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Phosphate Loading and Foam Formation in Urban Lakes

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Abstract
Phosphorus (P) is the most vital nutrient that regulates primary production and determines the trophic state of freshwater bodies. However, the concern over dwindling stock coupled with the consequences of eutrophication of water bodies due to enrichment of nutrients has been increasing worldwide. P is a very essential macronutrient required to meet the global food demands and to ensure food security in the future. The present study (i) reviews the global phosphate demand, (ii) assesses the extent of pollution in Varthur lake in Bengaluru district of Karnataka, (iii) causal factors of foam formation in lakes and (iv) suggest measures to mitigate eutrophication. The sustained inflow of untreated or partially treated sewage to water bodies (lakes) has led to enrichment of nutrients. The physicochemical analysis of foam and lake water revealed that foam consists of higher concentrations of chemical contaminants and nutrients than the lake water. The external and internal loading of phosphates in lakes stimulated foam formation, profuse growth of macrophyte and eutrophic conditions. Biomonitoring revealed that only pollution tolerant phytoplankton and zooplankton dominated the lake. India has limited rock phosphate resources and is the largest importer of phosphates. Hence, there is an urgent need to (i) restrict phosphate use in detergents manufacturing and (ii) explore cost-effective viable alternatives in order to minimize the dependency on imports of mined phosphorus. This study will help different stakeholders to implement prudent management strategies to prevent urban lakes from eutrophication.

Keywords: *Lake, Eutrophication, Foam, Plankton, Phosphorus, Pollution, Water quality*

Introduction

Phosphorus is a non-renewable source and is a vital element in the Earth's crust forming the basis for all life. It occurs in pentavalent forms such as orthophosphate, polyphosphates, pyrophosphate, organic phosphonates, organic phosphate esters and phosphate diesters in aquatic ecosystems. Functions of phosphorus include: i) major constituent of the skeletal bones and teeth (as calcium phosphates), ii) crucial role in the energy transport system in cells, iii) essential for photosynthesis, iv) forms a part of structural component of cell membranes (phospholipids), v) forms a part of DNA and RNA structure, helps in cell division and development of new tissue, vi) helps in the synthesis of proteins, vitamins and is a component in enzymes etc.[1,2]

Demand for phosphorus for agricultural activities, medicinal and industrial uses varies depending on population, food habit, soil quality, etc. However, the flow of phosphorus to the environment had increased substantially over the decades with the increased use of phosphate fertilizers, manures and detergents with burgeoning population.

Global phosphate demand

Globally, phosphate rocks have been used for the manufacture of fertilizers, animal feed, detergents, pharmaceutical products, insecticides, beverages, toothpaste, matches, fireworks, military operations, bombs, etc.

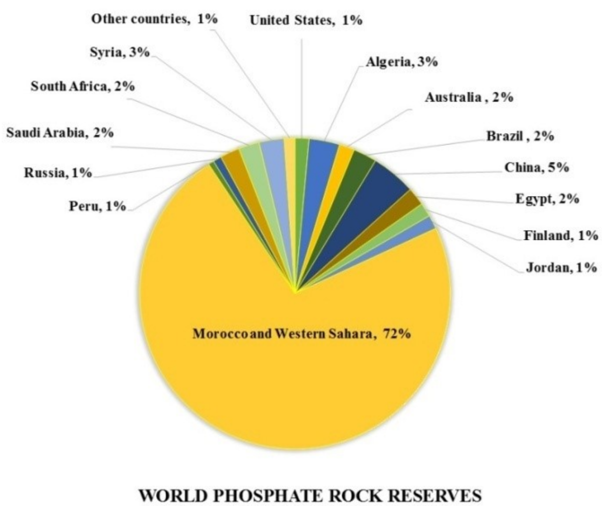

Fig. 1: Phosphate reserves (%) across many regions in the globe

Phosphate rocks/reserves occurs in few countries like United States, Algeria, Australia, Brazil, Canada, China, Egypt, Finland, Jordan, Morocco and Western Sahara, Russia, Peru, South Africa, Syria, Saudi Arabia and others. According to U.S. Geological Survey 2019[3], Morocco and Western Sahara has 50,000 million tonnes ~72% of world phosphate rock reserves (Figure 1). Phosphate reserves across countries are given in Figure 2, which indicates that most part of globe (India, Israel, Kazakhstan, Mexico, Senegal, Togo, Tunisia, Uzbekistan and Vietnam) has less than 1% of phosphate reserves and depend on imports.

Phosphorus is a very limited and non-renewable source. But, an increase in population, agricultural production, demand for more protein diet (like meat and dairy products), crop production, etc. have escalated the demand for phosphorus[4]. Factors such as income, price, prices of substitutes, technological change, consumer preferences, government activities, etc. need to be considered for assessing the demand for phosphate[5]. World consumption of phosphorus pentoxide (P_2O_5) projected to increase to 50.5 million tons in 2022 from 47.0 million tons in 2018. The countries such as Africa, India and South America would account for about 75% of the projected growth, whereas P_2O_5 consumption in U.S. remains as ~5 million tons per year[3]. According to IFASTAT 2019 data[6], the production, consumption and export of Grand total P_2O_5 is highest in China than other countries. Countries such as Brazil, followed by India and United States, are the largest importer of Grand total P_2O_5 (Figure 3).

P dependency in India

India has very limited reserves/resources of rock phosphates (RP) which are of low to medium grade quality and hence imports of P in the form of rock phosphate/phosphoric acid/direct fertilizers are necessary. India is the largest importer of RP (about 30% of global trade) in the world[7]. The total reserves/resources of rock phosphate account to 312.67 million tonnes (2015) and about 34% of it is in Jharkhand, 31% in Rajasthan, 19% in Madhya Pradesh, 8% in Uttar Pradesh and 8% in Uttarakhand, while states like Gujarat and Meghalaya has meagre quantities of resources[8]. In India, the demand for phosphatic fertilizer has increased gradually and as per the Fertiliser Association of India, the consumption of phosphorus pentoxide (P_2O_5) during 2008 to 2018 exceeded the production, necessitating imports (Figure 4).

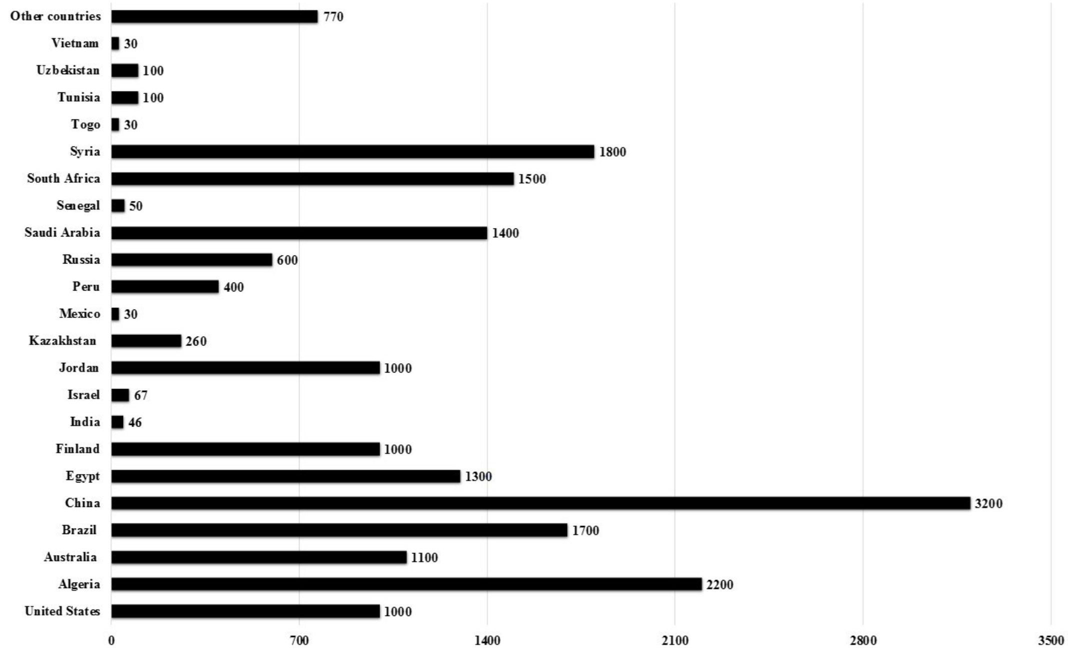

Fig. 2: Global phosphate reserves in million tonnes

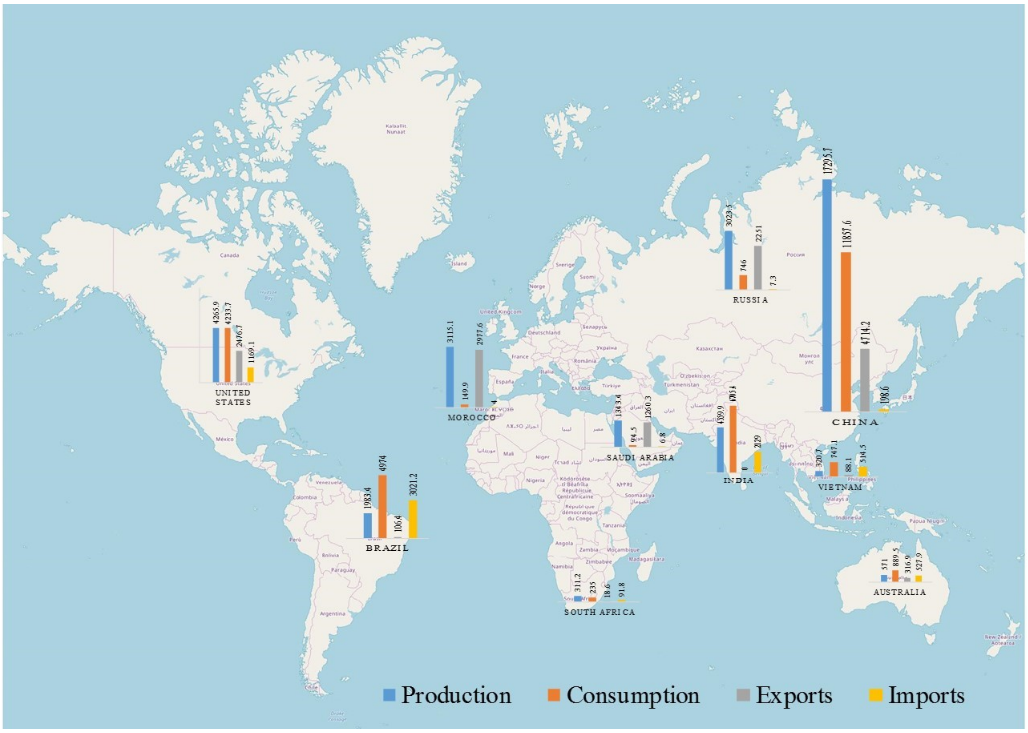

Fig. 3: Country wise production, consumption, export and import of total P_2O_5 (in 000 metric tonnes of nutrients)

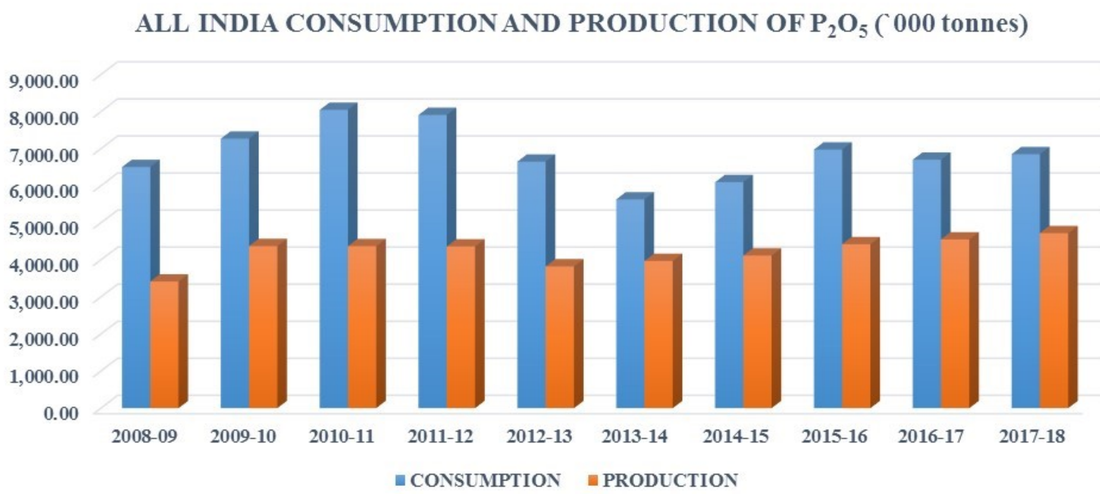

Fig. 4: Overall consumption and production of P_2O_5 ('000 tonnes) in India

Chemical fertilizers in India include Urea, Diammonium Phosphate (DAP), Single Super Phosphate (SSP), Muriate of Potash (MOP) and other complex fertilizers like Calcium Ammonium Nitrate (CAN) and various grades of NPK fertilizers. Indian Fertilizer Scenario, 2017[9] reported about 37 nitrogenous fertilizers (Urea, ASP and CAN) plants, 17 DAP and Complex Fertilizers plants and 105 Single Super Phosphate (SSP) fertilizer plants in India. As per the Department of Fertilizers, GoI[10], about 25% of Urea requirement, 90% of phosphate either as raw material or as finished fertilizers ((Diammonium Phosphate (DAP) or Monoammonium Phosphate (MAP) or Triple Superphosphate (TSP)) and potash requirement during the year 2017-2018 in India is completely met through imports. During 2016-17, the total production of urea, DAP and NP/NPK complex fertilizers was 24.33, 4.25 and 8.57 million tonnes respectively[8].

Phosphate fertilizer consumption in India includes both phosphoric acid based fertilizers and non-phosphoric acid based fertilizers. The non-phosphoric acid based fertilizers include phosphate in nitric acid based fertilizers and super phosphate. India is the third largest producer and consumer of fertilizers as per CARE Rating (2018)[11]. Recently, India has increased the domestic capacity and with easy availability of acid, the production of DAP has increased by 7.3% (38 to 46 LMT in FY16-18) whereas import of DAP had decreased by 3.8% during FY18. DAP is mainly imported from China (45%), Saudi Arabia (31%), USA (13%) and Jordan (5%).

The phosphate rock stocks are fast dwindling and there is no substitute for phosphorus, which is essential for agriculture and medicine, and hence it is necessary to minimize wasteful use of P for detergents manufacture apart from recovering from wastes. The main objective of the study is to assess (i) the water quality to understand the implication of sustained inflow of untreated sewage (rich in N and P), (ii) biomonitoring through assessment of plankton diversity, (iii) to understand the causal factors of pollution in Varthur lake leading to foam formation and (iv) to suggest remedial measures for lake protection.

Materials and Methods

Study area

Varthur lake (12°572 23.563 to 12°562 33.993 N, 77°432 08.713 to 77°442 41.723 E) is the second largest lake located towards the south of Bengaluru District in Karnataka, India and was built by the Ganga Kings over a thousand years ago to meet the local demand of domestic and irrigation water (Figure 5a). It covers a water-spread area of 190 ha and is the main source of water for irrigation for the nearby agricultural fields. The lake is located in Koramangala - Challaghatta (K&C) watershed and is a part of interconnected lakes (namely, Byappanahalli, Challaghatta, Agara, Bellandur, Haralur, Kasavanahalli, Kaikondanahalli, Doddanakundi, Vibhuthipura, Kundalahalli, Chinnappanahalli and Varthur) and canals that receive all the surface runoff, wastewater and sewage from the Bengaluru South taluk and finally drains into the Dakshina Pinakini River[12]. This had increased the pollution load of Varthur lake. The average annual rainfall of Bengaluru is 859 mm and temperatures vary from 14°C (minimum during December to January) to 33°C (maximum during March to May). There are two rainy periods, i.e. from June to September (south-west monsoon) and November to December (north-east monsoon).

Fig. 5a: Varthur lake - Sampling locations of water

Fig. 5b: Froth / foam formation in Varthur lake

Fertilizers and insecticides are being used in the lake catchment for cultivation of horticultural crops (Amaranthus, Coriander, Turnip, Palak, Spinach etc.), floriculture and agricultural crops (Maize, Paddy) and the runoff from the catchment with the nutrients reaches Varthur lake. Sustained inflow of untreated sewage, industrial effluents along with the nutrient rich catchment run-off has enhanced the nutrient content in the lake leading to eutrophication with the profuse growth of macrophytes covering the major part of the lake and foam/froth formation at outlets. Macrophytes in the lake include species such as *Eichhornia crassipes*, *Alternanthera philoxeroides*, *Colocasia esculenta*, *Cyperus* sp., *Ipomoea aquatica*, *Ludwigia* sp. and *Typha* sp. that occupied a large area of the lake. Heavy metals like copper, zinc, chromium, lead, nickel and cadmium were found to accumulate in lake sediments and in macrophytes in Varthur lake[13]. Decomposition of algae, fish and macrophytes releases a variety of organic compounds into the water body, which act as surfactants (foaming agents) with a hydrophilic end and hydrophobic hydrocarbon chain at the other end. Most surfactants originate from the detergents, oil and grease released from households or industries. These agents rise to the lake surface and interact with water molecules thus, reducing the surface tension of water. When the surface tension decreases, air mixes with the water molecules and foaming agents resulting in bubble formation. These bubbles aggregate together and forms foam in lakes. Foam generated in Varthur lake is sticky, white in color and spreads a foul smell to the surrounding area (Figure 5).

Water quality assessment

Water samples (V1 and V2 from two outlet points of the lake) and foam samples (V2) were collected from Varthur lake in clean disinfected bottles (Figure 5). In situ parameters like water temperature (WT), total dissolved solids (TDS), electrical conductivity (EC) and pH were measured on-site using handheld probes (Eutech: PCSTestr 35). Dissolved oxygen (DO) was determined on-site by Winkler's method[14]. The parameters like total alkalinity (TA), total hardness (TH), calcium (Ca), magnesium (Mg), chloride (Cl), chemical oxygen demand (COD), biochemical oxygen demand (BOD), sodium (Na), potassium (K), nitrate (N) and orthophosphate (OP) of water and foam samples collected from Varthur lake were analysed in the laboratory according to the standard protocols as per APHA[14].

Plankton identification

The plankton (phytoplankton and zooplankton) samples collected using standard plankton net (of mesh size 63 mm and 30 cm diameter) were transferred to clean sterile container and were preserved by adding 2 mL of 5% formalin. The planktons were identified microscopically according to the standard keys[15,16].

Results and Discussion

Water pollution in Varthur lake

Varthur lake series receives ~590 MLD (million liters per day) of untreated and partially treated sewage daily[17], which has sustained the level of nutrients (nitrogen, carbon and phosphorus) resulting in the pollution of the lake. TDS mainly consists of bicarbonates, carbonates, sulphates, chlorides, phosphates and nitrates of calcium, magnesium, sodium, potassium, iron etc. and small amount of organic matter. TDS at V1, V2 and foam were 448 mg/L, 454 mg/L and 7000 mg/L respectively. EC was 749 µS at V1; 764 µS at V2 and 17000 µS in foams. The conductivity increases due to the presence of chloride, phosphate and nitrate in wastewater entering Varthur lake. pH indicates whether water is acidic or basic, ranging from 0 -14. pH values at V1, V2 and foam were 7.46, 7.35 and 6.98 respectively.

DO is the amount of oxygen dissolved in water. Hypoxic/ anoxic condition prevailed in Varthur Lake due to low dissolved oxygen levels, attributed to the high pollution/ organic load, extensive macrophyte cover and organic matter decomposition. BOD was higher at all sites i.e., 24.39 mg/L at V1, 60.98 mg/L at V2 and 650.41 mg/L in foam. COD at V1, V2 and foam were 40 mg/L, 88 mg/L and 1140 mg/L respectively. The higher values of BOD and COD indicate increase in organic pollution due to wastewater from household and industrial waste discharges. Varthur lake behaves as an anaerobic - aerobic lagoon[18]. In addition, surface foams may block aeration of lakes, increase decomposition rate (BOD), and hence deplete DO levels[19]. Similar instances of foam/froth formation are reported in lakes of Bengaluru[20].

Alkalinity indicates the acid-neutralizing capacity of water and it was recorded as 336 mg/L at V1 and V2 and as 12000 mg/L in foam. The hardness mainly depends on the presence of calcium and magnesium salts and is linked with bicarbonates, carbonates, sulphites, sulphates etc. Total hardness at V1, V2 and in foam were 206 mg/L, 224 mg/L and 13000 mg/L respectively. Calcium content was 57.72 mg/L at V1, 64.13 mg/L at V2 and 3607.2 mg/L in foam whereas magnesium was 15.10 mg/L at V1, 15.58 mg/L at V2 and 974.25 mg/L in foam. Ionic content in water increases due to water pollution. Chloride concentrations at V1, V2 and in foam were 117.86 mg/L, 122.12 mg/L and 3195 mg/L respectively. Sodium levels at V1, V2 and in foam were 169.5 mg/L, 161 mg/L and 770 mg/L respectively whereas potassium levels at V1, V2 and in foam were 35 mg/L, 34 mg/L and 230 mg/L respectively. Phosphorus and nitrogen are essential nutrients required for all living organisms. Orthophos-phate levels at V1, V2 and in foam were 1.263 mg/L, 0.881 mg/L, 74.59 mg/L respectively. The high values of phosphate are mainly due to agriculture runoff, waste-water and detergents. Nitrate levels at V1, V2 and in foam were 0.541 mg/L, 0.361 mg/L and 129.72 mg/L res-pectively. The major sources of nitrate are fertilizers, agricultural runoff and wastewater. Thus, foam samples collected from the lake had higher concentrations of all the physicochemical parameters compared to lake water samples (at V1 and V2). These results coincide with earlier studies as foams in lakes were enriched with organic and inorganic forms of phosphorus, carbon and nitrogen; chlorinated hydrocarbons; heavy metals and cations[21]. Both the natural and synthetic foams can collect and concentrate chemical contaminants[22]. Detergents can increase the ionic/chemical contents in water. Powder detergents add more chemical contamination than liquid detergents by increasing the concentration of TDS, chloride, sulphate, carbonate, bicarbonate and pH of wash water[23].

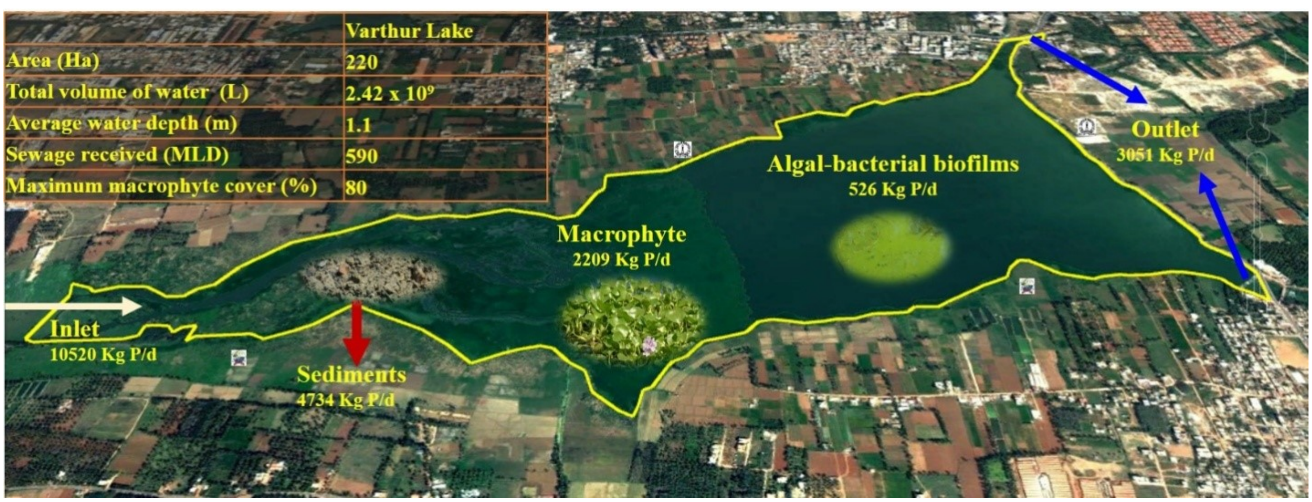

Fig. 6: Phosphorus content in Varthur lake

Varthur lake receives daily a considerable amount of untreated and partially treated sewage loaded with P, which gets trapped in sediments apart from assimilation by macrophyte, algal-bacterial biofilms etc. P uptake varies widely among biotic components. The foam formation is observed at outlet and is found to contain concentrated nutrients and ions (Figure 6).

Foam formation in lakes

White coloured foam is formed by the interactions between liquid phase, gas phase and surfactants in Varthur lake. Foams have low density and large surface area, exhibiting both solid and liquid like behavior[24]. Stable foams generated by the process of flotation involve three components (i) air bubbles, (ii) surfactants that reduce the surface tension and (iii) hydrophobic (bacterial) cells[25]. Foam in Varthur lake had total phosphate (TP) of >2 g/L and orthophosphate of 0.075 g/L which is due to the sustained inflow of sewage (containing detergents) and internal P loading from the lake sediments[26]. TP concentrations of uncontaminated surface waters range between 10-50 ìg P/L[27]. Even a concentration of phosphates (PO_4-P) greater than 0.5 ppm causes foam in surface water[28]. Phosphates are also responsible for the formation of white foam, which acts as a barrier to entry of oxygen and light in the water[29].

Surface-active agents of municipal wastewater include synthetic detergents, fats, oils, greases and biosurfactants. Synthetic detergents contain phosphates to soften water, increases pH and surfactant efficiency. Detergents cause foaming, eutrophication, limit oxygen production, reduce potable water sources and threaten aquatic life. Nature of the surfactants (whether, anionic/non-ionic synthetic detergents/biosurfactants) and their adsorption on interfaces, governed by electrostatic and steric repulsion determines the stability of foam[30]. The environmental risk associated with the use of surfactants depends on its final concentration in lake water[31] since it is toxic and persistent in nature[32].

The decomposition products of the phytoplankton, fulvic or humic acids, lipidic, proteic or colloidal substances present in water also act as surface-active compounds, producing foams both in marine and freshwater environments[33,34]. Even proteinaceous and carbonaceous matter from industrial and treatment plant effluents or from natural sources (plankton, higher plants and microorganisms) acts as a surface-active agent, reducing the surface tension and create foams[35]. Both surfactants and cells together form stable foams, whereas only surfactant (without bacterial cell) forms unstable foams in lakes. Foam formation never occurs in the absence of surfactants[36]. Surfactants have a polar, hydrophilic head group and a nonpolar, hydrophobic hydrocarbon tail group[37] and are of four types namely (i) anionic, (ii) cationic, (iii) amphoteric and (iv) nonionic, depending on the charge of their head group[38]. Surfactants form films on lakes and hinder evaporation of water and transport of gases across the aqueous interface[39]. *Skermania piniformis*, *Rhodococcus* sp., *Microthrix parvicella* and *Gordonia* sp. are foam-causing organisms growing on oil and hydrocarbons in wastewater[40]. Surfactants as well as foam are responsible for reducing oxygen levels[41], which affects aquatic life. Surfactants deteriorate water quality by creating foams in water bodies[42], which are harmful to fishes, vegetation and alsohuman beings. Foam transfers micro-contaminants and toxic metals into the food web, induces various chemical and physical interactions among components of foam and transports chemicals to the atmosphere through bubble breaking and wind-suspension processes[43].

Effect of pollution on aquatic organisms

The organisms such as primary producers (phyto-plankton) and consumers (zooplankton) of foodweb, which inhabit the surface of lake, will be exposed to these contaminants. Among phytoplankton, Chloro-phyceae members dominated Varthur lake indicating the presence of higher amounts of dissolved carbon content. The phytoplankton population comprised of *Chlorella* sp., *Monoraphidium* sp., *Dictyosphaerium* sp., *Chlamydomonas* sp., *Micracitinium* sp., *Scenedesmus* sp., *Pandorina* sp., *Schroederia* sp., *Pediastrum* sp., *Golenkinia* sp., *Oscillatoria* sp., *Chroococcus* sp., *Spirulina* sp., *Anabaena* sp., *Planktothrix* sp., *Merismopedia* sp., *Microcystis* sp., *Pinnularia* sp., *Nitzschia* sp., *Navicula* sp., *Amphora* sp., *Cyclotella* sp., *Aulacoseira* sp., *Synedra* sp., *Euglena* sp., *Phacus* sp., *Lepocinclis* sp. and *Trachelomonas* sp.

Zooplankton in Varthur lake includes *Brachionus quadridentatus*, *Brachionus plicatilis*, *Brachionus rubens*, *Brachionus calyciflorus*, *Brachionus diversicornis*, *Philodina* sp., *Brachionus angularis*, *Lecane luna*, *Platyias quadricornis*, *Cephalodella* sp., *Arcella* sp., *Vorticella* sp., *Paramecium* sp., Chironomid larvae, *Moina micrura*, *Chydorus sphaericus*, *Moina brachiata*, *Mesocyclops* sp., *Mesocyclops leuckarti* and *Microcyclops varicans*. Dominant are protozoa and rotifers, which indicates the deterioration of water quality with nutrient enrichments (eutrophic conditions).

Earlier, Varthur lake supported species like *Catla catla*, *Labeo rohita*, *Cirrhinus mrigala*, *Clarias gariepinus*, *Oreochromis mossambica*, *Clarias batrachus*, *Heteropneustes fosslis*, *Mystus dittatus* and Minor carps[44]. The sustained inflow of untreated or partially treated wastewater has contributed to nutrient enrichments leading to the profuse growth of macrophytes, which has hindered the solar energy penetration in most part of the lake and affected the producers. This has led to the decline of native species of fish and the frequent mortality of *Clarias gariepinus* has been reported. However, the fish culture involving exotic species of fish has led to the dominance of exotic invasive species.

Phosphate increases primary productivity but several studies showed the adverse effects of detergent on aquatic life[45-47]. Even low concentrations (0.003 mg/L) of detergent effluent induce various toxicological effects and histological abnormalities in *Clarias gariepinus*, which depends on exposure time and toxicant concentration[48,49]. Wastewater from automobile service stations (depending on wastewater concentration and exposure period) are toxic to freshwater fish, *Clarias gariepinus*[50]. Life Cycle Assessment (LCA) of detergents indicates that during production and consumption stages, affects severely ecosystems. Thus, recovery of detergents would help in reducing the environmental impacts of laundering industry[51].

Phosphate loadings and accumulation in urban lakes

Phosphorus (P) plays a crucial role in the productivity of aquatic ecosystems. Various abiotic and biotic processes control P dynamics in sediments containing varied quantities of organic, inorganic and microbial P[52]. Phosphorus input to water bodies occurs in rural areas through agricultural run-off from adjacent fields with an increased use of phosphate-containing fertilizers and manure, while in urban localities through anthropogenic activities involving excessive use of laundry detergents and discharges from industries. The threshold values for anionic, cationic and non-ionic detergents that are detrimental for aquatic life are 3-12, 20 and 3-38 mg/L respectively[53]. Increase in phosphorus concentration promotes algal blooms and aquatic plant (macrophyte/ weed) growth that adversely affects the biodiversity, water quality, fish population as well as the recreational value of lakes. During algal bloom, luxury P uptake by algae will occur and thus P accumulates as inositol polyphosphate. If concentration of orthophosphate in lake water reduces, about 90 percent of polyphosphates within the algal cell are released enzymatically back into lake water within 24 hours. Similar P release (60% of OP) occurs under anaerobic conditions within 3 hours[54].

Suspended particulate matter (SPM) includes all suspended particles, both inorganic and organic in freshwater ecosystems[55]. Generally, litter in water decomposes rapidly than standing dead material[56]. Both macrophyte and periphyton plays an important role in P retention and nutrient turnover. During photosynthesis and at high pH, periphytons induce P precipitation with calcium and increases P adsorption near the sediment surface[57]. Among periphytons, P uptake rate was higher in epiphyton compared to metaphyton and epipelon[58]. The P content in lakes varies widely (Figure 7 and Table 1). The organic phosphorus compounds include inositol phosphates, monoesters, diesters and phosphonates[59]. In India, total input of P through wastewater (from detergents) is between 41,000 to 145,555 tonnes/annum. These detergent phosphates in the form of STPP (sodium tri-polyphosphates) and phosphate from human waste (feces and urine) reaches surface water bodies and along with the sustained inflow of untreated wastewater promotes eutrophication and froth formation. During pre-monsoon, high velocity wind coupled with the high intensity rainfall leads to the churning of the lake with upwelling of sediments and release of trapped phosphates, which contributes to the large-scale frothing.

Figure 8 illustrates pollution in urban lakes with the sustained inflow of phosphorus enriched municipal wastewater and its consequent effects. Various sources of P like untreated domestic and industrial sewage, detergents and fertilizers from agricultural fields reach urban lakes through run-off and leaching. These phosphates will stimulate the growth of phytoplankton and aquatic plants (macrophyte). Phytoplankton forms the base of the food chain, provides food, and transfers energy to higher trophic levels (zooplanktons, fishes, birds and humans). This leads to eutrophication with the extensive and dense growth of macrophytes creating anoxic condition in the underlying layers with malodor generation, which chokes fishes eventually leading to their death, reducing the overall biodiversity and productivity of lake ecosystems.

Table 1: Phosphorus content in urban lakes

Components	Functions	References
Macrophyte	Bioaccumulation of nutrients from lake water and sediments; influence the nutrients (P) recycling in lakes upon macrophyte decomposition	60
	Nutrient uptake and cycling, immobilize the sediment, controls resuspension of sediment and improve water transparency in lakes	61
Flocs	Suspended in lakes by means of shear forces or bioturbation, which affect the phosphorus concentration in the overlying water	62
Organic matter	Serves as an electron donor and induces changes in redox and pH after mineralization of organic matter	63
Dead biomass (standing and fallen)	Internal P loading in lakes	64
Litter from aquatic plants	Decays rapidly which firstly get converted to organic matter and finally to minerals	65
Periphytons	Prefer inorganic phosphorus and serve as a sink for P in wetlands	66
	Nutrient uptake and cycling	67
Suspended solids and sediments	Act as a sink for P in lakes	68

P is found as particulate organic P (POP), dissolved organic P (DOP), particulate inorganic P (PIP) and dissolved inorganic P (DIP). Phytoplankton can readily utilize dissolved inorganic phosphates (DIP) which, later are incorporated into cells in the form of organic molecules. Upon excretion, death and decomposition of aquatic inhabitants, DOP releases. In the sediment part, heterotrophs mediate transformations from POP to DOP to DIP to PIP. The DIP and PIP again released back to water column. Conversion of POP to DOP is facilitated by phytoplankton and prokaryotes. These conversions are mainly dependent on pH, alkalinity, temperature, redox potential, mineral concentration and oxic/anoxic conditions (Figure 8). DIP levels increases to 50-100 μg P/L due to agricultural runoff and to above 1000 μg P/L from municipal sewage[69]. The pollution increase with the sustained loading of P leads to accumulation in sediments.

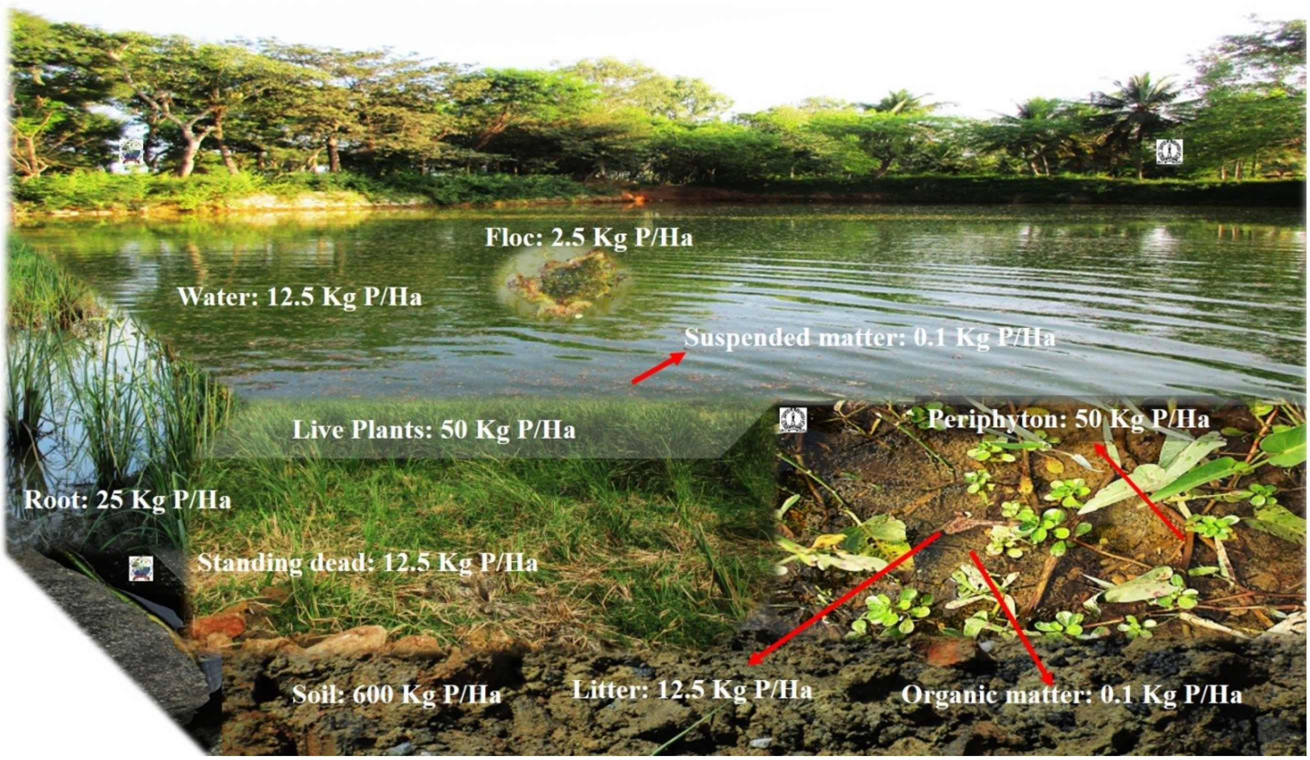

Fig. 7: Phosphorus dynamics in sewage fed urban lakes

Algae prefer non-apatite inorganic P for their growth and metabolism[70]. Dissolved organic phosphorus (DOP) can play an important role in biological and biogeochemical processes[71] and occurs commonly in agricultural, municipal and animal wastewaters[72]. Domestic and industrial wastewater contains increased level of P due to usage of detergents, soaps and cleaning materials[73], which may increase pollution load in lakes[74,75]. This will lead to algae bloom and massive growth of aquatic macrophytes[76] that threatens the freshwater resources and recreation[77]. Oxygen depletion due to increased decomposition of different aquatic macrophytes, weeds and phytoplankton leads to fish kill and loss of biodiversity in eutrophic lakes[78,79]. Approximately, 20% of phosphate rock is mined for making detergents, animal feeds and industries[80]. Thus, it is better to use green and eco-friendly detergents to avoid adverse effects on lakes[81].

The dynamics of phosphorus in sediments of lakes are shown in Figure 9. The external loading of nutrients from agricultural, horticultural and urban sources (wastewater) contributes to eutrophication. Inorganic orthophosphate (HPO_4^{2-} or H_2PO^{4-}) is the most bioavailable and mobile form of P exchanged between the lake sediments and water column. The bacterial community, algae, biofilms and aquatic macrophytes contribute to organic forms of P. Organic P is not available directly to aquatic organisms and thus the need to convert to inorganic orthophosphate. P transformations in sediments involve a series of processes (sorption/desorption; dissolution/precipitation; immmobilisation/ mineralisation) depending upon factors like temperature, pH, redox reactions and concentrations of available iron, calcium and aluminum.

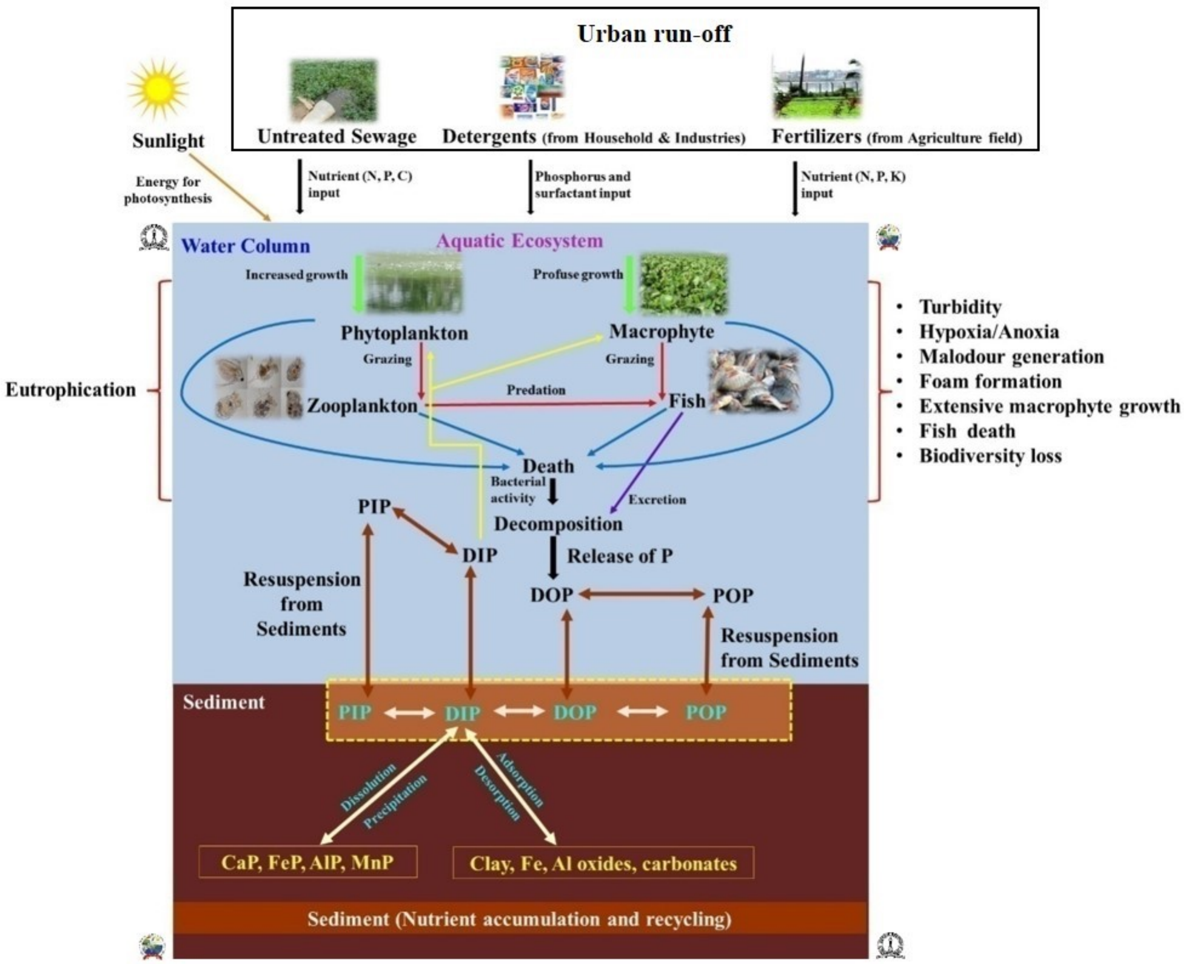

Fig.8: Sources of phosphorus and its adverse effects on lakes

Inorganic P can be either adsorbed (chemically bound) to suspended/settled sediments or desorbed (release of adsorbed P). During adsorption, phosphorus is bound to the sediment surface i.e., on clay surfaces or iron and aluminum oxides and hydroxides in sediments. While by desorption, the adsorbed phosphorus is released into the water. Orthophosphate remains adsorbed under aerobic conditions with high redox potential whereas gets desorbed under anaerobic conditions with low redox potential[54]. P gets precipitated with Ca (calcium), Fe (iron), Al (aluminium) and Mn (manganese) complexes (illustrated with equations below). Thus, ferric oxyhydroxides, calcium phosphate (apatite), aluminium oxyhydroxides, carbonates and clay are carriers of phosphates in lake sediments. These metal phosphates can release P back into water upon dissolution.

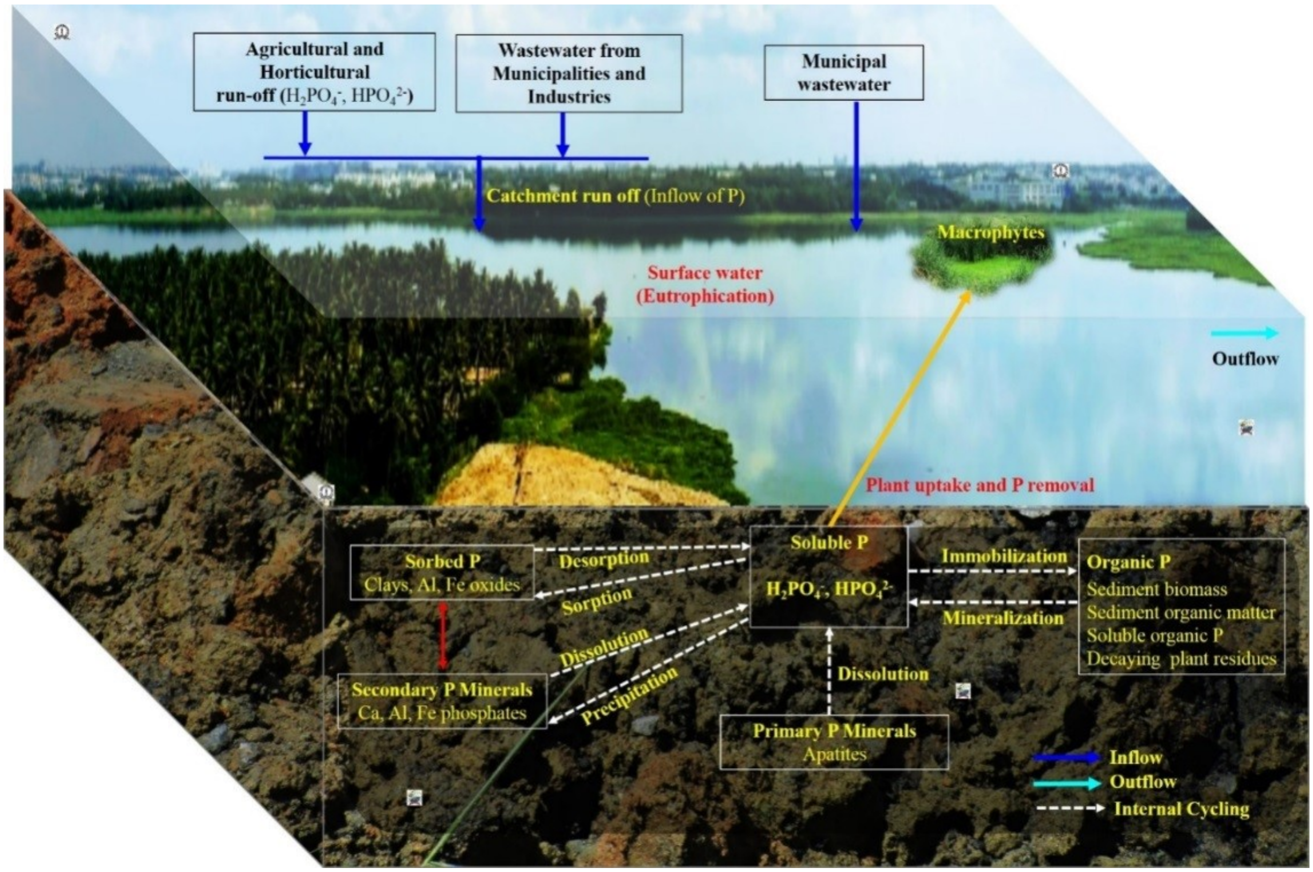

Fig. 9: Phosphorus cycling in lakes

$Ca(H_2PO_4)_2 + 2H_2O$ « $CaHPO_4 . 2H_2O + H_2PO_4^- + H^+$

$Ca(H_2PO_4)_2 + Ca_2^+ + 2OH^-$ « $2CaHPO_4 . 2H_2O$

$2CaHPO_4 + Ca_2^+ + 2OH^-$ « $Ca_3(PO_4)_2 + 2H_2O$

$2Ca(H_2PO_4)_2 + 2Ca_2^+ + 6OH^-$ « $Ca_4(HPO_4)_3 . 3H_2O + HPO_4^{2-} + 3H_2O$

$Ca_5(PO_4)_3OH + 7H^+$ « $5Ca^{2+} + 3H_2PO_4^- + H_2O$

$Al^{3+} + H_2PO_4^- + 2H_2O$ « $2H^+ + AlPO_4.2H_2O$ (Variscite)

$AlPO_4 . 2H_2O + OH^-$ « $Al(OH)_3 + H_2PO_4^-$

$Fe^{3+} + H_2PO_4^- + 2H_2O$ « $2H^+ + FePO_4.2H_2O$ (Strengite)

$3Fe^{2+} + 2PO_4^{3-} + 8H_2O$ « $Fe_3(PO_4)_2.8H_2O$ (Vivianite)

$FePO_4 + H^+ + e^-$ « $Fe^{2+} + HPO_4^{2-}$

$Mg^{2+} + PO_4^{3-} + NH_4^+$ « $MgNH_4PO_4.6H_2O$ (Struvite)

Organic phosphorus is converted into inorganic phosphorus with the help of microorganisms through mineralization process. Whereas, inorganic phosphorus is converted back to organic forms and are absorbed by the microbial cells through immobilization. The internal P loading from sediments to surface water increases the concentrations of P in water column even though there is a reduction in external loads (Figure 9).

Organic matter is a heterogeneous mix of decayed plant tissues and animal tissues, microbes (fungi and bacteria), humic substances, carbohydrates, lipids and amino acids. Organic matter competes with P for binding sites and inhibits the crystallization of Fe and Al oxides, thus, reducing the P sorption capacity[82]. Ionic strength affects phosphate sorption at the sediment-water interface[83]. Phosphate uptake and solubility in lake sediments is controlled by either redox potential/pH/both[84]. At high temperatures during summer, the pH at sediment-water interface increases whereas the redox potential decreases. Variations in redox potential also occur due to changes in DO (dissolved oxygen) and bacterial metabolism. Under anoxic conditions at the sediment-water interface, P release to overlying water is 7 to 10 times higher than under aerobic conditions[54]. Lastly, biological P uptake by benthic organisms also cause P removal from the lakes.

Phosphorus recovery from wastewater

The global phosphate demand can be met efficiently through recovering P from wastewater. Estimates indicate that phosphorus recovered from human wastes (urine and feces) could account for 22% of the total global phosphorus demand[85] as an individual excretes about 550 L urine/year, which is equivalent to 0.4 kg of phosphorus (P), 4 kg of nitrogen (N) and 0.9 kg of potassium (K) per year[86]. Urine is rich in nutrients and has high hygienic quality for utilizing as a fertilizer[87]. Urine contains ions like Na, K, NH_4, Ca, C1, PO_4, SO_4 and HCO_3[88].

Many studies have reported recovery of phosphorus from municipal wastewater, sewage sludge and sewage sludge ash[89-91]. Biomass ash derived from olive, sludge, meat and bone meal (MBM) and poultry litter has high P content (~5.4% by weight) useful for agricultural land[92]. P recovery from sewage sludge ash (SSA) is more promising than liquid phase and sewage sludge as it ensures high recycling rate, eliminates organic micropollutants, heavy metal decontamination, reduces gaseous emissions and energy demand[93,94]. Recovery of P from sludge is achievable by anaerobic digestion, wet chemical extraction (comprising either acid or alkaline dissolution) and incineration of sludge at high temperatures[95]. The overall P recycling efficiency from wastes was 51% in France, wherein the efficiency was 74.6% for food processing waste, 43.1% for household wastewater and 47.4% for municipal waste[96]. Recovering P from human discharge (a maximum of 3.7 Mt P) added to wastewater can satisfy major fraction of the global agricultural/fertilizer demand[97].

Phosphorus control and alternatives

In order to reduce the nutrient level in lakes, treated water from sewage treatment plants (STPs) should be allowed to pass through an integrated wetland model that consists of constructed wetlands and shallow algae pond as in Jakkur lake, Bengaluru[98]. Dredging of lakes will remove nutrient rich bottom sediments and reduce the internal phosphorus loading[99]. Phosphorus control measures include removal of phosphorus from municipal and industrial wastewater, ban of phosphorus in laundry detergents and other cleaning agents and control of agricultural and urban runoff[100]. Pollution prevention measures should be adopted by reducing phosphate use, reusing or removing phosphorus from wastewater through improved wastewater treatment plants which aids in the phosphorus recovery (by precipitating struvite) process. In addition, the use of locally recovered phosphorus can provide farmers with fertilizer as well as food security[101]. The replacement of sodium tripolyphosphate (STPP) as builder in detergents with Zeolite A helps to prevent eutrophication of surface waters. Since phosphate rocks are depleting, use of STPP need to be minimized as STPP is produced mainly from phosphate rock, sulphuric acid and sodium hydroxide/soda ash[102]. The internal loading of phosphate can be reduced by adopting different restoration methods such as dredging of lake sediments. P recycling (through urban wastewater treatment and food waste recycling) and use reduction (phosphorus substitution in beverages with alternatives, substitution of P in laundry detergents with zeolites, food wastage reduction, application of phosphorus solubilizing biofertilizing micro-organisms etc.) is expected to significantly improve the longevity of P resources.[103]

Restrictions on phosphate use in detergent manufacturing and ban on detergents containing phosphorous would lower the phosphate load. Entry of P rich detergents into aquatic environments needs to be restricted to avoid eutrophication[104]. The BIS (Bureau of Indian Standards)[105] has laid down the standards for eco-labelling of detergents (known as Ecomark) in India. The standards recommend that the product shall not contain phosphates and the need to replace phosphates with alternatives/ substitutes that are environment-friendly and biodegradable surfactants used for manufacturing of laundry detergent powders, and packaging material of the product must be recyclable, reusable or biodegradable. However, none of the detergent brands in the Indian market has opted for the Eco-mark or demonstrated environment-friendliness of a product or enlisted critical ingredients in terms of quantity (active ingredients, builders, soda ash, fillers and enzymes). In India, the expensive and popular brands of detergents still have high phosphates and STPP (sodium tripolyphosphate) compared to the cheaper detergents. This emphasizes the need for stringent environmental norms to mitigate wasteful use of phosphates in manufacturing detergents and ban on phosphate-based detergents to save fragile water bodies from eutrophication.

Conclusions

Poor water quality and frequent foam formation in Varthur Lake highlights of poor environmental status with nutrient enrichments due to the sustained discharge of partially treated or untreated sewage, industrial effluents, agriculture and floriculture run-off (non-point sources), solid waste dumping, etc. Foam with aerosols is being dispersed by winds has been affecting residents in the locality exposing them to health hazards and also traffic congestion. The surfactants are responsible for foam formation in lakes. Foam samples when compared to that of Varthur lake water have higher concentrations of chemical contaminants and nutrients. This underscores the need for preventing abuse of P use in detergents manufacturing as the global stock of P is limited and is required for manufacturing medicines and fertilizers (to sustain agricultural productivity). The current work underlines the need of P recovery from the lakes, which will be beneficial for different stakeholders to meet the food demand and to ensure food security. Measures like removal of phosphorus from municipal and industrial wastewater, adopting ways to recover P and ban of phosphorus in detergents and use of sustainable alternatives to P are essential to meet the burgeoning demand. There is an urgent need for enacting stringent legislations to regulate phosphate content in detergents and also ban of P based detergents in markets.

Recommendations

Different strategies need to be evolved to minimize eutrophication in water bodies through minimizing P in the environment, which help in saving waterbodies including Varthur lake in India and some of the suggestions are:

a) **Solutions at consumption level:**
- ban of phosphorus use in the manufacture of detergents and other cleaning agents,
- use of non-phosphate based builders like Zeo-

lite A to manufacture detergents,

- proper labeling of detergent packages (Ecolabel) including enlisting of all ingredients,
- awareness among customers to opt for detergents with minimum amount of polluting ingredients,
- stringent implementation of 'polluter pays' principle,
- minimize the use of phosphate fertilizers and use of sewage sludge ash as P source.

b) Measures to rejuvenate lakes include:

- Rejuvenation of lakes based on scientific principles,
- Dredging of lake removes nutrient rich bottom sediments, it can increase the storage capacity, aid in groundwater recharge, while reducing the internal nutrient loading,
- Restricting the entry of untreated solid and liquid waste/sewage directly into water bodies,
- Allowing only treated water to enter the lake through integrated wetlands to minimize the nutrient loadings,
- Creating constructed wetland of native species to treat partially treated or untreated wastewater,
- Adopting ways to control agricultural and urban runoff to lakes by creating buffer of riparian vegetation,
- Installation of aerators at different locations in the lake to enhance the dissolved oxygen levels and recreation services of water bodies,
- De-weeding at regular intervals to control the profuse growth of macrophytes and subsequent decay resulting to C, N and P inputs to water and sediments,
- Implementing pollution mitigation measures for reducing phosphorus (and nitrogen) loadings in the environment.

c) Recommendation for P recovery and reuse:

- Removal of phosphorus from municipal and industrial wastewater by passing through wastewater treatment plants to recover and reuse P and water,
- Recovery of phosphorus (and nitrogen) from domestic and industrial wastes to meet agricultural requirements,
- Extraction of microbial biosurfactants from wastes helps in industries, medicine, food processing industries, agriculture and phytoremediation.

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