

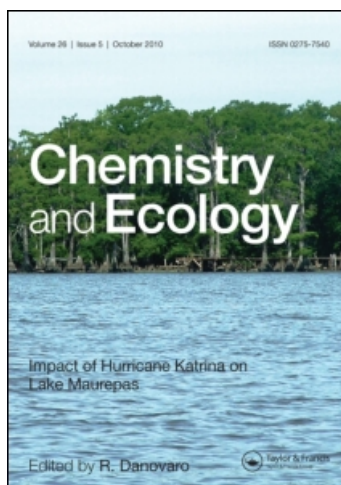
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Assessing the P fractionation in a tropical river-estuarine system of South India

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Seasonal variations in dissolved and particulate P forms were assessed in the estuarine system of Chalakudy River, Kerala, South India – a tropical river having substantial relics of riparian vegetation. The contribution of the reactive P form extended to 84–96% compared with the residual fraction. Geographical and human activities have had effects on the phosphorus-loading capacity at various locations, which reveal pronounced variability in P distribution. Not all forms of phosphate in suspended particulate matter are likely to be released, and thus the nature of the P forms within the stock is a sensitive factor that can be utilised. Ca-bound P in suspensates increases to a highly significant level in the estuarine area, whereas Fe/Al-bound P predominates at the riverine and catchment areas during both the monsoon and non-monsoon seasons. Thus, calcium compounds determine the availability of P in the alkaline estuarine environment, whereas in the riverine environment, Al and Fe control P solubility. The comparatively low P load in upstream waters indicates that, under ambient situations, vegetative riparian zones can be very important P filters.

Keywords: nutrient; phosphorus; fractionation; Ca-bound P; Fe/Al-bound P; riparian vegetation

1. Introduction

Phosphorus is a key nutrient in a river ecosystem. Recently reported studies on growth-limiting nutrients in aquatic systems endorse the view that phosphorus is the primary limiting nutrient in freshwaters, and nitrogen is the limiting nutrient in marine systems [1–3]. Phosphorus exists in different forms, but only those that are directly assimilated by algae can have a role in eutrophication. However, some forms of phosphorus (not directly available) may be converted into bioavailable orthophosphates [4]. Thus, the excessive enrichment of rivers with soluble inorganic phosphorus and nitrogen leads to the undesirable growth of algae, which in turn causes a reduction in water clarity and a deterioration in water quality.

Chalakudy River, in the state of Kerala, South India, has relics of thick riparian vegetation to a substantial extent and the river basin is also disturbed by human activities which certainly affect nutrient levels. Riparian forests in the proximity of Chalakudy River have revealed the existence of thick riparian vegetation > 10 m wide for a distance of 10.5 km downstream from Peringalkuthu,

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covering an area of 58.5 ha. Of this, 26.4 ha lie within the Vazachal area, including three large islands densely covered by riparian forests.

Vegetative riparian zones along the banks of rivers can act as ‘nutrient filters’, regulating the nutrients that enter the stream from both forested and agricultural landscapes. Riparian vegetation is undoubtedly one of the most important parameters affecting the varying riverine nutrients that define the aquatic ecosystem, as well as acting as the boundary between aquatic and terrestrial ecosystems. The moist and often wet soils and high water tables associated with riparian areas make them one of the most important and diverse parts of a river ecosystem.

In this study, an effort was made to identify the main factors that may potentially control contributions to the phosphorus species in the dissolved and particulate phases. Not all forms of phosphorus are likely to be released, and it is important to know which forms can be mobilised in both dissolved and particulate phases. This study was performed to: (1) separate the different forms of dissolved and particulate phosphorus using various recognised sequential or parallel chemical extraction techniques; and (2) understand the role of spatio-temporal features on their distributions in this tropical river estuary.

2. Materials and methods

2.1. Description of the study area and sampling stations

Chalaky River, the fifth longest (145.5 km) in Kerala (Figure 1), originates in the Western Ghats, ends at the Arabian Sea, and is geomorphologically diverse [5]. Its basin lies between

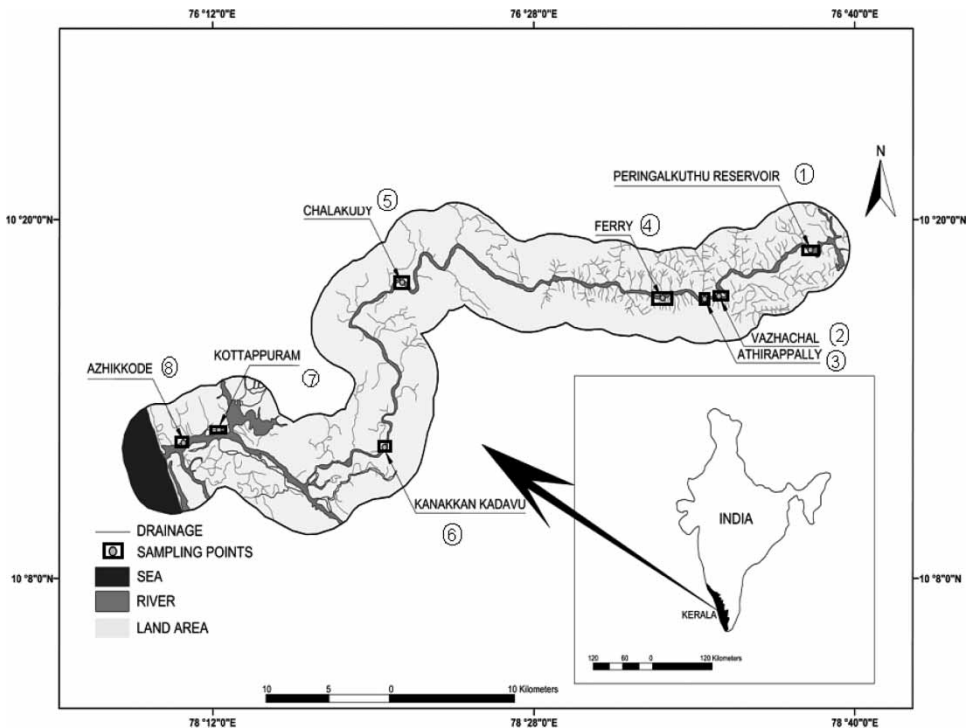


Figure 1. Chalaky River estuary showing the location of the eight sampling sites.

10°05'–10°35' N and 76°15'–76°55' E. The total drainage area of the river is 1704 km². The total average annual drainage discharge (1980–2000) was reported to be 1421.81 million m³ near Chalakudy town and the average annual rainfall in this area is ~3300 mm [6].

Samples were collected from eight stations (Figure 1) with entirely different physical features and varying levels of pollution. The stations differ in the amount of freshwater input and the degree of development in, and utilisation of, their catchments areas. Station 1, located in the deep forest, is the dam station of Peringalkuthu which generates hydroelectric power. Stations 2 and 3 lie downstream around the waterfall regions of Vazhachal and Athirappally, respectively. These sites, located at the entrance to the Sholayar forest ranges, are popular picnic spots. Station 4 is the Plantation Corporation of Kerala (PCK) ferry region at Ayyampuzha, which is characterised by considerable industrial and agricultural activity. Station 5 is below the Chalakudy Bridge, bordering Chalakudy town. Station 6 is in a village Kanakkankadavu, which is far from the crowded town. Before reaching the next station, the river confluences with the Periyar, the largest river in Kerala. Estuarine Station 7 is at Kottappuram where the river, affected by intrusion from Arabian Sea, turns saline seasonally. Station 8 is totally estuarine as the Chalakudy River merges into the Arabian Sea.

Tables 1 and 2 give the general setting of the river and the sampling sites. The distances of the sites from the estuary and general water-quality parameters such as temperature, pH and salinity are also presented in Table 2. Salinity was found to vary significantly at the estuarine end, whereas all other stations showed riverine values. Temperature and pH did not vary much. Table 2 also depicts the shallow nature of the river, surface and bottom samples thereby showing no significant differences.

Table 1. General features of the Chalakudy River.

Location	South India
Coordinates	10° 05' to 10° 35' N; 76° 15' to 76° 55' E
Length	145.5 km
Origin	Anamalai Hills
Source elevation	1250 m
Mouth	Arabian Sea
Basin area	1.704 km ²
Average discharge	52 m ³ ·s ⁻¹
Tributaries	Karappara River, Kuriarjuttu Aar Peruvirippallam Aar, Thunacadavu Aar, Sholayar River
Riparian vegetation	10 m wide, 10.5 km long covering an area of 58.5 ha
Total drainage area	1704 km ²

Table 2. General hydrographical features of sampling stations.

Station no.	Station name	Characteristics	Distance from Arabian Sea	Temp. (°C)	pH	Salinity	Depth (m)
1	Poringalkuthu Dam	Reservoir in the high range	80	27	7.2	<0.1	6
2	Vazhachal waterfalls	First waterfall	76	27	7.2	<0.1	0.5
3	Athirappilly	Second waterfall	74	28	7.3	<0.1	0.5
4	Ayyampuzha	PCK ferry region. Industrial and agricultural activity	70	28	7.2	<0.1	3
5	Chalakudy town	Below Chalakudy Bridge, town area	54	30	7.0	<0.1	3
6	Kanakkankadavu	Remote area unaffected by human intrusion	34	30	6.9	<0.1	3
7	Kottappuram	Start of estuary	6	31	7.4	10.5	6
8	Azhikodu estuary	Estuary	0	31	7.5	12.5	8

Table 3. Extraction schemes for the speciation of phosphorus in particulate matter.

Extraction step	Reagents	Form of phosphorus extracted
A	NaCl	Loosely adsorbed exchangeable phosphorus
B	Bicarbonate–dithionate (BD)	Fe/Al-bound phosphorus
C	NaOH (0.1 M)	NaOH-bound P (polyphosphates)
D	HCl (0.5 M)	Ca-bound phosphorus
E	Hot (85 °C); NaOH (1 M)	Refractory phosphorus

Note: If the BD step is not performed, NaOH (0.1 M) extracts Fe/Al-bound phosphorus plus polyphosphates.

2.2. Sampling and storage

Surface and bottom water samples were collected on a bimonthly basis from eight stations. The bimonthly sampling plan for 2005–2006 was divided into two seasons based on the precipitation rate: collections in May, July, September and November were in the monsoon period and collections in January and March were in the non-monsoon period. The reproducibility of sampling was checked by duplicate sub-sampling measurements at each of the eight stations. At the estuarine stations, samples were collected under similar tidal conditions (low/high tide) to avoid the influence of tidal faces on the loads of suspended particulate matter.

For surface sample collection, a clean plastic bucket tied with a nylon rope was used. A Hytech water sampler was used to collect bottom water samples. Water samples were stored in pre-cleaned 5L polypropylene bottles. After sampling, suspended particulate matter (SPM) for the analysis of nutrients was isolated by vacuum filtering of a particular volume of each water sample through a pre-combusted (450 °C, 4 h) glassfibre filter (25 µm; GF/F, Whatman). Water samples were analysed immediately for dissolved nutrients. Filtered suspended particulates were stored frozen until analyses were carried out.

2.3. Methodology

Determination of the dissolved phosphate-P from the filtrate was based on the molybdate–ascorbic acid procedure [7,8], using a Genesys 10UV thermospectronic spectrophotometer. Total phosphorus was estimated after oxidising the sample with potassium peroxodisulphate in sulphuric acid, where total phosphorus was converted to phosphate. The difference between total P and the phosphate-P is produced as residual P which is mainly organic P.

Chemical fractionation experiments on particulate matter were designed to separate and quantify specific forms of P using an operationally defined extraction sequence [9–13], displayed in Table 3. This technique, first developed for sediments, was extended to particulate matter. It utilises NaOH to solubilise polyphosphates and HCl to dissolve calcium-bound phosphorus. The pH of the final extracted solutions was adjusted, and the P concentrations were determined colorimetrically using the molybdate–ascorbic acid procedure [7]. Cell-to-cell and blank corrections were applied to all sets of readings. Triplicate analyses of each of the duplicated sub-samples were performed to check analytical reproducibility. Thus, the final analytical data are represented as standard deviation bases of six readings.

3. Results and discussion

P is usually found in its most oxidised state as a phosphate (PO_4^{3-}) ion. In riverine systems, P acts as the limiting nutrient and enters the ecosystem in different forms, depending on its origin. Spatial and temporal scales are important in determining the phosphorus supply from catchments.

Table 4. Station-wise variations of sediment structure during monsoon and non-monsoon seasons.

Season	Texture	Stations							
		1	2	3	4	5	6	7	8
Monsoon	% sand	30.08	93.04	80.91	21.04	29.379	43.94	76.35	27.09
	% silt	61.71	4.05	16.15	73.81	62.53	49.95	23.67	65.45
	% clay	8.20	2.90	2.93	5.14	7.68	6.11	3.85	7.45
Non-monsoon	% sand	56.35	89.65	65.02	11.92	12.12	14.36	65.33	11.73
	% silt	40.36	9.02	33.37	85.83	83.96	81.61	31.42	82.07
	% clay	3.29	1.32	1.61	2.25	3.92	4.03	3.25	6.20

Bioavailable P is the sum of immediately available P and P that can be transformed into an available form by naturally occurring processes. These factors are responsible for eutrophication in rivers. Dissolved P consists mainly of orthophosphates and is fully bioavailable to organisms.

Results of texture analyses performed on freeze-dried sediments are given in Table 4. Sand was the predominant form in waterfall stations 2 and 3 and also up-estuarine station 7 during both seasons. During the monsoon season, silt formed the major portion of the texture at reservoir station 1, but during the non-monsoon season, sand dominated the texture. Stations 4, 5, 6 and 8 had silt as the major constituent and its percentage was higher during non-monsoon seasons. The clay level was generally low at all stations, although a slight increase was seen at stations 1, 5 and 8 during the monsoon season.

Seasonal (monsoon and non-monsoon) variations in the distributional features of the reactive and residual P fractions are given in Figure 2 ($\mu\text{mol}\cdot\text{L}^{-1}$) and their percentage-wise compositions

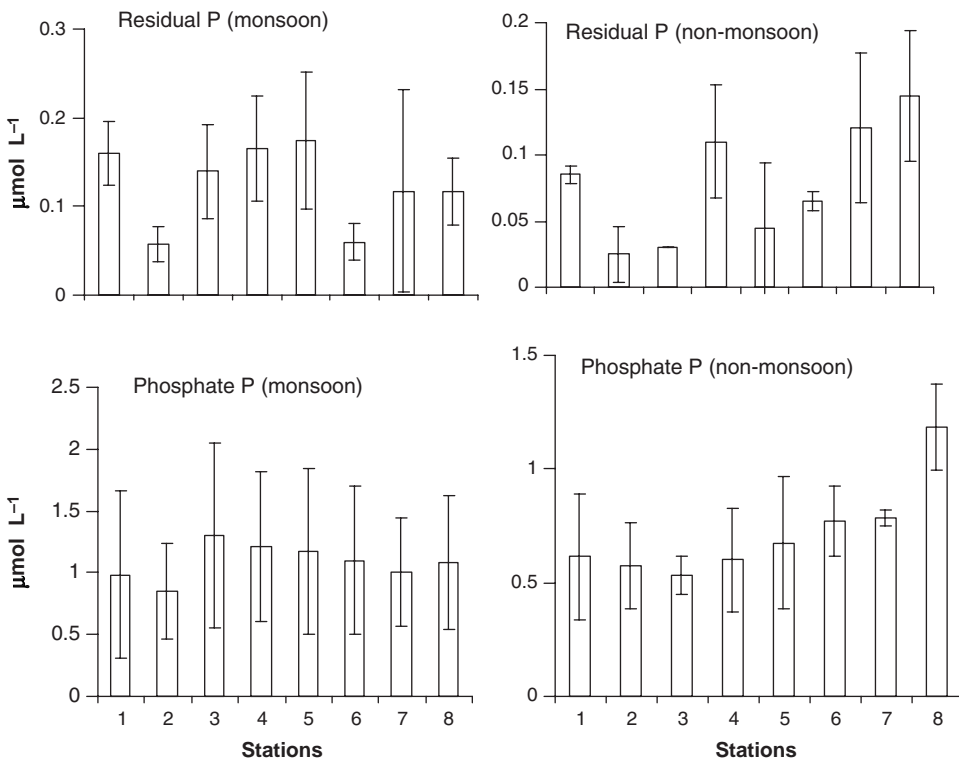


Figure 2. Seasonal distributions of dissolved reactive (phosphate P) and residual phosphorus at various stations.

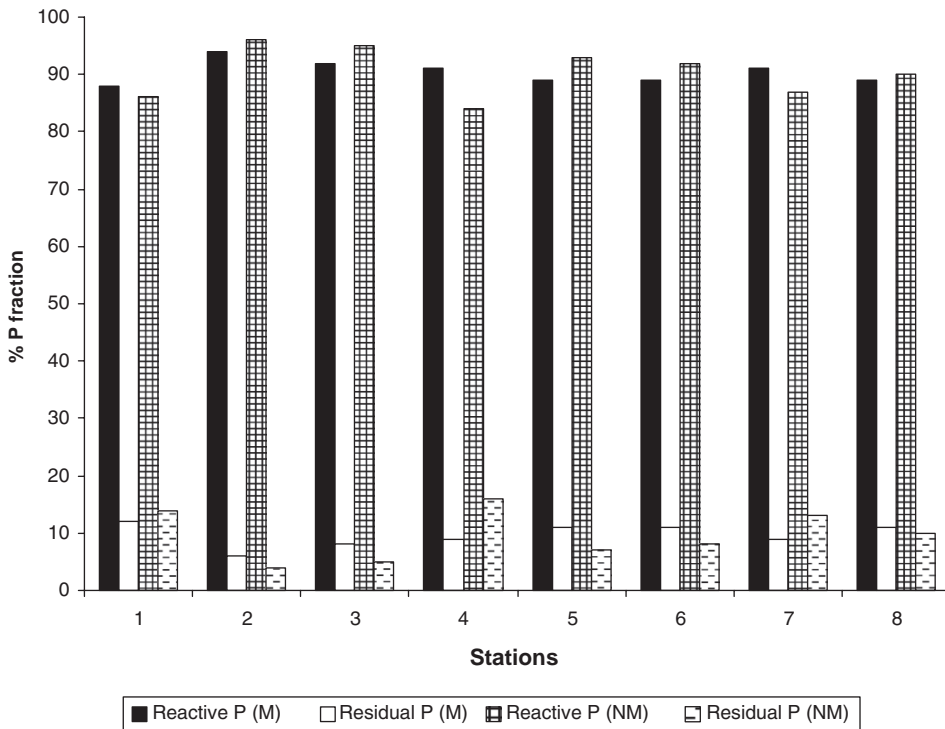


Figure 3. Percentage-wise distributions of dissolved P fractions at different stations (M, monsoon; NM, non-monsoon).

are compared in Figure 3. It can be seen that reactive phosphorus comprised a major portion of the total dissolved phosphorus, whereas the organic-rich residual-P was limited to 6–12% in the monsoon and 4–16% in the non-monsoon season, respectively. Soluble, reactive phosphorus is generally referred to as orthophosphate and is the form of phosphorus most readily utilised by algae; it is routinely measured to assess nutrient status and water quality in an aquatic system [14].

Two-way analysis of variance (ANOVA) was used to test the effect of months and stations on dissolved phosphate. The results of the ANOVA are given in Table 5. Although differences in the extent of dissolved phosphorus fractions during the monsoon and non-monsoon seasons may seem to be minor, it is worth noting that all of the stations sampled in this tropical river estuary showed considerable variations in the spatial distribution of the dissolved phosphorus fractions. The monsoon season favoured comparatively higher loadings of phosphate P and residual P in the hilly catchments areas, waterfall regions and mid-riverine sites. During the rainy season, dissolved P fractions are brought to these stations mainly through land run-off. The nonreactive residual fractions, loaded with organically bound P, never exceed 15% of the total dissolved phosphates. The lowest values of residual P were recorded at the waterfall regions (Station 2) which are characterised by high water turbulence/agitation – an environmental setting that is more favourable for the oxidative decomposition of dissolved residual P. Further, the waterfall regions had a rocky substratum (Table 4) compared with the sediments of other stations, which displayed an appreciable percentage of clayey fraction that showed high nutrient retention and wherein rapid recycling of P from organic matter in the sediments occurred. Phosphorus recycling mechanisms, including the release of phosphorus from the sediment–water interface, are some of the main pathways as far as concentrations of dissolved and particulate phosphates are concerned. During the non-monsoon season, an enhancement in the concentrations of total dissolved P towards the estuarine side of the water course was noticed, which focuses on the chemo-estuarine fluctuations.

Table 5. ANOVA results for station, season and depth-wise variations in dissolved phosphates in Chalakudy River during 2005 to 2006.

	Dissolved phosphate – surface						Dissolved phosphate – bottom					
	SS	df	MS	F	p-value	F _{crit}	SS	df	MS	F	p-value	F _{crit}
<i>Monsoon</i>												
Stations	4.84	3	1.61	13.3	0	3.07	5.77	3	1.92	15.2	0	3.07
Months	0.81	7	0.12	0.95	0.49	2.49	0.57	7	0.08	0.64	0.72	2.49
Error	2.55	21	0.12				2.65	21	0.13			
Total	8.2	31					8.99	31				
<i>Non-monsoon</i>												
<i>Particulates</i>												
Stations	0.01	1	0.01	0.19	0.68	5.59	0.14	1	0.14	5.72	0.05	5.59
Months	0.61	7	0.09	2.04	0.18	3.79	0.61	7	0.09	3.53	0.06	3.79
Error	0.3	7	0.04				0.17	7	0.02			
Total	0.92	15					0.93	15				

Notes: MS, mean square deviation; SS, sum of squared deviation.

The quantity of suspended particulate matter obtained from the water samples varied at different sampling sites. Low quantities of suspended particulate matter varying from 0.06 to 0.1 mg·L⁻¹ were obtained at the waterfall stations 2 and 3, whereas stations in the dam area and other riverine and estuarine locations recorded higher quantities (0.2–0.3 mg·L⁻¹). Not all forms of phosphorus in suspended particulate matter are likely to be released, and it is important to know which can be mobilised. Particulate P represents a long-term source of P for organisms by its existence as various species such as exchangeable P, P associated with Al and Fe oxides and hydroxides and Ca minerals, as polyphosphates, refractory (residual inorganic) P, etc. Stationwise average seasonal levels of the different forms of phosphorus in suspended particulates (μmol·L⁻¹) are given in Figure 4(a) and (b).

The particulate pools of the waterfalls station were deficient in all forms of P relative to other stations. Sediments collected from the waterfall regions are solely sandy in nature (Table 4) and it has been proved that sand typically has a very low P sorption potential because of its low amorphous Fe and Al concentrations [15]. The compositions of all fractions were found to be high at Station 4, ferry region, which is characterised by the presence of factories nearby. Thus, the higher values at Station 4 are partially attributed to the influence of pollutants from industrial effluence. The percentage-wise contribution of exchangeable P to the total particulate phosphorus in this river estuary was limited to 4–9% (Figure 5). The percentage of Fe/Al-bound P in particulates was higher from the reservoir to the riverine end (except for the waterfalls region), ranging from 39 to 51%. Noticeably, estuarine stations showed comparatively lower values (24–38%) of Fe/Al-bound P. Reservoir areas characterised by thick density of riparian vegetation show a high level of polyphosphates in the riverine suspensates (18–30%); whereas estuarine end stations had low levels (11–18%). Among the different particulate P forms quantified, inert refractory P was comparatively very low with a range of 3–9%, the lowest being at the waterfall regions.

The dominance of Fe/Al-bound P and an anomaly of Ca-bound P in riverine stations are also documented in other studies [16,17]. The percentage of Ca-bound P varied from 15 to 32% for all stations, except those located in the estuarine zone which showed a prominent increase, up to 58%. Ca-bound P concentrations were low during rainy season along the reservoir to river end with a slight increase at the ferry region. Afterwards, levels increased sharply at the estuarine end. Mixing with seawater, certainly, is one factor responsible for the increased load of Ca-bound P in estuarine particulate materials. Within the estuarine area, phosphorus is mainly associated with

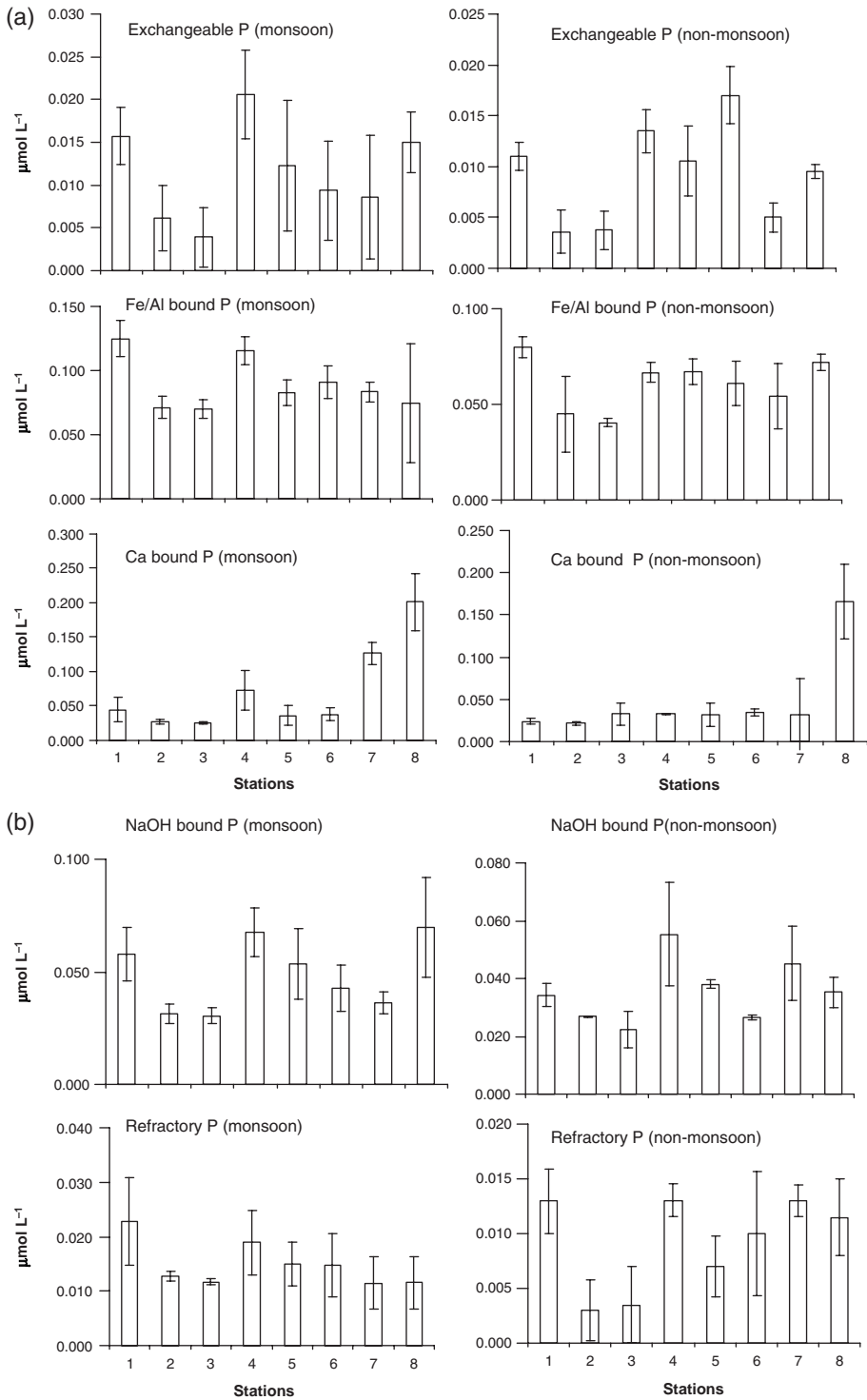


Figure 4. Seasonal variations in: (a) exchangeable, Fe/Al-bound and Ca-bound P fractions in particulates; (b) NaOH-bound P and refractory P fractions in particulates.

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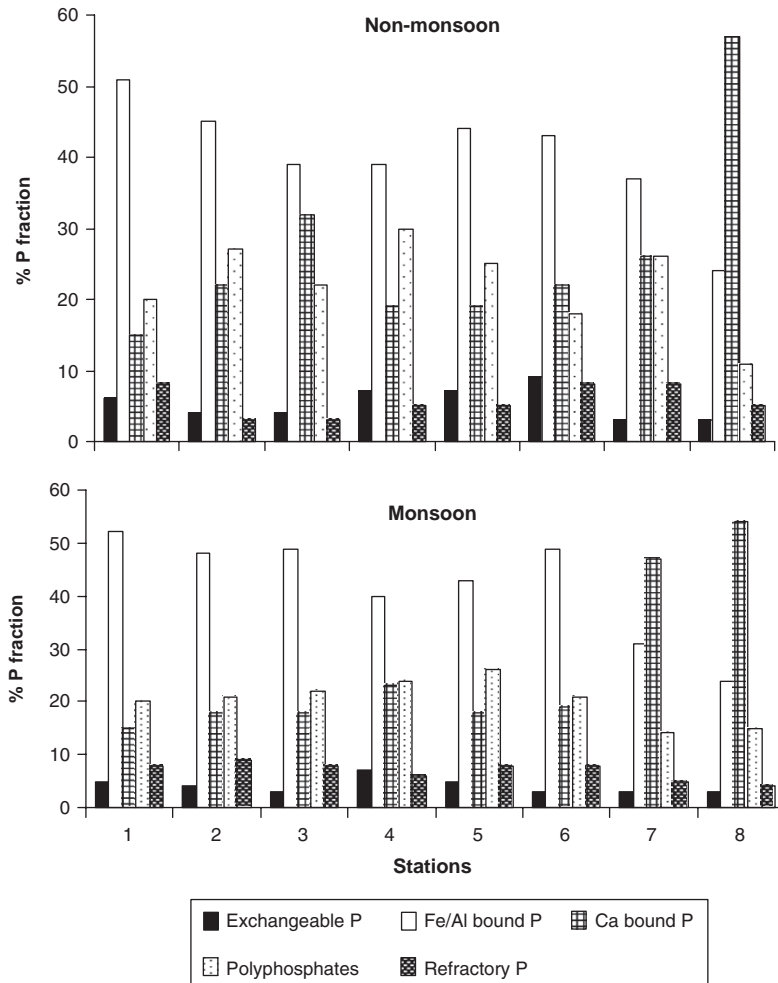


Figure 5. Percentage-wise distributions of particulate P fractions at different stations.

calcium minerals such as apatites. Hence, the formation and retention of apatites is the major process controlling phosphorus in the coastal biogeochemical cycle [16]. In view of its higher ionic concentration, various estuarine-chemical processes such as desorption, solubilisation and sedimentation play dominant roles in the spatio-temporal behaviour of particulate Ca-bound P in the estuarine zones. Thus, estuarine SPM is generally richer in the Ca-bound P fraction. Obviously, calcium compounds determine the availability of inorganic P in an alkaline aquatic environment, whereas in an acidic/neutral environment, Al and Fe control P solubility.

Stations located in the catchments area, mid-riverine region and estuarine vicinity faced a distinctly higher concentration of both dissolved and particulate phosphorus. Inputs from land, through the combined discharges of fertiliser inputs and urban discharges increased the nutrient load. In addition to the important role of exchanges with and inputs from the land and ocean, the local stoichiometric P ratios in the system were also dependent on local ecosystem processes. Nutrient assimilation by phytoplankton may lead to a decline in the bioavailable forms of nutrients.

An overall variation in the forms of P at the estuarine end was a noticeable phenomenon during the monsoon season. The exchangeable and refractory P fractions in SPM contributed only a minor part, which was too small to be significant during both seasons. Particulate P has two origins,

Table 6. Concentration of phosphorus species reported in studies elsewhere.

P form	Aquatic system	Conc. ($\mu\text{mol}\cdot\text{L}^{-1}$)	Ref
Phosphate P			
	Dam site of Acton Lake, OH, USA	<0.2 to >4	[21]
	River site of Acton Lake, OH, USA	8–12.3	[21]
	Ria Formosa coastal lagoon, south Portugal	0.3–1.6	[22]
	Liangxihe River discharge into Meiliang Bay, Lake Taihu, China	0.18	[23]
	S'Ena Arrubia Lagoon, central–western Sardinia	0.9–26.63	[28]
	Mgazana estuary, Eastern Cape, South Africa	4.86	[29]
	Fenton River, CT, USA	5.05	[30]
	Mount Hope River, CT, USA	0.38–6.80	[30]
	Natchaug Rivers, CT, USA	0.34–2.04	[30]
Total P			
	Dam site of Acton Lake, OH, USA	5–24	[21]
	Liangxihe River discharge into Meiliang Bay, Lake Taihu, China	1.5	[23]
	S'Ena Arrubia Lagoon, central–western Sardinia	2.87–39.38	[28]
	Danube River floodplain, Kopac ki Rit, Croatia	7.10–15.17	[31]
	Wuli Lake, China	0.67–5.48	[32]
	Fenton River, CT, USA	0.25–6.06	[30]
	Mount Hope River, CT, USA	0.48–7.58	[30]
	Natchaug Rivers, CT, USA	0.29–5.58	[30]
	Sahela Reservoir, Morocco	0.29–1.61	[33]
Particulate P			
	Northern and Central Adriatic	0.10–0.20	[34]
	Lake Vattern and Lake Vanern, southwest of Stockholm		[18]
	Filterable P (0.2 μm)	2.13–2.64	
	Fine colloidal P	0.09–0.61	
	Rostherne Mere, a British freshwater		[35]
	Total P	0.48–5.16	
	Orthophosphate	0–12.91	
	Danish rivers		[19]
	Exchangeable P	1.6–12.7%	
	Fe-bound P	38–79%	
	Al/clay-bound	4.3–36%	
	Ca-bound P	2.2–5.3%	
	Humic-bound P	2.4–4.4%	
	Extra. organic P	4.5–9.8%	
	Refr. organic P	2.7–6.6%	

i.e. external and internal. External P originates from point (industrial and domestic effluents) or diffuse (weathering, agricultural run-off) sources, but it is also released by sediments, which act as an internal source contributing phosphate to the overlying waters and particulates. Sedimentation and the filtering of suspended solid particles are removal mechanisms for particle-borne nutrients such as phosphorus [18]. Fe-bound P formed 38–79% and phosphate adsorbed onto aluminium oxides and clay 4.3–36% of particulate total P in Danish rivers, (Table 6) wherein exchangeable phosphate accounted for 1.6–12.7% and Ca-bound P to 2.2–5.3% of particulate total P [19]. Comparatively high amounts of phosphorus delivered from episodic land inputs enhance the relative phosphorus composition, showing an important role for high rainfall and river discharge in assessing nutrient partitioning within the water column. Finally, the texture of suspended as well as bed-load sediments may also potentially control the fractionation and stability of P, especially in estuarine areas dominated by fine-grain sediments. The large specific surface area, surface energy and electrostatic charge of small and colloidal particles are mainly driven by coagulation [20].

It can be seen from some of the studies referred to in Table 6 that the currently reported levels of dissolved inorganic P (<2 $\mu\text{mol}\cdot\text{L}^{-1}$) and total P ($\sim 2 \mu\text{mol}\cdot\text{L}^{-1}$) in the Chalakudy River estuarine

system were within the range observed in many other aquatic systems such as the dam site of Acton Lake (USA), Ria Formosa coastal lagoon (Portugal), Wali Lake (China) and Fenton River (USA) [21–35]. The upper limit of total P in the dam site of Acton Lake was $24 \mu\text{mol}\cdot\text{L}^{-1}$, whereas most of the water bodies referred in to Table 6 have dissolved and particulate P concentrations within the range $2\text{--}5 \mu\text{mol}\cdot\text{L}^{-1}$. The 38–79% of Fe/Al-bound P in particulate phosphorus in Danish rivers [19] is an attestation of the present finding of higher Fe/Al fractions in the riverine stations of Chalakudy River estuary. In general, it can be concluded that phosphorus pollution has not greatly affected the Chalakudy River estuarine system.

Marginal seasonal variability was observable, with higher phosphorus concentrations in the monsoon season, especially in the riverine sector. High dissolved inorganic phosphate levels have been found seasonally in river and mangrove systems in Kenya following rain or groundwater run-off [24,25]. During floods, the estuarine basin could be completely flushed of brackish water and the majority of the nutrient loads pass directly through the estuary. Estuaries mediate a large part of the nutrient flux from the land to the sea. As nutrients enter estuaries through tributary rivers, concentrations may often be maximal in the freshwater regions, because riverine freshwater was not diluted by relatively nutrient-poor seawater [26]. The results of our study did not conform to this for Ca-bound P and total inorganic P in suspensates during both seasons and for dissolved components in the non-monsoon season. The fluctuations in nutrient fractions in the dissolved, as well as particulate, forms were also impacted by the thick riparian buffer zones on the banks of riverine area. Vegetation productivity has a broad influence on riverine biogeochemical processes, related to the consequences of changing redox conditions occurring from upstream to downstream. However, surface and groundwater linkages are the predominant controls of landscape connectivity within riparian systems. The importance of riparian zones as sources and sinks of matter and energy was established in the context of structural and functional attributes, such as the sequestering or cycling of nutrients in sediments, retention of water in vegetation, and retention, diffusion or dispersal of biota [27]. Riparian vegetation is undoubtedly one of the most important parameters related to varying riverine nutrients which define the aquatic ecosystem. The moist and often wet soils and high water tables associated with riparian areas make them one of the most challenging parts of a river ecosystem. The riparian zones in the Chalakudy riverine ecosystem vary considerably in size, vegetation, species abundance and diversity. Rich riparian vegetation zones were observable at Station 1, (catchments area), Station 4 (ferry region) and Station 5 (town region), wherein comparatively higher nutrient loading was recorded. Towards the estuarine end, the increase in phosphorus concentration was established due to the chemo-estuarine mixing with seawater. Because riparian-driven organic matter, as well as different micro- and macro-components, are closely associated with the surface of suspended particulates, the fate and transport of particulate P are also affected throughout in this river estuary. Combining the data on dissolved phosphorus with that on particulate phosphorus shows that the organic and iron-bound phosphorus are not stable over longer time scales: $\sim 80\%$ is either transformed into dissolved phosphorus and exported from the estuary or transformed into apatites and buried [16].

The various correlation matrices of P forms in the particulate matter are depicted in Table 7. Correlation analysis identified a very strong correlation between two environmental variables: Ca-bound P and total inorganic P ($r = 0.87$). Poor correlations among all other measured nutrient fractions and the quantity of particulate matter suggest that biological processes and rainfall-mediated nutrient injections overwhelmed upstream sources over interannual time scales. When the amount of particulate matter increases, Ca-bound P and total inorganic P also increase, as shown in the scatter plots in Figure 6.

Nutrient loading during the study period appeared to be further substantially impacted by rainfall. Profound environmental change occurred in riparian river regions during the transition from monsoon to non-monsoon. Destabilisation and erosion of the riverbanks is one of the most

Table 7. Pearson correlation matrix of P fractions.

	Total N	Loosely bound P	Fe/Al-P	Polyphosphates	Ca-P	Refractory P	Total Inorganic P
Loosely bound P							
P	0.17						
Fe/Al-P	0.34	0.45					
Polyphosphates	0.19	0.58	0.49				
Ca-P	0.24	0.04	0.03	0.22			
Refractory P	0.27	0.23	0.50	0.31	0.09		
Total Inorganic P	0.37	0.40	0.52	0.60	0.87	0.38	
Mass of SPM	0.20	0.21	0.08	0.27	0.62	0.08	0.58

Note: SPM, suspended particulate matter.

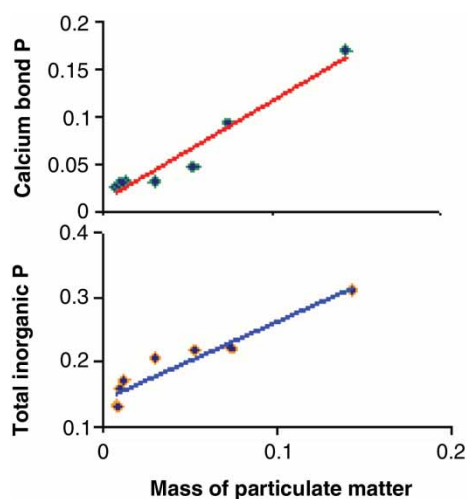


Figure 6. Relation of Ca-bound and total P ($\mu\text{mol}\cdot\text{L}^{-1}$) to the mass of particulate matter in the Chalakudy riverine system.

serious problems faced by rivers in general, and riparian vegetation has a crucial role in the protection of the riverbanks as well as maintaining the nutrient balance in the river.

4. Conclusion

P exhibits a strong concentration with increasing flow in all the river locations monitored. This feature indicates the dominance of point sources, especially from the rural and agricultural areas. Inorganic P is used as a fertiliser; it is probably strongly leached into the water courses. The consequences of interactions between various communities (animals and plants, microorganisms and plants) on biogeochemical processes need to be studied in detail, especially with respect to the control of landscape features. Multiscale approaches, coupling regional and local factors, are needed to model biogeochemical and community processes within the river–riparian–upland landscape of catchments.

The study identified a substantial input showing a greater ability to discriminate among variations in particulate, as well as dissolved, P in the Chalakudy River estuarine system. Maxima of $1.5 \mu\text{mol}\cdot\text{L}^{-1}$ phosphate-P indicate a noticeable degradation of the water quality in the river stretch along midstream, owing to high riparian vegetation and human-induced pollution sources, and

also at the estuarine end, due to chemo-estuarine fluctuations. Within the various locations, geographical and human activities have affected the dissolved phosphorus loading capacity, which shows ample variability in its spatial and temporal distributions. Suspended particulate matter (SPM) regulated the transport of all types of water pollutants in dissolved and particulate phases in the dam, river and estuary. The results show that the factors resulting in the distribution of nutrients in the total suspended matter were both complex and varying during periods of normal and high flow, suggesting that different controls operated in the individual catchments. Calcium compounds determine the availability of inorganic P in an alkaline estuarine environment, whereas in the riverine environment, Al and Fe control P solubility.

The comparatively low P load in upstream waters indicates that, under ambient situations, vegetative riparian zones can be very important P filters, and thus important tools in reducing nutrient input into streams with a major impact on the trophic status of this fluvial water body.

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References

- [1] D.J. Conley, *Biogeochemical nutrient cycles and nutrient management strategies*, Hydrobiologia 410 (2000), pp. 87–96.
- [2] R.J. Stevenson, S.T. Rier, C.M. Riseng, R.E. Schultz, and M.J. Wiley, *Comparing effects of nutrients on algal biomass in streams in two regions with different disturbance regimes and with applications for developing nutrient criteria*, Hydrobiologia 561 (2006), pp. 149–165.
- [3] P.A. Chambers, J.M. Culp, N.E. Glozier, K.J. Cash, F.J. Wrona, and L. Noton, *Northern rivers ecosystem initiative: nutrients and dissolved oxygen – issues and impacts*, Environ. Monit. Assess. 113 (2006), pp. 117–141.
- [4] F.R. Hauer, J.A. Stanford, and M.S. Lorang, *Pattern and process in northern Rocky Mountain headwaters: ecological linkages in the headwaters of the crown of the continent*, J. Am. Water Res. Assoc. 43 (2007), pp. 104–117.
- [5] R. Raghavan, G. Prasad, P.H. Anvar-Ali, and B. Pereira, *Exotic fish species in a global biodiversity hotspot: observations from River Chalakudy, part of Western Ghats, Kerala, India*, Biol. Invasion. 10 (2008), pp. 37–40.
- [6] S. Chattopadhyay, L. Asarani, and P.V. Sangeetha, *Water quality variations as linked to landuse pattern: a case study in Chalakudy River basin, Kerala*, Curr. Sci. 89 (2005), pp. 2163–2169.
- [7] K. Grasshoff, *Determination of nutrients*, in K. Grasshoff, M. Ehrhardt, and K. Kremling, eds., *Methods of Seawater Analysis*, Verlag Chemie, Weinheim, 1983, pp. 1–393.
- [8] K. Grasshoff, K. Kremling, and M. Ehrhardt, eds. *Methods of Seawater Analysis*, Verlag Chemie, Weinheim, 1999.
- [9] H.S. Jensen and B. Thamdrup, *Iron-bound phosphorus in marine sediments as measured by bicarbonate–dithionite extraction*, Hydrobiologia 253 (1993), pp. 47–59.
- [10] C. Paludan and H.S. Jensen, *Sequential extraction of phosphorus in freshwater wetland and lake sediments: Significance of humic acids*, Wetlands 15(1995), pp. 65–373.
- [11] H. Aghemian, *Determination of nutrients in aquatic sediments*, in A. Mudroch, J.M. Azcue, and P. Mudroch, eds., *Manual of Physico-Chemical Analysis of Aquatic Sediments*, CRC/Lewis, Boca Raton, FL, 1997, pp. 175–220.
- [12] Z. Libo, Y.E. Ying, and Z. Huaiyang, *Phosphorus forms in sediments of the East China Sea and its environmental significance*, J. Geogr. Sci. 14 (2004), pp. 113–120.
- [13] M. Ladakis, M. Dassenakis, and A. Pantazidou, *Nitrogen and phosphorus in coastal sediments covered by cyanobacteria mats*, J. Soils Sed. 6 (2006), pp. 46–54.
- [14] R.G. Wetzel, *Limnology*, 3rd edn, Academic Press, San Diego, CA, 2001.
- [15] S.D. Bridgman, C.A. Johnston, J.P. Schubauer-Berigan, and P. Weishampel, *Spatial controls over phosphorus sorption in soils and coupling with surface water in two riverine wetlands*, Soil Sci. Soc. Am. J. 65 (2001), pp. 577–588.
- [16] J.E.E. Van Beusekom and V.N. De Jonge, *Transformation of phosphorus in the Wadden Sea: apatite formation*, Ger. J. Hydro. 49 (1997), pp. 297–305.
- [17] J. Rao and R.A. Berner, *Phosphorus dynamics in the Amazon River and estuary*, Chem. Geol. 107 (1993), pp. 397–400.
- [18] B. Ulen, *Size and settling velocities of phosphorus-containing particles in water from agricultural drains*, Water Air Soil Pollut. 157 (2004), pp. 331–343.
- [19] H.S. Jensen, T. Bendixen, and F.O. Andersen, *Transformation of particle-bound phosphorus at the land–sea interface in a Danish estuary*, Water Air Soil Pollut. Focus 6 (2006), pp. 547–555.
- [20] G. Kapanen, *Phosphorus fractionation in lake sediments*, Estonian J. Ecol. 57 (2008), pp. 244–255.

- [21] W.H. Nowlin, J.L. Evarts, and M.J. Vanni, *Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir*, *Freshwater Biol.* 50 (2005), pp. 301–322.
- [22] D. Serpa, M. Falcao, P. Duarte, L.C. da Fonseca, and C. Vale, *Evaluation of ammonium and phosphate release from intertidal and subtidal sediments of a shallow coastal lagoon (Ria Formosa – Portugal): a modelling approach*, *Biogeochemistry* 82 (2007), pp. 291–304.
- [23] M.J. McCarthy, P.J. Lavrentyev, L. Yang, L. Zhang, Y. Chen, B. Qin, and W.S. Gardner, *Nitrogen dynamics and microbial food web structure during a summer cyanobacterial bloom in a subtropical, shallow, well-mixed, eutrophic lake (Lake Taihu, China)*, *Hydrobiologia* 581 (2007), pp. 195–207.
- [24] J.U. Kitheka, B.M. Mwashote, B.O. Ohowa, and J. Kamau, *Water circulation, groundwater outflow and nutrient dynamics in Mida creek, Kenya*, *Mang. Salt Marsh.* 3 (1999), pp. 135–146.
- [25] R.J. Lara and T. Dittmar, *Nutrient dynamics in a mangrove creek (North Brazil) during the dry season*, *Mang. Salt Marsh.* 3 (1999), pp. 185–195.
- [26] K. Muylaert, M. Tackx, and W. Vyverman, *Phytoplankton growth rates in the freshwater tidal reaches of the Schelde estuary (Belgium) estimated using a simple light-limited primary production model*, *Hydrobiologia* 540 (2005), pp. 127–140.
- [27] T. Eric, C.L. David, H. Richard, P. Gilles, P.T. Anne-Marie, and W.C. Robert, *Development, maintenance and role of riparian vegetation in the river landscape*, *Freshwater Biol.* 40 (1998), pp. 497–516.
- [28] F. Trebini, B.M. Padedda, G. Ceccherelli, A. Luglie, and N. Sechi, *Changes of nutrient concentrations and phytoplankton communities after morphological modification in the S'Ena Arrubia Lagoon (Central–Western Sardinia)*, *Chem. Ecol.* 21 (2005), pp. 491–502.
- [29] W. Emmerson, *The nutrient status of Mgazana, a warm temperate mangrove estuary in the Transkei, Eastern Cape, South Africa*, *Wetlands Ecol.* 13 (2005), pp. 405–418.
- [30] F. Nadim, G.E. Hoag, F.L. Ogden, G.S. Warner, and A.C. Bagtzoglou, *Water quality characteristics of two reservoir lakes in eastern Connecticut, USA*, *Lakes Reserv. Res. Manage.* 12 (2007), pp. 187–202.
- [31] G. Palijan and D. Fuks, *Alternation of factors affecting bacterioplankton abundance in the Danube River floodplain (Kopac ki Rit, Croatia)*, *Hydrobiologia* 560 (2006), pp. 405–415.
- [32] X. Jin, X. Jiang, Y. Yao, L. Li, and F.C. Wu, *Effects of light and oxygen on the uptake and distribution of phosphorus at the sediment–water interface*, *Sci. Total Environ.* 357 (2006), pp. 231–236.
- [33] B.A. Mhamdi, A. Azzouzi, M.A. Mhamdi, and T. Sime-Ngando, *Dynamics of the relative nitrogen and phosphorus concentrations in a reservoir situated in a semi-arid zone (Sahela, Morocco)*, *Water Res. Manag.* 21 (2007), pp. 983–995.
- [34] M. Gismondi, M. Giani, F. Savelli, A. Boldrin, and S. Rabitti, *Particulate organic matter in the northern and central Adriatic*, *Chem. Ecol.* 18 (2002), pp. 27–38.
- [35] V. Krivtsov and D.C. Sigeo, *Importance of biological and abiotic factors for geochemical cycling in a freshwater eutrophic lake*, *Biogeochemistry* 74 (2005), pp. 205–230.