Chapter 1
PHOSPHORUS IN THE GLOBAL ENVIRONMENT

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INTRODUCTION

Phosphorus is not one of the "global" elements, it does not enter the atmosphere like nitrogen, it does not spread like sulfur by acid rain and its solubility in water is so low that there is only a slow, steady movement of P down-stream as landscapes erode and weather, or P-containing pollutants are discharged. Yet, there are some global trends in the distribution of P. To understand these and their drivers it is useful to review some of the basic properties of P in the environment.

The earth's crust contains about 1,200 mg P kg^{-1}, making it the 11th most abundant element. Common concentrations for total P in soils are between 200 and 800 mg kg^{-1}, with older soils containing lower amounts of P and younger soils containing higher amounts of P. In primary rocks and young soils, P is largely bound to calcium or magnesium, giving P a typical water solubility near 0.5 mg P L^{-1}. The weathering of minerals changes the solubility of P, as Ca is preferentially leached out, the relative abundance of Fe and Al increases and the solubility of P becomes controlled by Fe- or Al-phosphates, which have much lower solubilities than Ca-phosphates. As a result, the sequestration of P in low-solubility Fe and Al-phosphate compounds and the effect of leaching and erosion, many older and tropical soils are P deficient, i.e. the availability of P to plants and other organisms restricts ecosystem processes such as N fixation or C sequestration.

The availability of P to plants is controlled by physical and chemical reactions, including sorption/desorption and precipitation/dissolution and biological processes such as immobilization (uptake by plants and microorganisms) and by mineralization (decomposition of residues). The sorption of P, followed by slower transformations, such as solid state diffusion into the matrix of the sorbent, reduce the solubility of P, sometimes to such a degree that P is said to become "fixed". Strictly speaking, P fixation is a misnomer, since all chemical reactions are to some degree reversible, but the amount and rate of release of "fixed" P may be so low that they are ecologically insignificant.

Over 99% of naturally occurring P is in the form of phosphate, either as inorganic phosphates or as organic phosphate esters. With its four oxygen atoms per P, phosphate has a high negative charge density, so it can readily bond to any positively charged

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cation or surface. This greatly restricts the mobility of P in the environment. When phosphate is bound into relatively large organic molecules, this charge is somewhat shielded. Consequently, organic forms of P are often more mobile in the environment than inorganic P. In most soils organic P accounts for 30–65% of the total P, although some soils contain up to 90% organic P (Harrison 1987). This accumulation of organic P implies low mobility, which is due to the sequestration of P in recalcitrant soil organic matter. The negative relationship between mobility and accumulation of organic P forms is seen in the abundance of inositol hexaphosphate, which may account for half the identifiable organic P in soils. Inositol hexaphosphate is sorbed more strongly than inorganic phosphate in soils due to the high charge density resulting from its six phosphate ester groups.

In water bodies, with few absorbing surfaces and constant mixing, organisms can take up P much more easily than from a soil matrix, where sorption is strong and transport towards uptake surfaces is limited by diffusion. Even low concentrations of P are therefore very effective in increasing the biological productivity of aquatic systems. This makes aquatic systems highly sensitive to P contamination. Phosphate losses from land to water, commonly have significant eutrophying effect on surface waters.

THE BIOLOGICAL IMPORTANCE OF P

Phosphorus is an essential element of biological systems. It is part of the genetic material and the phosphate ester bond is universally used for energy transfer reactions in organisms. Plants take up and concentrate P from near 0.1 mg P L^{-1} in soil solution to 100 mg P L^{-1} in xylem sap, and can accumulate near 4,000 mg P kg^{-1} in seeds. Mammals contain around 25,000 mg P kg^{-1} dry weight. Because of the importance of P in biological processes, changes in P availability can have major impacts on ecosystem function and structure. Often both N and/or P availabilities may be near limiting levels, but the dependence of biological N fixation on adequate P supply makes P the principal limiting element of ecosystems. The biological importance of P, means that ecosystems have developed mechanisms by which P is taken up, recycled and retained efficiently (Cole *et al.* 1977; Attiwill and Adams 1993). In dystrophic or oligotrophic tropical forests, a significant portion of P is cycled biologically within the plant biomass, thus it is protected from conversion to soil P of low solubility. Lal *et al.* (2001) estimated that between 20% to 91% of the P demand of Indian dry forest trees was satisfied by re-translocation of P prior to leaf abscission. The extent of re-translocation reflects soil nutrient availability (Tiessen *et al.* 1994). Recycling through mineralization of organic P from plant residues also contributes to plant P requirements (Frossard *et al.* 2000). Annual recycling of P to soil in above- and below-ground plant residues represented 18–38% and 15–80% (mean 55%) of plant P uptake in temperate crop and forest ecosystems, respectively (Hanway and Olsen 1980; Pritchett and Fisher 1987). In dystrophic forests, much of the P uptake by roots may be directly from plant litter via the hyphae of mycorrhiza. The biological and biochemical processes of P cycling are more important in tropical soils than in most temperate environments, because of the combination of lower inorganic P availability and greater biological activity in the tropics. The high biological potential of the humid tropics is evident in the large biomass production and rapid turnover of organic matter, and also in the very intensive land use. Up to four crops can be planted and harvested per year on a single plot, generating high nutrient demand.

THE AGRICULTURAL IMPORTANCE OF P

Much of tropical agriculture is undercapitalized with respect to P fertility. Mailly *et al*. (1997) illustrate a P-budget typical for most low input agriculture over a six-year cultivation cycle in Java. Of the 130 kg P ha^{-1} accumulated in plants during the cycle, half were removed in harvested materials. Fertilization replenished only 45 kg P ha^{-1}. In addition, P stocks of arable fields are frequently depleted further by erosion. In a study on the P fluxes in low input agriculture in northeast Brazil, Menezes and Sampaio (2002) showed the largest P flow was associated with erosion from cultivated fields (6 kg ha^{-1} $year^{-1}$), followed by the erosive flow from (generally overstocked) pastures. By comparison to these erosive flows, the output of P from the farm by crop (2 kg ha^{-1} $year^{-1}$) and animal (0.2 kg ha^{-1} $year^{-1}$) products was minor.

Biological cycling of P is rarely sufficient to supply P to highly productive cropping systems. Continued inputs of P in the form of fertilizers are required to sustain high levels of production after the initial mineralization of soil organic matter, commonly associated with bringing land under cultivation. On North American grasslands, this initial release of P from inherited soil organic matter lasted for some 60 years of cultivation without P inputs, and resulted in 20–30% decreases in soil organic P (Tiessen *et al*. 1982). Following these first 60 years of cultivation, fertilizer use in the region increased many-fold.

Crop P fertilizer requirement varies with soil type, from <1 kg P ha^{-1} in relatively unweathered soils of arid environments to 200 or 300 kg P ha^{-1} in oxide rich tropical or volcanic soils. As a result, oxidic tropical and subtropical soils, which are often in regions with low purchasing power, account for 50% of the world inorganic P fertilizer requirements for crop production. Crop production on such soils without inorganic P fertilisation will degrade the (agro-) ecosystem. The important role of P in maintaining ecosystem quality is demonstrated by the need for large P inputs in restoration strategies that combine P fertilisation with the planting of N-fixing legumes for degraded lands in Southeast Asia. During the plant succession following P application, P is recycled in plant residues, which decompose to release P in quantities and at rates greater than those determined by inorganic P availability. As a result, plants with higher P demand can grow, thus re-creating an organic P supply cycle that can effectively compete with inorganic P sorption and prevent P losses by runoff and leaching. Soil P availability will remain a major constraint on food production. Management of P fertilizer inputs, together with an understanding of organic matter cycling, should allow for the development of more sustainable agriculture practices.

ECOSYSTEM P AND THE IMPACT OF HUMAN ACTIVITY

The distribution of total ecosystem P between soils and plants varies widely. In a grazed permanent pasture, herbage P amounted to only 1% of the total P content of topsoil (0–20 cm; Williams and Haynes 1992), whereas above- and below-ground plant parts of a temperate forest accounted for 38% of total P in the ecosystem (Hart *et al.* 2003). In many dystrophic tropical forests, the largest reservoir of nutrient elements is in the plant biomass. In the total (300 t ha^{-1}) aboveground biomass, of a P-limited Colombian tropical rainforest, Rodriguez-Jimenez (1988) measured 40 kg P. Such differences in P contents and elemental ratios reflect plant community adaptation to geochemical constraints.

Elevated P concentrations in the environment are often an indicator of (past) biological or human activity. Megalithic and Khalahari campsites and Terras Pretas do Indio in the Amazon all show a clearly elevated P content. Even the "industrial" fertilizer P, mined from rock phosphate with a P concentration of approximately 150,000 mg kg^{-1}, is ultimately derived from biological processes. It is the product of the sedimentation and accumulation of marine organisms.

Human impacts have substantially altered global P transformations and transfers. Phosphorus transfers in the environment are closely correlated with human occupation, as shown by the regression between P exports from watersheds and their population density: loss rates of 0.3 kg P km^{-2} at a population density of 0.1 km^{-2}, rising to 30 kg P km^{-2} at densities of 300 km^{-2} (Caraco 1995). In the Canadian province of British Columbia, diatom records in lake sediments show a significant P enrichment since 1850, the time of European settlement. The advent of inorganic P fertilizers and concentrated livestock production in some areas has greatly increased P loads in surface waters (Anderson 1997). Particularly in richer nations, inorganic P fertilizer use and concentrated livestock production have increased P loads and transfers to surface waters. The P balance for a lake watershed in Sweden, a wealthy nation with a sound environmental policy, suggests 62% of P inputs came from inorganic P fertilizer, 30% from manure, 5% from sewage, 2% from atmospheric deposition and 0.3% from the natural weathering of rocks (Ryding *et al.* 1990). Phosphorus outputs were, 93% in crop exports, 6% in erosion from arable land and 0.6% was leached to ground water. The total P inputs were three times greater than outputs; i.e. the watershed showed a net P accumulation.

The surplus of P in highly developed regions is in stark contrast to the nutrient deficiencies in many developing countries. While P reserves in soils of highly developed agricultural areas are increasing, and even reaching saturation, many tropical soils have a large P deficit, aggravated by high P fixation capacities that reduce fertilizer availability. Increased food demands from old, weathered, often tropical soils has reduced the fertility of these soils beyond the traditional capacity for regeneration (such as under shifting cultivation) and land degradation is evident. Phosphorus availability in these soils is very low and will not sustain growing populations without extra P inputs.

World trade movements amount to some 10 million tonnes P year^{-1}, with 81% of trade in fertilizer, rock or phosphoric acid, 15% in plant and 1% in livestock commodities (Beaton *et al.* 1995). Since trade flows are uneven between world regions, these figures imply an important P enrichment in regions with large and wealthy populations, which import both fertilizers and other P-containing commodities. An equalization of P availabilities around the globe would require large resources, investments in effective P recycling and an increased value-added activity in primary producer regions. Shipping livestock products rather than soybean for instance, would avoid some of the nutrient concentration in rich intensive livestock production regions. While the need for efficient use of P has prompted human populations to evolve elaborate management strategies for maintaining P fertility in agriculture, recycling P and limiting P pollution from wastes, improvements in management and shipping patterns are still needed if increasing populations are to manage their environments sustainably.

Regions that import large P surpluses endanger the biological integrity of their surface waters. Although most watersheds will show a net P retention, even with substantial P inputs, they are leaky, and rates of P export are higher after P application than natural levels. Phosphorus inputs into fresh waters can increase growth of algae and aquatic weeds and lead to oxygen shortages due to their decomposition. Remedial action in such cases has focused on the role of P, although N is also essential for the growth of aquatic biota. The focus on P is due to the difficulty in controlling the fixation of atmospheric N by blue-green algae (Sharpley and Rekolainen 1997). Some 10% of P export from land occurs by leaching and ground water transport, while 90% is transported by overland flow as sediment or dissolved P. Despite the small proportion of leached P, it has a greater effect on eutrophication of receiving waters because it is soluble and therefore easily available to biota. Phosphorus losses by over-land transport range from 0.1 to 10 kg ha^{-1} year^{-1}, or more on highly erosive sites.

On average, surface runoff waters carry 10 μg L^{-1} of dissolved and 1,000 μg L^{-1} of sediment P (Melak 1995). While P is transported down-stream, sedimentation and re-suspension occur. Phosphorus is released from the sediment when solution P is diminished. The concomitant movement and recycling of P results in a “spiraling” of P as it moves down rivers. Inland lakes are affected by past fertilizer and animal waste management. More dialogue between freshwater and land use practitioners on the transfers of nutrients between systems is needed to develop regional plans to prevent P loss.

Globally some 33 million tonnes P year^{-1} are discharged into oceans, of which, more than half is carried by rivers and the remainder is coastal runoff (Howarth *et al.* 1995). Most of the input to oceans is ultimately buried in sediments, through processes lasting millions of years. Coastal seas receive both sediment-bound and dissolved P. The bio-available portion of P in fluvial transport is estimated to be approximately 2 million tonnes P year^{-1} and is responsible for the high productivity of near-shore waters. The sensitivity of coastal regions means that prevention should be favored over damage management. Water of the high oceans contains only 0.01 mg P L^{-1}, and P is critically limiting productivity of these waters.

One problem with quantifying the role of P in the global environment is the difficulty in measuring the biologically active or available portion of P. Phosphate availability is a function of chemical equilibrium-controlled solubilities and sorption reactions, and of rate-limited biological processes. Most methods for determining available P attempt to quantify only the chemical solubility of P using different extractants, but few relate this to P supply rates to plants. Soil test methods extract a portion of soil P that is related to plant available P, as estimated by regression equations established over years of agronomic experimentation and testing of fertilizer responses. Results obtained with this approach are rarely transferable between crops or soil types. The approach does not work at all when perennial plants or natural ecosystems are examined, because measurable pools are often small, and biological P re-cycling determines P availability. Since available P is constantly replenished, it is strongly time dependent. This makes available P a functional concept rather than a measurable quantity.

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