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Sediment Quality Assessment of Kavvayi Wetland in South Coast India with Special Reference to Phosphate Fractionation and Heavy Metal Contamination

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Abstract

Sediments play an important role in elemental cycling in the aquatic environment; it can be sensitive indicator for monitoring contaminants in aquatic environments. The heavy metal prominence, the amount and different forms of phosphorous present in the surface sediments of Kavvayi Wetland, which is in the south west coast of India was studied and reported in this paper. A total number of 10 surface sediment samples were taken from various regions of Kavvayi Lake and were subjected to heavy metal analysis and also phosphorous fractionation. Phosphorous forms in the sediment samples were determined by the modified sequential extraction procedure and among the inorganic phosphorous pool; Fe and Al bound phosphorous constituted the major portion while the Ca-bound phosphorous constituted the minor part only. Higher concentration of organic phosphorous was also detected in all the samples. The sediment samples were analyzed for heavy metals such as Fe, Mn, Cu, Pb, Cd, Ni, and Zn and the results showed comparatively higher concentration than the background values. The degree of contamination for each station was determined. Sediment pollution load index (PLI) values of the studied area ranged from 0.39 to 2.55 which indicated that the wetland sediments were polluted. Multivariate statistical techniques were applied to evaluate and characterize the analytical data. Spatial distribution maps of phosphorous fractions and heavy metals would help to identify the pollution sources and vulnerable sites.

Keywords

Kavvayi Wetland, Phosphorous Fractions, Degree of Contamination, Pollution Load Index, Multivariate Statistics

1. Introduction

Sediment has an important role in the nutrient cycle of aquatic environments. In some cases, sediment is responsible for transport of essential nutrients as well as pollutants [1]. Therefore, the assessment of sediment is more conservative than water quality assessment for determining the degree of contamination and toxicity.

Phosphorus is often the limiting nutrient for algal growth in lakes and may limit productivity [2]. The sources of phosphorus in lakes include phosphorus in runoff comes from rock weathering and soil transport and also the agricultural runoff (containing P from fertilizers and animal waste) and sewage (containing P from human waste, detergents and industrial waste) which are directly in the lakes and its inlet tributaries. Phosphorus may enter an aquatic system in the particulate form or dissolved-P may become associated with particles as they settle out of the water column. Sedimentation is a major P sink for the epilimnia of lakes, transporting P to the hyoplimnion and ultimately the sediments.

P content in the sediment can behave as a good predictor of the eutrophication probability of the water body [3]. Physical and chemical characterization of sediments is important for evaluating the phosphate exchange processes between bottom sediments and overlying waters [4]. The phosphorus content in sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of diagenetic processes. Total concentrations of phosphorus in sediments cannot predict the potential ecological danger. The fraction of available phosphorus is an important parameter for predicting future internal P-loading. The factors governing P release from sediments comprise redox reactions, adsorption, mineral phase solubility and mineralization of organic matter. Dissolved oxygen, nitrates, sulphates, pH, temperature and salinity are the major controlling parameters [5]. Moreover, P fractionation of the sediments based on sequential extraction schemes can provide valuable information on the origin of P, the degree of pollution from anthropogenic activities and the bio availability of P in the sediments [6].

Sediments were polluted with various kinds of hazardous and toxic substances, including heavy metals [7]. Pollutants are conserved in sediments over long periods of time according to their chemical persistence and the physical-chemical and biochemical characteristics of the substrata. River sediments, derived as a result of weathering, are a major carrier of heavy metals in the aquatic environment, the physico-chemical processes involved in their association being precipitation, adsorption, chelation, etc. Besides the natural processes, metals may enter into the aquatic system due to anthropogenic factors such as mining operations, disposal of industrial wastes and applications of biocides for pest. The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon the textural characteristics, organic matter contents, mineralogical composition and depositional environment of the sediments [8].

Accumulation of trace metals occurs in upper sediment in aquatic environment by biological and geochemical mechanisms and becomes toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity [9]. Assessment of heavy metal contamination in sediments is critical because of the associated bio-toxicity, high environmental stability and bioaccumulation of the heavy metals in the food chain.

This paper reports the sediment quality assessment of Kavvayi, one of the important wetlands in South India. The main objectives of the study were to evaluate different forms of phosphorous and heavy metal prominence of the surface sediments of Kavvayi Lake.

2. Methods

2.1. Study Area: The Kavvayi Wetland System

Kavvayi Wetland, a coastal backwater body spread out in 10.6 sq·km area, located in Kasargode and Kannur districts of Kerala. Geographically it is located between the coordinates: 75°06'48"E to 75°15'40"E longitudes and 11°59'52"N to 12°14'36"N latitudes. Some significant values of the wetland include flood control, diverse mangrove vegetation, rich biodiversity, fishery, coir retting, mussels culturing, pollution control, inland navigation, sacred groves and back water tourism.

Kariangode, Kavvayi, Perumba, Ramapuram, and Nileswaram are five major rivers draining into the Kavvayi Lake, in which only the Kariangode river originates from the eastern ghats of Kerala, all the other rivers originate from the lateritic hills of midlands. The Kavvayi Lake mixes with Arabian Sea near Mavilakadappuram of Valiyaparamba panchayath. More than 15 islands, namely Valiyaparamba, Kurippadu, Kochuthuruthu, Kavvayi,

Madakkal, Edayilakad, Thekkekad, Vadakkekad, Oriyam, Ori, Kokkal, Chembantemadu, Purathadu, Thuruthy, Achamthuruthy etc., are present in the Kavvayi wetland system. Surface sediment samples were collected from 10 sampling stations and are located in **Figure 1**.

2.2 Sediment Sampling and Analysis

The sediment samples were taken at a depth of nearly 10 cm and placed in polythene bags, preserved in ice and transported to the laboratory. The sediment samples were dried, powdered and sieved for the chemical analysis.

Fractionations of phosphorous in the sediment samples were done using the modified sequential extraction procedure [10]. The method fractionates sediment phosphorous into Fe and Al bound, Ca bound, organic and total phosphorous. 1M NaOH was used for the extraction of Fe and Al bound P (Fe-Al P). 1M HCl was used for the extraction of Ca bound P (CaP). Calcination of the samples followed by the extraction with 3.5 M HCl was used for the analysis of total P (TP). Extraction of the sediment samples with 1M HCl was used for the analysis of inorganic phosphorous (IP) followed by the calcination of the residual samples and another extraction with 1 M HCl was used for the analysis of organic phosphorous (OP).

Sediment pH was measured electrometrically with glass electrode pH meter in water using sediment/water ratio of 1:10. The wet oxidation method of Walkley and Black was used to determine the organic carbon (OC) content in the sediment samples. The sediment particle size was determined by hydrometer method. The total alkalinity (TA) of the sediment was measured by acid base titration (sediment/water ratio of 1:10).

For the heavy metal analysis, the sediment samples were collected and preserved as per the standard procedure [11]. The digestion was performed with a mixture of HNO₃ and HClO₄ acid [12]. The digested samples were analyzed for heavy metals by Thermo M5 series Atomic Absorption Spectrophotometer.

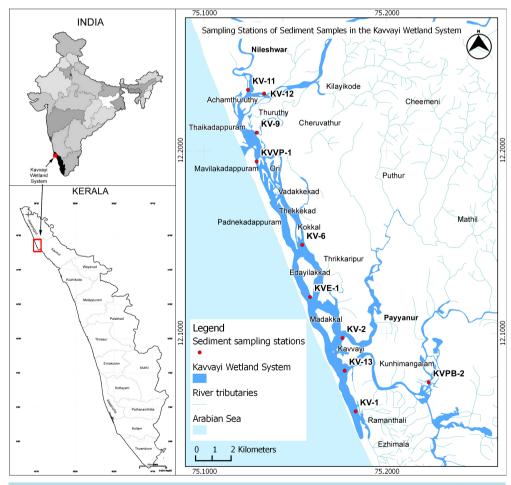


Figure 1. Study area with the sediment sampling stations in the Kavvayi wetland system.

2.3 Data Analysis

The Statistical Package for Social Sciences (SPSS version 19.0) was used for the statistical interpretation. Pearson correlation coefficients were calculated in order to study inter-elemental relationship with their sediment properties. Principal component analysis (PCA) and cluster analysis (CA) have been used for evaluation and characterization of analytical data. The PCA was performed using varimax normalized rotation on the dataset. The CA was applied to the standardized matrix of the samples using Ward's method and the results are obtained in the form of dendrograms. The principal component analytical (PCA) method, which is widely used to detect the hidden structure of sediment sources and to distinguish natural and anthropogenic inputs, was applied here to explore the origin and geochemical factors influencing their distribution [13]. Analytical results were elaborated by using the Geographical Information System (GIS) application, open-source software, QGIS 1.8.0. It was used to show geochemical indices and spatially explain the contaminated areas in the form of interpolated maps.

3. Results and Discussion

3.1. Phosphorous Fractionation of Sediment Samples

Table 1 shows the variation of pH, OC, TA and P fractions in the sediments of Kavvayi Lake. pH of the Kavvayi lake sediment samples ranged between 3.01 - 8.24. The highest values of the total alkalinity (CaCO₃) content in the study area were found at stations KV-6 and KV-2 and 4. The organic content of the sediment samples ranged between 0.5 - 8.08 percent; with an average of 3.46%. The highest organic carbon concentrations were found at the stations KV-6, KVE-1 and KV-2. High organic content should correlate with the aquatic productivity or anthropogenic output. The organic matter in the sediments of the open lakes was mainly endogenesis and the organic content in the surface sediments were correlated with the lake productivity [14].

Based on the data obtained for the analysis of sediment samples, the average TP concentration of the lake sediments was 10,420 mg/kg with a range of 3500 - 19,000 mg/kg. Comparing TP in all stations, a maximum concentration was observed in Thayyil kadappuram and a minimum in the sediment sample of Edayilakkad.

Among the inorganic phosphorus fractions, NaOH-P was found to be the major fraction in all the samples. The NaOH-P represents P bound to metal oxides, mainly of Al and Fe, which is exchangeable again with OH and inorganic P compounds soluble in bases and can be used for the estimation of both short-term and long-term available P in sediments. It is a measure of algal available P [15]. When the anoxic conditions prevail at the sediment-water interface, Fe-Al P will be released for the growth of phytoplankton [16]. The Fe and Al bound phosphorus is released during NaOH extraction and its average concentration in Kavvayi Lake sediments was 13.51 mg/kg. Higher concentration of NaOH-P (54.60 mg/kg) was observed in the sample collected from mixing point of Kavvayi River into lake and minimum concentration (2.10 mg/kg) was observed in the sample of

Table 1. Variation of pH, OC, TA and P fractions in the sediments of Kavvayi Lake.

Sampling stations	Fe-Al P (mg/kg)	CaP (mg/kg)	TP (mg/kg)	OP (mg/kg)	IP (mg/kg)	OC (%)	pН	TA (mg/kg)
KV-1	11.20	ND	19000.0	1000.0	ND	0.60	7.56	190.51
KV-2	54.60	0.50	10000.0	1200.0	6.0	5.49	8.16	730.30
KV-6	25.20	0.30	9000.0	2000.0	6.0	8.08	8.24	825.55
KV-9	5.60	ND	16200.0	1800.0	8.0	2.20	7.96	539.78
KV-11	11.20	0.80	9500.0	1600.0	2.0	1.50	7.82	285.77
KV-12	2.10	0.50	15000.0	1200.0	10.0	2.29	7.68	254.0
KV-13	4.20	1.30	5000.0	800.0	6.0	3.39	7.34	158.76
KVVP-1	15.40	0.20	12500.0	2800.0	8.0	4.89	7.76	412.78
KVE-1	2.80	ND	3500.0	1600.0	2.0	5.69	3.01	ND
KVPB-2	2.80	1.10	4500.0	1000.0	8.0	0.50	7.71	254.0
Average	13.51	0.47	10420.0	1500.0	5.60	3.46	7.32	405.72

ND-Not Detected.

Mixing Point of Kariyankode River into lake.

Calcium bound P (CaP) is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in sediments [17]. CaP is the least fractioned phosphorus form in Kavvayi lake sediments. CaP showed the range of Not detected to 1.3 mg/kg with maximum in the sample of Kottikadavu. Comparatively high concentration of CaP was detected in sediment samples of Kottikkadavu and Puthiyapuzhakkara; both sites were characterized by mangrove vegetation. CaP was not detected in the samples KV-1, KV-9 and KVE-1. Studies conducted by [6] suggest that when the sediment system is highly reducing it preferentially accumulates CaP and an acidic pH in sediment provides high stability to CaP. The lower concentrations of Fe-Al P and CaP in Kavvayi lake sediments suggest that these phosphorus fractions are readily available plant growth. The inorganic phosphorus (IP) content in the sediment samples ranged from 2 to 10 mg/kg and maximum value was found in the sample collected from the mixing point of Kariangode River into Lake (KV-12).

The fraction of available phosphorus is an important parameter for predicting future internal P-loading. The factors governing P release from sediments comprise redox reactions, adsorption, mineral phase solubility and mineralization of organic matter [18]. Iron and calcium bound inorganic fractions and acid soluble organic fractions of phosphorus are bioavailable [19]. If bulk of the total phosphorus is bioavailable then the sediments have the potential to act as source of phosphorus to overlying water.

Among the four fractions, organic phosphorus (OP) is the intensified fraction in Kavvayi lake sediments. OP contributes 5.3% - 45.7% of the total phosphorus. Maximum concentration (2800 mg/kg) was observed in the sample KVVP-1 (Mavilakadappuram) and minimum concentration (800 mg/kg) in the sample KV-13 (Kottik-kadavu). The average concentration of organic phosphorus observed was 1500 mg/kg. The high percentage of organic bound phosphorus indicates that the mineralization of phosphorus is less in the sediment samples.

Large amounts of fertilizers prepared from animal bones were applied by the farmers in the Kavvayi wetland area. The runoff from these agricultural lands may be the reason for high concentration of organic phosphorus in the Kavvayi lake sediments. The interpolated maps were created using QGIS 1.8.0. It describes the distribution of sediment bound phosphorus forms along the Kavvayi wetland system as shown in **Figure 2**, **Figure 3**.

3.2. Correlation of Different Phosphorus Fractions vs OC, Fe, TA and pH

The statistical analysis has been carried out by Pearson's correlation coefficient between different phosphorus fractions, organic carbon, total alkalinity and iron for the sediments from Kavvayi wetland system to find out the interdependence among the components. The results of correlation analysis indicates that Fe and Al bound P fraction is positively correlated with sediment organic carbon (r = 0.504) and Fe (0.804). There was a dependence of OC, iron and NaOH-P (Fe and Al bound P). Iron showed significant positive correlation with organic carbon (r = 0.647). This suggests that as the organic carbon in the sediment samples increases, the iron content also increases. OC showed weak positive correlation with Fe-Al-P and OP but insignificant correlation with CaP, TP and IP. pH did not show significant correlation with any of the phosphorus fractions. The CaCO₃ was the geochemical variable that showed significant correlation with Fe-Al-P; the potentially available form. TA also showed a strong positive correlation with Fe and Fe-Al P (Table 2).

Table 2.	Correlation	matrix of	correlation	of different	phosphorus	fractions.	OC. Fe.	TA and	nH.
T COLUMN	Communication	munition of	Communication	or arrierent	phosphorus	mactions,	- $ -$, III una	P

	Fe-Al P	CaP	TP	OP	IP	OC	Fe	pН	TA
Fe-Al P	1								
Ca P	-0.103	1							
TP	0.056	-0.555	1						
OP	0.101	-0.505	0.147	1					
IP	-0.028	0.241	0.014	0.184	1				
OC	0.504	-0.269	-0.316	0.484	0.080	1			
Fe	0.804**	0.050	-0.081	0.067	0.107	0.647^{*}	1		
pН	0.344	0.278	0.463	0.019	0.406	-0.204	0.387	1	
TA	0.736^{*}	-0.163	0.216	0.363	0.342	0.515	0.809^{**}	0.626	1

^{**}Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).

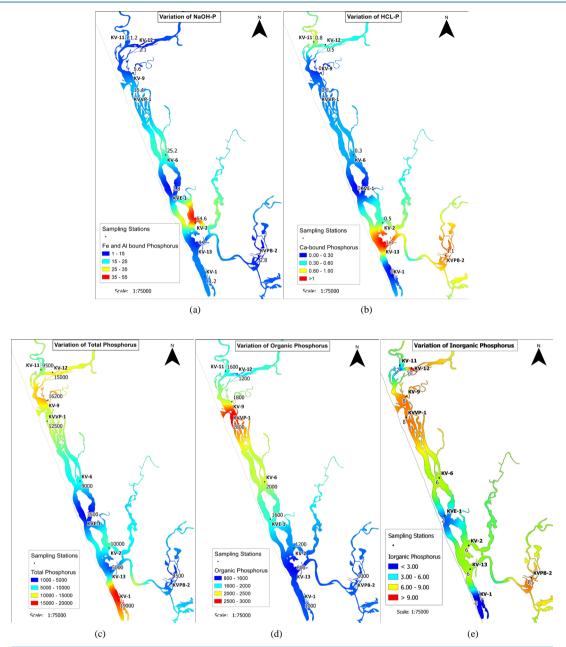


Figure 2. Spatial distribution of (a) NaOH-P (b) HCl-P (c) TP (d) OP and (e) IP in sediment samples of Kavvayi wetland system (in mg/kg).

3.3. Texture Analysis of Sediment Samples

The texture analysis of Kavvayi Lake sediment samples are shown in **Figure 4**. The sediment samples reported sandy texture in more than 90% with an average sand percentage of 95.1%. Maximum value of 98.25% of sand was found in the sample KV-12 (mixing point of Kariangode River into lake) and the minimum value of 92.5% of sand was found in the sample KV-6 (Ayittikadavu). The percentage of clay in the samples ranged from 1.0% to 5.50%. Highest percentage for clay was 5.50%, reported at KV-2 (mixing point of Kavvayi river into Lake) and lowest amount of 1.0% was reported at KVVP-1 (Mavila Kadappuram). The silt percentage in the samples varied from 0.5% to 3.25%. Highest percentage of silt (3.25%) was reported at KV-6 (Ayittikadavu) and lowest percentage of silt (0.50%) at KV-12 (mixing point of Kariangode River into Lake). The texture can provide information about water flow potential, water holding capacity, fertility potential, etc. Clay holds nutrients and

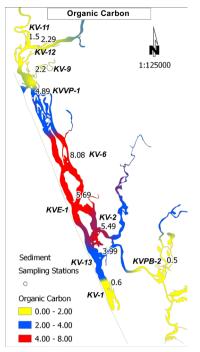


Figure 3. Spatial distribution of OC (in %) in sediment samples of Kavvayi wetland system.

water much better than sand. As water drains from sand, it often carries nutrients along with it. Silt has the best ability to hold large amounts of water in it.

3.4. Distribution of Heavy Metals in the Sediments

Concentrations of heavy metals in acid extracts of the sediments are given in **Table 3**. The heavy metal analysis data of the sediment samples revealed that dominant mean level of Fe (17,066 mg/kg), followed by Mn (93.3 mg/kg), while the average concentration of Cd (2.54 mg/kg) is the lowest. On the average basis, the metals follow a decreasing concentration order: Fe > Mn > Pb > Zn > Ni > Cu > Cd.

Iron concentration of samples varied from 1201 mg/kg to 57,626 mg/kg with an average value of 17,065 mg/kg. For the station KV-2; Kavvayi Lake (53308.0 mg/kg) and KV-6; in Ayittikadavu station (57,626 mg/kg) concentration of iron observed was higher than the Shale value (46,700 mg/kg). Geographic Information System was used to create interpolated maps to explain the extent of heavy metal content in the collected sediment samples. Using the technique the distribution of Fe, Mn, Cu, Pb, Ni, Zn and Cd concentration in the sediment samples is spatially represented in **Figure 5**.

Concentration of manganese in the samples ranged from 14 mg/kg to 368 mg/kg with an average value of 93.30 mg/kg. Highest concentration for manganese was recorded at station KV-2; Kavvayi Lake (368 mg/kg) and KV-1; Thayyil Kadappuram (302.5 mg/kg). Lowest concentration of 14 mg/kg was detected at station KVE-1; Edayilakkad. None of the samples showed a value greater than the Shale standard (900 mg/kg).

Copper showed a variation from 10.25 mg/kg to 54.25 mg/kg with an average value of 21.93 mg/kg. Concentration of copper in two stations KV-2; Kavvayi Lake (49.0 mg/kg) and KV-6; Ayittikadavu (54.25 mg/kg) were found to be higher than the Shale standard. (Shale value for Cu: 45 mg/kg).

Lead concentration in samples varied from 17.0 mg/kg to 104.25 mg/kg with an average value of 74.70 mg/kg. Except the sample at station KV-9; which is the mixing point of Orippuzha into lake (17.0 mg/kg), all the other samples showed significantly higher concentration of lead, than the Shale value. (Shale value for Pb: 20 mg/kg).

Cadmium in the samples varied between ND to 3.50 mg/l with an average value of 2.54 mg/kg. Maximum value of 3.50 mg/kg of cadmium was observed for the sample collected from the mixing point of Kavvayi River and lake (KV-2). Cadmium was not detected in the stations, KV-9, KV-12 and KVE-1. However, cadmium concentration in all the other samples was significantly higher than the Shale value concentration of 0.30 mg/kg.

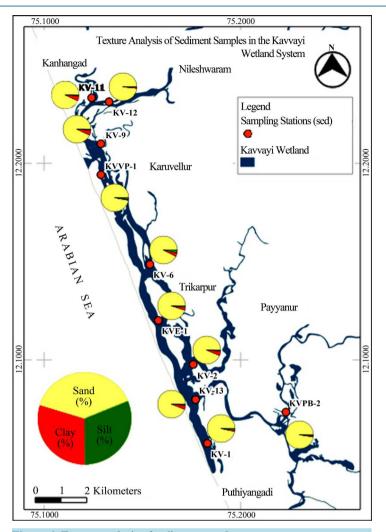


Figure 4. Texture analysis of sediment samples.

Table 3. Heavy metal comparison with average shale value and the pollution load index of Kavvayi wetland system.

Cli4-4i	Heavy metal (mg/kg)								
Sampling stations	Fe	Mn	Cu	Pb	Cd	Ni	Zn	- PLI	
KV-1	1912.0	302.50	10.25	80.25	2.0	0.50	31.50	0.43	
KV-2	53308.0	368.0	49.0	104.25	3.5	94.25	103.75	2.51	
KV-6	57626.0	18.0	54.25	111.50	3.0	94.5	110.50	2.55	
KV-9	3205.0	25.50	19.0	17.0	ND	ND	16.0	0.39	
KV-11	18726.50	58.75	22.25	78.25	3.25	41.0	68.50	1.56	
KV-12	16633.0	49.0	13.25	89.75	ND	32.50	45.25	0.79	
KV-13	9955.0	42.0	14.50	76.50	1.75	1.75	38.0	0.59	
KVVP-1	4907.50	21.75	12.0	76.50	2.0	5.75	36.50	0.74	
KVE-1	1201.0	14.0	10.50	37.0	ND	ND	20.50	0.45	
KVPB-2	3186.0	33.50	14.25	76.0	2.25	7.0	51.0	0.87	
Average shale	46,700	900	45	20	0.3	68	95		

ND: Not Detected.

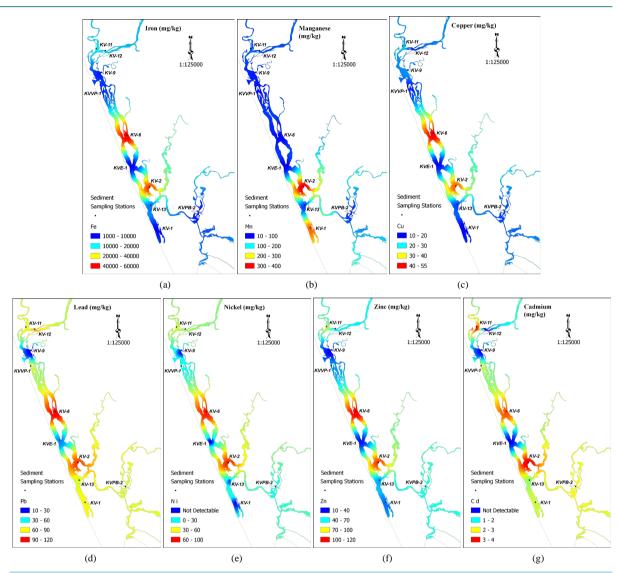


Figure 5. Spatial distribution of (a) Fe, (b) Mn, (c) Cu, (d) Pb, (e) Ni, (f) Zn and (g) Cd in sediment samples of Kavvayi wetland system (mg/kg).

Nickel concentration varied from ND to 94.50 mg/kg with an average value of 34.66 mg/kg. Nickel detected in the samples KV-9; which is the mixing point of Orippuzha into lake and Edayilakkad. Concentration of nickel in the samples Kavvayi Lake (94.25 mg/kg) and Ayittikadavu (94.50 mg/kg) were considerably higher than the Shale standard (68 mg/kg).

Zinc showed a variation from 16 mg/kg to 110.50 mg/kg with an average value of 52.15 mg/kg. Maximum concentration of 110.50 mg/kg was detected at the station Ayittikadavu and minimum of 16.0 mg/kg at mixing point of Orippuzha into lake. Concentration of zinc in samples KV-2 and KV-6 were found to be higher than the Shale standard (95 mg/kg).

3.5. Correlation Study

The correlation coefficient matrix of heavy metals and organic carbon is given in **Table 4**. Some heavy metals showed positive correlation with Organic Carbon (OC), such as Fe (r = 0.647), Cu (r = 0.646), Ni (r = 0.580) and Zn (r = 0.500). Humic materials have high adsorption influence on heavy metals [20]. The correlation analysis reveals the formation of organic complexes with heavy metals as a ligand. However, Mn and OC showed negative association revealing their opposing distribution in the sediments. Strong correlations of Fe with Ni, Zn

Fe Cu Pb Cd Ni Zn OC Mn Fe 1 0.323 Mn 1 Cu 0.969^{**} 0.298 1 0.707^{*} 1 Pb 0.373 0.571 0.713^{*} Cd0.605 0.429 0.608 1 Ni 0.985** 0.342 0.946** 0.714^{*} 0.620 1 0.809**0.779**0.961** Zn 0.949**0.319 0.914**1 0.647^{*} -0.097OC 0.646* 0.277 0.161 0.580 0.500 1

Table 4. Correlation coefficient matrix showing inter-element and element-organic carbon relationships in sediments (N = 10).

and Cu (significant at 0.01) and with Pb and OC (significant at 0.05) was observed. Some other significant relationships of Cu with Ni and Zn; Pb with Cd, Ni and Zn; Cd and Zn and Ni and Zn are also observed. Close association of these metals confirm their identical source or common sink in the sediments [21]. Mn does not show any significant correlation with other heavy metals suggesting its independent variations in the sediments [22].

3.6. Source Apportionment

The source apportionment of the metals in sediments was studied using PCA and CA. PCA extracted two factors and the principal component loadings of the heavy metals in the sediments are given in **Table 5**, whereas the corresponding CA is shown in **Figure 6**. Two factors explain 86.87% of the total variance for the surface sediment samples. PC1 (73.65% variance) showed strong positive loadings (>0.75) on Fe, Zn, Cu, Ni, Pb and Cd which are predominantly contributed by lithogenic processes, transportation activities, untreated urban wastes, and agricultural runoff. The cluster analysis also shows a joint cluster for these metals. PC2 (13.22% variance) reveals the natural/lithogenic contribution such as soil erosion and rock weathering, manifested by the prominent loadings of Mn only. Mn also shows almost independent pattern in dendogram of CA.

3.7. Contamination Factor and Degree of Contamination

Contamination factor (C_f^i) and the degree of contamination (C_d) are used to describe the contamination of given toxic substance [23] and is given by

$$C_f^i = C_{0-1}^i / C_n^i$$
 and $C_d = \sum_{i=1}^n C_f^i$

where, C_{0-1}^i is the mean content of the substance; C_n^i is the reference shale value for the substance. The contamination factor C_f and the degree of contamination were used to determine the contamination status of the sediment in the present study. The degree of contamination (C_d) is defined as the sum of all contamination factors. Contamination factor and their description are given in **Table 6**.

Sampling stations, KV-2 (mixing point of Kavvayi river into Lake), KV-6 (Ayittikadavu) and KV-11 (mixing point of Nileswar River into Kavvayi Lake) are considerably contaminated. The sampling stations of KV-1 (Thayyil Kadappuram), KV-13 (Kottikkadavu), KVVP-1 (Mavilakadappuram) and KVPB-2 (Puthiya Puzhakkara) were found to be moderately contaminated. The other stations, KVE-1 (Southern side of Edayilakkad), KV-9 (mixing point of Orippuzha into Lake) and KV-12 (mixing point of Kariangode River into Lake) showed low degree of contamination (Table 7 and Figure 7).

3.8. Assessment of Pollution by Calculating the Pollution Load Index (PLI)

Sediment pollution load index (PLI) was calculated using the equation, PLI = (product of n number of C_f values)^{1/n}, where, C_f is the contamination factor, n the number of metals and world average concentration of elements reported for shale was taken as their background values [7]. The PLI values calculated for each of the

^{**}Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).

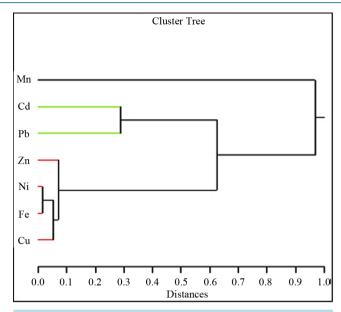


Figure 6. Cluster analysis of heavy metals in sediment samples of Kavvayi Lake.

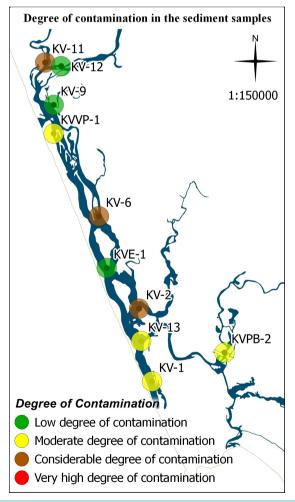


Figure 7. Degree of contamination in sediment sampling stations.

Table 5. Component loadings of heavy metal in the surface sediments.

Variables	Component				
variables	PC1	PC2			
Fe	0.957	-0.212			
Mn	0.450	0.815			
Cu	0.919	-0.246			
Pb	0.822	0.161			
Cd	0.789	0.285			
Ni	0.960	-0.184			
Zn	0.985	-0.120			
% of Variance	73.65	13.22			

Table 6. Contamination factor and their description.

C_f^i	C_d	Description
C_f^i < 1	$C_d < 7$	Low degree of contamination
$1 < C_f^i < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f^i < 6$	$14 < C_d < 28$	Considerable degree of contamination
$C_f^i > 6$	$C_d > 28$	Very high degree of contamination

stations were summarized. The PLI value of >1 is polluted whereas < 1 indicates no pollution [24].

The PLI values showed a high pollution load at stations, KV 2 (Mixing Point of Kavvayi River in to Kavvayi Lake), KV-6 Ayittikadavu and KV-11 (Mixing point of Nileswar River into Kavvayi lake).

The present study reveals that Kavvayi lake sediments are enriched with heavy metals. It could be due to the leaching of the metals into the water bodies from urban, agricultural and mining runoffs. In a study conducted by [25] reported that the increased rate of agricultural activities during the last few decades have deteriorated the soil entity and ground water quality of Kasargod district, Kerala. The laterite excavation in catchment areas is contributing high concentration of iron in to the lake sediments. The increased application of organic manure, the traditional agricultural fertilizer, could also cause elevated heavy metal concentration in the environment [26]. The application of pesticides such as the extensively used fungicide, Bordeaux mixture, considered as an important source of heavy metals. The application of pesticides and fertilizers are contributed most to the C_d input [27]. The automobile and other industries are also imparting the major sources of these heavy metals. Heavy metals may accumulate in a coastal wetland like the Kavvayi can cause many environmental problems.

4. Conclusion

This study evaluated the characteristics of P fractions and heavy metal accumulation in sediments of Kavvayi Wetland of northern Kerala, India. The fractionation study concluded that organic phosphorus (OP) was the intensified fraction in Kavvayi lake sediments. The correlation analysis provides evidence on the inter dependence of different phosphorus forms, Fe, OC and TA. Heavy metals exhibit random distribution and follow the order Fe > Mn > Pb > Zn > Ni> Cu > Cd in Kavvayi lake sediments. Humic materials have high adsorption influence on heavy metals (Sany *et al.* 2013). The Pearson correlation coefficients suggest the formation of organic complexes with heavy metals as a ligand in sediments. Multivariate PCA and CA manifest dominantly anthropogenic contributions of Pb, Cd, Cu, Ni and Zn in the sediments. Out of 10 samples, KV-2 (mixing point of Kavvayi river into Lake), KV-6 (Ayittikadavu) and KV-11 (mixing point of Nileswar River into Kavvayi Lake) are considerably contaminated and their PLI values also show a high pollution load. Since, the enrichment of heavy metals in sediment can cause many environmental problems, serious attention should be given to the sources that may cause the heavy metal pollution in the Kavvayi lake sediments.

Comple and		C_d				
Sample code	Cu	Pb	Cd	Ni	Zn	
KV-1	0.23	4.01	6.67	0.01	0.33	11.25
KV-2	1.09	5.21	11.67	1.39	1.09	20.45
KV-6	1.21	5.58	10.00	1.39	1.16	19.33
KV-9	0.42	0.85	0.00	0.00	0.17	1.44
KV-11	0.49	3.91	10.83	0.60	0.72	16.56
KV-12	0.29	4.49	0.00	0.48	0.48	5.74
KV-13	0.32	3.83	5.83	0.03	0.40	10.41
KVVP-1	0.27	3.83	6.67	0.08	0.38	11.23

ND

7.50

ND

0.10

0.22

0.54

2.30

12.26

Table 7. Contamination factor and degree of contamination of Kavvayi Lake sediments.

Acknowledgements

KVE-1

KVPB-2

0.23

0.32

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1.85

3.80

References

- [1] Mohd Ekhwan, T., Mohd Khairul, A.K., Mushrifah, H.I., Nor, R.J., Muhammad, B.G. and Nor, A.A.A. (2009) Sediment Concentration and Load Analyses at Chini River, Pekan, Pahang Malaysia. *Research Journal of Earth Sciences*, 1, 43-50.
- Balachand, A.N. and Nair, S.M. (1994) Fractionation of Sediments of a Tropical Estuary. *Environmental Geology*, 23, 284-294.
- [3] Manju, P.N. and Sujatha, C.H. (2013) Fractionation of Phosphorus in the Sediments of Kerala Coast. *Journal of Chemical, Biological and Physical Sciences*, **3**, 2274-2278.
- [4] Fytianos, K. and Kotzakioti, A. (2005) Sequential Fractionation of Phosphorus in Lake Sediments of Northern Greece. Environmental Monitoring and Assessment, 100, 191-200. http://dx.doi.org/10.1007/s10661-005-4770-y
- [5] Bigaj, I., Łopata, M., Dunalska, J., Szymański, D. and Zieliński, R. (2012) Bottom Sediments as a Potential Source of Phosphorus in the Riverine-Lacustrine System of the Kośna River (Northeastern Poland). *Limnological Review*, 12, 115-124. http://dx.doi.org/10.2478/v10194-011-0051-7
- [6] Joseph, M.M., Ratheesh Kumar, C.S., Ranjith, K.R., Gireesh Kumar, T.R. and Chandramohankumar, N. (2011) Phosphorus Fractions in the Surface Sediments of Three Mangrove Systems of Southwest Coast of India. *Environmental Earth Sciences*, **62**, 1209-1218.
- [7] Harikumar, P.S., Nasir, U.P. and Mujeebu Rahman, M.P. (2009) Distribution of Heavy Metals in the Core Sediments of a Tropical Wetland System. *International Journal of Environmental Science and Technology*, 6, 225-232. http://dx.doi.org/10.1007/BF03327626
- [8] Harikumar, P.S. and Jisha, T.S. (2010) Distribution Pattern of Trace Metal Pollutants in the Sediments of an Urban Wetland in the Southwest Coast of India. *International Journal of Engineering Science and Technology*, **2**, 840-850.
- [9] Olubunmi, F.E. and Olorunsola, O.E. (2010) Evaluation of the Status of Heavy Metal Pollution of Sediment of Agbabu Bitumen Deposit Area, Nigeria. *European Journal of Scientific Research*, **41**, 373-382.
- [10] Williams, J., Syers, J.K., Armstrong, D.E. and Harris, F. (1971) Fractionation of Inorganic Phosphate in Calcareous Lake Sediments. *Proceedings of Soil Science Society of America*, 35, 250-255. http://dx.doi.org/10.2136/sssaj1971.03615995003500020023x
- [11] UNEP (1985) Reference Methods for Marine Pollution Studies. United Nations Environment Program, Regional Seas, 31-39.
- [12] USEPA (1999) SW-846, Reference Methodology. Standard Opening Procedure for the Digestion of Soil/Sediment Sample Using a Hot Plate/Beaker Digestion Technique, Chicago.
- [13] Iqbal, J. and Shah, M.H. (2014) Occurrence, Risk Assessment, and Source Apportionment of Heavy Metals in Surface

- Sediments from Khanpur Lake, Pakistan. Journal of Analytical Science and Technology, 5, 28.
- [14] Liu, E., Shen, J., Yang, L., Zhang, E., Meng, X. and Wang, J. (2010) Assessment of Heavy Metal Contamination in the Sediments of Nansihu Lake Catchment, China. *Environmental Monitoring and Assessment*, 116, 217-227. http://dx.doi.org/10.1007/s10661-008-0739-y
- [15] Zhou, Q., Gibson, C.E. and Zhu, Y. (2001) Evaluation of Phosphorus Bioavailability in Sediments of Three Contrasting Lakes in China and the UK. Chemosphere, 42, 221-225. http://dx.doi.org/10.1016/S0045-6535(00)00129-6
- [16] Ting, D.S. and Appan, A. (1996) General Characteristics and Fractions of Phosphorus in Aquatic Sediments of Two Tropical Reservoirs. Water Science and Technology, 34, 53-59. http://dx.doi.org/10.1016/S0273-1223(96)00724-X
- [17] Gonsiorczyk, T., Casper, P. and Koschel, R. (1998) Phosphorus-Binding Forms in the Sediment of an Oligotrophic and an Eutrophic Hardwater Lake of the Baltic Lake District (Germany). *Water Science and Technology*, **37**, 51-58. http://dx.doi.org/10.1016/S0273-1223(98)00055-9
- [18] Kaiserli, A., Voutsa, D. and Samara, C. (2002) Phosphorus Fractionation in Lake Sediments—Lakes Volvi and Koronia, N. Greece. Chemosphere, 46, 1147-1155. http://dx.doi.org/10.1016/S0045-6535(01)00242-9
- [19] Diaz-Espejo, A., Serrano, L. and Toja, J. (1999) Changes in Sediment Phosphate Composition of Seasonal during Filling. Hydrobiologia, 392, 21-28. http://dx.doi.org/10.1023/A:1003557408640
- [20] Tavakoly Sany, S.B., Salleh, A., Rezayi, M., Saadati, N., Narimany, L. and Tehrani, G.M. (2013) Distribution and Contamination of Heavy Metals in the Coastal Sediments of Port Klang, Selangor, Malaysia. *Water*, *Air*, & *Soil Pollution*, **224**, 1476. http://dx.doi.org/10.1007/s11270-013-1476-6
- [21] Fianko, J.R., Laar, C., Osei, J., Anim, A.K., Gibrilla, A. and Adomako, D. (2013) Evaluation of Some Heavy Metal Loading in the Kpeshi Lagoon, Ghana. *Applied Water Science*, 3, 311-319. http://dx.doi.org/10.1007/s13201-013-0083-4
- [22] Selvam, A.P., Priya, S.L., Banerjee, K., Hariharan, G., Purvaja, R. and Ramesh, R. (2012) Heavy Metal Assessment Using Geochemical and Statistical Tools in the Surface Sediments of Vembanad Lake, Southwest Coast of India. *Environmental Monitoring Assessment*, **184**, 5899-5915. http://dx.doi.org/10.1007/s10661-011-2389-8
- [23] Hakanson, L. (1980) Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach. Water Research, 14, 975-1001. http://dx.doi.org/10.1016/0043-1354(80)90143-8
- [24] Sekabira, K., Oryem Origa, H., Basamba, T.A., Mutumba, G. and Kakudidi, E. (2010) Assessment of Heavy Metal Pollution in the Urban Stream Sediments and Its Tributaries. *International Journal of Environmental Science and Technology*, 7, 435-446. http://dx.doi.org/10.1007/BF03326153
- [25] Jyothish, K.T. and Sujatha, C.H. (2013) Characterization of Heavy Metal and Pesticide Contamination in Soils of Kasaragod District, Kerala. *International Journal of Geology, Earth and Environmental Sciences*, 3, 36-40. http://www.cibtech.org/jgee.htm
- [26] Luo, L., Ma, Y., Zhang, S., Wei, D. and Zhu, Y.G. (2009) An Inventory of Trace Element Inputs to Agricultural Soils in China. *Journal of Environmental Management*, 90, 2524-2530. http://dx.doi.org/10.1016/j.jenvman.2009.01.011
- [27] Wang, Y. and Bjom, L.O. (2014) Heavy Metal Pollution in Guangdong Province, China, and the Strategies to Manage the Situation. *Frontiers in Environmental Science*, **2**, 9. http://dx.doi.org/10.3389/fenvs.2014.00009