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Trace Metal Pollution in Estuaries of South India

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Abstract: Studies were conducted to determine the dynamics of heavy metals in selected stations of three major economically important estuaries of south India, viz, Vembanad, Ashtamudi and Veli. Heavy metals in the surface water of selected stations were analysed on monthly basis during April 2003 to March 2004. Significantly higher levels of copper and zinc were detected in most of the samples throughout the year. Trace levels of Cr, Cd, As, Sb, Se, Mn, Ni, V and Pb were detected and their occurrence was seasonal. The paper discusses in detail about the seasonal variations of different trace metals and the results revealed that these estuaries are less polluted.

Key words: Trace metals, water quality, estuaries, estuarine pollution.

Introduction

The estuaries around the world receive a large amount of waste from catchments that surround them and have become repositories for heavy metals, hydrocarbons and pesticides. In the state of Kerala, south India, interconnected estuary system comprises about 67% of the total 3600 sq km of water covered area in the state (Prabhakaran, 1992). Majority of the backwaters of Kerala are found in the southern half and the major estuaries along the coast are Vembanad, Ashtamudi and Veli. Vembanad backwater system is the largest of its kind on the west coast of India and is closely connected to the kol lands on its northern side. Almost all of the management interventions in Vembanad lake have been related to the development of paddy fields of Kuttanad. Ashtamudi is one of the largest wet land ecosystems in south India. Natural dynamics equilibrium and the biotic composition of the estuarine areas of this region are disturbed due to increased human influence by different reasons. These backwaters flourished with tourism, hospitality industry, increased human settlements, industries, etc., and these activities influence the rich biological production and accumulation of pollutants. Fertilizer consumption in Kuttanad region (the main agricultural field draining to Cochin backwater) alone is reported to be 20,239 t y^{-1} (Anon, 1998). The backwater receives organic wastes of about 260 t d^{-1} (Anon, 1998) Metals such as Fe, Cu, Co, Zn etc. are essential in small quantities for the healthy growth of marine organisms. These are toxic if present in excess. But metals such as Hg, Pb and Cd are said to have little or no biological role.

Recently large number of media reports state that these estuarine water qualities are deteriorating day-by-day due to different tourism and other economic activities. It is a major concern among government agencies and other policy making bodies. Not many studies have been conducted in the estuarine waters of south India with reference to the inorganic contaminants. This study was intended to provide data on dynamics of heavy metal concentration in major estuarine systems of this region. Aim of this study is to generate a data base on the dynamics of heavy metals concentration in selected stations from the three major estuaries of south India, viz. Vembanad, Ashtamudi and Veli.

Materials and Methods

Kerala is a tropical region which experiences annual rainfall of 3000-4000 mm and has three seasons viz.

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monsoon (June to September), post-monsoon (October to January) and pre-monsoon (February to May). The stations selected for the study were Punnamada (station 1), Puthanar (Station 2), Ayiramthengu (station 3), Sakthikulangara (station 4) and Veli (station 5). The surface water samples were collected from the above five stations during April 2003 to March 2004. Three samples were collected from each station and analysed separately. Water collected in thoroughly cleaned polythene bottles and kept in cold storage till the analysis. The water samples were filtered through Whatman No 40 filter paper and anlysed for heavy metals using Perkin Elmer Optima 2000DV Inductively Coupled Plasma Optical Emission Spectroscopy. Each sample was analysed for 11 elements viz. Cd, Cr, Cu, As, Sb, Se, Mn, Ni, V, Zn and Pb. NIST traceable multi element standard solution from Perkin Elmer [Quality Control Standard 21 (Lot No 26-51 AS, PE No N9300281)] was used for multi point calibration. Due to significant variation of salinity between the seasons, the metal analysis was carried out by standard addition method as described in AOAC (2003). 0.2 and 0.4 ml of 5 mg kg^{-1} multi element standards were pipetted in each samples separately and the concentration was calculated based on the intensity of the standard added and the original sample. The hydrographical parameters are also recorded in all the samples as per Strickland and Parson (1972) and the data used in the present paper is only for correlation analysis. Statistical analysis like two-way anova and correlation analysis was done using MS Excel available with Microsoft Office software. Statistical significance stated in the ensuing discussion is at $P \leq 0.05$ unless otherwise stated.

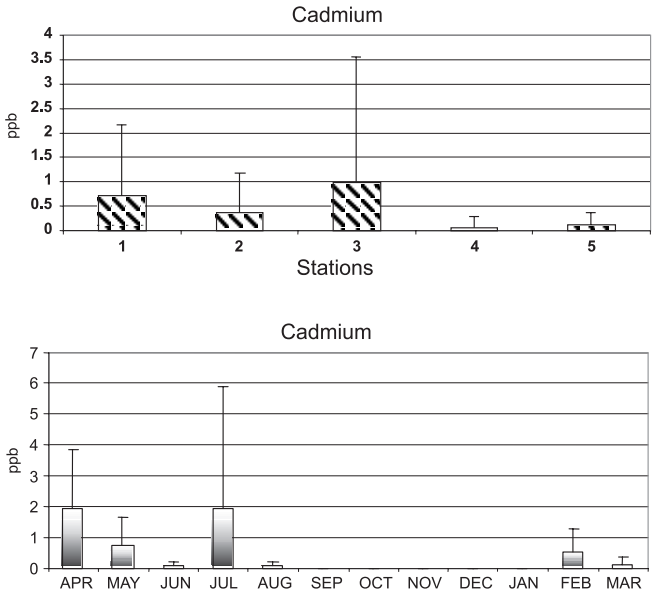

Figure 1: Variation of cadmium concentration (μg l^{-1}) in different stations and seasons.

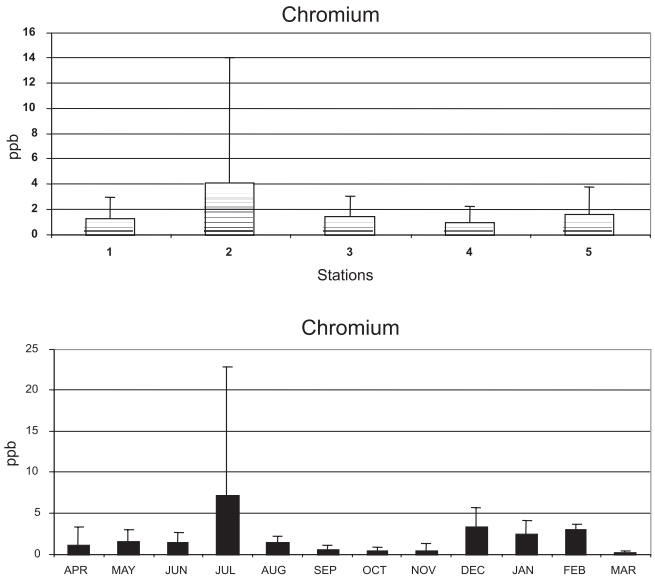

Figure 2: Variation of chromium concentration (μg l^{-1}) in different stations and seasons.

Results

Distribution and Seasonal Variation of Trace Elements

Cadmium concentration in water was varied between 0 and 9 μg l^{-1} during the year. Station 1 recorded increased concentrations of cadmium (0.714 ± 1.456 μg l^{-1}) especially during pre-monsoon period (Figure 1). In general pre-monsoon season recorded the presence of Cd in most of the stations. Correlation analysis revealed that there is a significant positive correlation with salinity (r=0.7688) and chromium (r=0.7849) in station 1 and also the salinity was maximum during premonsoon. Chromium content was recorded at 0-35.3 μg l^{-1} during the year and station 2 has recorded highest. Significantly higher levels of chromium (0.7-7.7 μg l^{-1}) were detected in station 5 during post-monsoon (Figure 2). Chromium varied between 0-5, 0-35.3, 0-4, 0-4.0 and 0-7.66 μg l^{-1} respectively in stations 1, 2, 3, 4 and 5 during the study. Very low levels of nickel (0-4.3 μg l^{-1}) were detected in some samples and in the remaining samples it was well below the detection limit. Its presence in most samples was during the pre-monsoon season (Figure 3).

Lead concentration in water varied between 0-19.7 μg l^{-1}, and the stations 1 and 2 recorded significantly higher values (Figure 4). Seasonal variation of Pb was in

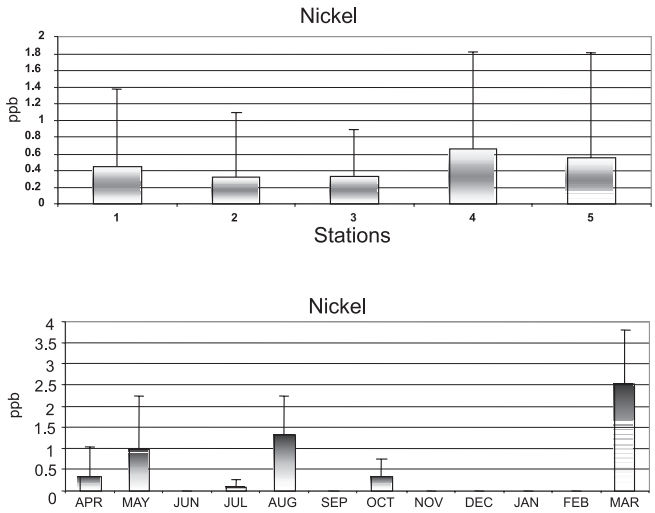

Figure 3: Variation of nickel concentration (μg l^{-1}) in different stations and seasons.

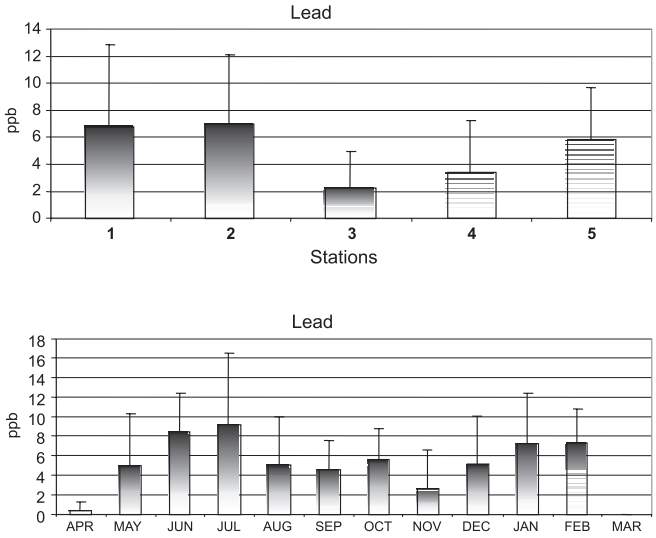

Figure 4: Variation of lead concentration (μg l^{-1}) in different stations and seasons.

the order, monsoon > post-monsoon > pre-monsoon. Pb was detected throughout the year in samples collected from stations 1, 2 and 5, whereas in stations 3 and 4, its presence was mainly during monsoon. Arsenic concentration ranged from 0 to 30 μg l^{-1} during the year and it was detected in stations 1 and 5 frequently and in other stations its presence was irregular (Figure 5). The concentration varied between 0-10.7 and 0-8.33 μg l^{-1} in stations 1 and 5 respectively. January to March season showed comparatively higher levels of arsenic in most of the stations.

Selenium concentration in water was detected mainly during post-monsoon in all the stations except in station 4. Selenium concentration varied between 0 and 33.33

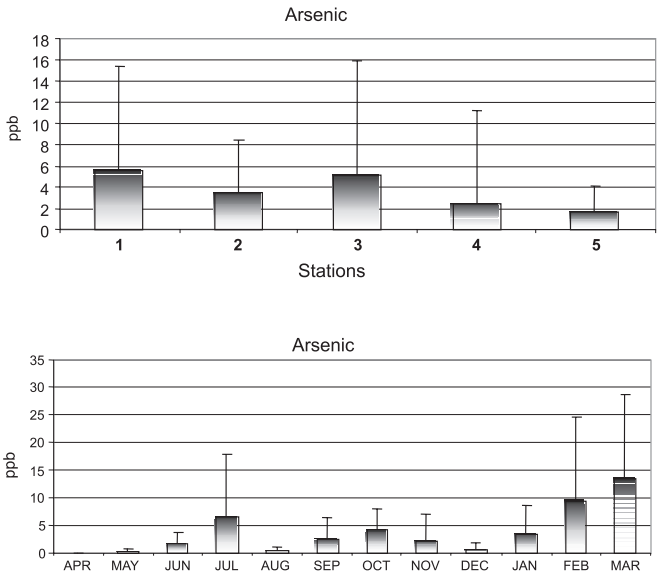

Figure 5: Variation of arsenic concentration (μg l^{-1}) in different stations and seasons.

μg l^{-1} during the study. Selenium concentration in station 2 increased slowly from October and reached maximum in January; it decreased after January (Figure 6). Antimony was detected mainly during post- and pre-monsoon period. It varied from 0 to 54.3 μg l^{-1} (Figure 7) during the study. Station 5 recorded maximum antimony concentration and it ranged from 0 to 54 μg l^{-1}. Trace levels of Sb were detected in station 4 and it was not detected during monsoon.

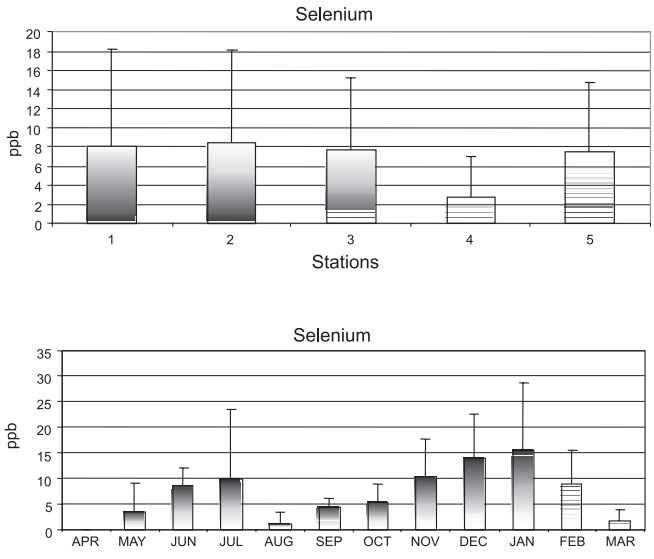

Figure 6: Variation of selenium concentration (μg l^{-1}) in different stations and seasons.

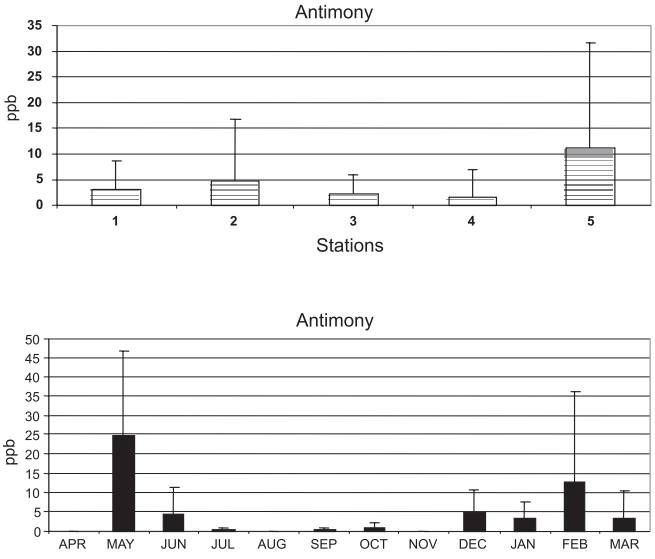

Figure 7: Variation of antimony concentration (μg l^{-1}) in different stations and seasons.

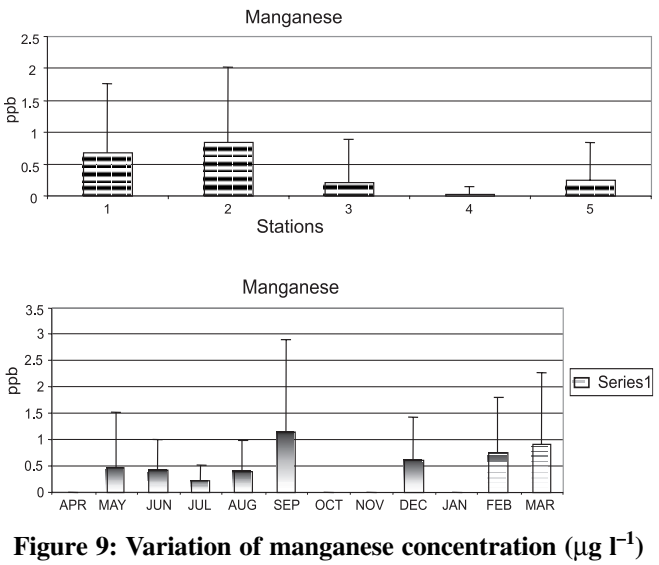

Figure 9: Variation of manganese concentration (μg l^{-1}) in different stations and seasons.

Distribution and Dynamics of Nutrient Elements

Copper concentration varied between 0-60.33 μg l^{-1} and it was maximum in station 1 (Figure 8). Significantly higher levels of copper were recorded during June-September (monsoon) period. In station 1, copper varied between 0 and 60.33 μg l^{-1} and its concentration in monsoon > post-monsoon > pre-monsoon. Copper showed positive correlation with Pb, V, Se and turbidity in most stations. Trace levels of manganese was detected in some of the samples and it varied between 0 and 3.2 μg l^{-1} (Figure 9). Increased levels of manganese were detected in station 1 during February-March, the pre-monsoon period. Vanadium was detected in most of the samples and it ranged from 0 to 55 μg l^{-1}. Its presence was significantly higher in stations 2, 3 and 4. Vanadium varied from 0-31.3, 0-32.7, 0-48.0, 0-28.5 and 0-26 μg l^{-1} in stations 1, 2, 3, 4 and 5 respectively (Figure 10). Station 1 and 5 recorded an irregular variation of V concentration between the samples collected and increased levels were recorded during post-monsoon. Zinc was detected in all the stations and seasons and its concentration varied between 0.8 and 87.8 μg l^{-1}. Pre-monsoon season recorded significantly higher levels of Zn and station 2 has recorded comparatively higher levels among stations (Figure 11). Zinc concentration ranged

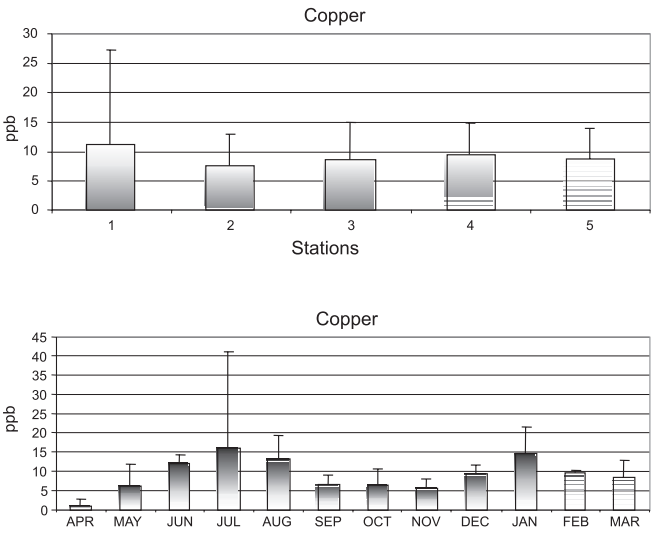

Figure 8: Variation of copper concentration (μg l^{-1}) in different stations and seasons.

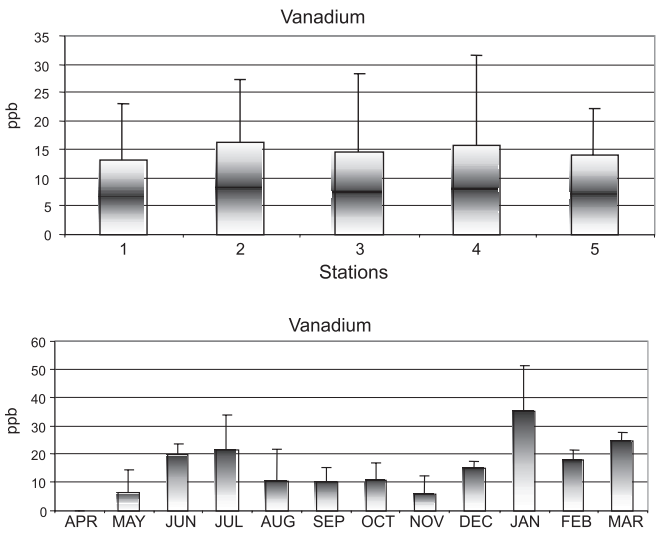

Figure 10: Variation of vanadium concentration (μg l^{-1}) in different stations and seasons.

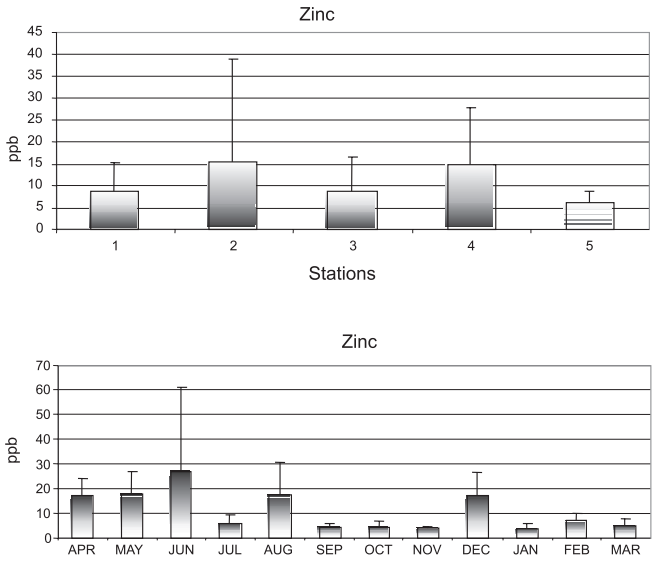

Figure 11: Variation of zinc concentration (μg l^{-1}) in different stations and seasons.

1.67-21.0, 0.80-87.83, 0.80-27.57, 2.00-40.00 and 2.67-10.67 μg l^{-1} in stations 1 to 5 respectively. The higher standard deviation in stations 2 and 4 was due to the irregular variation of zinc during the study.

Discussion

Metallic Residues

Increased concentrations of cadmium during pre-monsoon season were attributed to increased salinity and low fresh water discharge prevailing in this region. Studies on the seasonal changes of cadmium and manganese in Hudson River by Yang and SaZudo-Wilhelmy (1998) revealed that the higher Cd was detected during low fresh water discharge season which implies that limited hydraulic flushing allows a build-up of metals in the water column. Krishnakumar et al. (2004) reported that the mean cadmium concentration in seawater samples collected on monthly basis from the hotspots of Cochin and west coast of India were 8.14 μg l^{-1} and 2.95 μg l^{-1} respectively. Standard for the protection of fresh water and marine life of UK is respectively 0.002 mg kg^{-1} and 0.003 mg kg^{-1} (salt water, total Cd) of dissolved Cd. Generally total chromium is detected at low concentration in fresh waters. Chromium(VI) is water soluble and always existing in solution as a component of complex anion. Higher levels of chromium were detected during the month of July, which is peak monsoon month in the region. The higher influx of fresh water produce a washing effect and re-dissolve the metal ions accumulated in sediments during summer.

Lead was specific in seasons and stations. The stations 1 and 2 belong to Vembanad estuarine system and the region is known for rice cultivation and tourism industry. Use of lead in fuels is decreased considerably in recent years. The primary sources of lead in water are generally from manufacturing processes, atmospheric deposition and domestic waste water. According to Nriagu (1989) approximately 96% of all the lead emission originates from anthropogenic sources particularly combustion of lead containing products. The input of lead into remote waters is primarily due to atmospheric deposition (Urban et al., 1987). Lead is stable at +2 and +4 oxidation states. In fresh water Pb forms a number of soluble complexes with many of the major anions, including hydroxides, carbonates, sulfides and sulphates. At pH10 $Pb(OH)^{+}$ dominates over all other species. Speciation shifts to favour chlorides and hydroxide complexes in salt water. Approximately 75% of the Pb in rivers is in suspension and 25% in solution but in salt water the corresponding ratio is approximately 50:50. Maximum lead concentration during monsoon season may be explained based on the abovesaid phenomenon as the salinity was highest during summer and salinity was reduced to minimum during monsoon due to the high inflow of fresh waters. Krishna Kumar et al. (2004) and Banat et al. (1998) reported Pb in 5.94 and 0.84-1.25 μg l^{-1} in sea water from Cochin, India and UAE coastal waters respectively. Ajmal and Uddin (1986a) reported that Pb residue in running water at the Aligarh University campus ranged from 0.5 to 2.5 μg l^{-1} compared to 0.8-5.5 μg l^{-1} for standing tap water. Hand pump water from Aligarh city had higher Pb residue up to 25 μg l^{-1}. The prescribed maximum lead concentration in inland waters by Environmental Protection Rules of Environmental Protection Act (1986) is 0.1 μg l^{-1} and lead in surface waters of all the abovesaid stations recorded well below the limit.

Selenium is a potentially toxic contaminant of surface water and may bioaccumulate to relatively high levels in fishes and other aquatic species. In general, post-monsoon being the most productive season in this region may have influenced the higher availability of Se along with other elements. Cutter (1989) noted that dissolved Se residues in fresh waters range from <0.1 to 5 μg l^{-1} when there are no major anthropogenic inputs. Average Se concentrations between the stations were 2.70 and 8.46 μg l^{-1} and the occurrence was seasonal. Several selenium complexes with different chemical and toxicological properties exist in the environment, and detailed information regarding the fate of those compounds is lacking.

The average copper levels ranged from 7.57 to 11.19 $\mu g\ l^{-1}$ and are present in the river system in all the seasons. It may be noted that station 1 is an important back water tourist destination where about 300 number of house boats are berthed and also the area is having different small scale industrial units. Copper contamination in the estuarine system mainly comes from agricultural inputs like copper containing pesticides, fungicides, antifouling paints from tourist/recreational crafts, increased human intervention from tourism and hospitality industry etc. According to Ph.Monbet (2004) long term intensive manure application can be responsible for elevated copper content in the surface soils. During rainy season the copper stored in the soil leached out and joined in the hydrological system. This agrees with our findings as the monsoon season recorded maximum copper in all the stations since these estuarine areas are very close to agricultural catchments. Ajmal and Uddin (1986a, b) reported 0.001-0.015 mg kg^{-1} of copper in running water samples of Aligarh University, India. Copper is regarded as an essential micronutrient because of its key role in many enzymatic reactions. The minimum dietary requirement of human beings is 0.0001 mg/day (Federal Registers, 1985).

Manganese concentration in all the estuaries were in trace levels and its occurrence was only during pre-monsoon season. Studies on the seasonal changes of cadmium and manganese in Hudson River by Yang and SaZudo-Wilhelmy (1998) showed that higher Mn was detected during low fresh water discharge season which implies that limited hydraulic flushing allows a build-up of metals in the water column. According to them dissolved Mn levels (range: 0.033-1.46 mM) have remained relatively constant over the same period of time, suggesting that anthropogenic sources have very limited impact on Mn concentrations in the estuary. Manganese exists in oxidation states Mn^{2+} (manganous) and Mn^{4+} (manganic) states are most important in aqueous system.

Vanadium is an essential micronutrient for chlorophyll development and its presence indicates the productivity. Vanadium residues in fresh water generally range from <0.5 to 50 $\mu g\ l^{-1}$ (Moore, 1991). In Srilanka, Dissenayake et al. (1987) reported that concentration in an urban canal averaged 18 $\mu g\ l^{-1}$ with range of 2-45 $\mu g\ l^{-1}$. The canal received waste water from both industrial and municipal sources. Vanadium has a number of possible oxidation states V^o, V^+. V^{2+}, V^{3+}, V^{4+} and V^{5+}. The pentavalent form is most stable and is primary agent of transport in surface waters. Vanadium can be oxidized to V^{5+} from V^{4+} and becomes soluble in water. Vanadium concentration does not pose a threat to surface waters except in localized stations. There is no evidence that concentrations of vanadium through the food chain and all compounds appear to be relatively non-toxic to aquatic species (Moore, 1991). Zinc is another nutrient element present at significantly higher level in all the stations and seasons. Zinc concentration in Cochin (Krishnakumar et al., 2004) and Mumbai (Dhage et al., 2005) coastal waters was 318 and 0-46 $\mu g\ l^{-1}$ respectively. Higher concentration of zinc in pre-monsoon was due to the concentrating effect of the dissolved metals occuring in the water due to evaporation. Sridhar (1986) reported that the total zinc in the influent of Awba lake, Nigeria ranged from 2.4 to 6.4 $\mu g\ l^{-1}$, but declined to only 0.4-5.1 $\mu g\ l^{-1}$ after passing through a growth of the water lettuce *Pistia stratiotes*, that gave a reduction of 20-83%. Zinc is classified as borderline metal which means that it forms bonds with oxygen as well as N and S donor atoms. Under aerobic conditions $Zn^{2+}$is the predominant species at acidic pH, but is replaced by $Zn(OH)_2$ at pH 8-11 and $Zn(OH)^{3-}/Zn(OH)_4^{2-}$ at pH >11 (Vymazal, 1985). Anaerobic conditions lead to the formation of ZnS regardless of pH within the range of 1-14.

Comparison of Data with Other Estuarine Systems

Comparative evaluation of heavy metal concentration reported in the estuaries different region are compiled and presented in Table 1. The ranges of metals given in the table are higher but closer evaluation of the data clearly revealed that the occurrence of metals is purely on seasonal and also the averages of each elements in a year are in traces. The presence of zinc and copper reported by the authors are higher among the other metals studied. The data of the present study revealed that the contaminations of metals in the estuaries of south Kerala are comparable with other regions. Trace metals are essential micronutrients and required for various body functions and well being of the immune system. In a detailed review Chaturvedi et al. (2004) presented the interaction of viral diseases vs heavy metals. In one of our study we found that the exchangeable zinc, potassium and magnesium were higher in the sediments of a viral disease affected aquaculture system (Ashraf and Edwin, 2003). No concrete study has been carried out on the role metal constituents present in the water and sediments against viral diseases in aquaculture system except microbial pollution. There is an urgent need of an integrated study on the role of heavy metals along with microbiological and virological aspects.

The study revealed significantly higher level of zinc and copper and their presence was maximum during pre-monsoon and monsoon seasons respectively. Increased

Table 1: Comparative evaluation of heavy metals reported in estuaries of different regions of the world with present study

Location	*Cd*	*Cu*	*Zn*	*Pb*	*Cr*	*Mn*
Present study	0-9 μg l^{-1}	0-60.3 μg l^{-1}	0-88 μg l^{-1}	0-19.7 μg l^{-1}	0-35 μg l^{-1}	0-3.2 μg l^{-1}
Cochin coastal waters (Krishanakumar et al., 2004)	8.14 μg l^{-1}	17.14 μg l^{-1}	318 μg l^{-1}	5.94 μg l^{-1}	-	-
Mumbai coastal waters (Dhage et al., 2005)	2-24 μg l^{-1}	-	0-46 μg l^{-1}	Nd	0-30 μg l^{-1}	-
UAE coastal waters (Banat et al., 1998)	0.2-0.3 μg l^{-1}	2.6-3.4 μg l^{-1}	8.6-11.9 μg l^{-1}	0.84-1.25 μg l^{-1}	0.2-0.29 μg l^{-1}	0.7-1.3 μg l^{-1}
East river (Dongjiang) (Ho and Hui, 2001)	-	0.05-0.58 μg g^{-1}	0-1.35 μg g^{-1}	-	-	-
Rio Grande (Rios-Arana et al., 2003)	-	-	0.128 μg g^{-1}	0.077 μg g^{-1}	-	-
Hudson river (Yang and Sañudo-Wilhemy, 1998)	0-1.19 nM	-	-	-	-	0.11-1.46 nM

levels of lead and vanadium were detected during monsoon and trace levels of Ni, Mn, As, Se, Cd and Sb recorded in different seasons. Metal concentrations in most of the samples/stations were well below the limit prescribed.

Acknowledgements

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