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Research Article

Assessment of heavy metal contamination in the surface sediments of Neyyar River- Kerala, South India

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Abstract

Neyyar River (Latitude 8°16' to 8° 40' N and Longitude 77° 5' to 77° 16' E) with 56 Km length originating from the Agasthyamala, flows through the midland, low land and joins with the Lakshadweep Sea at Poovar Pozhi. Neyyar is the primary source of drinking water supply to entire Neyyattinkara taluk of Thiruvananthapuram district, Kerala. Study focused on the analyses of heavy metals in the surface sediments of Neyyar River and samples were collected from 10 previously identified station locations of the River for a period of one year and subjected for different heavy metal analysis. The study sites were categorized into fresh water zone (stations 1-8) and estuarine (9-10) zone depending on saline influence. Dried and powdered sediment samples are extracted using acid digestion method with concentrated nitric acid and perchloric acid (4:1 ratio). Analyses of various heavy metals such as copper, zinc, cadmium, chromium and lead were done using Atomic Absorption Spectrophotometer. Decrease in concentrations was observed in the estuarine zone for all five metals analyzed. Among them cadmium and lead showed comparatively higher concentration than internationally accepted standard values indicating the contaminative nature of the river sediments with respect to cadmium and lead. However, copper, zinc and chromium reported remained within the accepted standard values for particular metals. Spatial and temporal variations remained significant for all metals except copper where only monthwise variations were significant. Sediment contamination was assessed by enrichment factor and geo-accumulation index, and observed that sediments in Neyyar River are moderately contaminated.

Keywords: Contamination; Anthropogenic; Autochthonous; Spatial; Temporal

Introduction

Sediments play an important role in aquatic ecosystems and act as major sink and source for various chemical components as well as absorb and release these compounds to the overlying water column. Sedimentary organics of the system consist of autochthonous inputs resulting from primary production and allochthonous imports from neighbouring ecosystems. Trace metals are important components of the environment that become either beneficial or toxic depending upon their concentration. They are soluble in water and may be readily absorbed by plant or animal tissue and can become toxic in certain cases. A river has two sources of heavy metals: lithogenic sources from weathering of rocks and anthropogenic sources from urban centers. Accumulation of heavy metals in sediments of various aquatic systems were well documented all over the world: Singh (2001) [1] in Yamuna river; Kumar and Kalsotra (2001) [2] in Mandakini River; Anilakumary., *et al.* (2001) [3] in Poonthura estuary; Achyuthan and Mohan (2002) [4] in estuary and tidal zone between Chennai and Pondicherrry; Rajasegar., *et al.* (2002) [5] in Vellar estuary; Panda and Sahu (2002) [6] in Chilika lake; Mermi and Merchiwa (2003) [7] in mangrove sediments in Tanzania; Manjappa., *et al.* (2005) [8] in River Bhadra; Raman., *et al.* (2007) [9] in mangrove sediments of SE coast of India; Wang., *et al*. (2010) [10] in marine sediments from Jinzhou Bay, China; Marathea., *et al* (2011) [11] in surface sediment of Tapti River; Sudhanandh., *et al.* (2011) [12] in coastal estuarine sediments in Veli, Kochi and Mangalore; Chakraborty *et al*. (2013) [13] in south-

ern coast of the Hooghly estuarine system; Astatkie., *et al.* (2021) [14] in Awetu Watershed of Southwestern Ethiopia; Basooma., *et al*. (2021) [15] in River Rwizi in western Uganda; Desiree., *et al.* (2021) [16] in Mefou River sediments, West-Africa; Nishitha., *et al.* (2022) [17] in a tropical river estuary, Southwestern India, Dante., *et al.* (2023) [18] in Lake Rinconada in the Southern Andes, Peru. As Neyyar is the primary source of drinking water supply to one of the Taluks in Thiruvananthapuram districts, it is essential to analyze the heavy metal content in the surface sediment samples in the river. Therefore, the present study focused on the systematic analyses of different heavy metals such as copper, zinc, cadmium, chromium and lead in the surface sediments of Neyyar River in order to assess the contamination rate of the river sediment with respect to heavy metals.

Materials and Methods

Neyyar, the southernmost river of Kerala, originates from the Agasthyamala flows through the midland, lowland and finally joins with the Lakshadweep Sea at Poovar. It lies between the latitude 8^0 16' to 8^0 40' N and Longitude 77^0 5' to 77^0 16' E (Plate1). It is the primary source of drinking water supply to entire Taluk of Neyyattinkara of Thiruvananthapuram district, the capital city of Kerala. Sediment samples were collected from 10 previously identified station locations once a month for a period of one year. Stations 1 to 8 are referred to as fresh water stretches of the river and stations 9 and 10 the estuarine zone. Study period was divided into three seasons- pre monsoon, monsoon and post monsoon based on the rain fall data which were procured from the Meteorological Dept. Govt. of India, Thiruvananthapuram.

Plate 1

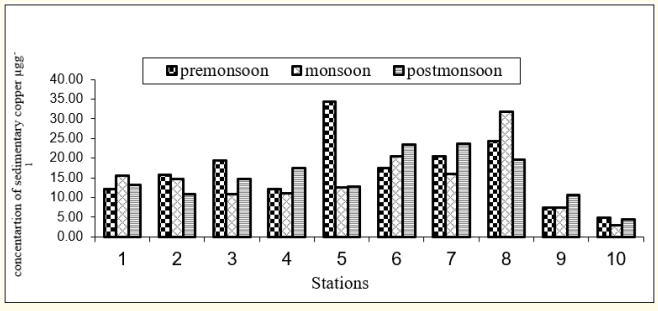

Figure 1: Seasonal distribution of sedimentary copper content in Neyyar River.

Through well planned collection trips, sediment samples were collected in pre-cleaned polythene bags and brought to the laboratory for analyses. After removing leaf litters and other organic debris, the sediment samples were allowed to shade dry for two days and oven dried at 50 ^{0}C, powdered and kept in Dessicator for analyses. All glass and plastic wares used for extraction were pre-cleaned with detergent first and dipped in dilute nitric acid for 2 days and rinsed with double distilled water before oven drying. All the reagents used were of analytical grade. Extraction of sediment samples were done by adopting the method in APHA (2017) [19]. A known quantity of the powdered sediment sample was carefully transferred to pre-cleaned and oven dried 100 ml conical flask through funnel and added 10 ml mixture of nitric acid and perchloric acid (4:1 v/v) and placed in a pre heated sand bath at 90 ^{0}C. Gradually the temperature was increased and when the whole content in the flask turned white/colorless, it was removed from the sand bath and kept for cooling. After cooling the whole content in the conical flask was made up to a known volume by adding double distilled water in a volumetric flask through a funnel with Whatman No.1 filter paper. The made-up solution was transferred to a pre-cleaned polythene bottle and kept in refrigerator until analysis.

Analyses of different heavy metals from the extract were done using Atomic Absorption Spectrophotometer (Perkin Elmer Model 2380) against standard stock solutions and the data obtained in ppm were converted in to µg/g. Estimation can be done using the formula.

$$\text{Concentration of heavy metals} = \frac{\text{data obtained in ppm}}{\text{sample taken for extraction}} \times \text{made up volume}$$

Quality of the analytical data was assured through the implementation of laboratory quality assurance and quality control methods such as the use of standard operating procedures, stan-

dard analytical reagents, calibration with standard stock solutions, analyses of reagent blanks solutions, analyses of replicates etc. Data were subjected to season wise as well as annual average basis. Statistical analyses were done using appropriate software.

Sediment contamination rate were assessed by enrichment factor and geo-accumulation index. Choice of background values remained significant for the assessment of sediment contamination. In the present study the data obtained at station 1 is selected as background value as it is located in comparatively pristine environment.

Enrichment factors (EF) were computed for each metal in the sediment at Stations 2 to 10 that are apparently exposed to anthropogenic inputs by dividing the respective concentrations against background values at Station 1 which is located in comparatively pristine environment. EF >1 indicates the contaminative nature of the river sediment with respect to particular metal. Enrichment factor is computed using the equation

$$EF = \frac{\text{heavy metal content in sediment sample}}{\text{heavy metal content in background}}$$

Geo-accumulation index (*Igeo*) was calculated adopting the formula

$$Igeo = \frac{Cn}{1.5\,(Bn)}.$$

Where *Cn* is the concentration of metal observed in the sample, and *Bn* is the geochemical background concentration of metal. Factor 1.5 is the background matrix correction factor due to lithospheric effects.

Results and Discussion

Seasonal data on different heavy metals in the sediments of Neyyar River are shown in (Figure 2-6), annual data (Figure 7), data on different heavy metal concentrations in various aquatic systems along with present findings (Table 1), sediment texture (2), enrichment factor in (Table 3) and geo-accumulation index (Table 4).

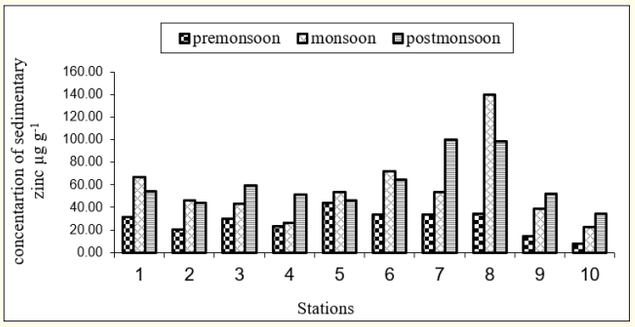

Figure 2: Seasonal distribution of sedimentary zinc content in Neyyar River.

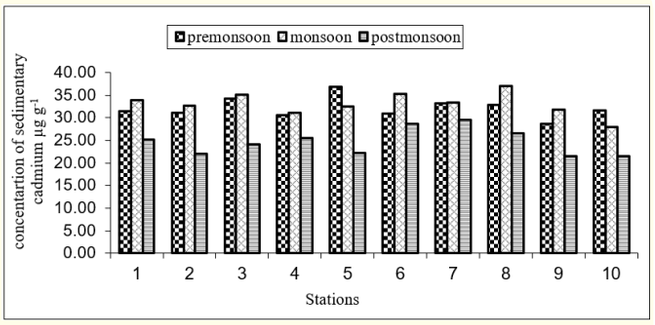

Figure 3: Seasonal distribution of sedimentary cadmium content in Neyyar River.

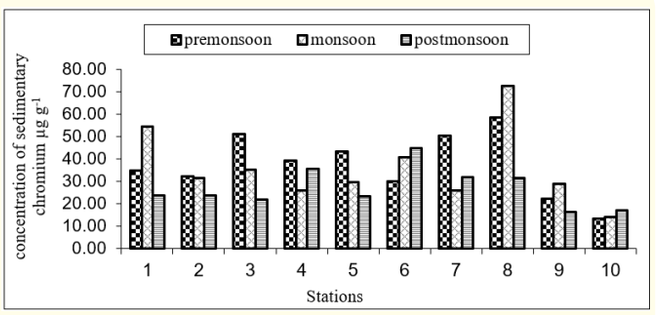

Figure 4: Seasonal distribution of sedimentary chromium content in Neyyar River.

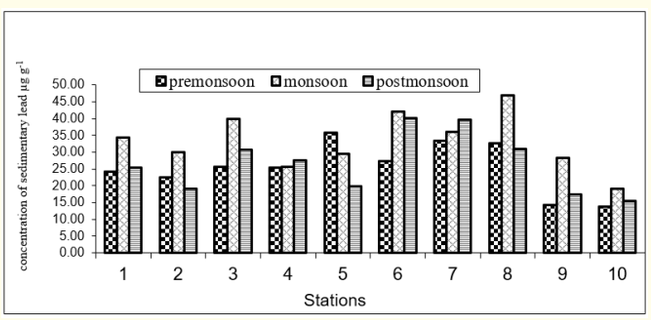

Figure 5: Seasonal distribution of sedimentary lead content in Neyyar River.

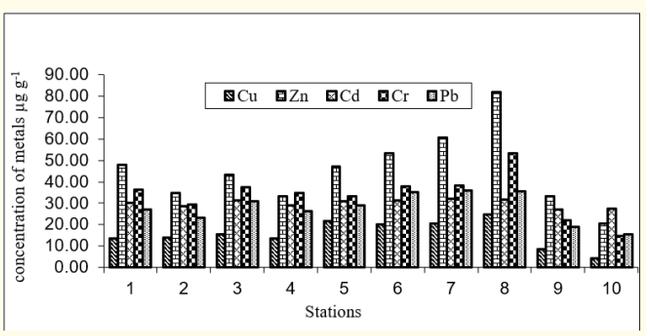

Figure 6: Annual average values of trace metals in the sediments of Neyyar River.

Reference		Copper	Zinc	Cadmium	Chromium	Lead
Nishitha., *et al*. (2022)	Tropical river estuary, Southwestern India (µg/g)	0.7 - 15.58				
Astatkie., *et al*. (2021) Mean	Awetu waste watershed Ethiopia (mg/kg)			151.09	375	2005.94
Pan., *et al*. (2018)	River, Miyun, China (mg/kg)	72.34	21.01	0.18	31.53	33.01
Zarezadeh., *et al*. (2017)	Hara Biosphere Reserve, Qeshm Island (Persian Gulf) (mg/kg)	20.98 ± 0.04	49.39 ± 0.04	2.63 ± 0.04	194.29 ± 0.04	7.94 ± 0.04
Xu., *et al*. (2016)	Jiaozhou Bay catchment, Qingdao, China (mg/Kg)	23.6	64.6	0.159	69.3	20.2
Sim., *et al*. (2016)	Bakun Hydroelectric Reservoir, Malaysia (mg/Kg)	4.26–16.26	6.54–62.28			
Islam., *et al*. (2015).	Korotoa River Bangladesh (mg/kg)	71 ± 27 82 ± 26		1.0 ± 0.5 1.5 ± 0.77	99 ± 38 118 ± 50	54 ± 15 - 63 ± 16
Zarei., *et al*. (2014)	Hara Biosphere Reserve, southern Iran (µg g^{-1})	16.09±4.18	39.54±7.27		73.09±1.20	37.80±6.61
Rahman., *et al*. (2014) Mean	Bangshi River (Bangladesh) (mg/kg)	31		0.6	98	60
Topi., *et al*. (2012)Mean	BUTRINTI LAGOON (ALBANIA)mg/kg	23.4		0.125	56.5	31.2
Suresh., *et al*. (2012)	Veeranam lake, India (mg/kg)	94.12	180.08	0.81	88.20	30.06
Ekeanyanwu., *et al*. (2010)	Okumeshi River			1.32	0.87	0.45
Drusilla., *et al*. (2006)	River Chittar (ppm)				BDL to 0.03	BDL to 0.004
Manjappa., *et al*. 2005)	Bhadra River, Karnataka (µg/g)	7.00 to 9.7				
Dutta and Saxena (2004)	Hoogly Rriver (µg/g)		52 to 90	BDL to 6.5	6.70 to 15.70	
Singh, 2001	Yamuna River(mg Kg^{-1}).	40 to 1204		0.50 - 114.8	157 to 817	
Samanta (2000)	River Ganga (µg/g)	3.8 to 46		3.2		
Biksham and Subramanian (1988)	River Godavari (µg/g)	0.003 - 0.030	13			
Bertin and Bourg (1995)	Lot River basin France (µg/g)			20 -100		
Subramanian., *et al*. 1985	Indian average (µg/g)	28	16			
Taylor, 1964	Earth's crust (µg/g)	44	70	0.2		
Turekian and Wede-pohl (1961)	World geochemical background value in average shale (µg/g)	45	95	0.3	90	20
Present study	Neyyar River (µg g^{-1})	2.98 -34.38	7.91 - 139.74	21.43 - 37.02	13.38 - 72.74	13.82 -46.93

Table 1: Sediment heavy metal concentration in various aquatic systems along with present findings (Units are shown against each reference).

Stations	Season	Nature of sediment	sand %	silt %	clay %
1	Pre monsoon	Loamy sand	86.47	0.89	12.59
	Monsoon	Sandy clay loam	77.57	0.31	22.14
	Post monsoon	Loamy sand	84.91	1.63	13.46
2	Pre monsoon	Sandy clay loam	94.73	0.78	4.48
	Monsoon	Sand	96.34	0.07	3.56
	Post monsoon	Sand	94.46	0.75	4.79
3	Pre monsoon	Sand	91.39	0.91	7.70
	Monsoon	Sand	91.23	0.36	8.41
	Post monsoon	Sand	91.15	0.56	8.29
4	Pre monsoon	Loamy sand	87.90	1.60	10.50
	Monsoon	Loamy sand	86.74	1.98	11.28
	Post monsoon	Sandy loam	79.86	2.08	18.06
5	Pre monsoon	Sandy loam	80.69	0.72	18.60
	Monsoon	Sand	96.37	0.72	2.91
	Post monsoon	Sand	95.21	1.06	3.72
6	Pre monsoon	Sandy clay loam	73.19	1.92	24.89
	Monsoon	Sandy clay loam	73.70	0.93	25.38
	Post monsoon	Sandy clay loam	58.86	10.25	30.90
7	Pre monsoon	Sandy clay loam	62.93	5.01	32.07
	Monsoon	Sandy clay loam	70.34	4.66	25.00
	Post monsoon	Sandy clay	53.15	8.06	38.79
8	Pre monsoon	Sandy clay loam	64.54	5.34	30.13
	Monsoon	Sandy clay loam	62.81	3.84	33.35
	Post monsoon	Sandy clay loam	73.51	1.14	25.36
9	Pre monsoon	Sand	94.94	3.18	1.89
	Monsoon	Sand	96.60	0.24	3.11
	Post monsoon	Sand	93.19	0.89	5.91
10	Pre monsoon	Sand	98.92	0.55	0.54
	Monsoon	Sand	98.43	0.11	1.46
	Post monsoon	Sand	98.94	0.30	0.77

Table 2: Seasonal data and texture of sediment in Neyyar River.

	Copper			Zinc			Cadmium			Chromium			Lead		
Stations	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon
1*															
2	1.33	0.87	1.02	0.69	0.77	0.88	0.99	0.97	0.86	0.99	0.97	0.86	0.94	0.98	0.74
3	1.29	0.95	1.39	1.49	0.98	1.43	1.10	1.05	1.11	1.10	1.05	1.11	1.17	1.28	1.72
4	0.65	0.96	1.24	0.80	0.59	1.11	0.90	0.94	1.08	0.90	0.94	1.08	1.02	0.64	1.03
5	3.00	1.18	0.71	2.08	2.10	0.72	1.20	1.00	0.85	1.20	1.00	0.85	1.43	1.17	0.65
6	0.55	2.05	1.70	0.79	1.35	1.37	0.85	1.24	1.28	0.85	1.24	1.28	0.78	1.61	2.11
7	1.17	0.78	1.11	1.01	0.88	1.71	1.07	1.00	0.98	1.07	1.00	0.98	1.26	0.89	1.00
8	1.18	1.69	0.71	1.02	2.43	0.74	0.99	0.98	0.94	0.99	0.98	0.94	0.99	1.23	0.75
9	0.31	0.24	0.66	0.43	0.26	0.71	0.87	0.83	0.81	0.87	0.83	0.81	0.43	0.48	0.61
10	1.12	0.40	0.47	0.65	0.77	0.65	1.10	0.91	1.01	1.10	0.91	1.01	1.09	0.83	0.85

Table 3: Enrichment factor.

1* data from station 1 is selected as background value and hence there is no enrichment factor at station 1.

	Copper			Zinc			Cadmium			Chromium			Lead		
Stations	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon
1*															
2	0.89	0.77	0.68	0.46	0.40	0.38	0.66	0.65	0.64	0.65	0.57	0.54	0.63	0.58	0.58
3	0.86	0.80	0.77	0.99	0.99	0.98	0.73	0.74	0.74	1.04	1.08	1.02	0.78	0.80	0.82
4	0.43	0.45	0.52	0.54	0.45	0.43	0.60	0.58	0.57	0.55	0.46	0.45	0.68	0.60	0.55
5	2.00	1.91	1.41	1.39	1.38	1.18	0.80	0.81	0.78	0.74	0.75	0.70	0.95	0.97	0.87
6	0.36	0.44	0.60	0.53	0.62	0.73	0.56	0.55	0.59	0.50	0.55	0.67	0.52	0.58	0.71
7	0.78	0.78	0.75	0.67	0.63	0.58	0.71	0.71	0.69	1.16	1.06	0.86	0.84	0.78	0.70
8	0.79	0.96	1.05	0.68	0.74	0.97	0.66	0.69	0.70	0.81	1.31	1.53	0.66	0.68	0.71
9	0.21	0.20	0.22	0.28	0.39	0.39	0.58	0.59	0.60	0.24	0.30	0.35	0.28	0.36	0.41
10	0.75	0.65	0.28	0.43	0.34	0.28	0.73	0.71	0.68	1.11	0.97	0.27	0.73	0.66	0.53

Table 4: Geo-accumulation index.

1* data obtained in station 1 is selected as background value and hence there is no geo-accumulation index at station 1.

Seasonal data on copper content in the surface sediments of Neyyar River varied between 2.98 and 34.38 µg/g. Results are more or less in agreement with the findings of Manjappa., *et al.* (2005) [8], Nishitha., *et al.* (2022) [17], Samantha (2000) [20], Topi., *et al.* (2012) [21], Zarei., *et al*. (2014) [22], Sim., *et al.* (2016) [23], Xu., *et al.* (2016) [24] and Zarezadeh., *et al*. (2017) [25]. Comparatively higher copper concentrations than the present study was reported by Suresh., *et al.* (2012) [26], Islama., *et al.* (2015) [27] and Pan., *et al.* (2018) [28]. In River Yamuna, Singh (2001) [1] reported exceptionally higher copper content (40-1204).

The present result found to be within the range of the standard value of Indian average (28 µg/g – Subramanian., *et al*. 1985) [29] in all the ten stations except at stations 5 and 8 where a little increase in concentration was observed during pre-monsoon and monsoon seasons. However, both seasonal and annual data were within the standard values of Earth's crust (44 µg/g - Taylor, 1964) [30] and Average shale (45 µg/g -Turkian and Wedepohl, 1961) [31] indicating the uncontaminated nature of the river sediments with respect to copper.

ANOVA showed significant monthwise variation (F = 13.425, *d.f.* = 9, $p \leq$ 7.93E-14) in the distribution of sedimentary copper. Copper showed a positive correlation with zinc (r = 0.476, y = 10.626 + 0.11x, $p \leq$ 3.999E - 08, n = 120), cadmium (r = 0.426, y = -4.610 + 0.677x, $p \leq$ 1.250E - 06, n = 120), chromium (r = 0.720, y = 2.825 + 0.379x, $p \leq$ 1.838E - 20, n = 120) and lead (r = 0.698, y = -0.242 + 0.571x, $p \leq$ 7.623E - 19, n = 120) and a negative correlation with sand (r = -0.718, y = 48.364 – 0.392x, $p \leq$ 2.762E - 20, n = 120). Among the various factors analyzed, copper correlated more strongly with chromium > lead > zinc > cadmium suggesting a dominant mineralogical affinity with these metals.

Concentration of zinc ranged between 7.91 and 139.74 µg/g with monsoon/post monsoon high values. Present findings are in concurrence with the reports of Samantha (2000) [20], Zarei., *et al*. (2014) [22], Sim., *et al.* (2016) [23], Xu., *et al.* (2016) [24], Zarezadeh., *et al.* (2017) [25] and Pan., *et al.* (2018) [28], Biksham and Subramanian (1988) [32] and Dutta and Saxena (2004) [33]. Suresh., *et al*. (2012) [26] reported exceptionally higher concentration from Veeranam Lake sediments. Zinc concentration in the Neyyar river sediments remained within the standard values of Earth's Crust (Taylor, 1964) [30] and Average Shale (Turkian and Wedepohl, 1961) [31] except at stations 7 and 8 during monsoon/post monsoon. It can be reasonably stated that Neyyar river sediments are possibly be free from pollution by zinc reflecting only the background levels.

Significant spatial and temporal variations were observed in the distribution of zinc (ANOVA: stationwise – F = 6.591, *d.f.* = 9, $p \leq$ 2.51E - 07; season wise – F = 11.028, *d.f.* = 2, $p \leq$ 7.47E - 04). Regression analysis showed a positive correlation with copper (r = 0.476, y = 10.626 + 0.11x, $p \leq$ 3.999E - 08, n = 120), chromium (r = 0.323, y = 20.727 + 0.735x, $p \leq$ 3.225E - 04, n = 120) and lead (r = 0.659, y = -19.278 + 2.333x, $p \leq$ 2.672E - 16, n = 120 and a negative correlation with sand (r = -0.501, y = 144.439 – 1.184x, $p \leq$ 5.422E - 09, n = 120).

Cadmium ranged between 21.43 (Station 10) and 37.02 µg/g (Station 8). A tendency in declining the values after monsoon observed is in unison with the reports of Kumar., *et al.* (1998) [2] in the sediments of River Kali. Cadmium concentration remained higher when compared to the observations of Rahman., *et al.* (2014) [9], Samantha (2000) [20], Topi., *et al.* (2012) [21], Xu., *et al.* (2016) [24], Zarezadeh., *et al.* (2017) [25], Suresh., *et al.* (2012) [26], Islama., *et al.* (2015) [27], Pan., *et al.* (2018) [28], Dutta and Saxena (2004) [33] and Ekeanyanwu., *et al.* (2010) [34]. Relatively higher cadmium concentrations in sediments were reported by Singh (2001)[1] and Astatkie., *et al.* (2021) [14].

The present result corroborates with the findings of Bertin and Bourg (1995) [35] in the Lot River basin, France (20 to 100 µg/g). However, the results were very high when compared to the internationally accepted reference standards of Earth's Crust (Taylor, 1964) [30] and Average Shale (Turekian and Wedepohl, 1961) [31]. As there were no specific source of cadmium contamination in the catchment area of the river, urban particulates originating from the burning of oil, plastics, pigments and paints may account for the elevated cadmium content as suggested by Coquery and Welbourn (1995) [36]. In general, sedimentary cadmium content recorded in the sediments of Neyyar River remained higher which warrants further investigation as it is non-essential toxic element with unknown function.

Spatial and temporal variations in the distribution of sedimentary cadmium were significant as revealed by ANOVA (stationwise- F = 6.461, *d.f.* = 9, $p \leq$ 3.47E - 07; seasonwise- F = 45.283, *d.f* = 2, $p \leq$ 9.47E - 08). Regression analysis showed positive correlation of cadmium with copper (r = 0.426, y = 10.626 + 0.677x, $p \leq$ 1.250E - 06, n = 120), chromium (r = 0.601, y = 23.175 + 0.199x, $p \leq$ 3.899E - 13, n = 120) and lead (r = 0.480, y = 23.039 + 0.247x, $p \leq$ 2.935E - 08, n =120) and negative correlation with sand (r = -0.279, y = 37.896 – 096, $p \leq$ 2.020E - 03, n = 120).

Chromium concentration varied from 13.38 to 72.74 µg/g during pre monsoon and monsoon respectively. There is no definite seasonal trend in the accumulation of chromium. The present findings is in agreement with the reports of Topi., *et al.* (2012) [21], Zarei., *et al.* (2014) [22], Xu., *et al.* (2016) [24], Pan., *et al.* (2018) [28] and Dutta and Saxena (2004) [33]. Compared to the present findings higher chromium concentration were reported by Singh (2001) [1], Astatkie., *et al.* (2021) [14], Zarezadeh., *et al.* (2017) [25], Suresh., *et al.* (2012) [26] and Islama., *et al.* (2015) [27], and lower concentration by Drusilla., *et al.* (2006) [37]. The results were found within the world geochemical background value of Average Shale (90 µg/g-Turekian and Wedepohl, 1961) [31] indicating the less polluted nature of the river sediments with respect to chromium, which may be due to the absence of any point sources like industries along the entire stretches of the riverine system.

ANOVA showed significant stationwise variations in the distribution of sedimentary chromium (stationwise- f = 9.050, d.f. = 9, p ≤ 7.16E – 10). Chromium exhibited a positive correlation with copper (r = 0.720, y = 2.825 + 0.379x, p ≤ 1.838E - 20, n = 120), zinc (r = 0.323, y = 20.727 + 0.735x, p ≤ 3.225E - 04, n = 120), cadmium (r = 0.601, y = 23.175 + 0.199x, p ≤ 3.899E -13, n = 120) and lead (r = 0.642 y = 6.066 + 0.997x, p ≤ 2.791E -15, n = 120); and a negative correlation with sand (r = -0.583, y = 84.278 – 0.605, p ≤ 2.733E - 12, n = 120).

Lead content ranged between 13.82 and 46.93 µg/g during pre monsoon and monsoon seasons respectively. Results agree with the reports of Topi., *et al.* (2012) [21], Zarei., *et al.* (2014) [22], Xu., *et al.* (2016) [24], Suresh., *et al.* (2012) [26] and Pan., *et al.* (2018) [28]. Zarezadeh., *et al.* (2017) [25], Ekeanyanwu., *et al.* (2010) [34] and Drusilla., *et al.* (2006) [37] registered comparatively lesser cadmium concentration than the present study while Islama., *et al.* (2015) [27] observed little more. However, lead content in Neyyar river sediments at almost all stations remained higher than the Earth's crust (12.5 µg/g - Taylor, 1964) [30] and world Aaverage Shale (20 µg/g - Turekian and Wedepohl, 1961) [31] indicating the polluted nature of the river sediments with respect to lead. As there were no point sources of lead contamination noticed in the catchment area as well as in the study sites, indications of lead contamination observed in the present study may be due to organic matter content and pH influences both solubility and mobility of lead. Airborne particulate lead inputs resulting from vehicular transport may also be responsible for the increase in the concentration of lead as reported by Bertin and Bourg (1995) [35].

Spatial and temporal variations were found significant by ANOVA (station wise- F = 16.904, $d.f$ = 9, p ≤ 1.51E -16; season wise- F = 7.259, $d.f.$ = 2, p ≤ 5.27E - 03). Lead exhibited positive correlations with copper (r = 0.698, y = -0.242 + 0.571x, p ≤ 7.623E - 19), zinc (r = 0.659, y = -19.278 + 2.333x, p ≤ 2.672E - 16), cadmium (r = 0.480, y = 23.039 + 0.247x, p ≤ 2.935E - 08, n = 120), chromium (r = 0.642, y = 6.066 + 0.997x, p ≤ 2.79E - 15, n = 120) and a negative correlation with sand (r = -0.721, y = 67.961- 0.481x, p ≤ 1.622E - 20, n = 120).

In general, on an annual basis it shows that copper is less accumulated in the sediments at all stations and zinc the most accumulated at the majority of the stations. Textural characteristics and organic carbon content in the sediment were found to affect the accumulation of metals. The study revealed that the river is relatively free from contamination by copper, zinc, and chromium. However, indications of contamination by lead and cadmium evident in the present study may be under the influence of forest fires, burning of plastics, air borne particulates, soil weathering, erosion, municipal effluents and automobile exhausts. Decrease in concentration noticed at the estuarine stations irrespective of season may be due to low clay content and high sandy nature of the sediment. The textural characteristics and organic carbon content in the sediment have significant role in adsorption, desorption and accumulation of metals. This may also be due to the non-availability of metal due to flocculation and precipitation under marine influence [38] and subsequent removal. Monsoon/post monsoon high values observed at majority of stations may be due to the influence of land run off brought in by flood water carrying agricultural pesticides and other contaminants. Comparatively higher concentration observed at Stations 6, 7 and 8 irrespective of season may be attributed to the textural characteristics of the sediment.

Higher enrichment factor (Table 3) indicates higher metal contamination and the values >1 indicates the contaminative nature of the sediment with respect to particular metal. Comparatively higher enrichment was observed at station 5 irrespective of metal as well as season. Enrichment factor >1 observed at most of the fresh water stretches of the river indicates the contaminative nature of the river sediment with respect to heavy metals. This may be due to the entry of contaminants through anthropogenic inputs.

According to Muller (1981) [39] geo-accumulation index have (*Igeo*) seven classes: Class 0 (practically uncontaminated: *Igeo* ≤0), class 1 (uncontaminated to moderately contaminate: 0 < *Igeo* 1), class 2 (moderately contaminate: 1< *Igeo* <2), class 3 (moderately

to heavily contaminate: 2 < *Igeo* < 3), class 4 (heavily contaminated: 3 < *Igeo* < 4), class 5 (heavily to extremely contaminate: 4 < *Igeo* <5) and class 6 (extremely contaminated: 5 > *Igeo*). Geo-accumulation index (Table 4) observed in the present study indicates moderately contaminate nature of river sediment for all the five metals irrespective of stations.

Conclusion

Significant spatial as well as temporal variations were observed in the distribution of all metals except copper. Spatial variability may be attributed to the change in relative contribution of sediment draining from different geological formations and sorting of size fractions during transport process along with human influences. The source of copper and lead might be mineralogical as well as anthropogenic, whereas cadmium and chromium were predominantly anthropogenic and zinc might be mineralogical. Uniform trend in decrease in metal concentration irrespective of season observed at the estuarine Stations 9 and 10 which may be attributed to the combined action of salinity induced desorption of metals concentrated in fresh water clay minerals and also by physical action by waves and currents. The only possible sources of metals in Neyyar River were agricultural inputs, domestic influences, forest fires and airborne particulates of urban origin settling in the catchment area. Comparatively higher concentrations of lead and cadmium observed in the Neyyar River sediments warrant further investigation as these metals can become toxic to the flora and fauna. Through food chain biomagnification these toxic heavy metals finally enter in the human body leading severe health issues. The protection of this aquatic system from heavy metal contamination is an urgent need as it is the primary source of drinking water supply to entire Neyyattinkara Taluk of Thiruvananthapuram district, the capital city of Kerala, God's own country. The purification of this precious aquatic system can be done by promoting the growth of bioindicator plant species for particular metal.

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