus cycle (all values are in Mt P year^{-1})

Fluxes	Natural	Preindustrial (1800)	Recent (2000)
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

2. settlements and transportation links;
3. recycling of organic wastes – crop residues, animal manures and human urine and faeces – to fields;
4. releases of untreated, or insufficiently treated, urban and industrial wastes to streams and water bodies;
5. applications of inorganic fertilizers; and combustion of biomass and fossil fuels (Smil, 2000; Table 2).

Although the last process is the least important source of phosphorus, it is the largest anthropogenic source of carbon and a large source of fixed nitrogen (*see* **Phosphorus Water Quality Objectives**, Volume 3) Trace amounts of phosphorus present in wood and coal remain overwhelmingly in the ash and less than 0.3 Mt P are released annually in airborne particulate matter.

Recycling of organic wastes has always been a mainstay of traditional farming and it remains an important ingredient of well-balanced modern agriculture. Progressing urbanization and diffusion of sewers have gradually reduced the often intensive recycling of human wastes, once characteristic of many regions of Asia and Europe. Nevertheless, the recycling of crop residues remains highly desirable, not only because of the return of plant nutrients but also because of its contributions to better tilth, higher water absorption capacity and reduced soil erosion. During the 1990s, global crop harvests produced about 3.75 Gt (dry matter) of residues (mostly cereal straws). About half this phytomass was recycled, returning (with average content of 0.05–0.1% phosphorus) 1–2 Mt P to arable soils.

Animal wastes are potentially a very large source of recyclable phosphorus. Every year, over four billion large mammals and some 10 billion domestic birds produce together about 2 Gt of dry waste containing up to 20 Mt P. Only the wastes produced in confinement are recyclable but, because of their bulk, uneven distribution and excessive cost of application beyond a limited radius from the source, not all of this manure is actually applied to fields. The best estimates indicate annual return of up to 8 Mt P, with the highest applications (exceeding 50 kg P ha^{-1}) in such regions of high animal density as the US Corn Belt, Northwestern Europe and East Asia.

The global population of six billion people now discharges every year about 3 Mt P in its wastes. Nationwide production densities of human waste are as high as 9 kg P ha^{-1} of cultivated and settled land in densely populated countries (Egypt, Japan), and more than 100 kg P ha^{-1} in large cities. A large share of human waste produced in rural areas of the low-income countries is deposited on land, but progressing urbanization puts a growing share of human waste into sewers and then, treated or untreated, into streams or water bodies. Since the 1940s phosphorus-containing detergents have added another major source of waterborne phosphorus. Neither the primary sedimentation of urban sewage (which removes only 5–10% of the initial phosphorus in the sludge), nor the use of trickling filters during the secondary treatment (removing 10–20% phosphorus) withhold enough of the nutrient to prevent eutrophication, undesirable enrichment of waters with the nutrient that most often limits the growth of phytoplankton.

Conversion of forests and grasslands removes the canopies and litter layer that protect the soil and opens the way for accelerated soil erosion which increases typically by one or two orders of magnitude, from $0.1-2\,t\,ha^{-1}$ to $10-20\,t\,ha^{-1}$ a year; overgrazing of permanent pastures has a similar effect. The additional phosphorus lost due to these changes is difficult to quantify with any degree of confidence. I have estimated that over $20\,Mt$ more phosphorus are lost annually from farmland and pastures than erosion would have removed from the same area of land if it were covered by undisturbed natural ecosystems. Enhanced anthropogenic loss of dissolved phosphorus adds another $1\,Mt\,P\,year^{-1}$.

Production of inorganic fertilizers began during the 1840s with the treatment of P-containing rocks with dilute sulphuric acid. The resulting ordinary superphosphate (OSP) contains $7-10\%$ phosphorus, ten times as much as recycled phosphorus-rich manures. Discovery of huge phosphate deposits in Florida (1870s), Morocco (1910s) and Russia (1930s) laid the foundation for the rapid post-World War II expansion of the fertilizer industry. Consumption of phosphatic fertilizers reached $5\,Mt\,P$ in 1960 and it peaked at more than $16\,Mt\,P$ in 1988. After a 25% decline by 1993 the global use began rising once again (International Fertilizer Industry Association, 1999; Figure 2). The top three producers (USA, China and Morocco) now account for about 2/3 of the global output. Major fertilizers besides OSP include triple superphosphate (TSP, containing about 20% P) produced by treating phosphate rock with phosphoric acid, and combinations with nitrogen (mono- and diammonium phosphate), calcium and potassium (UNIDO and IFDC, 1998).

DEPENDENCE ON INORGANIC FERTILIZERS

Modern cultivars whose harvests now dominate the production of food and feed remove annually between $15-35\,kg\,P\,ha^{-1}$ of cereals, $15-25\,kg\,P\,ha^{-1}$ of leguminous and root crops and $5-15\,kg\,P\,ha^{-1}$ of vegetables and fruit (Pierzynski and Loan, 1993). Global food harvests now assimilate about $12\,Mt\,P$ in crops and in their residues while no more than $4\,Mt\,P$ are supplied annually by weathering of P-bearing rocks and by atmospheric deposition (Smil, 2000). Applications of phosphatic fertilizers have thus become indispensable for producing today's harvests and this dependence will only increase.

Combination of an early stabilization of human population at less than 10 billion people, less meaty diets in affluent countries (where about 60% of all cereals are now used as animal feed), and relatively modest increases in animal food consumption in low income countries would significantly lower the growth rate of global food demand during the first half of the 21st century – but they would still result in a substantial rise of overall phosphorus requirements.

During the 1990s global applications of inorganic fertilizers averaged just over $10\,kg\,P\,ha^{-1}$ of arable land, with continental means ranging from a mere $3\,kg\,P\,ha^{-1}$ in Africa to over $25\,kg\,P\,ha^{-1}$ in Europe (International Fertilizer Industry Association, 1999). These means hide enormous inter- and intra-national differences, as well as uneven use on different crops. For example, in Africa applications are adequate on some plantation crops while tens of millions of the continent's subsistence peasants have never applied any phosphorus at all. International surveys indicate that nearly 2/3 of all applied phosphorus is used on cereals, 10% on oilseeds and about 5% on vegetables (Harris, 1998). Crops receiving the highest applications are corn in the US Corn Belt (around $60\,kg\,P\,ha^{-1}$), Japanese rice (over $40\,kg\,P\,ha^{-1}$) and Chinese and West European winter wheat (about $35\,kg\,P\,ha^{-1}$).

PHOSPHORUS IN AGRICULTURAL SOILS

Phosphorus applied in both organic and inorganic fertilizers is involved in complex reactions that transform a large
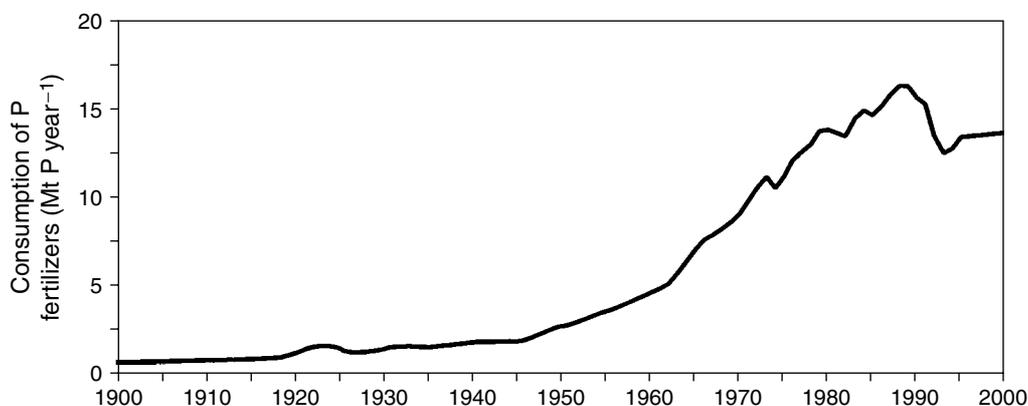

Figure 2   Consumption of inorganic phosphatic fertilizers, 1900–2000
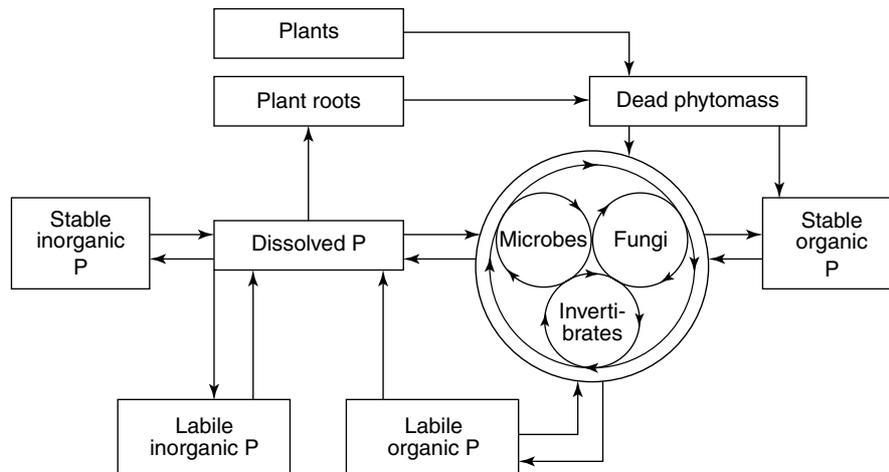
Figure 3 Phosphorus cycle in soil

part of soluble phosphates into much less soluble compounds (Figure 3). Particularly important in this regard are reactions between superphosphates and Al, Fe, K and Mg. The resulting compounds are relatively insoluble and hence immobile in soil. This process of P fixation has been known since 1850 and it has received an enormous amount of research attention (Khasawneh *et al.*, 1980; Morgan, 1997). The traditional argument is that the fixation is rapid, dominant and irreversible. Accordingly, phosphate applications were seen as overwhelmingly futile – albeit laborious and costly – exercises of moving the element from extracted rocks to insoluble soil compounds (Tinker, 1977).

This misconception resulted in decades of excessive use of phosphorus in agriculture: global N : P ratio of applied fertilizers was just around 1.5 by the late 1940s. Mounting evidence of relatively high efficiency with which crops use the nutrient has finally changed that wasteful practice (Karlovsky, 1981; Isermann, 1990). By the late 1990s the global fertilizer N : P ratio stood around 6 : 1. Recovery rates of 50–60% of applied phosphorus are not uncommon, and maxima are above 70%. Even the global mean appears to be close to 50%, virtually the same as the rate for inorganic nitrogen. Decades of relatively high P applications and the gradual release of a part of the initially fixed nutrient have resulted in many fertilized agro–ecosystems have considerable surpluses of available phosphorus (Edwards *et al.*, 1997). Present annual accumulations commonly amount to several $kg\,P\,ha^{-1}$, surpassing $30\,kg\,P\,ha^{-1}$ in the most intensively cultivated regions.

PHOSPHORUS IN WATERS

The low solubility and high sorption rates of phosphorus compounds limit their leaching into ground waters, leaving diffuse runoff from fertilizers and manures and direct, point discharges of urban and industrial wastes as the two principal ways of enriching surface waters with phosphorus. Because a single atom of phosphorus supports the production of as much phytomass as 16 atoms of nitrogen and 106 atoms of carbon, even relatively low additions of the nutrient can cause eutrophication (*see* **Eutrophication**, Volume 2), excessive nutritional enrichment of waters (Harper, 1992; McComb, 1995; Tunney *et al.*, 1997). Mere $10\,\mu g\,P\,l^{-1}$ will support algal growth that will greatly reduce the clarity of water. As total phosphorus in water increases, the standing phytomass goes up linearly. It may include unsightly scum-forming algal blooms and filamentous cyanobacteria, as well as thick coats of algae on any submerged surfaces.

Concentrations above $50\,\mu g\,P\,l^{-1}$ will result in deoxygenation of bottom waters during the decomposition of the accumulated biomass; this can cause extensive summer fish kills and reduce or eliminate many aquatic species: pike may disappear while bream and roach, species adapted to turbid waters, become dominant. Offensive taste and odor of water filled with algae requires expensive treatment before drinking, and neuro- and hepatotoxins released by decomposition of some of these blooms may be a serious health hazard to livestock and people. Studies of polluted lakes and estuaries have shown that excessive eutrophication can be generally prevented if annual loadings are lower than $1\,g\,P/m^2$ ($10\,kg\,P\,ha^{-1}$) of water surface – but much higher loadings may not cause serious problems as long as the average retention time of imported nutrients is short.

Eutrophication also seriously disrupts coastal ecosystems in regions receiving high P inputs. For example, it has affected the growth of corals in parts of the Australian Great Barrier Reef (Bell and Elmetri, 1995). In the North Sea it repeatedly creates anoxic conditions and toxic algal blooms while a third of the sea bottom of the Baltic Sea proper (its southern part) is now intermittently deprived of oxygen, the condition which also results in formation

of toxic H_2S by S-reducing bacteria and precludes the survival of previously very common mussels and bottom fish (Jansson and Dahlberg, 1999) (*see* **Water Resources: Baltic**, Volume 3; **Baltic Sea**, Volume 4).

MODERATING THE HUMAN IMPACT

There is no shortage of ways to lower the anthropogenic loss of phosphorus. By far the most effective measure would be to reduce the intake of animal foods in affluent countries where *per capita* consumption is now commonly above $60\,kg\,year^{-1}$ of meat and that of dairy products above $100\,kg\,year^{-1}$. Lowering these intakes by $15-35\%$ would still allow the enjoyment of diets with plenty of animal foods. In addition, since 2/3 of all phosphatic fertilizers are used on cereals and 3/5 of all grains in rich countries are used as animal feed the need for phosphatic fertilizers would decline by $5-15\%$ without any investment.

An approach that is much more likely to be successful relates to best management practices aimed at reducing phosphorus applications or limiting the post-application losses (Sharpley and Withers, 1994). Indirect measures include reduced tillage, crop rotations and recycling of crop residues; direct ways include applications of phosphatic fertilizers derived from repeated soil testing, balanced amounts of the three macronutrients, maintenance of appropriate soil pH, and incorporation, rather than broadcasting, of phosphorus compounds.

Phosphorus in sewage can be effectively controlled either by the use of coagulating agents or by microbial processes (Imperial College of Science, 1997). Addition of flocculating reagents (most commonly salts of iron or aluminum) can remove $70-95\%$ of all phosphorus initially present but the increased bulk of the resulting sludge and high cost of reagents favor microbial treatment of waste water. This treatment relies first on anaerobic conditions for phosphorus release and then during the aerobic stage on a rapid uptake of soluble P by phosphate-accumulating microorganisms. While conventional sludge has $1.5-3\%$ phosphorus, activated sludge contains up to 7% phosphorus and the effluent has less than $1\,mg\,P\,l^{-1}$. Phosphorus-rich sludge can be either recycled or it can be dried and incinerated and the nutrient recovered from ash.

The best way to deal with waste phosphorus is to precipitate it in discrete crystalline products of reasonable purity that can be used either directly as fertilizers or as raw materials. Nearly a dozen of these processes are now commercially available or in an advanced research stage; they produce magnesium ammonium phosphate or calcium phosphate (which is ideal for further processing as it is indistinguishable from phosphate rock), and they release effluent with less than $0.5\,mg\,P\,l^{-1}$. Naturally, the eventual mass deployment of these efficient controls will depend on their cost and on the standards set by national environmental regulations.

In many cases, perhaps most notably in the Great Lakes, eutrophication has been greatly reduced due to the elimination or restricted use of phosphorus-based detergents and increased phosphorus removal from sewage. In other cases it remains a serious problem: although total Dutch phosphorus inputs were cut by about 50% by 1995 compared to the year 1985, phosphorus-saturated soils remain a large source of excessive runoff and many surface waters have phosphorus concentrations an order of magnitude above the natural levels (Uunk, 1991). And while phosphorus loadings may have stabilized, or even substantially declined in many lakes in North America, Europe and Japan, they are rising in China and India, and eventually they will increase also in Africa.

Yet another long-term environmental problem associated with applications of phosphatic fertilizers and recycling of manures and sewage sludges is the presence of cadmium (Van Kauwenbergh, 1997). Cadmium is the most enriched element in phosphate rocks, occurring in concentrations almost 70 times higher than in average shale. Maximum daily intake should not exceed $50-70\,\mu g\,Cd\,day^{-1}$ for most adults while the recent European intakes are already as high as $40\,\mu g\,Cd\,day^{-1}$. Consequently, about a dozen countries (including Australia, Denmark, Germany, Japan and the Netherlands) have already set Cd limits for fertilizers.

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