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Environmental Risk of Heavy Metals in the Southern coast of Kerala, India

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ABSTRACT

The study assessed the environmental and ecological risk of heavy metals such as Iron (Fe), Lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni), Zinc (Zn) & Mercury (Hg) in the south west coast of Kerala, India. Site 1 – considered by tourist arrival and a spiritual pilgrimage centre ensuing in domestic and organic pollution. Site 2 is characterized by oil contamination since it is a fishing harbour with immense motor boat / trawler traffic. Site 3 characterized by inorganic effluence of heavy metals and trace metals due to release of sewages from the KMML Titanium dioxide manufacturing plant. Site 4 since it is alleged to be near primeval being post tsunamic and also lacking any manufacturing / agronomic to enterprise in the area. The area of study which extends from the stretch of coastal belt is a vital part of the Arabian Sea. The study clearly indicates that there is a substantial accretion of heavy metals within the water column and sediment. Heavy metal concentrations were found to exhibit significant spatio-temporal variations in the water column ($p<0.01$), but only Pb showed significant spatiotemporal variations in sediment ($p<0.099$). Cd, Cr, and Ni did not exhibit significant spatiotemporal variations, but Zn showed significant variations during the study periods. These findings validate severity of pollution status of Kerala's southern coast.

Introduction

Heavy metal contamination is now a major concern on a global scale. Due to urbanization and industrialisation, the quantity of heavy materials is inevitably rising. Due to their bio accumulative nature, they constitute a persistent contaminant of the aquatic ecosystem. Heavy metal contamination is less common than other types of water pollution, but it has a much wider range of effects on the aquatic ecology. The increased environmental concentrations discovered in coastal waters are mostly attributable to many natural as well as anthropogenic sources. Since these particles are most likely quite minute, they remain in water bodies for a very long time. However, since they will eventually end up in the sediments, their concentrations there are often 10 to 100 times higher than in water. Even after the primary source of contamination has vanished, these particles may still contribute significantly to contamination in the sediments [4,5]. Mostly in seawater, the majority of marine invertebrates collect heavy metals. Mollusks, crustaceans, and other marine invertebrates are known to collect excessive levels of heavy metals in their tissues even if they continue to survive in contaminated areas. Environmental researchers are interested in tracing the most significant or potentially hazardous metals because they are limiting nutrients (Fe, Zn, Mn, Cu, Co, and Ni), play critical roles in enzyme systems that require metals or are activated by them, and are poisonous when present in high amounts [6]. Heavy metals are unsafe components of air and water pollution. The vast literature on the consequences of metal contamination in water attests to the truth, that it is more a worldwide situation

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developing in scale and degrading of global habitat[7]. The distribution of dissolved cadmium in the water follows a pattern similar to that of nutrients (phosphates and nitrates), according to studies conducted by many researchers [8,9,10]. These studies also demonstrated the establishment of oceanographically regular profiles [11,12 & 13].

In addition to increased shipping activity, higher amounts of Cd and Cu are reported to be released by anti-fouling paint used on most vessels, as well as from various sources (industrial effluents and untreated sewage). The application of biomarkers reveals an early reaction in chosen target animals, according to Chiarelli and Roccheri's (2014) study of marine invertebrates as bio-indicators of heavy metal contamination[14]. Youssef (2015) studied the geographic distribution and heavy metal contamination of benthic foraminifera from the Red Sea coastal area[15] and noted that several foraminiferal species showed abnormalities in their coiling chambers and apertures, which may be related to the higher absorptions of Fe, Zinc, Mn, Cu, Co and Ni in assessments of live *Sorites marginalise* and *Peneroplis planatus*, which confirmed that the coastal areas are being influenced by anthropogenic impacts. Tan *et al*. (2016) examined the heavy metal levels in the water and sediments in the coastal regions of Tuaran, Sabah, and Malaysia. They found that each station's heavy metal levels in the water and sediment varied as a result of anthropogenic and natural disturbances[16]. Gur and Ozan (2017) investigated over the physico-chemical composition of heavy metal faces in water and sediment from Türkiye Isikli lake[17]. Ardila *et al* (2023) assessment of heavy metal pollution in marine sediments from southwest of Mallorca island, Spain. Anjali *et al*. (2023) examine the effects of heavy metal contamination on the environment and human health. A summary of the heavy metal pollution in Kenya's western Indian Ocean (WIO) region was presented by Neymora *et al*. in 2023. These studies suggested that many scientists have investigated the human-caused consequences of heavy metal pollution on the coastal ecosystems along Kerala's and India's coasts [18, 19, 20, 21, 22 & 23].

To assess the levels of heavy metals at three selected sites in the Kollam region, this study was conducted. The study aimed to evaluate pollution levels and understand the associated health implications and thus the study paves the information of impact of heavy metal toxicity on the marine ecosystem.

Materials and methods

Study area

The study region extends from the coastal waters off Varkala in Thiruvananthapuram to the shore of Alappad in Kollam, South Kerala. This coastal strip, which spans 60.5 km, is an essential part of the Arabian Sea. The investigation was conducted in Varkala, Neendakara, Chavara-Titanium, and Alappad (see Table 1 and fig. 1).

Table 1 Lists study area - Latitudes and Longitudes.

Site No.	Locations	Latitude	Longitude
1	Site 1	8° 43' 48.00" N	76° 42' 36.00" E
2	Site 2	8°56'12.2"N	76°32'13.9"E
3	Site 3	9º.03'50.7"N	76º58'.24"E
4	Site 4	9º.11'6"N	76 º 29' E

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Figure 1: Kerala map with study locations

SITE 1 -VARKALA

Locals and visitors from various countries frequently visit the Varkala seashore (Papanasam) to throw burnt relatives' ashes into the water. Despite the burying activity, swimmers from both domestic and foreign countries continue to go to this popular beach. In addition, it serves as a destination for pilgrims and tourists. Naturally, a lot of household and organic pollutants are discharging into the ocean at this location due to heavy foot traffic and direct garbage inputs (figs. 2 and 3)

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Figure 2 & 3. Site 1

National Geopark status will soon be granted to the area surrounding the geological monument, which was chosen because it is litter-free and has no close manufacturing or mining operations (fig. 4). A permission procedure from the Union Ministry of Environment and Forests may be required if there are any additional activities in the area. The opportunity to place oneself on the UNESCO's worldwide list of geohistorical landmarks stands out in Varkala. The UNESCO Global Geopark Programme requires residents of regions with exceptional geological significance to take part in order to preserve the cliff and its surroundings, which have been classified as a protected area. Construction work and rubbish disposal are strictly prohibited in the area [27].

Figure 4. Section of the site 1

SITE 2 -NEENDAKARA

The Location is a picturesque fishing community 9 km north of Kollam City, surrounded to the east by Ashtamudi Lake and to the west by the Arabian Sea. Another Ramsar site is the Ashtamudi estuary, which empties into the sea at Neendakara. In Kollam, Neendakara Harbour is renowned for being one of the premier domestic tourism sites.



Figures 5 – 7. Site 2

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Neendakara harbor currently has the potential to handle about 3300 boats from various regions of Kerala 28 to amenities like ice and freezing plants, processing centers, exporting centers, diesel and petrol bunks, boat building repairing yards, and industrial fishery segments. Eutrophic conditions have been created in Neendakara as a result of the increasing volume of sewage (nitrogenous wastes), and the aquatic system's health has been impaired by oil pollution (oil spills from boat motors) [fig. 7].

SITE 3 - CHAVARA-TITANIUM

In India, presently KMML is the only manufacturer (through chloride process) and distributor of rutile grade titanium dioxide. The plant is located on the western side of national highway (NH 47) between Kollam and Kayamkulam, situated at Sankaramangalam, Chavara located in the midst of a thickly populated area. Ever since KMML began functioning, serious pollution issues were raised by the general public and media who campaigned against the pollution through the gaseous and liquid effluents expelled from the manufacturing facility endangering to the life and environment of the locality. The production of Titanium dioxide from ilmenite through the chloride route resulted in huge quantities of effluents containing hydrochloric acid and ferric chloride, which were released into the surrounding water bodies without proper treatment. The mineral separation plant (fig 8) seems to be the main culprit of the deterioration in the quality of water in the surrounding areas. The pollution in the area was also found to have badly affected the vegetation including and fauna.

Figure 8. Mineral Separation Plant

KMML effluents are discharged into the Arabian Sea from two-points viz, the mineral separation plant at Anchumanakal and at Upukunnu, situated 2 kms away from the main plant [29]. The location was also found to be badly affected up to an area of about 15 square kms with its pollution slowly spreading in all directions (figs 9).

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Figures 9 & 10. Acid fields and Effluents

The effluents discharged from KMML and MS plant at intermittent intervals had been found to pollute the surrounding water bodies before reaching the sea (fig 1.10). Investigations carried on the northern part of the factory were found to contain pools of brownish yellow, floating smelly effluents which were highly acidic and reactive in nature [30]. Identical effluents have also been noticed within the surrounding wells and ponds in vicinity of the factory. Water in and around the factory region was observed to be of inferior quality, silently spreading in the direction of the opposite areas via alluvial aquifers and effluents channels, opening into the sea spreading in the coastal waters.

Site 4 - Alappad

Alappad is a coastal village sandwiched between the Arabian Sea and TS Canal, approximately 16 km in length, with its narrowest point as narrow as 33 m. It is a low-lying coastal belt comprising a sandbar with a width of about 50-200 m and with an elevation of area 0.5 to 1.5 m above the level of the sea (fig 11).

Figure 11. Site 4

It was on 26th December 2004 at 12.45 pm, that tsunami waves struck the coastal regions of Kerala, inflicting death and destruction. The complete barrier next to the sea was inundated, badly affecting agriculture and assets due to seawater seepage and salt accumulation by way of summer season evaporation[31]. Alappad became one of the worst-affected villages in Kerala with numerous people losing their lives. However, there are absolutely no industrial units or agricultural land in the vicinity and so it can be safely assumed that the coast along Alappad

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is not prone to contamination and may be considered as a pristine site.

Duration of the study

The study was carried out over the course of three seasons, from 2013 to 2015: pre-monsoon (March to May), monsoon (June to August), and post-monsoon (Nov to January).

SAMPLING DESIGN

For heavy metal (HM) analysis, surface and bottom water (SW & BW) samples were taken, suspended debris was removed, and samples were filtered (Whatman GF/C) and analysed [32,33,34]. sediment samples were taken (Van Veen grab, 0.1m^2), deposited in polyethylene plastic bags, and maintained frozen at 4°C.

Heavy metals in water column (Fe, Pb, Cd, Cr, Ni, Zn & Hg)

Seawater samples (between 300 and 1000 ml) were moved for extraction 35. The aqueous phase was collected for analysis after phase separation in pre-cleaned plastic vials. ICP-AES was used to measure the presence of heavy metals in seawater.

Heavy metals in sediment (Fe, Pb, Cd, Cr, Ni, Zn & Hg)

The total concentrations of heavy metals were determined using a microwave-assisted acid digestion procedure. The concentrations of Fe, Pb, Cd, Cr, Ni, Zn & Hg were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; PerkinElmer DV4300), and the precision was within10 % of the relative standard deviation [30-33].

Statistical analysis

The statistical analysis was carried out using PAST 3 (PAleontological STatistics Version 3.14) and SPSS Version 24. Multivariate analysis of variance (MANOVA) was used to analyze the interaction between the heavy metals and determine whether there are any significant spatio-temporal fluctuations in the concentrations of heavy metals (SW, BW, and sediment) along the study sites during the study periods. Studying two or more factors (Spatio-temporal variations) simultaneously increases the model's efficiency and the enduring variation is reduced.

RESULTS & DISCUSSION

Heavy metals in water column SW and BW during 2013-15

The spatio-temporal variation in heavy metal concentrations along the study sites are represented in Tables 2 & 3 and figures 12 – 25 (premonsoon (PREM), monsoon (MON) and post monsoon (POSM).

Table 2 Spatio-temporal comparison of heavy metals (SW & BW) during 2013–2014

source	Dependent Variable	Type III sum of squares	df	Mean square	F	sig.
SITES*	Fe SW	27.022	3	9.007	22.207	0.000
	FeBW	116.228	3	38.743	26.273	0.000
	Pb SW	75.319	3	25.106	16.978	0.000
	PbBW	60.797	3	20.266	13.482	0.000
	Cd SW	255.549	3	85.183	25.592	0.000
	CdBW	211.42	3	70.473	23.183	0.000
	CrSW	33.178	3	11.059	30.362	0.000
	CrBW	19.033	3	6.344	18.395	0.000
	NiSW	2.596	3	0.865	13.69	0.000
	NiBW	3.751	3	1.25	9.346	0.000
	Zn SW	4.098	3	1.366	8.721	0.000
	ZnBW	7.649	3	2.55	10.113	0.000

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	HgSW	0.579	3	0.86	0.605	0.000
	HgBW	1.392	3	0.797	3.763	0.000
SEASONS*	Fe SW	4.647	2	2.324	5.729	0.006
	FeBW	13.556	2	6.778	4.596	0.015
	Pb SW	8.191	2	4.096	2.77	0.073
	PbBW	10.17	2	5.085	3.383	0.042
	Cd SW	2.203	2	1.102	0.331	0.72
	CdBW	6.787	2	3.394	1.116	0.336
	CrSW	1.626	2	0.813	2.232	0.118
	CrBW	1.803	2	0.902	2.614	0.084
	NiSW	0.983	2	0.492	7.778	0.001
	NiBW	0.644	2	0.322	2.408	0.101
	Zn SW	0.64	2	0.32	2.043	0.141
	ZnBW	0.028	2	0.014	0.056	0.945
	HgSW	0.127	2	0.064	0.396	0.675
	HgBW	0.216	2	0.108	0.534	0.59
SITES * SEASONS	Fe SW	5.764	6	0.961	2.369	0.044
	FeBW	29.758	6	4.96	3.363	0.008
	Pb SW	8.653	6	1.442	0.975	0.452
	PbBW	12.17	6	2.028	1.349	0.254
	Cd SW	6.362	6	1.06	0.319	0.924
	CdBW	10.652	6	1.775	0.584	0.741
	CrSW	7.169	6	1.195	3.28	0.009
	CrBW	3.592	6	0.599	1.736	0.133
	NiSW	0.92	6	0.153	2.426	0.04
	NiBW	2.119	6	0.353	2.639	0.027
	Zn SW	2.652	6	0.442	2.822	0.02
	ZnBW	1.955	6	0.326	1.292	0.279
	HgSW	1.253	6	0.209	1.303	0.274
	HgBW	7.991	6	1.332	6.581	.000

Table 3 Spatio-temporal comparison of heavy metals (SW & BW) during 2014 - 2015

source	**Dependent variable**	**Type III sum of squares**	**df**	**Mean square**	**F**	**sig.**
SITES	Fe SW	11.791	3	3.930	18.266	.000
	Fe BW	20.523	3	6.841	41.313	.000
	Pb SW	39.659	3	13.220	22.435	.000
	Pb BW	28.464	3	9.488	11.769	.000
	Cd SW	66.532	3	22.177	20.799	.000
	Cd BW	63.242	3	21.081	16.501	.000
	Cr SW	22.948	3	7.649	17.163	.000
	Cr BW	13.753	3	4.584	16.037	.000
	Ni SW	8.718	3	2.906	34.283	.000
	Ni BW	6.999	3	2.333	21.387	.000

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	Zn SW	4.850	3	1.617	7.514	.000
	Zn BW	5.844	3	1.948	5.996	.001
	Hg SW	1.951	3	.650	2.853	.047
	Hg BW	5.140	3	1.713	8.425	.000
SEASONS	Fe SW	1.214	2	1.607	2.822	.069
	Fe BW	3.923	2	1.961	11.845	.000
	Pb SW	10.074	2	5.037	8.548	.001
	Pb BW	20.343	2	10.171	12.616	.000
	Cd SW	12.706	2	6.353	5.958	.005
	Cd BW	24.548	2	12.274	9.607	.000
	Cr SW	6.251	2	3.125	7.012	.002
	Cr BW	3.997	2	1.998	6.991	.002
	Ni SW	1.785	2	.892	10.528	.000
	Ni BW	1.558	2	.779	7.139	.002
	Zn SW	1.596	2	.798	3.708	.032
	Zn BW	1.768	2	.884	2.721	.076
	Hg SW	.307	2	.153	.673	.515
	Hg BW	1.191	2	.595	2.927	.063
SITES* SEASONS	Fe SW	1.152	6	.192	.892	.508
	Fe BW	4.453	6	.742	4.482	.001
	Pb SW	31.512	6	5.252	8.913	.000
	Pb BW	12.540	6	2.090	2.592	.029
	Cd SW	8.068	6	1.345	1.261	.293
	Cd BW	21.878	6	3.646	2.854	.019
	Cr SW	5.544	6	.924	2.073	.074
	Cr BW	1.464	6	.244	.854	.535
	Ni SW	.876	6	.146	1.722	.136
	Ni BW	1.741	6	.290	2.660	.026
	Zn SW	.910	6	.152	.705	.647
	Zn BW	1.220	6	.203	.626	.709
	Hg SW	0.223	6	.204	.894	.507
	Hg BW	1.285	6	.381	1.872	.105

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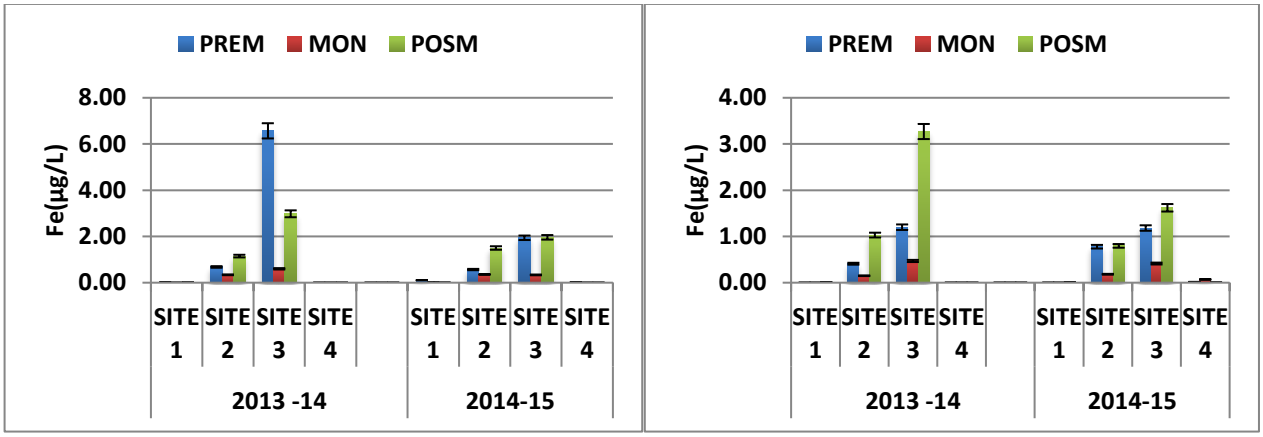
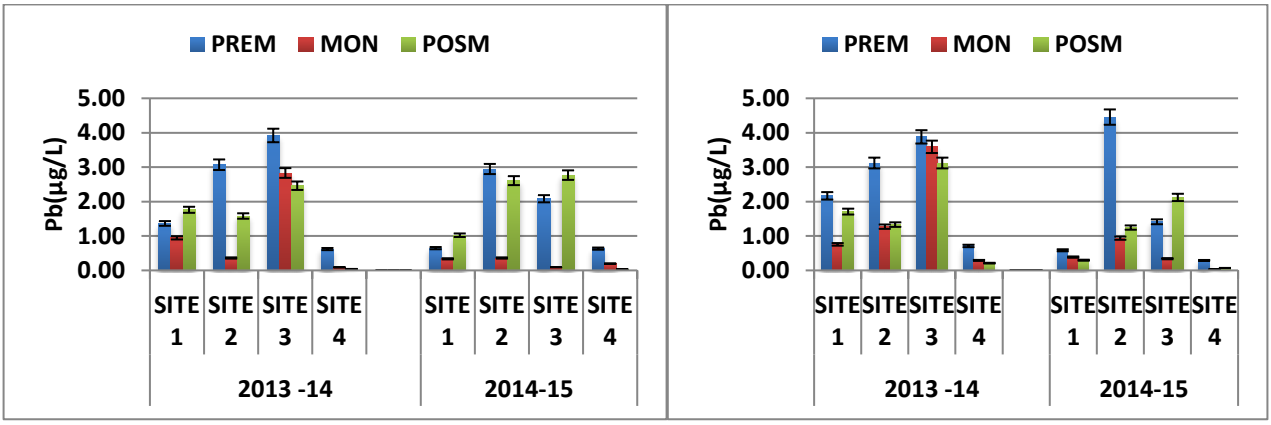
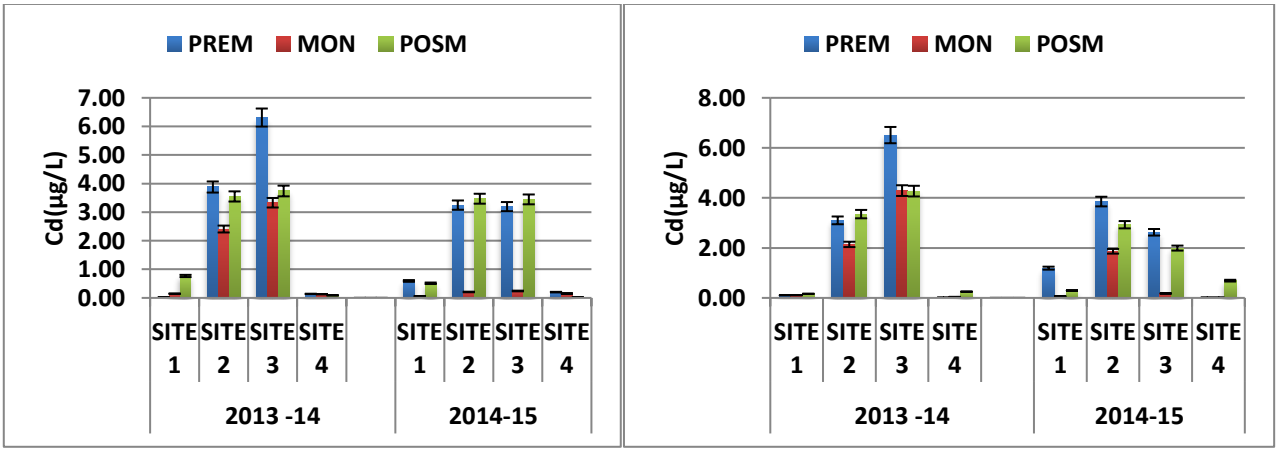


Figures 12 and 13. Spatio-temporal variations of SW Fe (µg/L) and BW Fe (µg/L)



Figures 14 and 15. Spatio-temporal variations SW Pb (µg/L) and BW Pb (µg/L)



Figures 16 and 17. Spatio-temporal variations of SW Cd (µg/L) and BW Cd (µg/L)

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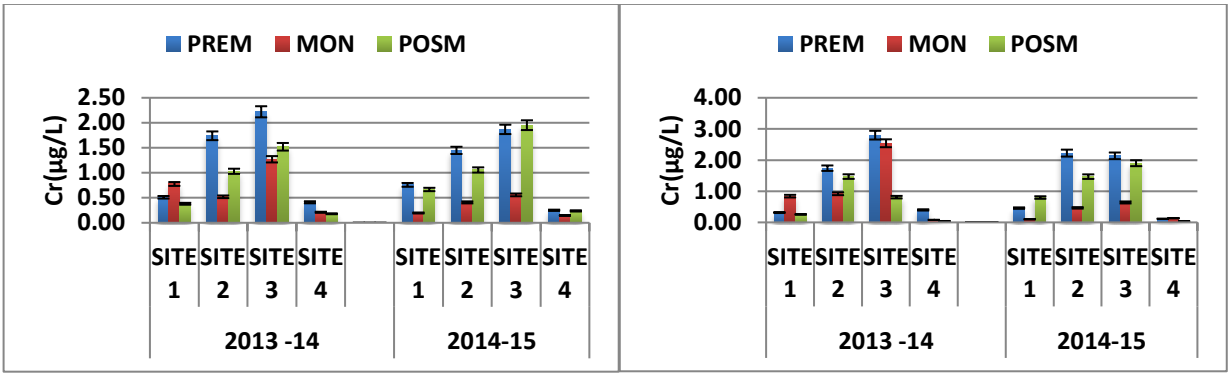
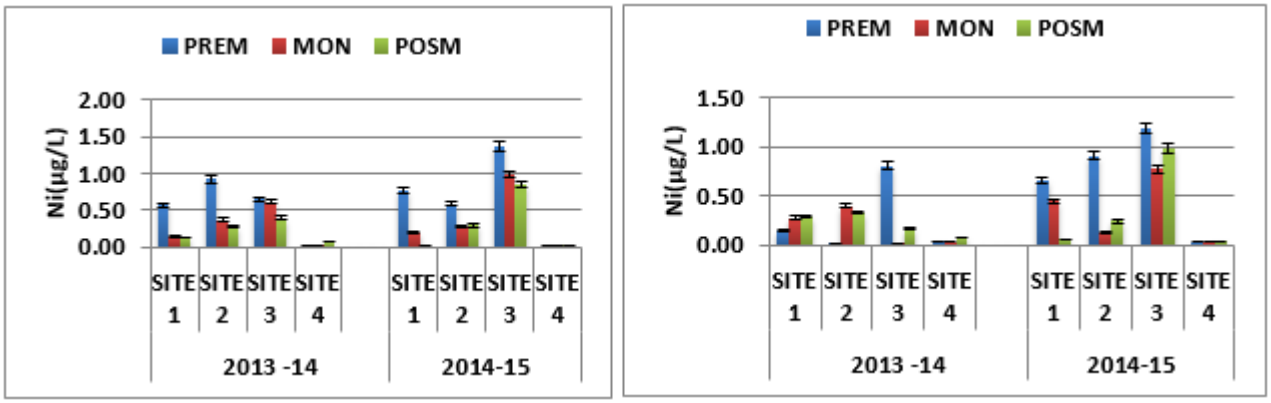
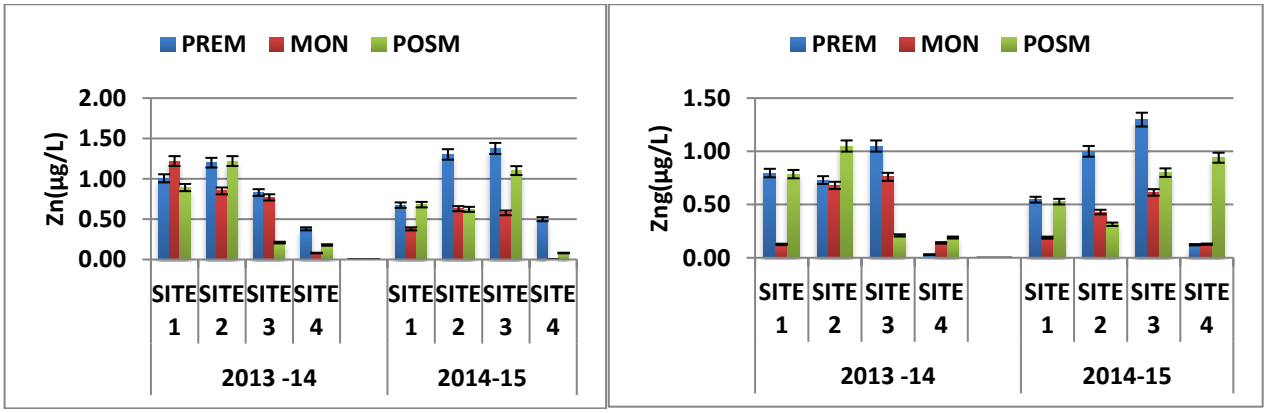


Figures 18 and 19. Spatio-temporal variations of SW Cr (µg/L) and BW Cr (µg/L)



Figures 20 and 21. Spatio-temporal variations of SW Ni (µg/L) and BW Ni (µg/L)



Figures 22 and 23. Spatio-temporal variations of SW Zn (µg/L) and BW Zn (µg/L)

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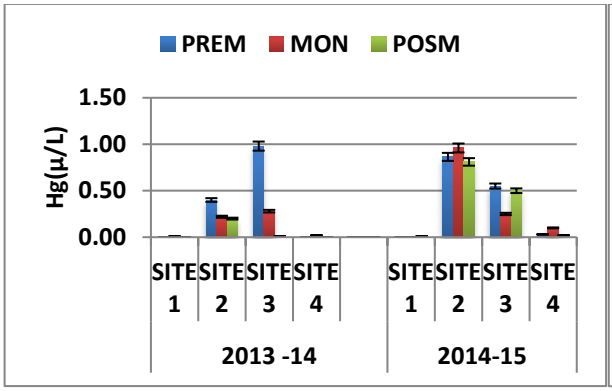

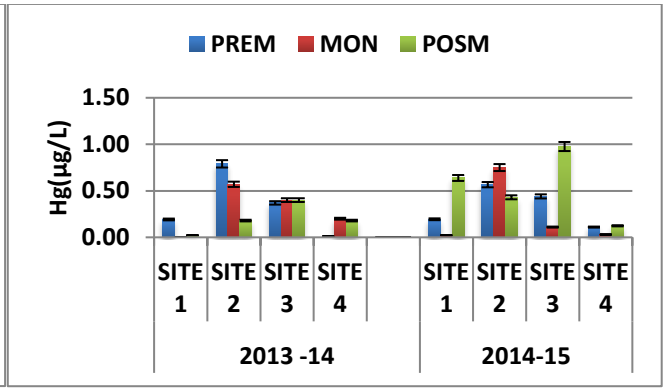

Figures 24 and 25. Spatio-temporal variations of SW Hg (µg/L) and BW Hg (µg/L)

Heavy metals in sediment

The spatio-temporal variation in heavy metal concentrations in sediment along the study sites are given in Tables 4 & 5 and figures 26 – 33.

Table 4. Spatio-temporal variation in sediment heavy metals during 2013–2014.

Source	Dependent variable	Type III sum of squares	df	Mean square	F	sig.
SITES	Fe	19.842	3	6.614	59.095	.000
	Pb	91.057	3	30.352	57.022	.000
	Cd	66.062	3	22.021	10.072	.000
	Cr	11.579	3	3.860	13.630	.000
	Ni	8.030	3	2.677	32.445	.000
	Zn	8.281	3	2.760	11.506	.000
	Hg	6.434	3	2.145	9.965	.000
SEASONS	Fe	7.080	2	3.540	31.628	.000
	Pb	21.195	2	10.598	19.909	.000
	Cd	10.634	2	5.317	2.432	.099
	Cr	.030	2	.015	.053	.948
	Ni	.311	2	.156	1.888	.163
	Zn	3.148	2	1.574	6.561	.003
	Hg	.606	2	.303	1.408	.255
SITES* SEASONS	Fe	10.289	6	1.715	15.322	.000
	Pb	31.539	6	5.256	9.875	.000
	Cd	25.107	6	4.184	1.914	.098
	Cr	5.818	6	.970	3.424	.007
	Ni	2.067	6	.344	4.175	.002
	Zn	1.901	6	.317	1.320	.267
	Hg	1.757	6	.293	1.361	.250

Table 5. Spatio-temporal variation in sediment heavy metals during 2014–2015.

Source	Dependent variable	Type III sum of squares	df	Mean square	F	sig.	Partial Eta squared
SITES	Fe	59.771	3	19.924	35.945	.000	.692
	Pb	338.998	3	112.999	75.899	.000	.826
	Cd	146.797	3	48.932	18.642	.000	.538
	Cr	14.222	3	4.741	13.924	.000	.465
	Ni	3.007	3	1.002	8.438	.000	.345

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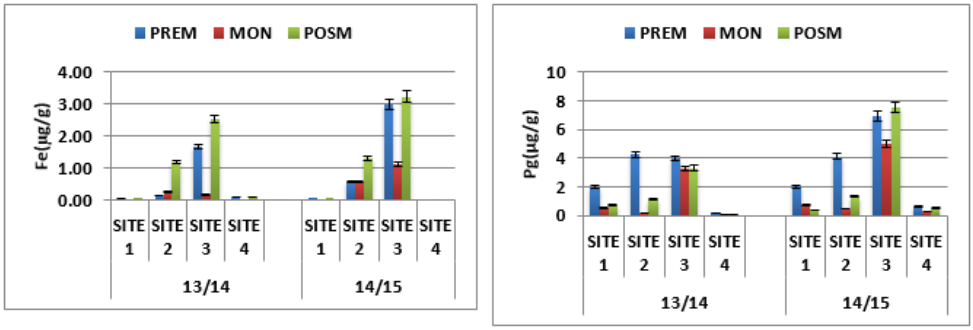
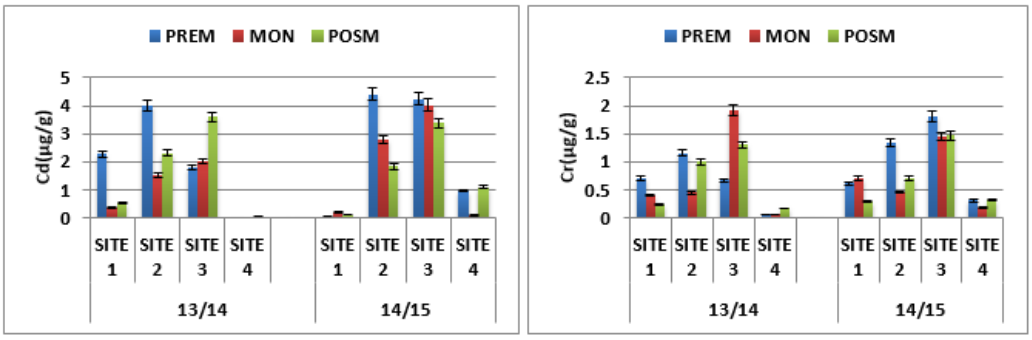
	Zn	.877	3	.292	1.217	.314	.071
	Hg	9.695	3	3.232	16.784	.000	.512
SEASONS	Fe	5.586	2	2.793	5.039	.010	.174
	Pb	33.675	2	16.837	11.309	.000	.320
	Cd	7.332	2	3.666	1.397	.257	.055
	Cr	1.366	2	.683	2.006	.146	.077
	Ni	.382	2	.191	1.608	.211	.063
	Zn	.281	2	.141	.586	.561	.024
	Hg	.120	2	.060	.311	.734	.013
SITES* SEASONS	Fe	9.771	6	1.628	2.938	.016	.269
	Pb	28.519	6	4.753	3.193	.010	.285
	Cd	14.809	6	2.468	.940	.475	.105
	Cr	1.636	6	.273	.801	.574	.091
	Ni	.389	6	.065	.546	.771	.064
	Zn	3.731	6	.622	2.590	.030	.245
	Hg	4.602	6	.767	3.984	.003	.332



Figures 26 and 27. Spatio-temporal variations of Fe and Pb in sediment (µg/g)



Figures 28 and 29. Spatio-temporal variations of Cd and Cr in sediment (µg/g)

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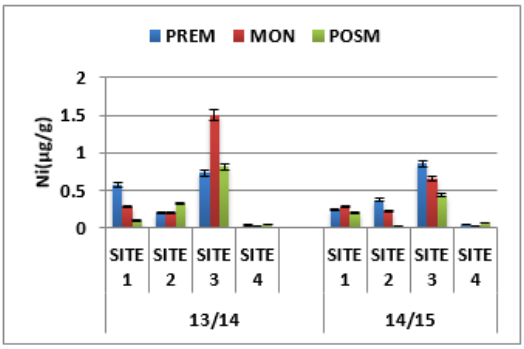

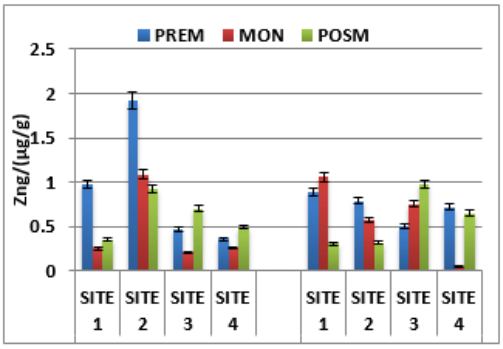

Figures 30 and 31. Spatio-temporal variations of Ni and Zn in sediment (µg/g)

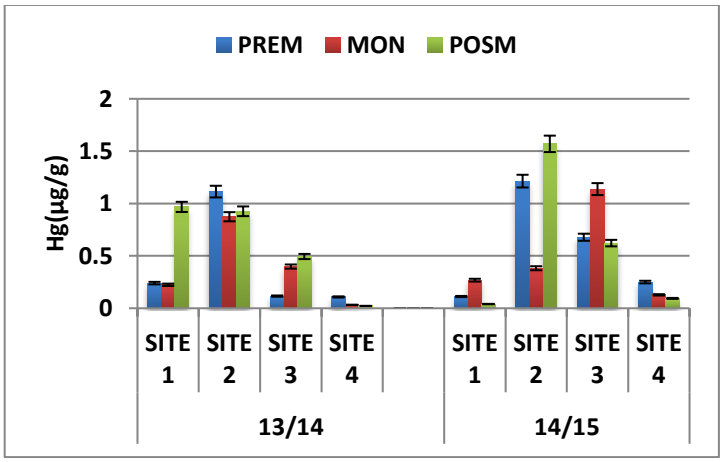

Figure 32. Spatio-temporal variations of Hg in sediment (µg/g)

Table 6. Maximum permissible limit (MPL) of Heavy Metals

HM	Water (µg/l)	References	Sediment (µg/g)	References
Fe	0.30	WHO, 2011	35.30	WHO, 2011
Pb	0.01	WHO, 2011	0.03	WHO, 2011
Cd	0.01	WHO, 2011	6.00	WHO/USEPA,1999
Cr	0.05	EPA, 2002	20-30	USPHS, 1997
Ni	0.02	WHO/USEPA,1999	5.40	McDonald, 1995
Zn	0.30	EPA, 2002	24.74	WHO/UNEP, 1999
Hg	0.50	EU/EC, 1881/2006	2ng/g	EU/ EC, 1881/2006

Discussion

Heavy metal contamination in aquatic habitats has caused havoc during the last few decades [44,45,46]. Many studies have tried to connect industrial and municipal discharges to heavy metal water pollution[47]. Potentially, both anthropogenic and natural processes could raise the burden of heavy metals. The accumulation of metals in water and sediments affects a variety of environmental species, which significantly affects how well they function [48]. Heavy metal concentrations were found to exhibit significant spatiotemporal variations in the water column ($p<0.01$), but only Pb showed significant spatiotemporal variations in sediment ($p<0.099$). Cd, Cr, and Ni did not exhibit significant spatiotemporal variations, but Zn showed significant variations in 2013–2014. These findings validate severity of pollution status of Kerala's southern coast.

Varkala's water column and sediment were found to

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contain the following heavy metals, in decreasing order: Pb>Zn>Cd>Cr>Ni>Hg>Fe(SW),Pb>Zn>Cd>Cr>Ni>Hg>Fe(BW),and Pb>Cd>Zn>Hg>Ni>Cr>Fe(Sed). Over the course of the three seasons of the full study period, it was discovered that SW and BW had greater Pb concentrations. In the pre-monsoon, BW had a higher concentration (6.07 0.75 g/L) than SW (5.9 0.80 g/L). Zn was found to be present in BW at the highest concentration (4.85 0.05 g/L) compared to SW.

While the concentrations of Cr, Ni, Cd, and Hg were more or less consistent over the course of the three seasons, the concentrations of BW were greater than SW, ranging from 4.03 to 6.06 g/L. In SW, Fe and Hg concentrations were always below the level of detection (BDL), while during the pre-monsoon, Fe concentration in BW was observed to be slightly elevated. This may be due to much higher Fe concentration ratios of sinking material in the high dust deposit regions. Iron concentrations reflect a steadiness between sources and sinks [49], with organic complexation more likely to play a position, and noted that the shrink in surface iron concentrations was once strongly influenced by sediment re-suspension activities, which released dissolved iron into the water column [50].
In the water column and sediment at Neendakara, heavy metals were discovered in the following decreasing order:Cd>Pb>Cr>Zn>FeNi>Hg(SW),Cd>Pb=Zn>Cr>FeNi>Hg(BW),and Cd>Pb>Zn>Cr>HgFeNi (Sed). While BW Cd concentrations decreased from 3.87 g/L (2013–2014, pre–monsoon) to 0.20 g/L (2014–2015, monsoon), SW Cd concentrations ranged from 1.86 g/L (monsoon) to 3.85 g/L (pre–monsoon). Comparison between SW, BW & Sed Pb concentrations, maximum (4.45 µg/L±1.28) value was recorded in SW during pre-monsoon and minimum (0.18 µg/L ± 0.09) value was recorded in sediment during monsoon. The maximum permissible limit of Pb is 0.01µg/L in water and 0.03 µg/g in sediment respectively. According to recent studies, heavy metal concentrations are much greater than they were in the past [51,52,53].

However, the atmospheric pathway is also significant for several elements, particularly in the open ocean, such as Hg, As, and Pb. The profile of heavy metal distribution at Neendakara confirms that land runoff, oil spills from powered boats, and harbor sewage wastes are the main sources of most trace metals associated to coastal locations. Despite the fact that these elements originate from neighboring rivers and outflows, it is usually seen that they dominate the coastal inflow.

The concentrations of heavy metals in the water column and sediment at Chavara-Titanium were discovered to be decreasing in the following order: Cd>Pb>Cr>Fe>Ni>Hg>Zn(SW),Cd>Fe>Pb>Cr>Zn>Ni>Hg(BW),and Pb>Cd>Fe>Cr>Zn>Ni (Sed). Normally, traces of Pb are transported to the ocean's surface by atmospheric wet and dry particle deposition. However, even for these parts, regional outflows.

Pre-monsoon had greater seasonal metal concentrations than monsoon and post-monsoon. Similar observations were made in the Bay of Bengal 56. Higher concentrations during the summer may be attributable to low flow conditions and rapid temperature caused by industrialized air dumping wastes from the sector that result in desiccation. At Alappad, heavy metal concentrations were discovered in the water column and sediment in the following decreasing order: Pb>Zn>Cd>Cr>Hg>Ni>Fe(SW),Pb>Cd>Cr>Zn>Ni>Fe>Hg(BW),and Zn>Ni>Pb>Cd>Cr>Fe>Hg (Sed). In this region throughout both years, levels of Cd, Cr, Ni, and Hg were almost identical. While Cr and Ni loads are larger in BW, Cd and Hg concentrations in SW vary less than in BW.

Concentrations of heavy metal loads have been recorded at Neendakara and Chavara-Titanium whereas, at Varkala and Alappad, the coastal waters are comparatively less polluted. The direct discharges of industrial effluents, after partial treatment in the effluent settling ponds, from Chavara-Titanium dioxide pigment plant to the seas shore spreads over a broad area in the coastal sea. Other outlets from the factory compound also discharge the toxic effluents to the neighboring land area and TS canal. The local areas namely Panmana, Mekkad and Chittoor adjacent to the factory compound are thus heavily polluted (air, soil and water). Since the production facility was first established in 1984, the poisonous effluents of the KMML factory in Chavara have been allowed to flow wild. The iron-oxide sludge that has been discovered there is mixed with acid and heavy metals and is seen oozing from old sewage ponds, where it had been building for decades, posing major health risks to the surrounding population.

Ilmenite, a mineral that is plentiful in the black sand of the Chavara belt, is used by the plant to make titanium dioxide. Previously crystal-clear canals are now filled to the brim with foamy trash. Pale effluents had flooded domestic wells and ponds. Almost all of the greenery has been exhausted. Previously a green location along the sea, Panmana now symbolizes the pollution load. This situation is in agreement with other researchers' studies

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[57,58,59]. The existence of heavy metal load along the coastal waters [60] is caused by the usage of metal and metal components, the leaching of metals from solid waste, and the offshore dumping of home sewage, sludge, and industrial wastes. Other contributing factors include businesses that manufacture organic and inorganic chemical compounds, ferrous and non-ferrous metals, including businesses that plate metal, and businesses that manufacture organic and inorganic chemical compounds. Temporal variations in the trace metal distribution in the water at the four study sites. Localized inputs, like river flow, have a substantial impact on the fluctuating metal concentration.

The public health risk in the contaminated areas of the study sites was further substantiated by a comparison of the metal concentrations in the water column and sediments using the maximum permissible limit (MPL) established by various organizations (Table 6). The analysis unequivocally shows that there has been a large buildup of heavy metals in the soil and water column. It can be seen that it is necessary to create a system for ongoing physical, chemical, and biological monitoring of coastal waters and sediment in order to provide the industrial houses and general public with the knowledge they need to develop strategies for the safe disposal of industrial effluents and domestic sewage, with the overarching goal of preventing the spread of toxicity in the environment. A critical step in creating efficient emission control methods and identifying polluted sites for remediation is identifying the sources of anthropogenic heavy metals that contribute to their buildup at any specific site. For this purpose, the utilization of heavy metal stable isotopes (such as copper, lithium, and zinc) has increased [61,62,63, & 64]. As a result, these innovative and promising methodologies were employed as a potent environmental quality detection tool that can be used in the future for additional source documentation studies.

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