REVIEW ARTICLE

Phosphorus dynamics in mangroves of India

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Phosphorus (P) is an essential nutrient which plays a key role in global biogeochemical cycles. Coastal ecosystems such as mangroves are an important sink which can trap significant quantities of P. The phosphorus as such deposited in sediments is not available to the organisms, but is converted to bioavailable forms as dissolved orthophosphate through a series of biogeochemical reactions. Several studies on phosphorus reservoirs, transport rates (fluxes) and residence times are reported from different ecosystems across the world. In the present article, an effort has been made to compile and review the scientific research carried out on phosphorus biogeochemistry in the mangroves of India.

Keywords: Biogeochemistry, fractionation, mangroves, nutrient cycling, phosphorus.

BEING circumtropical in distribution, coastal ecosystems such as mangroves are found along transient zones of intertidal regions of the world. The geomorphic location of mangrove ecosystem forms an intermittent platform for efficient nutrient regeneration mechanisms. One such mechanism is geological weathering of minerals from the catchment enhancing their nutrient levels from rivers. Mangrove creeks are responsible for tidal exchange of dissolved and particulate matter between the forest and adjacent coastal waters[1]. These ecosystems play a dual role in acting as sinks of sediments and nutrients, but also as sources of organic matter of low nutrient quality[1,2]. They are also considered to be the most productive wetlands; the total productivity from mangroves (leaf litter, wood and root production combined) has been estimated as roughly 149 mol C m^{-2} yr^{-1} (although these data are often considered as underestimates)[3]. It is suggested that mangrove net primary productivity may reach as high as 20–50 t C ha^{-1} yr^{-1}; and with such a high productivity, they export detritus to the adjacent oligotrophic marine food webs, supporting valuable estuarine and coastal fisheries[3,4]. Furthermore, high productivity of mangrove forests, their geomorphological position at stronger tidal regime with regular freshwater riverine input, and non-litter retaining feature of mangrove vegetation support the 'outwelling' of nutrients in the mangrove ecosystem[5].

Organic matter degradation carried out by microorganisms results in the recycling of essential nutrients in the sediments, owing to rapid immobilization of nutrients during decomposition in mangrove forest sediments and other sediments as well[6–8]. Input from various anthropogenic activities (such as agricultural run-off, aquaculture run-off and municipal wastewater) into mangrove fringed creeks may increase the rate of decomposition of organic matter by increasing the nutrient conditions suitable for bacterial growth. This in turn leads to an increase in the phosphorus (P) load to the sediments. Hence, Redfield ratio (C : N : P) serves as a crucial tool to identify the phosphorus load/biogeochemistry in a system[9]. In many tropical estuarine and coastal systems, primary production appears to be limited by phosphorus[10].

The absence of gaseous phases makes the phosphorus cycle relatively simple in nature, although the relationship between microbial activities and changes in phosphorus geochemistry can be highly complex and difficult to measure. A summary of various components of P cycling is represented in Figure 1. The major pools of P include aboveground and belowground biomass and soil, the input involves atmospheric (dry and wet deposition), mangrove (canopy nutrient transfer and litter fall), mineralization from soil and anthropogenic sources (sewage, agriculture, aquaculture, etc.). The removal of P (output) involves mangrove plant assimilation, microbial uptake, uptake by macro-feeder, tidal exchange and soil immobilization.

Synthesis

Mangroves are estimated to cover 137,760 sq. km in 118 countries and territories in the tropical and subtropical regions of the world[11]. Mangroves in India are spread over an area of 4661.56 sq. km, which accounts for 3% of world's total mangrove vegetation[12]. The east coast of India covers about 57%, west coast covers 23% and the Andaman and Nicobar islands account for 20% of the total mangrove area. It has been found that Sundarbans and Bhitarkanika mangroves are tide-dominated allochthonous

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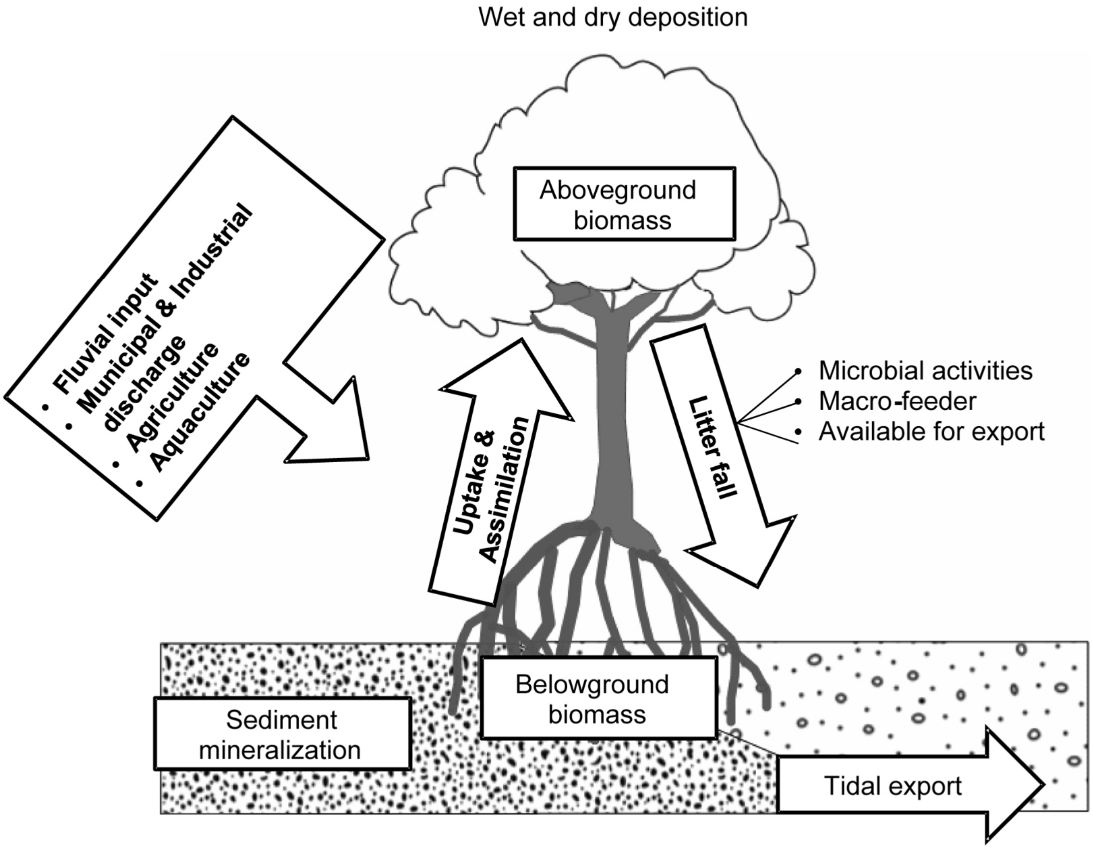

Figure 1. Schematic representation of various components (pool, input, output) of phosphorus cycling in mangrove ecosystem.

type having high tidal range with strong bidirectional current as well as funnel-shaped river channels with extensive tidal flats, colonized by the mangroves. However, Corianga mangroves of Andhra Pradesh and Pichavaram–Muthupet mangroves of Tamil Nadu are river-dominated allochthonous type characterized by rapid deposition of terrigenous material from the river[13–15]. Gujarat mangroves (Gulf of Kutch and Khambat) are of peculiar bedrock valley type, drowned by rising sea level; relatively small delta area could be seen at the head of the valley. The Andaman and Nicobar Islands are low-energy coast type of mangroves with carbonate platform, which are slowly accreting due to the accumulation of marl (calcareous) and peat, coral reef or sand. The shallow water areas of these islands are characterized by luxurious growth of fringe mangrove.

The objective of this article is to provide an overview of the current knowledge on quantitative aspects of phosphorus dynamics of mangroves in India. We carried out an intensive literature survey for data related to sources and sinks of phosphorus and currently available estimates on phosphorus export, burial and mineralization rates from Indian mangroves. We propose a number of processes and pathways that might have been overlooked or underestimated in the current knowledge from Indian literature, and confer how these important gaps in the phosphorus dynamics for these systems may be resolved through future insights of research.

Dynamics of phosphorus in mangrove water

Concentrations of dissolved (dissolved inorganic phosphorus, DIP) and particulate (dissolved organic phosphorus, DOP) phosphorus in mangrove sediments are usually <40 μM and <4 μM respectively[16]. Seasonal changes in plant uptake and microbial growth, temperature, rainfall, oxygen availability and sediment type have a profound effect on concentration over time and intertidal position[17]. Dissolved inorganic phosphorus (soluble reactive phosphate) exists mainly as a nutrient salt (HPO_4^{2-}) at the pH of sea water. A study affirmed that unpolluted pristine mangrove water has concentration of DIP ranging from <0.1 to 20 μM, whereas total P content varies between 100 and 1600 $\mu M\ g^{-1}$ in mangrove sediments[18]. Soluble reactive phosphate is readily assimilated by bacteria, algae and higher plants, including mangroves. However, most of dissolved P in aquatic systems consists of various organic phosphates (primarily phosphate esters originating from living cells), which have limited availability due to their resistance to enzymatic hydrolysis[18].

Generally, phosphate bound to matrix in mangrove sediments is often released at low redox potential and particularly at low pH ($\mathrm{pH} < 1$). The following factors are suggested to contribute towards the release of phosphorus in the system[19]:

(i) Redox processes, namely reduction of ferric phosphate (insoluble) and hydrated ferric oxide to more soluble ferrous form and subsequently releasing occluded phosphate.
(ii) Displacement of phosphate from ferric and aluminium complexes by organic ion.
(iii) Anion exchange reactions between phosphate and organic anions.
(iv) Hydrolysis of ferric and aluminium phosphate.

Water quality assessment and nutrient status in aquatic ecosystems on the Indian coast are widely studied. Though dissolved inorganic phosphorus has been often studied as a component of water quality, it is worthy to note that the dissolved organic phosphorus in the Indian mangroves has been rarely studied[20]. Very few studies are exclusively available on phosphorus dynamics in the Indian mangroves. The variability of dissolved phosphorus in the Indian mangroves with reference to land-use practices, nutrient loadings, pollution and climate change[9] has been summarized in Table 1. The release of the allochthonous nutrients from human perturbations significantly increased the dissolved P concentrations in Sundarbans from 2001 to 2006, altering the nutrient biogeochemistry[9]. Remote sensing studies further augmented that increased human activities are the major factors in both the Indian and Bangladesh Sundarbans[21], which exacerbated eutrophication and subsequently harmful algal blooms (e.g. Dinoflagellates and Cyanophyceae) in the Sundarban waters[22]. Increased incidences of algal blooms, sedimentation of organic matter and oxygen depletion and ultimately, deterioration in water quality in Pichavaram were reported to be the cumulative outcome of all these factors altering the ecosystem dynamics and biogeochemical processes[15,23–25]. In Pichavaram, there has been a rapid increase in the number of aquaculture ponds during the last few decades followed by changes in agricultural practices. This resulted in significant increase of dissolved phosphate concentration in Pichavaram after the 2004 tsunami, which is attributed to the retreating water that carried waste from the agricultural fields and aquaculture ponds to this ecosystem (Figure 2).

Table 1. Variation of dissolved phosphorus in mangroves of India

Mangrove system	Range (μM)	Reference
East coast of India		
Sundarbans	42.3–85.16	52
Bhitarkanika	5.04–73.29	57
	3.15	58
Gautami Godavari	1.89–5.85	59
Uppnar	7.25–38.64	30
Pichavaram	21–136	25
Pichavaram	74.55–103	55
Muthupet	0.14–1.21	20
West coast of India		
Gulf of Kutch, Gujarat	3.36–29.5	31
Mumbai	2.31–157	32
Navi Mumbai	0.18–0.57	33
Kali estuary, Karwar mangrove	0.08	34
Udyavara mangrove	0.74–2.37	60
Cochin mangroves (Puthuvypeen and Nettur)	14.79–30.61	61

A recent study[26] indicated that the implementation of strict norms by the concerned environmental agencies has restricted the amount of nutrient loading in Pichavaram (Figure 2).

The fluvial loads from the River Godavari are the main driving factor for enhanced nutrient levels in the Coringa mangroves, which is due to accelerated chemical weathering rate in the Godavari catchment than any other major Indian rivers[27]. The Godavari supplies substantial amount of dissolved geogenic phosphorus to the estuarine system. Further, agriculture and aquaculture practices also add up a considerable amount of allochthonous nutrients and increase the biological oxygen demand and seasonal algal blooms in the Coringa mangrove water[28]. Besides this, high terrestrial nutrient loadings through climate change-induced extreme events also are reported to aggravate eutrophication and alter the biogeochemical processes in the Coringa mangroves[29].

In the Uppanar mangroves, the observed high concentration of phosphate was attributed to the regeneration and release of total phosphorus from the bottom mud into the water column by turbulence and mixing[30]. Studies on the west coast are scanty and scattered. The variations in the dissolved nutrient concentrations in mangroves of the Gulf of Kutch have been attributed to wastewater discharge[31]. In the Mumbai mangroves, land drainage as well as anthropogenic input played a vital role in governing phosphorus chemistry in water; monsoons were usually associated with maximum load[32,33]. Low values during pre-monsoon were due to decreased run-off, adsorption to sediments and utilization by phytoplankton[33]. In the Kali estuary, Karwar mangrove, the concentration was more during post-monsoon and the southwest monsoon; however, the variations were not pronounced[34].

Role of sediments in controlling phosphorus chemistry

Mangrove sediments act as a sink for phosphorus with high retention capacity as confirmed by numerous studies[35–37]. About 85% of the added P was retained in the sediment mangrove area of Shenzhen, China, dominated by *Kandelia candel* and *Aegiceras corniculatum*[38]. A

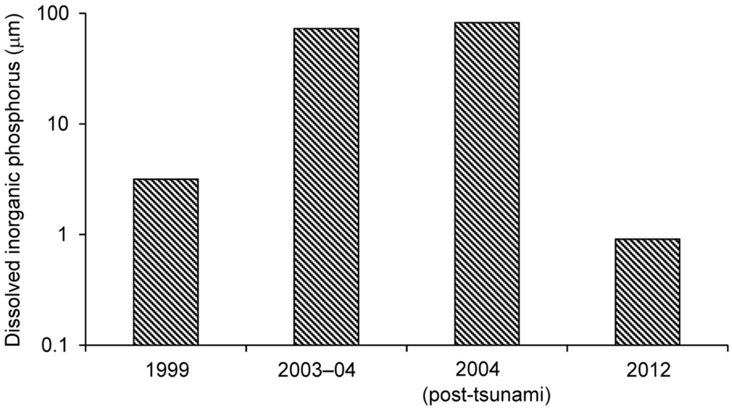

Figure 2. Decadal variation in dissolved inorganic phosphorus (μM) in Pichavaram mangroves (1999, 2003–04 and 2004 post-tsunami)[26,41,55].

Table 2. Variation in geochemical fractions of phosphorus in mangroves of India

Mangrove system	Total-P*	Inorg-P#	Org-P	Methodology (reference)
Sunderbans, West Bengal[52]	804–910	Ex-P: 18–42 Fe-P: 152–267 Au-P: 121–176 Det-P: 187–313	OP: 146–306	44
Bhitarkanika, Odisha[49]	300–536	Ex-P: 51–146 Fe-P: 69–208 Au-P: 32–91 Det-P: 7–39	OP: 31–172	62
Pichavaram, Tamil Nadu (Pre-tsunami)[15]	451–552	Ex-P: 49.6 Fe-P: 172 Au-P: 122 Det-P: 92	OP: 58	44
Pichavaram, Tamil Nadu (Post-tsunami)[42]	653–927	Ex-P: 15–44 Fe-P: 117–419 Au-P: 121–210 Det-P: 72–270	OP: 48–290	44
Cochin mangroves, Kerala[63]	2,226–28,665	Fe-P: 825–2080 Au-P: 505–24764	ASOP: 201–1555 AlkOP: 428–735 ROP: 48–92	50

All P concentrations are expressed in μg g^{-1}.
#Inorganic phosphorus (Inorg-P) includes: Ex-P, Exchangeable-bound P; Fe-P, Iron oxide-bound P; Au-P, Authigenic/calcium-bound P and Det-P, Detrital-bound P. OP, Organic phosphorus; ASOP, Acid soluble organic phosphorus; AlkSOP: Alkali soluble organic phosphorus; ROP, Residual organic phosphorus.

significant correlation of the aboveground biomass with the soil exchangeable phosphorus was found in a mangrove ecosystem, thereby confirming the removal of a significant amount of phosphate from the soil by these mangroves[39]. Mangrove sediments in Australia have been reported to have adsorption maxima in the range 250–700 mg P kg^{-1} dry wt of sediment, while total phosphorus content varied in the range 100–1600 mg kg^{-1} of dry sediment[19].

In general, the capacity of mangrove sediments to immobilize phosphorus depends on the amount of organic matter, its C : P ratio, and the type and amount of clay minerals present. It has been estimated that up to 88% of the forest P pool is retained within the system in tropical mangroves[40]. Physio-chemical characteristics such as pH, available sulphides, alkalinity and redox state also affect dissolution of mineral phosphate[17,41]. These factors are often affected by the activity of microbes and larger organisms. It has been found that the release rate of phosphorus from mineral phosphates and refractory organic materials is transient in comparison with the turnover time for P uptake, utilization and excretion by living organisms[15,16]. In the Sundarbans, total phosphorus was observed to be more in dense mangrove forest sediments with no human activity, suggesting plant litter as the major source of total phosphorus in the sediments (Table 2). Similar results were observed from Bhitarkanika mangroves where high total phosphorus (TP) concentrations in the sediment were associated with dominance of *Avicennia* species which have easily degradable organic matter and pronounced diagenetic activity. The variability of TP in mangroves is sensitive to biogeochemical changes; slight alteration often results into significant changes in the concentration. For example, the 2004 tsunami resulted in drastic increase in the concentration in total phosphorus in Pichavaram mangroves[42].

Chemical speciation of phosphorus in mangroves

Transformation of P can be categorized as: (1) abiotic (precipitation, dissolution, desorption, adsorption, chemisorption), and (2) biotic (assimilation, excretion and hydrolysis). Biotic transformation by means of excretion of soluble reactive phosphorus, mineralizing organic phosphates is the characteristic way of participation of living organisms in the P-cycle. Biogeochemical cycling of phosphorus in the sediments largely depends on chemical speciation of phosphorus[43]. It occurs in the sediment either associated with calcium or iron or aluminum hydroxides, or can be adsorbed on the surface of minerals, or present in organic compounds[44].

Significant removal of phosphorus into the large mineral pool through phosphate immobilization by precipitation as Ca, Fe and Al salts also limits its availability to living systems. In flooded salt marshes and mangroves, P is trapped as $FePO_4$ due to oxygenated microenvironment which is created by oxygen excreted from the root system by grass and mangrove trees[45]. However, during the dry season, increased Fe^{3+} concentration leads to the precipitation of ferric hydroxide, resulting from atmospheric exposure of the sediments[45,46]. The concentration of Fe-bound phosphorus is also affected by the smaller grain size and longer tidal inundation periods.

The primary producers mainly depend upon internal source of phosphorus which is mobilized from the sediments. Other external sources of phosphorus in coastal environment such as atmosphere deposits, agricultural run-off and wastewater discharges also make significant contribution[47,48]. Adsorption of the phosphate ions in dissolved phase to clay particles (particular to clay containing iron or manganese oxyhydroxides through different chemical and physical interactions) has been recorded. In particular, clay such as kaolinite which is abundant in tropical soils and sediments is efficient in phosphate adsorption[16]. Greater amount of total organic P concentration in the surface (0–25 cm) sediments indicates the proportionate influence of the roots, whereas the gradual increase in inorganic fractions, mainly Fe–P, proportionally and in real terms, with depth reflects the influence of increasing anoxia, particularly below the root layer[18,49].

The solubility of apatite in water controls the precipitation of phosphate with Ca^{2+} as well as the adsorption of phosphate onto $CaCO_3$ (ref. 50). In addition, mobilization of phosphorus from hydroxyl-apatite may also be increased by the lowering of pH[45,46]. The extent to which organic matter is preserved in the sediments is critical in determining how far the diagenetic sequence progresses, since the decomposition of organic carbon is driven by redox reaction.

Operationally defined sequential extraction of phosphorus fractionation in sediments is an important method to understand the mechanisms controlling the dynamics of phosphorus[51,52]. Various operationally defined approaches have been applied to understand the geochemical association of phosphorus in the mangroves of India (Table 2).

In the Sundarbans and Bhitarkanika, adsorbed phosphorus was >10% of TP and the variability was linked to the direct discharge of waste into the ecosystem[49,52]. The significant relationship of exchangeable/adsorbed fraction with iron in Pichavaram suggests that Fe in the estuarine zones regulates the amount of adsorbed P in the sediments. However, significant decrease in adsorbed P compared to other fractions was recorded after the 2004 tsunami (Figure 3). It has been established that such reduction is due to rise in salinity concentration and oxic environment. The oxic conditions facilitate the dissolution of adsorbed phosphorus from the sediments, while in high salinity of the overlying water, the phosphate sorption capacity of the surface sediments decreases leading to release of phosphorus into water during the tsunami[42].

The Fe–P fraction is usually observed to be the most dominant fraction in mangrove sediments representing the redox-sensitive mobile fraction in the coastal sediments[15,42,49,52]. In general, comparatively high concentrations of Fe–P fraction are observed in the estuarine sediments than the mangrove sediments; this trend may result from several processes[53]. The concentrations of Fe-oxides/hydroxides are reduced in sulphide-rich mangrove environment by the formation of solid Fe sulphides[54]. Hence an increase in the dissolved oxygen (as in the case of, tsunamigenic water in Pichavaram) will favour the transformation of Fe(II) to Fe(III) and subsequent sorption of P to iron on the oxidized surface of the sediments. These oxidized sediments may have scavenged P from the overlying water column[55].

Authigenic-$CaCO_3$-bound phosphorus and biogenic apatite (Au-P) can be related to the formation of calcium phosphate compounds and/or co-precipitation of phosphorus with calcium carbonate and mainly derived from digenesis[52]. Rivers play an important role in the carrying and deposition of the sediment load in the deltaic lowland, suggesting that detrital apatite can be a major pool of phosphorus in the eroded soils and sediments. The variability of detrital phosphorus was attributed to the fluvial transport of sediments to Pichavaram by distributaries of the Cauvery, viz. Coleroon and Vellar[42].

The variability in organic-bound phosphorus was high in the Indian mangroves and was dependent upon organic matter load, anthropogenic discharge and biogeochemical

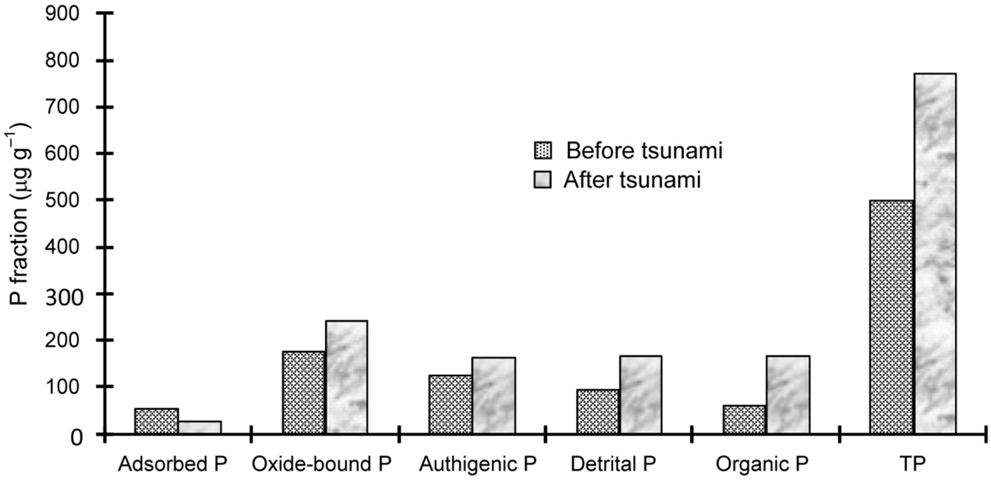

Figure 3. Impact of tsunami on phosphorus fractionation in Pichavaram mangroves[42].

conditions. Org-P was low in the Pichavaram sediments, accounting for <12% of the total phosphorus[15]. However, the increase in the organic-bound fraction in post-tsunami sediments is most likely due to flooding of adjoining aquaculture ponds during the event[55]. High concentration of Org-P in the mangrove zone compared to the estuarine zones was observed in the Sundarbans and Bhitarkanika mangroves, suggesting that retention and cycling of organic matter are high in the interior mangrove zone. Hence, significant amount of P is adsorbed within the organic matrix which is subsequently released by microbial degradation into the overlying water column, thus influencing the dissolved phosphorus dynamics.

Biological control on phosphorus geochemistry and phosphorus burial rates

Phosphorus is an essential and integral component of every living organism for its growth and maintenance. The organic phosphates could either be taken directly or assimilated after hydrolysing them by extracellular alkaline phosphatases. Few studies have been conducted on the Indian mangroves depicting the essential role of microorganisms in burial and release of phosphorus into the system. In the Sundarbans, it has been observed that solubility of phosphorus is induced by microbes either in the presence of P solubilizing bacteria or due to degradation of organic matter[52]. Similar observations were recorded from the Gujarat mangroves[31].

Studies on phosphorus accumulation rates in sediments on the Indian coast are limited. The total P burial rates ranged between 5.41 and 6.38 μM P cm^{-2} yr^{-1} in the Pichavaram mangroves[56]. P burial rates were high in the interior zone (7.27 μM P cm^{-2} yr^{-1}) of the Pichavaram mangroves; however, high burial rates of Fe–P and Au-P were recorded in the estuarine regions[15]. In Pichavaram, the diffusive benthic P fluxes ranged from 0.122 to 0.233 μM P cm^{-2} yr^{-1}, whereas phosphorus burial efficiency rate was ~99%. This suggested that in mangroves environment, majority of phosphorus is buried in sediments with less than 1% being available for recycling within the system; thus it becomes a limiting nutrient for primary productivity[15]. However, it is important to note that these fluxes are subject to high uncertainty and various biogeochemical and environmental factors play an important role in governing the mobility and burial in the mangroves.

Future outlook

The fragile ecosystems such as mangroves are a topic of major concern due to enhanced geogenic as well as anthropogenic activities in the river catchment. In the event of rapid urbanization, comprehensive knowledge of the impact of anthropogenic coastal-zone nutrient cycling and its implications to coastal eutrophication and hypoxia is mandatory. So far, limited information is available for groundwater and pore water P turnover within these transitional ecosystems. Thus, a holistic scientific approach on overall phosphorus budget is needed to elucidate the relative importance of various pools as a source or sink of P. Extensive ocean and marine modelling studies also provide insights in phosphorus biogeochemistry and related oceanic primary productivity, which illustrates the regional variability and limiting nutrients dynamics in the coastal/ocean ecosystem. Furthermore, unambiguous relationship between microbial activities and changes in P geochemistry needs to be investigated in detail. Increased hypoxia due to decrease in oxygen solubility and advanced water-column stratification resulting from climate change is presumable in the future. Also, progressive salinization of many brackish and freshwater coastal systems due to sea-level rise associated with global warming is expected to result in enhanced availability of P in the water column. Hence, further research is needed to understand the interaction of hypoxia, salinization and other environmental factors, including the activity of benthic organisms.

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