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Heavy Metal Sequestration in an Urban Wetland of Kerala, India

Dipu Sukumaran[1,*], Ajith K V[2]

[1]Centre for Water Resources Development and Management, Kozhikode, Kerala, India
[2]Kerala University of Fisheries and Ocean Studies, Kerala, India
*Corresponding author: dipu@cwrdm.org

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Abstract This study provides a comprehensive understanding of water quality, sediment and core sediment characteristics in Paroppadi wetland, Kozhikode, Kerala. Water samples were collected and analyzed for physico-chemical and bacteriological parameters. The physico-chemical parameters were within the acceptable limit as per Indian standards for drinking water except microbial contamination. The sediments were contaminated with heavy metal like iron. Core samples were also contaminated with heavy metals particularly with iron. As suggestion to reduce wetland pollution, people must avoid disposal of household waste in the wetlands. Initiate proper monitoring programs to identify water pollution sources which discharged in to wetland waters directly or indirectly and provide awareness class to the native people on importance of wetland.

Keywords: *Paroppadi wetland, heavy metals, core samples, sediments*

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1. Introduction

Natural wetlands play a key role in functioning of biotic communities and maintaining the quality of the environment [1]. The value of the world's wetlands is progressively increasing as they contribute to a healthy setting in some ways. They retain water throughout dry periods, thus keeping the watertable high and relatively stable. In addition, wetlands are important feeding and breeding areas for wildlife and provide a stopping place and refuge for waterfowl [2]. Sediments can act as active sensors for monitoring contaminants in aquatic environment. Pollution in these sediments can be caused by various hazardous and toxic substances, including heavy metals. These substances accumulate in sediments via several processes, including disposal of industrial effluents, runoff and chemical leachates originating from various urban and agricultural sectors, also due to atmospheric deposition [3]. Reference [4] reported qualitative evaluation of Sasthamkotta Lake reveals that the lake is facing degradation due to human activities such as direct disposal of human waste into the lake, higher rate of soil erosion due to lack of vegetation, land use changes etc. As a result of increase in urban population wetlands are continuously depleting day by day. The depletion of these wetlands is resulting in many environmental problems in urban areas [5].

In aquatic environments, sediments play an important role in cycling of nutrients. In several cases, sediments are also responsible for transport of both nutrients as well as pollutants [6]. Total metal distribution in the core sediment of Cochin estuarine system studied by reference [7] collected two core sediments from environmentally distinct zones and identified greater metal contents were found in core collected from the industrial area. Accumulation status of five toxic metals: Cadmium, Cobalt, Chromium, Copper and Lead were analyzed for the study. Trace metals accumulate in the upper sediment of aquatic system by various biological and geochemical processes and which in turn affect sediment dwelling organisms and fishes, resulting in their death, reduced life span and less species diversity [8]. When these contaminants enter into the body of benthic organisms through the process of bioaccumulation which in turn passes to large organism through food chain with increasing concentrations known as bio magnifications [9]. In a study conducted by reference [10] on heavy metal analysis in surface sediments and water samples of Kabar Tal wetland, identified that the wetland ecosystem was continuously disappearing due to agricultural conversion and land use.

Sediments can accumulate trace metal contaminants which may leads to serious environmental problems to the surrounding areas. These kind of contaminations in sediments could affect the quality of water body and also leads to bioaccumulation in aquatic species, ultimately resulting in long term problems on human health and environment. Elements such as cadmium, arsenic etc. exhibit extreme toxicity even at low concentrations [11].

2. Materials and Method

2.1. Study Area

The study was conducted in Paroppadi Wetland of Kozhikode district, Kerala. It lies geographically between coordinates 11°17'33.08''N and 75°48'37.06". It is an urban wetland although it was rich in its biodiversity. Paroppadi wetland act as fertile ground for many migratory birds and has a free connection with Poonoor River. The Samples were labeled as PWS1, PWS2, PWS3 and PWS4. The Geological location of sampling points is given in Table 1.

2.1.2. Geographical Location of Sampling Stations

Table 1. Surface water and sediment sampling locations in Paroppadi wetland

Sample code	Latitude	Longitude
PWS1	N 11°17' 33.0"	E 075°48' 34.7"
PWS2	N 11°17' 42.0"	E 075°48' 37.2"
PWS3	N 11°17' 53.0"	E 075°48'39.6"
PWS4	N 11°17' 32.1"	E 075°48' 43.0"

Table 2. Physicochemical characteristics of surface water

Sample code	PWS1	PWS2	PWS3	PWS4
pH	6.14	5.59	6.1	6.59
Temperature(°C)	28.8	28.7	28.4	28.2
Turbidity (NTU)	70.1	6.49	165	194
EC (µS/cm)	165	75.76	121.8	227.8
TDS (mg/l)	108.6	48.91	78.45	163.3
Salinity (mg/l)	71.1	37.7	56.7	71
Total hardness (mg/l)	35.28	11.76	27.44	97.08
Total alkalinity (mg/l)	30.41	7.92	23.76	47.52
Chloride (mg/l)	34.23	15.76	11.53	15.88
Sulphate (mg/l)	2.9	10.2	8.4	10.4
Nitrate (mg/l)	6.01	2.16	5.083	2.431
Phosphate (mg/l)	BDL	BDL	BDL	BDL
Calcium (mg/l)	9.40	3.136	7.84	31.36
Magnesium (mg/l)	2.85	2.09	4.76	15.96
Sodium (mg/l)	18.93	11.04	15.48	14.2
Potassium (mg/l)	1.08	1.01	1.65	2.41
Iron (mg/l)	1.49	0.69	2.35	2.4
Dissolved Oxygen(mg/l)	1.41	3.68	0.36	0.14
BOD(mg/l)	2.4	2.69	1.43	2.20
COD (mg/l)	8	16	8	8

2.2. Collection and Preprocessing of Samples

Total 8 water samples, 8 sediment samples and 4 core samples were collected from Wetland. Parameters like pH, Electrical conductivity and salinity were measured *insitu*. Water for analysis of all other parameters was collected in pre rinsed polythene bottle and was taken to the laboratory under refrigeration. Water sample were analyzed for various physico-chemical and biological parameters as per the standard procedure [12]

The sediment samples were collected from four different sampling stations which are strategically positioned at four distinct corners in wetland. Surface sediment samples were taken at a depth of 0-10 cm which was quickly packed in airtight polythene bags that were free from heavy metals or organics and well covered while transporting from field to the laboratory to avoid contamination from the environment. A portion of the samples were air dried and ground to fine powder using motor and pestle. Sediment cores are collected with the help of a core sampler (80 cm length and 5 cm diameter) by gently pushing in to the sediments. The core length size differs between the stations due to variations in nature of the substratum. For the digestion of core sample, 0.2 gram of dried sediment samples was weighed and placed in to an acid washed PTFE digestion vessel. The digestion was performed with a mixture nitric acid and per chloric acid. The digested samples were analyzed for heavy metals by Thermo M5 series AAS.

3. Results and Discussion

3.1 Water Quality of Paroppadi Wetland

Four samples were collected from Paroppadi wetland to study the surface water quality. The samples were labeled as PWS1, PWS2, PWS3 and PWS4. The results of physico chemical parameters are given in the Table 2.

pH ranged from 5.59 to 6.58 during sample analysis. Three sampling stations have pH concentration less than 6.5. Electrical conductivity of the samples was in the range 75.76µS/cm to 227.8µS/cm. The highest concentration for EC observed for PWS4 and lowest for PWS2. A total dissolved solid refers to any minerals, salt, cations or anions dissolved in water. Total dissolved salt comprise of inorganic salts like calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates. The concentration of TDS is found to be between 48.91 mg/l and 163 mg/l. The acceptable limit for TDS as per Indian standard [13] is 500 mg/l, all samples are with in desirable limit. The turbidity was recorded in the range 6.49 NTU to 194 NTU. Maximum turbidity was observed at PWS4 and minimum at PWS2.

Salts are highly soluble in both surface and ground water and can be transported with water movement. High levels of salinity in water may cause threat to environment as well as affecting agriculture and infrastructure [14]. The observed concentration of salinity ranged from 37.7 mg/l to 71.1 mg/l. the sample pws1 has highest concentration of salinity and the sample PWS2 has lowest concentration of salinity. The total alkalinity of collected samples ranged from 7.92mg/l to 47.52mg/l. The acceptable limit of total alkalinity for drinking water proposed by BIS is 200mg/l.

Hardness of water is the total concentration of calcium and magnesium. The hardness concentration of samples lies between 11.76mg/l and 97.08mg/l. The acceptable limit of calcium is 75 mg/l as per BIS. All samples reported calcium within acceptable limit as per BIS. The acceptable limit of magnesium is 30 mg/l as per BIS. All samples observed were under acceptable limit of 30 mg/l as per BIS. It is usually expressed as equivalent quantity of calcium carbonate [15]. The hardness of water provides the nature of geological formations with which it has been in contact [16].

The acceptable limit of chloride in drinking water is 250 mg/l as per BIS. The chloride concentration ranged

from 11.53 mg/l to 34.23 mg/l. all samples are within acceptable limit of drinking water as per BIS and all samples can be considered as good drinking water quality in terms of chloride. The sample PWS1 has highest contamination of chloride and PWS3 sample has lowest contamination of chloride. The phosphate concentration was found below detection level in all samples. The nitrate values in between 2.16 mg/l to 6.01 mg/l. The concentration of iron in the sample ranged from 0.69 mg/l to 2.35 mg/l. The PWS3 has the highest concentration of iron.

Dissolved Oxygen (DO) of samples was less than 5 mg/l, the concentration of samples ranged between 0.14 mg/l to 3.68 mg/l. The PWS2 samples have highest concentration of dissolved oxygen. BOD values of the samples ranged between 1.43 mg/l to 2.69 mg/l. The COD values were ranged from 8 mg/l to 16 mg/l. High COD may cause oxygen depletion on account of decomposition of microbes to a level detrimental to aquatic life. All water samples are found to be contaminated with microbes. Total coliform count in water samples lies between 240 MPN/100ml to 2400 MPN/100ml. The highest contamination of total coliform found in PWS2 and lowest contamination in PWS3. The total coliform count found in these water samples are above the drinking water quality standards [13]. Faecal coliforms count in samples ranged from 28 MPN/100ml to 2400 MPN/100ml. Presence of *E.coli* was detected in all four samples.

3.2. Correlation Analysis

The correlation coefficient (r) between various pairs of the physico-chemical parameters of surface water samples in Paroppadi wetland are shown in table. EC shows strong positive correlation with TDS (r = 0.9971) salinity (r = 0.9004), total hardness(r = 0.9426), total alkalinity (r = 0.9925) and calcium(r = 0.9229). TDS shows positive correlation with total hardness (r = 0.9644), total alkalinity (r = 0.9878). Total hardness show strong positive correlation with total alkalinity (r = 0.9397), calcium (r =0.9985) and magnesium (r = 0.9712).

3.3. Sediment Quality of Paroppadi Wetland

Sediment quality of a wetland also plays a significant role in assessing the overall quality of water in the wetland. As the part of sediment quality assessment in Paroppadi wetland, eight samples were collected from different stations. Physico-chemical parameters and heavy metal analysis were carried out.

The pH concentration lies between4.72 to 6.99, which is in agreement with pH of Sediments in Agbede wetlands [17]. Chloride of the sediment samples ranges from 11.53 mg/l to 15.37 mg/l. Due to anthropogenic activities such as sewage contamination, use of water softeners etc cause increase in chloride concentration of Rhode Island. TOC of the sediment samples ranged from 3.35% to 6.19%. The maximum concentration of TOC is obtained in PWS3.

3.3.1. Soil Texture

Texture analysis of the collected eight sediment samples was carried out and the percentage composition of sand, clay and silt in the various samples were given in the Table 3.

Table 3.Texture analysis of sediments

Sample code	Sand (%)	Clay (%)	Silt (%)	Type of soil
PWS1	81	14.25	4.75	Sandy loam
PWS2	74.5	20.2	5	Sandy clay loam
PWS3	84.5	11.75	3.5	Loamy fine sand
PWS4	74.75	16.75	8.5	Sandy loam

From the texture analysis it was found that percentage of sand in Paroppadi wetland ranged from 74.5% to 84.5%. The percentage of silt in sediment samples ranged from 3.5% to 8.5% in Paroppadi wetland. Type of soil varied between stations except PWS1 and PWS4 which has sandy loam soil while PWS2 has sandy clay loam soil and PWS3 has loamy fine sand. The textural properties of sediment revealed that sandy texture predominate all sampling station throughout the period of study, which is in agreement with the result of sediment characteristics of Polachira Wetland, Kollam [18].

3.3.2. Heavy Metals in Sediment Samples

Generally heavy metals occur naturally in sediments, which are formed by geological processes, such as alteration and erosion of the geological underground materials. Besides the parent material, the sources of contamination in sediment are multifarious and include agricultural and industrial pollution. The high levels of sediment pollution recently become a major issue. The chemical analysis of sediment is important tool in environmental monitoring and legislation. Sediments normally contain heavy metals like ferrous, manganese, copper, lead, cadmium, nickel and zinc. Excessive amounts of these heavy metals may leads to death of aquatic microorganisms and other species. The results of heavy metal analysis are given in the Table 4.

Table 4. Heavy metals in sediment samples

Heavy metals (mg/kg)	PWS1	PWS2	PWS3	PWS4
Manganese	0.029	0.043	0.141	0.045
Zinc	0.173	0.189	0.339	0.215
Iron	507.2	172.9	246.6	201.8
Lead	BDL	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL	BDL
Copper	0.161	0.135	0.146	0.137
Nickel	0.135	0.151	0.149	0.112

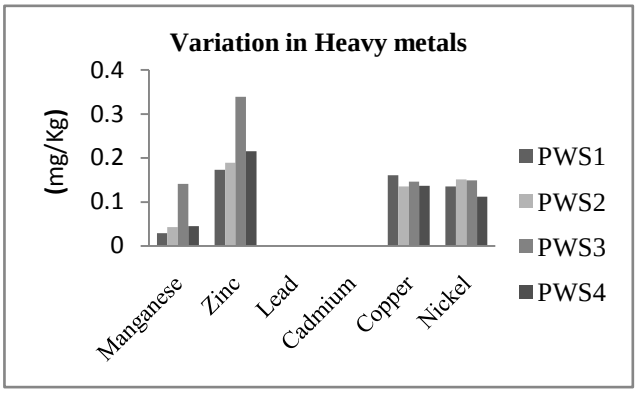

Figure 1. Variation of Heavy metals in sediments

The concentration of iron is very high in all the samples. Iron concentration ranged from 172.9 to 507.2 mg/kg. All the concentration reported were higher than the concentrations reported for sediments in Aras River [19]. The variation of heavy metals in the sample is represented in Figure 1

In heavy metal analysis, most of the heavy metals were present in soil samples except Lead and Cadmium. Heavy metals like copper, manganese, zinc and nickel are present in very low concentration in all samples while the concentration of iron found to be very high in all samples. Concentration of manganese varied from 0.029 to 0.141 mg/kg. Concentration of zinc varied from 0.173 mg/kg to 0.339 mg/kg. Concentration of Cadmium and lead were found to be below detection level. All the values reported for Manganese, Zinc, Nickel, Copper, Lead and Cadmium were found to be lower than the value reported in Dhaka wetland [20].

3.4. Core Sediment Quality

Core sample collected from first sampling station were divided into three layers and marked by sample code PW1/L1 for lowermost layer, PW1/L2 for middle and PW1/L3 for uppermost layer. TOC of the core samples ranged from 0.71 % to 2.5% (Figure 2). All concentrations of TOC observed in the wetland are higher than the concentrations reported on sediment cores of Sundarbans Mangrove wetland [21].

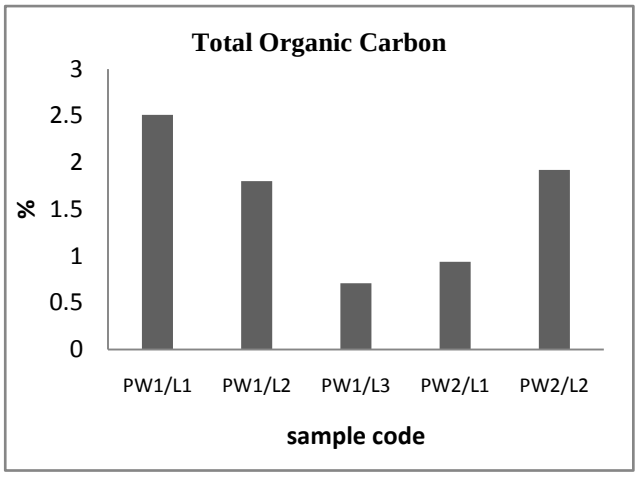

Figure 2. Variation of TOC in Paroppadi wetland

3.4.1. Soil Texture

The core sediment samples in Paroppadi wetland reported sandy texture in more than 65% with an average sand percentage 69.45%. Maximum value of 72.5% of sand was found in the sample PW1/L1 and the minimum value of 66.25% of sand was found in the sample PW2/L2. The percentage of clay in Paroppadi wetland ranged from 22.75% to 27.75%. Highest percentage of clay was 27.75%, reported at PW2/L1 and lowest amount of 22.75% was reported at PW1/L1. The percentage of silt in sediment samples ranged from 4.75% to 6% in Paroppadi wetland. Highest percentage of silt (6%) was reported at PW2/L2 and lowest percentage of silt (4.75) at PW1/L1.All soils of Paroppadi wetland is characterized by Sandy Clay Loam.

3.4.2. Heavy Metals in Core Sediment

The concentration of iron varied from 168 to 283.3 mg/kg. The average distribution of iron in two core sediments collected from Paroppadi wetland was 238.26 and 233.2mg/kg respectively. Concentration of manganese varied from 0.003 to 0.053 mg/kg. The mean value of manganese in core1 and core2 collected from Paroppadi wetland are 0.020 mg/kg and 0.038 mg/kg respectively. The concentration of copper varied from 0.106 to 0.167mg/kg. The concentration of nickel varied from 0.168 to 0.213mg/kg. The highest distribution of nickel was found in PW2/L1. The results of heavy metal analysis are given in the Table 5.

Table 5. Heavy metal in core sediments

Heavy metals (mg/kg)	Paroppadi wetland				
	Core sample1			Core sample2	
	PW1/L1	PW1/L2	PW1/L3	PW2/L1	PW2/L2
Mn	0.036	0.022	0.003	0.053	0.023
Zn	0.173	0.162	0.221	0.207	0.278
Fe	283.3	168	263.45	242.95	223.45
Pb	BDL	BDL	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL	BDL
Cu	0.167	0.110	0.106	0.127	0.131
Ni	0.168	0.174	0.199	0.213	0.198

4. Summery and Conclusion

The study on wetlands revealed that water quality of Paroppadi were degraded and are subjected various pollution and microbial contaminations. Most of the surface water samples found to be contaminated with faecal coliforms. Very high count of total coliform (≥2400) was reported in sample PWS2. E. *coli* was detected in all water samples. The concentrations of organic matter were high in Paroppadi wetland. Sediment was characterized by Sandy Clay Loam. The concentration of iron was found to be high in all core samples but other heavy metals were present in low concentrations. As suggestion to reduce wetland pollution, people must avoid disposal of household waste in the wetlands. Initiate proper monitoring programs to identify water pollution sources which discharged in to wetland waters directly or indirectly and provide awareness class to the native people on importance of wetland.

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