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Research Article

Evaluation of Metal Contamination in Water Samples by Inductively Coupled Plasma Atomic Emission Spectroscopy

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Abstract

Background and Objective: Contamination of heavy metals in water is regarded as a global crisis with a large share in developing countries like India. The objective of this study was to evaluate the levels of heavy metals found in water samples of Kattiparambu mangrove area, Ernakulam district, Kerala. **Materials and Methods:** Hydro-chemical parameters were carried out following standard methods prescribed in APHA-AWWA-WPCF. The estimation of heavy metals in the water samples were done using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Data were analyzed by one-way ANOVA using DMRT and SPSS. **Results:** During pre monsoon and post monsoon, the concentration of heavy metals in water were reported high. Fe concentration of mangrove water (46.13 mg L^{-1}) was high in station 1 during post monsoon. Zn (21.81 mg L^{-1}), Mn (2.94 mg L^{-1}), Co (0.91 mg L^{-1}), Pb (1.03 mg L^{-1}) and Ni (1.36 mg L^{-1}) reported high concentration during post monsoon (station 3). **Conclusion:** According to International Standards (WHO), the area contain high metal concentrations is water. The decreasing trend of metals were observed in water as Fe> Zn>Mn>Cu>Ni>Cr>Cd>Pb>Co.

Key words: Anthropogenic, mangroves, ICP-AES, hydro-chemical parameters, pre monsoon, post monsoon

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity[1-3]. Both natural and anthropogenic activities are responsible for the abundance of heavy metals in the environment[4,5]. Heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities and humans are exposed to them through various pathways, especially food chain. The essentiality of Fe, Mn, Cu and Zn are based on their role as metallo enzymes. These metals are cofactor of large number of enzymes[6]. In order to assess the health risks, it is necessary to identify the potential of a source to introduce risk agents into the environment. Urbanization and population growth have generally increased non-point source pollution of coastal waters. A diversity of pollutants via rivers adversely affect the health of the people around and the beneficiaries of the water body, to estimate the amount of these hazardous agents that come into contact with the human-environment boundaries and quantify the health consequence of the exposure[5].

Pollutants are the causes of major water quality degradation around the world. Major water pollutants include microbes, nutrients, organic chemicals, oil, heavy metals and sediments. Heavy metals are important environmental pollutants. Metal contamination of the environment results both from natural sources and industrial activities. Metals in soil and water may enter the food cycle with an additional contribution from air[7]. The increasing pollution by heavy metals have a significant adverse health effects for invertebrates, fish and humans[8-13]. The metal pollution of aquatic ecosystems was increasing due to the effects from urbanization and industrialization[10,14-17.] The water and soil contamination with heavy metals is well proven in various studies. This study was conducted in Kattiparambu, a mangrove area of Ernakulam district, Kerala to determine the concentration of metals in water and sediments. In total, the levels of 9 potential toxic or toxic metals (Fe, Mn, Zn, Mn, Cr, Cu, Ni, Cd and Pb) have been assessed. The study receives huge amount of untreated effluents from small scale industries such as fish processing units, oil refineries and others. High concentration of heavy metals such as chromium (Cr), cadmium (Cd) and lead (Pb) are discharged into the Kattiparambu water body which pollute the water and sediments. To date, no scientific research regarding heavy metal pollution in water and sediment of the study area has been conducted so far. Therefore, the objectives of this study were to evaluate the water quality parameters of the Kattiparambu mangrove river and to determine the levels of heavy metals in water.

MATERIALS AND METHODS

Study area: Kattiparambu is situated between 9.8072100°N and76.277427°N. This mangrove area is affected by municipal and industrial pollution during recent days. Three sampling stations were selected on the basis of water quality parameters, human and environmental factors and the probability of anthropogenic pollution.

Selection of sampling stations and sample collection: The study was conducted from 2014-2016. Three points were selected and marked along Kattiparambu mangrove region. The three stations were within an approximately 500-600 m section and about 100-150 m distance between locations. During pre monsoon, there is no rainfall and the water levels decrease; during post monsoon, river water levels increase due to heavy rainfall. Considering the water flow in the studied water body, post monsoon season exhibited higher than winter season which can cause the variation of metals concentration in water and sediment. Total 72 samples were collected from the lake (three samples of water every month) for 2 years. Pre-cleaned sampling bottles were immersed about 10 cm below the water surface in the periphery, 25 m away from the periphery and from the center of the lake. About 1 L of the water samples were taken at each sampling site. Samples were acidified with 10% HNO_3, filtered and kept at 4°C until analysis.

Analytical methods: On site, measurement and laboratory analyses were carried out as per standard methods. The parameters include pH, alkalinity, salinity, chloride, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) were done by titrimetric method. Phosphate (PO_4^{3-}), ammoniacal-nitrogen (NH_3N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N) and sulphate (SO_4) by UV-Visible Spectrophotometer. Sodium and potassium by flame photometer[18]. The analysis of metals using inductively coupled plasma atomic emission spectrophotometer[19] after pretreatment of the samples with microwave digestion system. The values were expressed in mg L^{-1}. The average and mean values were calculated seasonally. The concentrations of heavy metals in water between the seasons tested statistically. The correlation coefficient was calculated between water among different seasons.

Statistical analysis: The data were statistically analyzed by the statistical packages viz., Microsoft EXCEL-2007, SPSS 20.0 (SPSS Inc., Chicago, IL, USA). Three independent measurements of each experiment were pooled and subjected to statistical analysis. The means, standard deviations, one-way ANOVA and correlations of the heavy metal concentrations in water followed by Duncan's multiple range test (DMRT) to find out any significant differences resulting from the analytical experiments were carried out. p-value less than 0.05 were adopted as statistically different.

RESULTS AND DISCUSSION

Physicochemical parameters of water samples: Descriptive analyses of physicochemical variables at selected sampling stations in the Kattiparambu water body during the period of July, 2014-Jun, 2016 are summarized in Table 1. In order to understand the spatiotemporal variations between three seasons in the study area, statistical analysis of the collected data were interpreted using one-way analysis of variance to determine the level of significance among the measured variables. The climate condition was characterized by pre monsoon, monsoon and post monsoon seasons. The pre monsoon season set in between March and May, monsoon season in between June and September while post monsoon season in between October and February. The weather in study area was quite cool, however the water temperature plays an important factor which influences the chemical, bio-chemical characteristics of water body. The physicochemical parameters are very important because they have a significant effect on the water quality. Further-more, aquatic life also suffers due to degradation of water quality. Among the external factors, temperature is one of the most important factors which influence the aquatic ecology.

Recorded data of water temperature, pH and dissolved oxygen confirmed a seasonal cycle during the period of study. Temperature effects on water quality can be of physical, chemical and biological. Temperature affects the physical properties of water such as density, vapour pressure, viscosity and surface tension. Water temperature shows more significant variations seasonally than spatially and it correlates with salinity. The maximum temperature of 30°C was recorded in pre monsoon and a minimum of 26°C was recorded in monsoon. The mean value of water temperature was found within the permissible limits set by WHO[20], which was between 25 and 30°C. Water temperature in pre monsoon was high due to low water level and clear atmosphere[21]. The pH values ranged between 6.73 (station 1) and 8.2 (station 2) of monsoon and post monsoon season with the highest values in high-flow period and the lowest in low-flow period. The reduced rate of photosynthetic activities reduces the assimilation of carbon dioxide and bicarbonates which are ultimately responsible for the increase in pH. The higher pH values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physico chemical condition[22]. The fluctuations in pH can be related with removal of CO_2 by photosynthesis through bicarbonate degradation, reduction of salinity, decomposition of organic matter and dilution of sea water by fresh water influx.

Table 1: Physicochemical parameters of water

	KW-1			KW-2			KW-3		
Parameters	Pre	Monsoon	Post	Pre	Monsoon	Post	Pre	Monsoon	Post
Temperature	27.00	30.00	29.00	27.00	26.00	28.00	28.00	26.00	28.00
pH	8.14	6.73	7.40	7.64	6.86	8.20	7.51	7.03	7.92
Total alkalinity (mg L^{-1})	68.70	41.00	71.50	28.80	31.00	46.30	32.90	37.00	49.70
Salinity (ppt)	4.62	2.91	3.74	4.99	3.01	3.47	4.25	2.49	2.85
Total dissolved solids (mg L^{-1})	1382.00	2418.00	1874.00	1016.00	2073.00	2371.00	1592.00	1342.00	1724.00
Total CO_2 (mg L^{-1})	53.80	39.90	46.39	45.20	23.19	35.90	59.30	26.00	32.14
Calcium (mg L^{-1})	40.64	33.10	39.30	26.90	17.26	40.20	29.60	18.50	23.27
Magnesium (mg L^{-1})	27.12	19.80	20.46	30.40	14.18	27.80	19.80	10.40	19.82
Sodium (mg L^{-1})	133.67	73.21	123.00	79.40	74.21	96.40	69.40	71.90	83.15
Potassium (mg L^{-1})	44.24	32.18	39.80	31.60	17.26	31.70	22.10	20.20	26.32
Free ammonia (mg L^{-1})	2.91	2.63	2.88	1.96	1.79	2.83	2.03	3.00	3.31
Nitrite (mg L^{-1})	3.77	3.90	4.69	2.99	2.08	4.04	2.68	2.14	5.19
Nitrate (mg L^{-1})	3.84	2.74	3.91	4.10	2.67	3.88	3.59	3.04	4.24
Chloride (mg L^{-1})	10.63	21.90	28.70	13.60	5.86	24.18	11.49	5.73	16.34
Sulphate (mg L^{-1})	5.88	3.66	4.21	3.970	3.03	3.96	5.07	2.66	3.96
Phosphate (mg L^{-1})	12.08	4.20	9.83	22.85	13.19	11.30	17.93	11.30	17.38
Dissolved oxygen (mg L^{-1})	4.72	3.21	4.69	3.89	4.38	4.12	3.94	3.42	4.12
Biological oxygen demand (mg L^{-1})	9.63	5.87	8.11	8.31	8.69	8.32	7.66	6.92	8.14
Chemical oxygen demand (mg L^{-1})	7.27	4.35	5.80	6.88	7.03	6.35	6.03	5.37	6.81

KW: Kattiparambu water

Salinity is a measure of the salt content of the water. The salinity of freshwater is always less than 0.5%. This range of salinity is generally termed brackish as distinct from marine or fresh waters. High salinity (4.99 mg L^{-1}) was observed in samples collected from the middle of the lake (station 2, pre monsoon). Total alkalinity ranged from 31-71.5 mg L^{-1}, the maximum value (71.5 mg L^{-1}) was recorded in station 1 (post monsoon) and minimum (31 mg L^{-1}) in station 2 (monsoon). Maximum alkalinity in post monsoon due to increase of bicarbonates in water[23] and minimum in monsoon due to high photosynthetic rate. Total dissolved solids were almost lower in high-flow period in upstream. Poor vegetation cover, high agricultural activities and inappropriate management are potential factors that cause much runoff and soil loss[24].

The total dissolved solids (TDS) fluctuated from 1342-2418 mg L^{-1}. Maximum TDS was recorded in station 1 (monsoon) due to heavy rainfall and minimum in station 3 (pre monsoon). Total carbon dioxide was reported maximum (59.3 mg L^{-1}) in station 3 during pre monsoon and minimum (23.19 mg L^{-1}) in station 1 during post monsoon. It depends upon alkalinity and hardness of lake water and related to the high rate of decomposition of organic material in pre monsoon season[25]. Maximum Ca concentration (40.64 mg L^{-1}) was reported in station 1(pre monsoon). The range of Ca content was 17.26 mg L^{-1} (station 2, monsoon) to 40.64 mg L^{-1}. Mg concentration was low when compared to Ca, ranged between 10.4 mg L^{-1} (station 3, monsoon) to 30.4 mg L^{-1} (station 2, pre monsoon). High concentration of Na (133.67 mg L^{-1}) and K (44.24 mg L^{-1}) were reported in station 1 (pre monsoon).

More pollutants with dissolved conducting minerals are transferred from the farms to the river. Thus, the concentrations of nitrite nitrogen and nitrate nitrogen showed similarity in results (2.08 mg L^{-1}-5,19 and 2.67 mg L^{-1}-4.24 mg L^{-1}), where was vicinity to farm lands and N-P-K fertilizers or chicken dung[26] were common to apply for agricultural activities[27] which were similar to results reported[28]. Nitrogen compounds were reported high in station 3 (post monsoon). In station 1 during post monsoon season, nutrients like chloride was reported high (28.7 mg L^{-1}) and maximum sulphate (5.88 mg L^{-1}) reported during pre monsoon in station 1.

The more land is converted into agricultural site, the more pollution of nitrate is expected to be increased in recent years. Phosphate concentration ranged from 4.2 mg L^{-1} (station 1, monsoon) to 22.85 mg L^{-1} (station 2, pre monsoon). Phosphate concentrations point out the presence of anthropogenic pollution[29]. Domestic wastewaters and industrial discharges, particularly those containing detergents and fertilizer runoff, or changes in land use in areas where phosphorous is naturally abundant in the soil would be lead the higher levels of phosphates in the water column[30,31].

There was however an increasing trend in dissolved oxygen values at all the stations during the transition to monsoon period as observed in Table 1. Maximum dissolved oxygen (4.72 mg L^{-1}) recorded during pre monsoon in station 1. Dissolved oxygen is in fact the most important indicator of water quality and is essential for the survival of all aquatic organisms. The high DO is due to increase in temperature and duration of bright sunlight influence on the % of soluble gases (O_2 and CO_2). The intense sunlight during hot season accelerate photosynthesis by phytoplankton, utilizing CO_2 and giving off oxygen. This possibly accounts for the greater qualities of O_2 recorded during summer. This may be due to the fact that algae use from the high amount of phosphate and nitrate and other substances and multiply rapidly. This massive growth of algae leads to pollution. When the algae die they are broken down by the action of the bacteria which quickly multiply, using up all the oxygen in the water[32]. Minimum and maximum BOD reported (5.87-9.63 mg L^{-1}) in station 1 during monsoon and pre monsoon season. There was fluctuated variation of chemical oxygen demand observed in sampling sites. COD reported high (7.27 mg L^{-1}) in station 1. This condition was highly expected in this station duo to its vicinity to residential area, farm lands and industrial centres.

Heavy metal concentration in water: Heavy metals levels in water depend on the physicochemical parameters such as pH, alkalinity, salinity and TDS. It is well known that the solubility of toxic metals increases with the decrease of pH (from surface to depth, from alkaline to acidic)[33]. The mean of heavy metals concentrations (Fe, Zn, Mn, Cu, Cd, Pb, Ni, Cr and Co) in water samples are presented in Table 2. There were significant relationship between salinity, Ni, Cd and Cr levels. It can found negative relationship between pH and metals such as Ni, Cr and Mn. It could be concluded that the changes of physicochemical parameters depend on how seasons affect the levels of some metals.

Generally, Fe is the most abundant and common element in the earth's crust. This can be one of the reason for which iron was obtained in highest levels in water and sediment samples[34]. It is well known that the pyrite by oxidation can produce sulphate (Fe^{2+}) and then Fe^{2+} ion, is oxidized to Fe^{3+} by microorganisms[35]. In water samples, Fe concentration was high (17.93-40.19 mg L^{-1}) in all the samples compared to other

Table 2: Heavy metal concentration in water samples (mg L^{-1})

Sites	Seasons	Fe	Cu	Zn	Mn	Cr	Cd	Co	Pb	Ni
KW-1	Pre-monsoon	40.19±5.04	2.09±0.83	13.27±1.83	1.96±0.89	0.94±0.89	1.13±0.73	0.66±0.19	0.32±0.15	0.64±0.17
	Monsoon	27.99±2.11	1.04±0.86	9.32±4.86	1.1±0.92	0.58±0.17	0.55±0.14	0.47±0.15	0.57±0.14	0.73±0.12
	Post monsoon	46.13±5.1	2.15±0.25	20.17±2.66	2.88±0.14	1.20±0.79	0.62±0.17	0.74±0.17	0.89±0.13	1.17±0.11
KW-2	Pre-monsoon	18.38±2.63	1.32±0.79	8.36±4.32	0.84±0.84	0.72±0.12	0.85±0.12	0.91±0.16	0.54±0.14	1.00±0.1
	Monsoon	18.03±2.4	0.99±0.89	6.22±3.12	1.03±0.93	0.51±0.14	0.36±0.14	0.28±0.15	0.47±0.13	0.42±0.13
	Post-monsoon	26.27±2.18	1.40±0.85	11.38±1.19	1.95±0.89	0.81±0.27	0.68±0.18	0.32±0.15	0.71±0.16	0.81±0.16
KW-3	Pre-monsoon	22.52±2.31	1.13±0.33	9.73±4.81	2.01±0.85	1.00±0.1	0.60±0.18	0.80±0.13	0.93±0.18	0.90±0.14
	Monsoon	17.93±2.3	0.75±0.27	4.39±0.36	1.65±0.88	0.73±0.77	0.59±0.17	0.53±0.14	0.40±0.11	0.58±0.12
	Post-monsoon	31.34±3.04	1.85±0.82	21.81±2.2	2.94±0.13	1.02±0.13	1.04±0.11	0.91±0.18	1.03±0.1	1.36±0.13
WHO		3.00	0.4	0.01	-	2.00	0.003	0.07	0.05	-

Each value is expressed as Mean±Standard deviation done in triplicates. Data were analysed by ANOVA SPSS version 20.0 for windows followed by Duncan Multiple Range Test (DMRT) for comparison at p = 0.05 level of significance. KW: Kattiparambu water

metals. This is due to the nature of the substratum, ie, the clayey substratum of mangrove at Kattiparambu has accumulated more metals than the sandy substratum[36]. Maximum Fe concentration was shown in station 1 (pre monsoon) and minimum in station 3 (monsoon). Maximum Cu concentration (2.15 mg L^{-1}) was reported in station 1 (post monsoon) and minimum (0.75 mg L^{-1}) reported in station 3(monsoon). A high level of Zn was reported in the samples. Station 3 showed high Zn content (21.81 mg L^{-1}) during post monsoon. Maximum concentration of Mn, Co, Pb and Ni (2.94, 0.91, 1.03 and 1.36 mg L^{-1}) were reported in station 3 during post monsoon, which could be due to the effect from point and non-point sources; such as petroleum, municipal runoffs and atmospheric deposition[37] near the study area. The level of chromium in water samples was ranging between 0.51and 1.2 mg L^{-1}. The same level of Cr (0.13-1.04 mg L^{-1}) was reported in the water samples of Chirackal lake[38]. Cd content (1.13 mg L^{-1}) was found to be far above the WHO/EU permissible limit levels of 0.003 mg L^{-1}.

In the present investigation, heavy metals in water collected from three stations of Kattiparambu were in the decreasing order of Fe > Zn >Mn> Cu Ni > Cr > Cd > Pb> Co. The variation in accumulation of metals in water was due to their geographical location. The difference in the pattern of accumulation could have been influenced by the discharge of varying amounts of sewage and municipal wastes[39]. It was implied that meteorological parameters such as rainfall has negative influenced on deterioration the water quality at the parts of the river where near the residential area and farmlands. So, much more pollutants were carried out into the river. Analysis of variance and comparison of means of physicochemical variables and concentration of heavy metals at different stations, it could be construed that the river water quality primarily influenced by effluents of residential area, industrial centres and agricultural runoff disposed directly or indirectly into the river.

The increasing level of pollution at Station 1 and Station 3 indicated progressive anthropogenic pressure in these sites. Land use changes either legal or illegal, inefficient and poor management, low awareness of local community and unplanned and uncontrolled development cause that the present environmental conditions of Kattiparambu watershed are already stressed, along the whole river. This study will provide a scientific support for water pollution control and help in the decision making process and providing a holistic watershed management plan to survive and recover the quantity and quality of this important mangrove area. In order to reduce the degree of pollutant of this water body, setting up of sewage treatment system in the residential and industrial areas and regulating the use of excessive fertilizers in cultivation activities are highly recommended.

Statistical analysis of data samples: The observed results were statistically analyzed using computer aided packages viz., Microsoft EXCEL-2007, SPSS 20.0. Data were analysed by ANOVA followed by Duncan multiple range test (DMRT) for comparison at p = 0.05 level of significance. Different stations were compared based on the similarity of their chemical compositions and concentrations. Weak correlations were found between the concentrations of the heavy metals in water. Correlations between specific heavy metals in water may reflect similar levels of contamination and/or release from the same sources of pollution, mutual dependence and identical behavior during their transport in the river system[40-43].

CONCLUSION

It is concluded that water accumulate metals above the permissible level. The accumulation and bio-transformation of toxic metals are a significant factor for the reduction of mangrove biodiversity.

The variation of metal concentration in water and depends on the activities of the human communities. In this study a significant relationship between physicochemical parameters and heavy metal concentrations were assessed. These results showed that the people living and working in and around this area encounter major health problems. Hence we highly recommend that policy makers should formulate laws and regulations to assess these anthropogenic activities to caution the health risk. This study suggested that point sources of heavy metals in the water should be closely monitored; improvement of conditions and industrial effluent and domestic sewage discharge should be reduced.

SIGNIFICANCE STATEMENT

Metals are considered as the serious pollutants due to their environmental persistence and their ability to concentrate in aquatic organisms. So this study on the assessment of metal contamination is an eye opener to the authorities for the new steps in pollution free environment.

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