Chapter

Phosphorus: A Boon or Curse for the Environment?

D. Sayantan and Sumona Sanyal Das

Abstract

Phosphorus, a limiting nutrient of biosphere, exists as dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP), particulate inorganic phosphorus (PIP) and particulate organic phosphorus (POP) in water of soil as well as ponds, lakes, etc. The only available phosphorus for plants are DIP, while the other forms need to be converted to DIP by the decomposing microorganisms of the soil. The heavy metals (such as arsenic and chromium), which are the menace of both terrestrial and aquatic environment, are taken up by the plants and animals causing toxicity at physiological level. However, the metal (Cr and As) toxicity can be mitigated competitively by phosphorus, since the latter is a structural analogue. Since, phosphorus is an essential nutrient, plants prefer it over Cr or As. At the same time, if excess of phosphorus is applied in the soil in the form of fertilisers, it gets discharged into the water bodies (ponds, lakes, etc.) through agricultural runoff, causing eutrophication followed by harming the health of the water bodies. This can be further mitigated by employing the phenomenon of luxury uptake by the aquatic plants such as *Pistia stratiotes.*

Keywords: arsenic, chromium, eutrophication, luxury uptake, phosphorus

1. Phosphorus: an introduction

Phosphorus (P) (*fos'furus* = light-bearing) is a reactive, non-metallic, multivalent chemical element of the nitrogen family group 15 [Va] of the periodic table, along with arsenic, antimony and bismuth and moscovium [1]. The atomic number of phosphorus is 15, and it has a density of 1.823 g/cm^3 (298 K), an atomic volume of 17 cm^3/mol, an atomic mass of 30.97 g/mol, three main oxidation states (−3, +3 and +5) and one naturally occurring isotope (^{31}P) (http://epathshala.nic.in/QR/books/12Chemistry/7.1.pdf). Phosphorus has 15 protons and there are 17 known isotopes. It is the 11th most abundant element in the earth's crust, consisting approximately of 0.1% by weight [2]. It was discovered and named by Hennig Brand who was a Hamburg merchant and alchemist by profession in 1669 by boiling and evaporating about 1100 l of urine and heating the residue with sand (which yield hot gases and vapour) and condensing it with cold water. The final substance to condense was soft, waxy white solid material which glowed in the dark. This element was named phosphorus [3, 4]. Phosphorus exists in several allotropic forms showing different properties, three of which are white phosphorus, red phosphorus and black phosphorus, which commonly exists [5].

White phosphorus consists of tetrahedral P_4 molecules, in which each atom is bound to the other three atoms by a single bond. This form generally exists (in liquid and gaseous) as tetrahedral P_4 molecules at temperature up to 800°C that change to P_2 molecules at temperature higher than 800°C [6]. White phosphorus is the most reactive and least stable; for this reason it should be stored under water, as it is dangerously reactive in air, and it must be handled with forceps, as contact with the skin may result in severe burns. Due to its high reactivity, white phosphorus is never found as a free element on earth. It is also very poisonous, 50 mg of which constitutes an approximate fatal dose. Exposure to white phosphorus should not exceed 0.1 mg/m^3 (8-h time weighted average—40-h work week) [7]. It is the most volatile and least dense of all allotropes [8]. Because of its dehydrating nature, it has a corrosive property [9].

Red phosphorus is polymeric in structure. It is non-poisonous, odourless and insoluble in water. It can be viewed as a derivative of P_4. It can be produced by heating white phosphorus to around 250°C within the sight of daylight. Freshly prepared, bright red phosphorus is highly reactive and ignites at about 300°C, though it is still more stable than white phosphorus, which ignites at about 30°C.

Black phosphorus is a layered semiconducting material similar in appearance to graphite with numerous uses in optoelectronic, semiconductor and photovoltaic applications. In a two-dimensional form, black phosphorus is known as phosphorene and has similar properties to other 2D semiconductor materials such as graphene. Among other allotropes, this form is the most thermodynamically stable and densest allotropes under ambient temperature and pressure.

2. Sources of phosphorus

Phosphorus is a naturally occurring element that exists in minerals, soil, living organisms and water. Phosphorus occurs in nature as orthophosphate (PO_4^{3-}), principally in the mineral apatite $Ca_5(PO_4)_3(F, Cl, OH)$ but also in monazite (Ce, La, Nd, Th) (PO_4, SiO_4) and xenotime YPO_4. It is widely dispersed at trace levels in minerals such as olivine, pyroxene, amphibole and mica and is also present in biological materials such as the bone. Phosphorus is a major element in all plants. In the natural world, phosphorus is never encountered in its elemental form but only as phosphates, which consists of a phosphorus atom bonded to four oxygen atoms. This can exist as the negatively charged phosphate ion (PO_4^{3-}), which is how it occurs in minerals, or as organophosphates in which there are organic molecules attached to one, two or three of the oxygen atoms. Phosphorus exists in many different forms in soil. In general, these sources can be grouped into three general forms: (i) organic phosphorus, (ii) soluble phosphorus and (iii) adsorbed phosphorus. Phosphorus (in the forms hydrogen phosphate [HPO_4^{2-}] and dihydrogen phosphate [$H_2PO_4^-$]) is least mobile in soil. The comprehension of forms of phosphorus will enable to understand mobility of phosphorus in soil and the extent to which phosphorus can move within the environment.

Organic phosphorus account for 15–80% of the phosphorus in soils, the exact amount being dependent upon the nature of the soil and its composition. It is the principal form of phosphorus in the manure of most animals. About two-thirds of the phosphorus in fresh manure is in the organic form. Nucleic acid constitutes 1–5% of total organic phosphorus in soil.

Soluble phosphorus or available inorganic phosphorus include small amounts of organic phosphorus, as well as the orthophosphates, $H_2PO_4^-$ and HPO_4^{2-} (the primary forms of phosphorus), taken up by algae and plants (aquatic and terrestrial). The soluble form accounts for the smallest proportion of the total phosphorus

in most of the soils. When fertiliser or manure (both containing mostly soluble phosphorus) is added to soil, the soil's pool of soluble phosphorus increases. With time, soluble phosphorus is transformed slowly to less-soluble forms. The effluents of sewage treatment plants contain mostly soluble phosphorus. Phosphorus is adsorbed by plants in the ionic forms $H_2PO_4^-$ and HPO_4^- [10]. The adsorbed phosphorus does not leach. In fact, it moves very little, even with large amounts of precipitation or irrigation. Attached phosphorus includes labile or loosely bound, and "fixed," or tightly bound, phosphorus compounds.

Agricultural fields lose adsorbed phosphorus in a mechanism to transport phosphorus to water bodies. Phosphorus travel to surface water attached to particles of soil or manure. Phosphorus can also dissolve into runoff water as it passes over the surface of the field. Soil particles strip soluble phosphorus from the water as it moves through the soil profile. Leaching of phosphorus usually is not a significant concern. The concentration of phosphorus in soil leachate is significantly less than surface runoff concentrations [10].

However, special situations can produce higher concentrations of phosphorus in groundwater. The capacity of soil to absorb phosphorus can be overwhelmed on sandy soils or when the water table is close to the soil surface. Also, cracking in soils creates channels allowing surface water to travel directly to groundwater.

Increased use of phosphorus in fertiliser had unsustainable consequences. Since phosphorus remains a finite, diminishing and irreplaceable resource, this is affecting global phosphorus cycles. Phosphorus in rocks is unavailable to organisms, but now increased used of phosphorus in fertilisers has tripled the rate at which biologically available phosphorus enters the ecosystem.

3. Presence of phosphorus in environment

The phosphorus cycle (**Figure 1**) is the process by which phosphorus moves through the lithosphere, hydrosphere and biosphere. Phosphorus being a constituent of nucleic acids as well as cell membranes and phosphate/phosphorylated compounds is a nutrient of major importance for the biosphere. Calcium phosphate is also the primary component of mammalian bones and teeth and is used in a variety of other biological functions. The phosphorus cycle is an extremely slow process, as various weather conditions (e.g. rain and erosion) help to wash the phosphorus

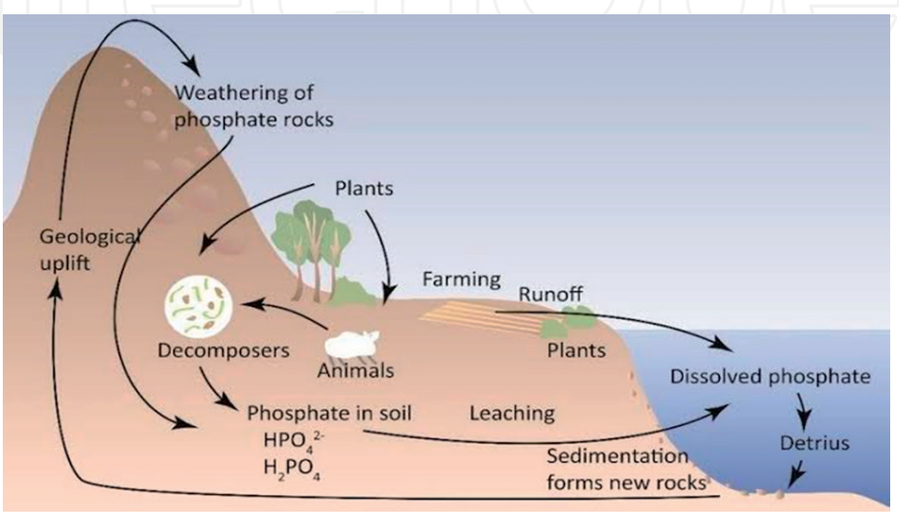

Figure 1.
Phosphorus cycle (image source: Ref. [11]).

found in rocks into the soil. In the soil, the organic matter (e.g. plants and fungi) absorbs the phosphorus to be used for various biological processes [11].

Phosphorus is an important element for all forms of life. As phosphate (PO_4^{3-}), it makes up an important part of the structural framework that holds DNA and RNA together. Phosphates are also a critical component of ATP, the cellular energy carrier, as they serve as an energy release for organisms to use in building proteins or contacting muscles. Like calcium, phosphorus is important to vertebrates; in the human body, 80% of phosphorus is found in teeth and bones [11].

The phosphorus cycle differs from the other major biogeochemical cycles in that it does not include a gas phase, although small amounts of phosphoric acid (H_3PO_4) may make their way into the atmosphere, contributing, in some cases, to acid rain. The water, carbon, nitrogen and sulphur cycles all include at least one phase in which the element is in its gaseous state. Very less amount of phosphorus circulates in the atmosphere because under normal temperatures and pressures condition of the earth, phosphorus and its various compounds are not gases. The largest reservoir of phosphorus is found in the lithosphere [11].

Weathering: since the main source of phosphorus is found in rocks, the first step of the phosphorus cycle involves the extraction of phosphorus from the rocks by weathering. From weathering the released phosphorus is transported to the soil by wind or water as inorganic phosphate. Absorption by plant and animal: inorganic phosphate is absorbed and assimilated by plants. In most soil, the amount of available phosphorus is about 0.01% of the total phosphorus in soil. From the plant, phosphorus moves through the food chain in the organic form. Once the living organisms die, the organically bound P is returned to the environment by the process of degradation by the decomposition. Organically the dead organic matter is acted upon by the phosphatising bacteria to release inorganic phosphorus from bound organic form. Phosphorus is also returned from shallow marine deposits in fish harvest and guano deposits in fish-eating birds and geological uplift. Turnover of organic phosphorus occurs due to phosphatase activity associated with root activity and microbial populations. The precipitation of phosphorus in marine habitats limit primary productivity [1, 11].

4. Role of phosphorus in mitigating arsenic and chromium toxicity from plants

Since phosphorus is a limiting nutrient for terrestrial biological productivity, it commonly plays a key role in net carbon uptake in terrestrial ecosystems. Although the inorganic phosphorus of soil causes harm to the environment in the form of eutrophication, it has some beneficial effects too. The phosphorus present in soils helps in mitigation of heavy metal toxicity in plants. Increasing population; rapid urbanisation; rapidly expanding industrial areas; use of fertilisers, pesticides and manures; and atmospheric decomposition have added lots of pollutants in the soil [12, 13]. Heavy metals like arsenic (As) and chromium (Cr) are highly toxic and cause ill effects at very low concentrations [14]. They are posing a major environmental challenge; since they do not undergo microbial and chemical degradation, they become persistent and bioaccumulative in nature [15, 16]. They affect soil chemistry by altering pH and conductivity of soil and also cause oxidative and physiological toxicity in the plants [17]. Many technologies like electrokinetic (EK) technique [18], electrokinetic-geosynthetic approach [19] and excavation and physical removal of the soil [20] are used to clean heavy metal pollutants. Each remediation technology has its specific benefits and limitations, but in general none of them is cost-effective [21]. Phytoremediation has the benefit of being a relatively

low-cost, natural solution to an environmental problem [22]. Some plants are hyperaccumulators of metal. If the hyperaccumulator plants are edible, the roots will take up the heavy metals from the soil, leading to bioaccumulation of heavy metals in the entire plant body, which will ultimately enter into the food chain and pose health hazards to higher organisms. So, in order to stop the entry of heavy metals into the food chain, it is excellent to apply phosphorus in the soil that will alleviate the uptake and accumulation of heavy metals in food crops growing in the soil contaminated with heavy metals like arsenic and chromium (**Figure 2**) [23–25].

Literatures suggest that arsenate and phosphate share a common transport pathway via roots of the higher plants [23, 26, 27]. Since phosphate is a growth-supporting nutrient, plants prefer its uptake over arsenate. With the understanding of the above molecular analogy between arsenate and phosphate, the most cost-effective method for amelioration of arsenic toxicities, at the oxidative and physiological levels, in the agriculture would be the prevention of its entry in the food chain using phosphate amendments. Thus, a study by Sayantan and Shardendu [23] has been designed to determine the effect of arsenate-phosphate amendments on the variation in the physiological and oxidative toxicities in the root and shoot tissues of *Amaranthus viridis L*. By differentiating the total As accumulation at the tissue level, it was found in the present study that the roots of *A. viridis* accumulated up to twofold higher amount of total As than that in shoot. When the PO_4^{3-} was amended along with the AsO_4^{3-} supplies, the total As accumulated in the root and shoot tissues was significantly ($p < 0.001$) reduced by the maximum of 68.18 and 64%, respectively, with respect to control (0 μM PO_4^{3-} amendment). These observations were further supported statistically by obtaining significant ($p < 0.05$) negative correlation coefficient values between the total As accumulation and the total P stored in root and shoot tissues.

Sayantan and Shardendu [24] showed the role of different levels of phosphorus amendments on chromium toxicity in *Raphanus sativus L.* The experiments were done with the design in which five different concentrations of Cr have been taken and at each Cr level; there were five amendments of P concentration. After completion of experiment, results showed chromium accumulation in plant roots

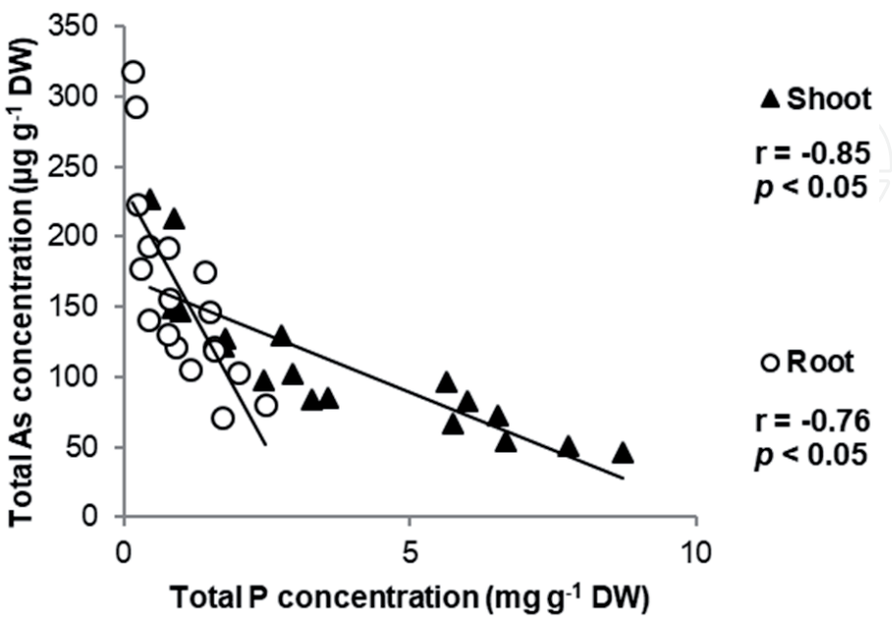

Figure 2.
Relationship between total As and P accumulations in root and shoot tissues of A. viridis*, each with representations of Pearson's correlation coefficient (r-value) and level of significance (p value) (image source: Ref. [23]).*

was dose-dependent and increased as the concentration of Cr supply is enhanced. However, the impact of amendment of phosphorus concentration on Cr accumulation was notable. At each Cr supply, accumulation of Cr decreased as the levels of P increased, showing a reciprocal correlation ($-0.960 \leq r \leq -0.762$) among these two parameters.

Qian et al. [28] showed that chromium could damage the thylakoid structure and impinge on the chloroplast, therefore affecting algal growth. P availability can alleviate Cr toxicity in *C. vulgaris* by decreasing the absorption of Cr and changing the absorption of other metal ions. It is, therefore, necessary to consider the phosphorus availability when the toxicity of metal compounds is evaluated.

It is known that the nutrients present in the soil influence the Cr uptake by *Raphanus sativus* [24]. Sayantan and Shardendu [25] examine the role of Cr toxicity on root and shoot tissues of *Spinacia oleracea* L. (spinach) and its variation when different levels of P were amended with the Cr supply. The path of movement of Cr and P is similar in plants; however, P is preferred over Cr. Thus, P competitively inhibits the Cr uptake. With the phosphorus amendment in the growth medium, accumulation of chromium decreased up to 55% in root and 50% in shoot tissues. These results showed two general observations, i.e. increasing Cr concentrations induced an enhancement in toxicity at both physiological and oxidative levels; and the amendment of P at each Cr supply ameliorated the toxic effects in both kinds of tissues of *S. oleracea.*

Phosphorus is essential to all living beings also; it is one of the main nutrients for animal and plant growth. Phosphorus is used by plants in photosynthesis. When there is less phosphorus during photosynthesis, the production of sugars is restricted. This directly affects the colour of the plant. Phosphorus-deficient plants will not be green but have a purple hue to them. A lack of sugar in the plants will restrict the growth of the plant since sugar is the main source of energy in a plant.

Phosphorus acts as a catalyst. When fertiliser is added to plants, it is often thought of to assist in allowing them to grow quicker and stronger. This is due to the phosphorus in the fertiliser. Phosphorus speeds up plant growth as well as the quality of plant growth.

Phosphorus is also a key component in the structures of life. It is found linking DNA and RNA together and being found in bones of animals. Phosphorus is also involved in ATP that forms during photosynthesis.

Phosphorus is vital to the environment because it allows plant growth that is necessary to keep the ecosystem balanced and flourishing. It allows plants to grow robust to feed the animals that eat them. Healthier plants also allow more oxygen to be released in the air. In manageable amounts, phosphorus can help any ecosystem thrive by providing more food and oxygen. The only measure to check the use of phosphorus for the environment is to reduce the usage of chemical fertiliser and shift towards organic farming. This will reduce eutrophication and, in other words, improve the health of lakes.

5. Eutrophication

When sewage and agricultural runoff containing phosphates or other nutrients enter water bodies, they cause overnutrition, leading to eutrophication. "Eutrophication is an enrichment of water by nutrient salts that causes structural changes to the ecosystem such as: increased production of algae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use" (Organisation for Economic Cooperation and Development). Eutrophication is a major environmental issue

as it causes degradation in the quality of water and is one of the major hindrances for achieving the quality objectives established by Designated Best Use Water Quality Criteria by Central Pollution Control Board, India, 2019 [29]. As per the International Lake Environment Committee Foundation, Japan, about 54% of lakes are affected by the phenomenon of eutrophication in Asia ("http://www.eniscuola.net/en/2016/11/03/what-is-eutrophication-causes-effects-and-control/"; "https://www.ilec.or.jp/en/") [30]. Eutrophication occurs naturally over centuries as lakes age and is filled in with sediments [31]. However, anthropogenic activities like discharge of growth-limiting nutrients like phosphorus have accelerated the rate and extent of eutrophication. Any aquatic body starts its life cycle as oligotrophic, i.e. clear body of water. Eutrophication is distinguished by a remarkable increase of algae (very simple, non-flowering aquatic plant) due to the considerable availability of one or more growth factors obligatory for photosynthesis, such as sunlight, carbon dioxide and nutrients (primarily phosphorus) [32]. With the introduction of nutrients through runoff, algae start to grow in an uncontrolled manner. With this growth, increasingly large biomass is formed which is destined to decay. In deep water, pond collects a good amount of organic substance, represented by the algae having reached the end of their life cycle. Eventually, there is algal bloom when the lake becomes marsh or debris. An excessive consumption of oxygen is required by microorganisms to destroy all the dead algae. This created an oxygen-free environment in the lake bottom, anaerobic organisms being responsible for the degradation of the biomass [33]. The microorganisms, decomposing the organic substance in the absence of oxygen-free compounds that are toxic, such as ammonia and hydrogen sulphide (H_2S), were formed. The absence of oxygen reduces biodiversity causing, in certain cases, even the death of animal and plant species. All this happens when the rate of degradation of the algae by microorganisms is greater than that of oxygen regeneration, which in summer is already present in low concentrations. The stage is eutrophic, when the lake is filled with sediment, while aquatic animal life will perish. It will then turn into dry land. The rate of eutrophication strikes a balance between the production of aquatic life and its destruction by bacterial decomposition. With large input of nutrients from human sources, bacterial decomposition cannot keep pace with productivity and sedimentation is accelerated whereby eutrophication is favoured. Lakes can be protected from eutrophication by providing measures for sewage treatment and preventing the sewage and agricultural runoff from entering the water bodies. Another method is to use aquatic plants as their high relative growth rates efficiently absorb nutrients from their surrounding media, thereby providing a simple and inexpensive solution for phosphorus-polluted water bodies. Experiments done by Shardendu et al. [34] proved that *Pistia stratiotes* L. accumulated the highest amount of tissue P (1 .06 ± 0 .22 mg/g dw) than other common wetland species like *Eichhornia*, *Phragmites* and *Typha*. They further found out that up to 91% phosphate was removed from the surrounding medium within 60 days at 50 mg/L supply.

Author details

D. Sayantan[1*] and Sumona Sanyal Das[2]

1 Department of Life Sciences, CHRIST (Deemed to be University), Bengaluru, Karnataka, India

2 Department of Zoology, Patna University, Patna, Bihar, India

*Address all correspondence to: sayantan.d@christuniversity.in

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