Foaming or Algal Bloom in Water bodies of India: Remedial Measures - Restrict Phosphate (P) based Detergents

Summary

Algal bloom or foaming is a consequence of nutrient enrichment (N and P) due to untreated sewage (mostly from human and household waste and detergents) and industrial effluents. The phosphorus from several sources reaching water bodies causes pollution leading to algal blooms, frothing, etc. Phosphorus represents both a scarce non-renewable resource and a pollutant for living systems.

Primary nutrient, such as carbon, nitrogen, phosphorus, etc. contribute to eutrophication. In fresh water ecosystem, primary producers are able to obtain N from the atmosphere and hence phosphorus is the primary agent of eutrophication. Moreover, elements carbon, nitrogen and phosphorus can generate its weight by 12, 71 and 500 times, and hence phosphorous is the limiting element in primary producers. Nutrients enrichment often leads to profuse growth of invasive species (water hyacinth, etc.), which forms thick mat hindering the sunlight penetration. In absence of sunlight, photosynthetic activities cease affecting the food chain. Absence of sunlight penetration leads to the decline of primary producers (algae) in the region below the macrophyte mat. Most part of nitrogen available in the sewage and industrial effluents is assimilated by producers, while phosphorous gets trapped in the sediment. During pre-monsoon with high intensity winds, churning of lake water happens, leading to the release of phosphorous from sediments forming froth. Foaming is the manifestation of interactions among air bubble, surfactant and hydrophobic particles. The hydrophobic particles congregate at the air-water interface and strengthen the water film between air bubbles. Meanwhile, the particles also serve as collector for surfactant which stabilizes the foam. Surfactants contain slowly biodegradable surfactants and hydrophobic particles are the filamentous bacteria with a long-chain structure and hydrophobic surface. Thus, frothing is due to the presence of slowly biodegradable surfactants (eg. household detergents) from industrial or municipal wastewater, excess production of extracellular polymeric substance (by microorganisms, proliferation of filamentous organisms) and air bubble (wind).

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Constituents of Detergents: The surfactant nonylphenol ethoxylate (**NPE)**, an endocrine disruptor and estrogen mimic; phosphates, which help remove minerals and food bits but cause harmful algal blooms in waterway.

Chemical analyses of field samples reveal that, foams are enriched with particulate organic and inorganic compounds such as nutrients (Nitrogen, Phosphorus and Carbon), cations (Sodium, Potassium, Calcium and Magnesium). Foam generated is normally sticky and white in color. Most surfactants originate from the detergents, oil and grease that are used in households or industry. Surfactant could stabilize the foaming and allow foam to accumulate.

Physico-chemical parameters of water and foam samples from Varthur lake (01/05/2015)

Parameters	V1	V2	Foam
Water temperature (^{0}C)	27.1	26.9	27.2
TDS (mg/l)	448	454	7000
EC (µS)	749	764	17000
pH	7.46	7.35	6.98
DO (mg/l)	2.6	0	-
BOD (mg/l)	24.39	60.98	650.41
COD (mg/l)	40	88	1140
Alkalinity (mg/l)	336	336	12000
Chloride (mg/l)	117.86	122.12	3195
Total Hardness (mg/l)	206	224	13000
Ca Hardness (mg/l)	57.72	64.13	3607.2
Mg Hardness (mg/l)	36.03	38.85	2282.45
Phosphate (mg/l)	1.263	0.881	74.59
Nitrate (mg/l)	0.541	0.361	129.72
Sodium	169.5	161	770
Potassium	35	34	230

Algal Bloom: due to Nutrient enrichment in lentic ecosystem

Foam/Frothing: Nutrient enrichment in lotic ecosystems and in lentic ecosystem (with movement of water).

Fire associated with foam in Bellandur lake (@ Yamalur):

Flammability is the ability of a substance to burn or ignite, causing fire or combustion. Incidences of foam catching fire are due to compounds with high flammability i.e. (i) mostly hydrocarbons and organic polymers from nearby industries in the vicinity of Bellandur lake and (ii) phosphorous from detergents. High wind coupled with high intensity of rainfall leads to upwelling of sediments with the

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churning of water as it travels from higher elevation to lower elevation forming froth due to phosphorous. Discharge of untreated effluents (rich in hydro carbon and phosphorous) with accidental fire (like throwing cigarettes, beedi) has led to the fire in the lake. Colour of the flame and subsequent analyses of black particles (burnt residues) confirms the source (long chain hydro carbons).

Phosphorus (P) is one of the nutrients essential to sustain biota on the Earth and is a non-renewable resource. The indiscriminate exploitation and abuse of this resource is threatening the sustenance and its availability for future generations is becoming obscure. There has been a series of events (frequent frothing, etc. in water bodies) and subsequent research have clearly highlighted the linkages of enhanced usage and influx of P with a phenomenal increase in P enrichment in surface and ground waters. Consequence of extensive phosphorus usage in contemporary urban societies is the nutrient enrichment or eutrophication of water bodies. Studies across the globe highlight of nearly 2.4–2.7-fold increase in nitrogen and phosphorus driven eutrophication of freshwater and marine ecosystems with the current level of human-induced stresses. The main sources of phosphate in aquatic environment, is through household sewage water containing detergents and cleaning preparations, agricultural run-off containing fertilizers, as well as, industrial effluents from fertilizer, detergent and soap industries.

The consumption of synthetic detergents is rapidly increasing with urbanisation and most of them contain phosphate as a ‘builder’, which has been increasing phosphate loading in water bodies. The estimated annual consumption of phosphate-containing laundry detergents for the current population in India is about 2.88 million tonnes and the total outflow of P is estimated to be 146 thousand tonnes per year. The environmental consequences necessitate immediate policy interventions for checking eutrophication of water bodies, through reduction in

Phosphate based detergents and hence P inputs to surface waters. All the detergent manufacturers need to adhere to minimise the use of P in the manufacture of detergents while the authorities need to restrict with stringent norms. Strict control with the vigilant and environmentally conscious public only could ensure that Indian water bodies remain safe and healthy.

During seventies and early eighties, 19^{th} century such instances had brought about an increase in global consensus and the public awareness mostly in the European nations and triggered regulations on P loads from Industry and Urban sources. In India there has been a widespread use of P based detergents that has resulted in contamination of ground and surface waters rendering the water unsuitable for any use. One of the major constituents that form a bulk of the detergents is the builder material that is often made up of Sodium tripolyphosphate (STPP) that significantly contributes to P enrichment. The levels of P enrichment in urban water systems is enormous ranging from 0.5 to >10 mg/l of labile P. Abundant P in these systems have substantially contributed to increased biomass productivity and a leap in the net primary productivity of the urban aquatic systems that ahs resulted in rampant proliferation of aquatic macrophytes and weeds at the same time aided in the large scale algal blooms often seen sin the surfaces of these urban water bodies. The sludge P values in the initial reaches of the wastewater fed water bodies like Bellandur is ~1-3 %. During shifts in redox environments these P becomes bioavailable and results in increased primary productivity of the system. The sediment P levels varies from 0.1 – 0.28 %, mostly as NaOH soluble P forms indicating high fraction of mineralisable P in these lake systems. Two main solutions for cutting short rapid and high P influx into the system is a) Introduction of non-P based builders in detergents for example Zeolite, that can completely replace Sodium tripolyphosphates (STPP - amounts to ~50% bio-available P in municipal wastewaters) commonly seen in detergents and b) Augmenting the existing wastewater treatment system for nutrient removal and recovery. This requires various measures that aids in framing and implementatation of laws to completely replace P based builders to alternative non-P based household laundry detergents. Already the European Commission (EC) has implemented non-P based culture in detergents through the European Union (EU) and recommends appropriate measures to improve the present P enrichment scenario. The two main essential P sources in urban conglomerates are the municipal wastewaters and to a lesser extent agriculture. In most of the Bangalore's catchment that has an inadequate treatment facility and treatment is mostly up to tertiary levels. Municipal wastewaters represent the single largest P source in urban municipalities. In case of certain areas where people practice agriculture, horticulture and floriculture, a minute amount of P (synthetic fertilisers) escapes from these landscapes, where top soil erosion and land run off are the crucial means of entry of fertiliser P into the channels and freshwater lakes. It has been estimated that P from detergents contributes to an estimated 65% of P in municipal wastewaters and the rest are from excrements etc. Based on the field sample analyses, the recommendations are a) A ban on production of polyphosphate based detergents in Indian systems which will help in usage of trusted non-P based detergents, that would bring down the P loads contributed from detergents in municipal wastewaters and also significantly reduce P loads from all garment, textile and other industries that uses detergents substantially; b) Nutrient removal and recovery mechanisms to be augmented into the existing treatment systems by the help of phyto-phyco modules.

The study highlights the need for immediate intervention towards the reduction in the amount of sodium tripolyphosphate (STPP) used in detergent builders and switch to 'alternative' non-phosphate based builders, such as Zeolite A; and, improving wastewater treatment taking advantage of constructed wetlands in urban wastewater treatment.

Keywords: Lakes, water bodies, nutrient enrichment, eutrophication, detergents, phosphorous

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Introduction

Phosphorus is the most crucial nutrient in living systems and is a key component of the genetic make up of living organisms known as gene that essentially comprises of DNA and RNA. The phosphates in the bound forms as reducing powers are also the only energy currency to the cells in the form of ADP/ATP, that helps in production of metabolic energy and there by sustaining various coupled and biochemical processes in the cells. Belonging to the group V of elements, Phosphorus with its unique capacities of delivering and storing energy in pyrophosphates bonds is irreplaceable. The P acts as a limiting nutrient in agricultural and aquatic processes, and is thus indispensable as a source of food source and essential nutrients depended mostly on mineral inputs as phosphatic fertilisers. ~85 % of the mineral phosphates mined from various regions across the globe have been used for manufacturing fertiliser, detergents, medicine, etc. At such unprecedented rate of mining P for meeting the global food demands and ensuring the food security in future, the natural lithological/terrestrial P pools in the system is diminishing at an alarming rate. If no action is taken to quell misuse of phosphorous, demand is likely to increase exponentially. The fact that P resources are non renewable and the world p reserves are scant, it becomes highly imperative to identify potential P pools in nature and use sustainability concepts to pool back P reuse and recycle from the P enriched sub-systems. The P distribution in nature in unlike other essential nutrients as N and C, where the P is mostly in mineral origin, where as the major nutrient pools for N and C are the atmosphere. This makes P very unique and critical in terms of limitation in availability and as rare sources. Globally ~26-34 % i.e. 11-15 % of P by weight are found in P rock minerals (Steen, 1998)where P_2O_5 content is ~31 %, which means ~ 13.5 % P on a weight basis (Kratz et al, 2007). The global mining of P has been reported to be at a rate of ~160 million tonnes/annum and the total P deposits in these areas are ~16 billion tonnes (USGS, 2010) which is going to last for another 120 years at the present rate of exploitation and has been well documented and predicted by a number of scientific studies (Wagner, 2005; Rosmarin, 2004). During the mining process, numerous environmental externalities are witnessed a) with large open pit mines, continuous operations results in huge dust emissions and the generation a large quantities of mining wastes and ore tailings; b) during the production of H_3PO_4 from the P rich rocks, extensive acidification through sulphuric acid is undergone that produces voluminous phosphogypsum (5 ton/ton of phosphates) which is often disposed into large water systems as sea and oceans; c) the by-products produced during the mining and processing operation have squat utility due to the presence of hazardous substances as heavy metals like Cd and other naturally occurring radioactive elements as Ur and Th (Villabla et al., 2008).

During mineral processing phosphoric acid is formed by treating phosphate ore (apatite) with sulfuric acid that produces phosphogypsum a by-product

$Ca_5(PO_4)3X + 5\ H_2SO_4 + 10\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4.2\ H_2O + HX$

where X includes OH, F, Cl, or Br

The mining and extraction of P are being practised only at a few locations that are known to be the global reserves of P i.e. China, Morocco, parts of Western Sahara, South Africa, Russia and the U.S. The major producers of P are China, U.S, Morocco and Russia (USGS, 2010). The geographical distribution of P reserves is highly uneven like oil wells and can be the reasons for instabilities across the major economies of the world, where western European nations and countries like India have to incur huge costs on import of P, having literally no domestic P generation. With the present extent of mining, as we go deeper into the lithological strata's the phosphate ore quality drastically deteriorates, evident from an increase in Cd and Ur, that are highly hazardous and practically impossible to separate from these P rich minerals (Kratz & Schnugg, 2006).

Industrial processing without proper removal of these heavy metals from these minerals will result in extensive deposition of these hazardous elements in agricultural and farm lands. It has been observed that the organic matter content of the soil (fertility) has been rapidly declining with the natural denudation and erosion process coupled with anthropogenic soil utilisation. This has led to a very poor nutritional status of the soil witnessed mostly in the developing nations. In order to achieve higher food productivities and ensure global food security in future for a better quality of life and higher standard of living, a high demand for these rock based fertilisers are essential. Moreover to achieve this there is a shift from agrarian food culture to a meat and diary based diet pattern that increase the present load on fertilisers to several folds. Reports suggest an annual growth rate of ~1 % until 2030 that would lead to >25 % more rock phosphate utilisation compared to present usage (FAO, 2000).

Table 1. For the production of 1 ton of P_2O_5 (0.44 ton of P), the type of energy and materials consumption required (modified from Villabla, 2008)

	Mining	Mineral Processing	Total
Input	Electricity 697 MJ Diesel 125 MJ Explosives 3,3 MJ	Water Electricity 1,128 MJ Flotation reagents Diesel 396 MJ	Total Primary energy consumption 5,500 MJ

			Total Solid waste generation 28 tonnes
Output	Waste 21.8 tons Mine water Diesel exhaust gases	Waste water Tailings 6.5 tons Diesel exhaust gases	

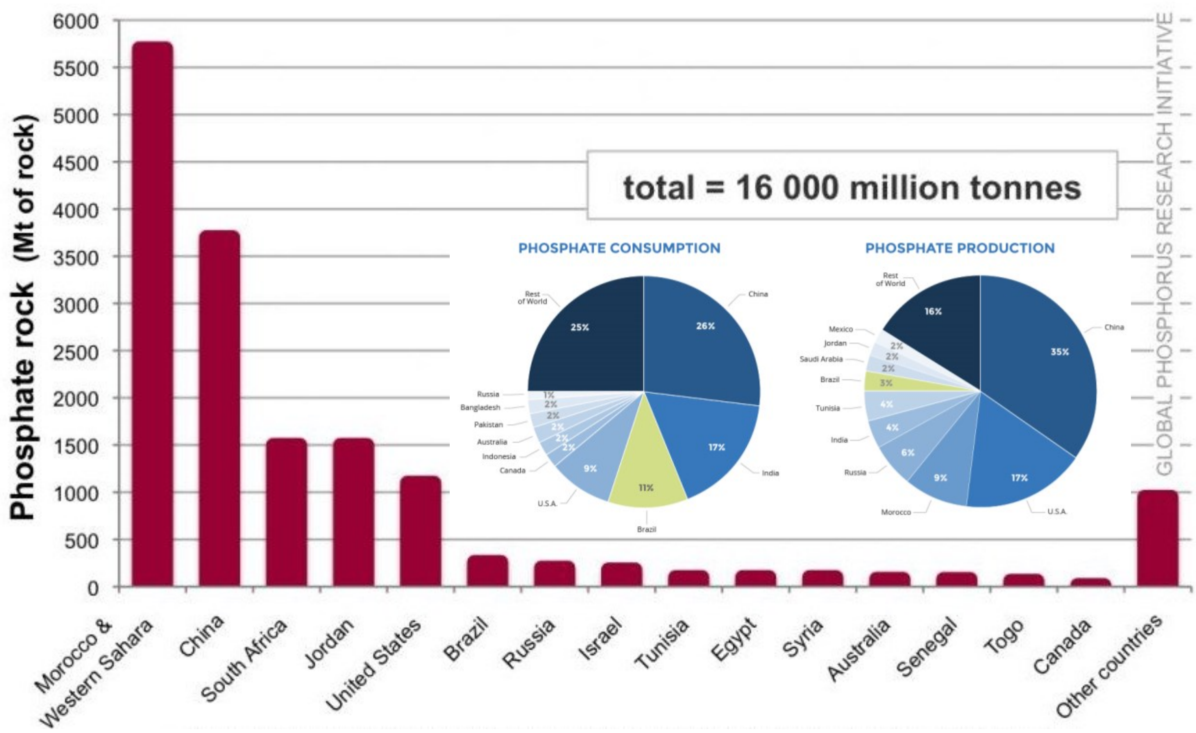

Figure 1. Rock Phosphate abundance and distribution, USGS (Jasinki, 2010)

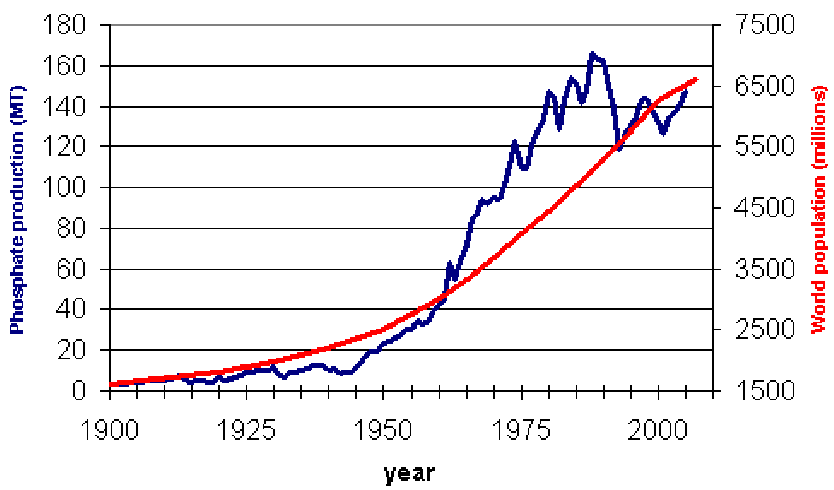

Figure 2. Increase in P production with increased population growth, USGS, 2010

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As apparent from the above curves, the population and the increasing demand for P goes hand in hand. However when it comes to the utilities if these P based resources, these systems are rather very inefficient. According to studies conducted on P budgeting and balance across various sub-systems (Bacinni and Brunner, 1991) only 10 % of P that is intended to be used for agriculture goes into food, there by incurring huge losses into the pedosphere and the hydrosphere, from where mining back P becomes complicated and difficult. Thus efficient P management in these spheres becomes utmost important to conserve the present day nutrient pools.

One of the major sources of P in wastewaters are the human excrements, household detergents and p from other commercial and industrial sources. Urban runoff contributes to a very small amount of P loads. The P inputs from both the vegetative sources and the animal sources in our food both accounts to each ~ 0.8 – 1.2 g, while the P contributed by the detergents in around 0.2 g per day per person. An average Indian household generated ~ 1.8 – 2 g of P per capita per day, where bulk of the P in these waste are present in urine ~0.8 – 1.2 g; feces ~0.4 – 0.6 g and others utilities ~0.3 grams.

P role in surface waters: P is transported into surface water bodies from various non-point sources as agricultural runoff and from point sources like municipal and industrial wastewater discharges. In India due to lack of norms / standards in P levels in household detergents used in laundry and dishwashers, these detergents contain bulk of phosphates as builders and interestingly ~50 5 of the labile P (inorganic and soluble forms) present in municipal wastewaters are from these sources alone.

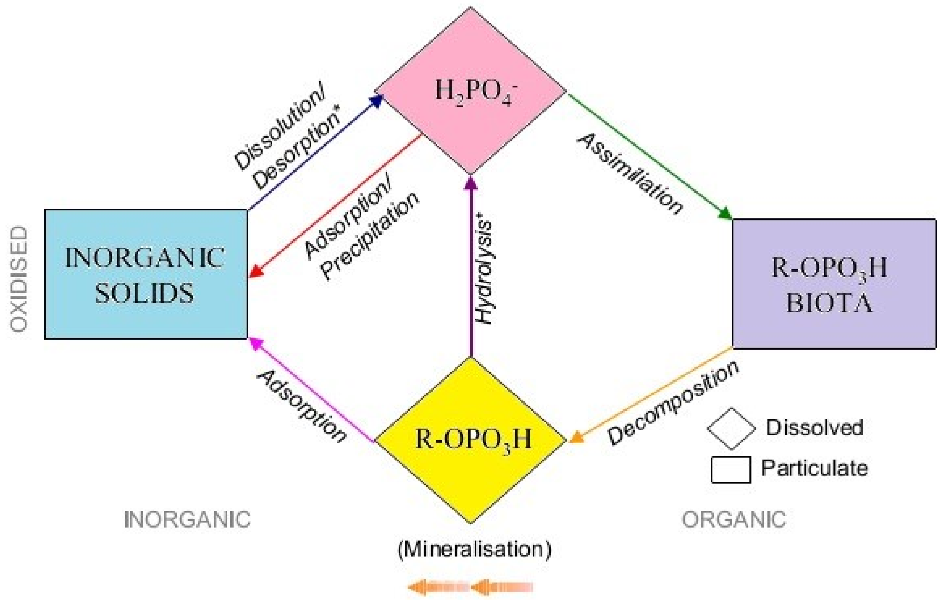

Figure 3. P biochemical Cycle (terrestrial and aquatic environments)

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N and P are very basic nutrients trigger aquatic plant and algal growth and increase in the primary productivity in surface waters. A combination of organic nutrients with various ionic radicles and metals act as important metabolic precursors for bio-synthesis of vital energy rich molecules as fats and proteins required for the growth and development. Phosphorus is usually known as limiting nutrients that restricts the growth, and is the most crucial element that addresses nutrient enrichments in surface waters. Bulk of the p in aquatic systems are in the form of Organic P (70 %) mostly found in the living and dead biomass and the rest comprise of the soluble and the particulate P.

Internal P cycling

In most of the lakes or surface waters, the sediments play a vital role in flux regulations and role in soluble P in waters. Annually large quantities of P are deposited in the bottom sediment owing to various physical and chemical processes; at the same time there is an ample remobilisation/resuspension of P from these sediments under certain conditions that maintains a minimum level of soluble P in these aquatic environments. Various factors affect the P exchanges across the sediment-water interface. Some of these important factors are dissolved oxygen levels, nature of the redox environment, pH, complexometic reactions, precipitations and activities of sediment microflora.

It has been observed that P concentrations in these sediments are much higher compared to those present in overlying waters. The mechanism of resuspension of P is directly linked with the dissolved oxygen concentration in these environments, where DO levels below 2 mg/l helps in the release of soluble P from these sediment pools. Under anaerobic conditions this phenomena increases manifolds. But, the P release flux is dependent on various factors as the surface properties of the particles/minerals in the sediments, acidic or basic environments, their abilities of adsorption and desorption, the oxidising/reducing nature of the overlying waters, the nature of organic C and the various biotic components in these systems.

P chemistry is very interesting with its unique abilities of forming bonds with various metal oxides, as Fe, Mn, Zn and Cu. The affinity of P to these metal oxides is governed by the prevailing redox environment at the interface between the sediment and the water layers. In aerated water systems, P readily binds with Fe oxides. However, in contrasting conditions under anaerobic environment, the Fe with the highest oxidation state i.e. +3 gets reduced to +2 ferrous, thereby releasing the soluble P into the overlaying waters. This is one of the major mechanisms of re-suspension of p from the bottom sediments under low redox conditions with high residence time. Studies conducted in the major lakes of Bangalore city showed 11-37 mg/l TP; 1.8-16 mg/l OP; 2-4 g/kg TP in sediments; 1.2-2.8 % TP in sewage sludge; 84-111 mg/l in interstitial waters. The total P influx into Bellandur and Varthur lake systems was computed to be around ~ 18 – 10 tonnes/day. Of which ~45 % of P is trapped in the sediment pool.

Changing tropic conditions in lakes due to P accumulation: Based on the P concentrations and the prevailing trophic conditions the lake can be divided into five different categories as per OECD norms for trophic classification

Table 2. Trophic status of surface waters with P concentrations

Class	Trophic Level	Total P (µg/L)
1	Oligotrophy	<10
2	Oligo-mesotrophy	<20
3	Mesotrophy	<50
4	Eutrophy	<100
5	Hypertrophy	>100

The primary productivity in the surface waters is mainly dependent on the external nutrient loads. However the trophic status of the water in also to a larger extent dependent upon the internal p loading for those water bodies that have history of nutrient enrichment. However to curtail algal blooms and macrophytes invasion, the first step should be to minimise the external loadings. However the trophic conditions in an aquatic system is influenced by the bathymetry, morphometry, mixing, flushing rates, the nature and the type of the catchment as well as the sediments, the trophic status and the history of nutrient loads.

Soaps and Detergents as one of the major reasons for P enrichment in urban conglomerates

Soaps and detergents primarily comprise of surface active groups generally called as surfactants made of chemicals that aids in cleaning dirt. Soaps when used with hard water, have low cleansing action due to the presence of minerals. Thus builders that help in improving the efficiency of these surfactants have become major ingredients in soaps and detergents. These builders enhance the surface activity by counteracting minerals responsible for hardness in water, oil and grease emulsification, soil particle/dirt re-suspension and avoiding deposition. Phosphates have been by far the most extensively used builders in detergents, primarily acting on as water softener and agent for suspending dirt in aqueous systems and has been also responsible for nutrient enrichment in surface waters (Feisthauer et al., 2004).

A look at the utilities of detergents in India, shows tremendous use of these detergents, but facilities for recovery of detergent constituents and treatment being extremely scarce. India realises the implication of detergents as a potential chemical pollutant on the surface and various receiving waters through the Environment protection act (1986) as in other nations. Despite norms, phosphorous is being used even today, evident from frothing in Yamuna river, Bellandur lake, Varthur lake, etc. Studies indicate a 1.5 fold decadal growth in the use of detergents (2.8 kg/cap/annum, 1994; >4 kg/cap/annum, 2005). Moreover, there is a high utility of the detergent bars, with annual growth of ~8 %, where ~35% of the detergents comprise of Sodium tri-polyphosphate (STPP). Most laundry detergents in India are phosphate based, as there are no norms, control or regulation of phosphates use resulting in deterioration of receiving waters. This highlights grave situation due to misuse of phosphorous and consequent accumulation of P in aquatic systems, evident from frequent frothing episodes.

Today, the Nations action plan towards the control of nutrient enrichment is very meagre. Recent increased awareness among public, have led to the establishment of sewage treatment plants, but these plants treat water only up to secondary levels, and the issue of nutrient removal remains largely ignored. The Environment Protection policy (1986) and the Hazardous Waste Rules (1998) that clearly categorises the major forms of P as phosphine and phosphates as toxic chemicals and attempts to prohibit the usage of phosphates in the day to day chemicals is still weak and these rules are not yet applied in the manufacturing of the household laundry soaps and detergents. The Bureau of Indian Standards (BIS) has set up certain grades/standards for eco-labelling with the help of Ecomark in 1991. These eco-labelling necessitates the detergents to use surfactants that are biodegradable and packaging in recyclable and biodegradable materials. However, for Indian systems where there are no norms for the use/disposal of P linked commodities, separate legislation is required to limit the P content in detergents or potential substitution of P in detergents (such as Zeolite) is required. European nations, the US and Canada had imposed restrictions on the sale of P-rich detergents (since 2010) and devised several strategies to minimise runoff and P input into aquatic systems. The detergents may vary depending upon utilities for example laundry detergents used in washing clothes (hand/washing machine); fabric conditioners; dish wash detergents and liquids. Generally these detergents include a set of basic compounds as the builders, the surfactants and the stain removal agents.

The builders firstly helps in providing a platforms for the water softeners imparting best water interfaces for the operation of surfactants, mostly by deactivating the freely wandering minerals in hard waters, that restricts the action of surfactants. The surfactants help in separation of phases by solubilising the dirt, by getting attached with it that renders them for mixing in water phase. These can be of various categories i.e. cationic, anionic, neutral/amphoteric. In Indian markets there is a widespread use of these anionic based surfactants in the household detergents which mostly comprise of linear alkyl benzene sulphonate (LAS) and Do-decyl benzene sulphonate (DBS). The stain removers act as very crucial agents comprising of bleaching agents and enzymes that help in the rapid degradation/oxidation of the dirt/coloured/sticky materials ultimately removing the colour or the stain from the fabric. Other than these (surfactants, builders), various other constituents used in detergent are fragrance imparting agents, enzyme activators, bleach activators, fabric conditioners, alkali etc. Builders are one of the key components of detergents, which help in reducing water hardness, while enhancing surfactant efficiency by catching ca and Mg ions and encrust the surface of fabrics. Secondly, these builders stabilise excessive pH conditions that are required for dirt/soil removal. Thirdly, they help in improving the overall solubilisation of the various components in the detergents, moreover the dirt in the fabric gets dispersed and move out into the solution. Most importantly the builders offer a platform or skeleton for holding together the powder grains in the detergent. Present day builders are mostly made up of STPP that are environmentally detrimental as they cause nutrient enrichment. Possible substitutes to these builders can be zeolite (Zeolite A) and combination of polycarboxylic acid and sodium carbonate. Zeolites are non hazardous as these are made up of alumino-silicates. Citrates can also be used as potential builders, but the cost for synthesis is pretty much high. The various builders that are used presently and can be potentially used with their possible impacts on environment are provided in Table 3.

Table 3: Available builders and alternatives to STPP for detergents

Sl No.	Builder components	Org/Inorg	Abbreviation	Actions and Impacts
1	Sodium tripolyphosphate	Inorg.	STPP	Contains 25% P, main cause of eutrophication in rivers, lakes and coastal waters
2	Zeolites (A, P, X, AX)	Inorg.		No environment effect. Increases sludge quantity. Co-built with other additives, especially PCAs.
3	Polycarboxylic acids	Org.	PCAs	Poorly-biodegradable, adsorb to sludge. Fate in environment – limited studies and yet to be realised; potentially used with zeolites.
4	Citrates	Org.		Act as a potential chelator, more effective on Mg than Ca ions, contributes substantial BOD load at wastewater treatment works. Can be used especially for liquid detergents
5	Nitrilotriacetic acid	Org.	NTA	Increased dissolved heavy metals - Rapidly solubilises heavy metals through chelation. Is banned in EU
6	Carbonates	Inorg.	CO_3^{2-}	Aids in water softening by precipitating free Ca ions; in hances and stabilises alkalinity
7	Silicates	Inorg.	SiO_X	Avoids corrosion – supplying oxygen and increases alkalinity
8	Phosphonates	Org. P	$C\text{-}PO(OH)_2$ / $C\text{-}PO(OR)_2$ R-alkyl, aryl	Poorly biodegradable, metal ion chelator, anti-redeposition agent
9	Soap	Org. salts	RCOO-X X-Na/K	Inhibiting excess foaming in mechanically driven system
10	Ethylenediaminotetracetic acid	Org.	EDTA	Poorly degradable. Dissolves metal ions
11	Carboxymethyloxysuccinate Carboxymethyltartronate	Org.	CMOS CMT	Weak chelator also observed with STPP. Poor biodegradation, not trapped in primary solids; not generally used in EU.
12	Carboxymethyl cellulose	Org.	CMC	Does not allow re-deposition, helps in repulsion of soil/dirt particles from fabric

There can be a lot of variations in the components of these detergents and differs across brands. While the conventional powders have similar constituents the advanced/concentrated/compact detergent powders may vary. The STPP based conventional detergent powders generally have 15-30 % STPP with <5% PCA, where as the advanced concentrated detergent forms can have many combinations of STPP i.e. 5-15 % or > 30 with 5 % PCA or 30 % STPP, with carbonates and silicates (~10 %). However in case of Zeolite based conventional powders 15-30 % Zeolites with < 5% PCA is used compared to concentrated detergents where roughly similar proportion of Zeolite i.e.e 15-30 5 is used with addition of Percarbonates (15-30 %). A comparison of the difference in various constituents in detergents conventional and advanced is provided in the Table 4.

Table 4. Constituents of detergents conventional and compact (advanced)

Constituents (%)	Detergents (Conventional)		Detergents (Advanced)	
	P rich	P free	P rich	P free
Sodium tripolyphosphate (STPP)	20-25	0	50	0
Zeolite	0	25	0	20-30
Polycarboxylates (PCAS)	0	4	0	5
Organic phosphonates	0 to 0.2	0.4	0	0.2
Sodium silicate	6	4	5	4
Sodium carbonate	5	15	4	15-20
Surfactants	12	15	14	15
Sodium perborate**	14	18	10	13
Activator	0 to 2	2.5	3	5
Sodium sulphate	1 to 24	9	4	5
Enzymes	1	0.5	0.8	0.8
Anti-redeposition agents	0.2	1	1	1
Optical brightening agents	0.2	0.2	0.3	0.3
Perfume	10	0.2	0.2	0.2
Water	--	5	8	5

**monohydrated perborate is used in advanced detergents as high impact bleach
**tetrahydrated perborate used in conventional detergents

Compared to STPP based detergent systems, the Zeolite A based systems are environmentally friendly and does not fertilise aquatic resources. Zeolite A is inert and insoluble alumino-silicate, and can only contribute to high total suspended solids (TSS) and would lead to high quantity of sludge generation. If all the household detergent systems are substituted by Zeolite based systems, the mix of Zeolite and PCA can constitute up to 10 % of the dry solids in the sludge. The only concern for Zeolite based systems i.e. Zeolite A is its little affinity for heavy metals, however no evidences have been discovered yet. Zeolites have been known ti improve sludge settleability. In case of high heavy metal concentrations in the sludge/sediments, the hydrolysis of Zeolite A can potentially re-release these metals in soluble forms to the overlying waters. Similarly the PCA'a comprise of synthetic polymers, whose biodegradability in very low (~20 %) [Morse et al., 1994]. PCA's are mostly captured in sludge/sediments with having no impact on the environment, and the detection of these compounds in the effluents is difficult as are a mixture of compounds.

Set of Solutions and Recommendations for avoiding P influx into aquatic systems:

Rapid deterioration of aquatic systems due to environmental impacts of P presses the need for implementing various measures/control strategies and restrictions on the use of possible P sources as household detergents to bring down P loads into surface waters. The last two decades have witnessed a global consensus on the impacts of P on fast declining freshwaters reserves on earth. As an effort of resurrection and checking the environmental implications several nations have implemented schemes and legislations to avoid P based ingredients in detergent commodities. The growing consensus across nations and increasing studies on P based pollution in aquatic systems suggests a reduction by 80-90% to restore the trophic status in many of the aquatic systems. Restrictions of p based detergents can bring down the 40% of the P loads in aquatic systems that would contribute significantly towards safeguarding water resources. Furthermore, improved wastewater treatment facilities with effective N and P capture mechanisms as Algal modules further aid in another 30 % restrictions of P influx into aquatic systems. In many of the countries a stringent law on restrictions on use of p in detergents and efficient wastewater treatment facilities has already resulted in the improved surface waters. In this regards identifying a suitable alternative to P based ingredients in detergents i.e. builders is essential. Zeolite A-PCA; Sodium citrate, ethylenediaminotetraacetic acid (EDTA) and Nitrilotriacetic acid (NTA) are some of the possible alternatives for substituting phosphorus completely from detergents. Sodium citrate is expensive and are ineffective in removal of hardness in water primarily caused by abundance if Ca and Mg cations. As builders EDTA and NTA have reduced efficiency in dispersion of particulates compared to P based detergents as STPP. In addition to this NTA have abilities to bind to cancer causing heavy metals in sewage sludge and enhance the mobility of these hazardous trace elements.

However detailed studies on its impacts in environments, economy and feasibility as a potential substitute to P based detergents have to be undertaken. Many of the European nations and US have completely substituted STPP by Zoelite and this intervention has rendered improved water quality in many of the freshwater systems in Europe and US. Taking lessons from the above mentioned success stories, the developing nations as India must also strictly restrict the use of P in detergents and parallel plan for economic and efficient nutrient removal systems during wastewater treatment to curtail any further P enrichment and resulting environmental degradation. Zeolite A (aluminium silicates) has been proved by far as the most acceptable and safe alternative to STPP, being inert, non toxic in aquatic systems. Many developed economies as US, Germany, Switzerland and other European nations have extensively adopted zeolite A as environmentally friendly substitute for STPP. Based on the studies of preponderance of phosphates in domestic wastewater, surface waters and sludge/sediments and the increasing enrichments of these urban surface waters with large quantum of nutrient loads from untreated wastewaters comprising of P inputs from detergents and human excrements, the following actins needs to be implemented

1. Immediate reduction, and eventual eradication of phosphates in detergents;
2. Awareness among consumers to select washing products with the least amount of polluting ingredients;
3. prompt promulgation of regulations requiring appropriate labelling of detergent packages listing of the ingredients and information about use of detergents in soft and hard water.
4. Enacting legislations to regulate/remove p based ingredients in household laundry detergents, as almost all detergents brands available in market invariably constitutes bulk of p based ingredients,
5. Identification of P detergent manufacturing units and inventorisation of phosphates based products in these units. Together with this a national accounting of total P imports, distribution, manufacturing into various end products and disposal of these commodities encompassing all sectors has to be documented.
6. More research and development on fate of P based ingredients in aquatic systems, from various sectors (Agricultural, Municipal etc.) has to be undertaken.
7. Incorporating mandates for nutrient (N and P) removal and recovery to the existing wastewater treatment systems that only focuses on BOD/COD and TSS removal as a criterion for disposal of water into streams and other surface water bodies.

8. Seeking participation from the local communities in surface and ground water quality monitoring and management and strictly applying the "polluter pays principle" to the rapidly declining surface waters would ensure conservation and protection of the fresh water resources.

P enrichment in River - CASES	Initiation (History)	Actions taken /implemented	Reduction of P inputs achieved	Effect on quality/ improvements
Belgium – Wallonia Meuse and Schelt rivers	STPP based detergents Poor standard of sewage treatment	Change to Zeolite based detergents Improvements in sewage treatment	Not quantified	Partial improvement
France - Seine and Loire rivers	STPP based detergents Sewage treatment does not remove P Intensive agriculture locally	Partial change to Zeolite based detergents Improvements in sewage treatment	~50% for the Seine Marginal for the Loire	Partial improvement
Germany - Rhine river	STPP based detergents Sewage treatment does not remove P	Change to Zeolite based detergents Complete implementation of the UWWT directive including P removal	55-60%	Partial improvement
Hungary - Danube & Black Sea	Mainly STPP based detergents Poor standard of sewage collection& treatment	At an early stage	Unknown	Unknown
Italy - Po river and N. Adriatic	STPP based detergents Sewage treatment does not remove P	Change to Zeolite based detergents Improvements in sewage treatment	30-40%	Partial improvement in quality of the N. Adriatic
Netherlands	STPP based detergents Sewage treatment does not remove P Intensive agriculture	Change to Zeolite based detergents Sewage treatment removes P Measures to control agricultural P sources	50%	10% reduction in Chlorophyll a
P enrichment in Lakes - CASES	**Initiation (History)**	**Actions taken /implemented**	**Reduction of P inputs achieved**	**Effect on quality/ improvements**
France - Lac du Bourget	Catchment runoff, detergents	Regulations on use of detergents	70%	Eutrophic to meso/eutrophic. Still in transition
Germany - Lake Haussee	Detregents	Ring sewer. No domestic sewage input	90 %	Eventual recovery of the lake, >5 years after reducing P inputs
Italy - lago d'Iseo	STPP based detergents Sewage treatment does not remove P	Change to Zeolite based detergents P removal at main STW and diversion of some flow	60%	Lake still in transition from eutrophic condition
Italy - lago Endine	Mainly STPP based detergents Poor standard of sewage collection& treatment	Change to Zeolite based detergents Ring sewer	80%	Lake still in transition from eutrophic to oligotrophic conditio
Switzerland - lake Geneva	STPP based detergents Sewage treatment does not remove P	Change to Zeolite based detergents sewage treatment works remove P	60%	Significant improvement
USA - lake Erie	STPP based detergents Sewage treatment does not remove P	Change to Zeolite based detergents Major sewage treatment works Remove P	85% from municipal wastewater, 50% overall	Significant improvement, recovery not complete