Journal of Environment and Earth Science www.iiste.org
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol 1, No.1, 2011

Identification of heavy metals contamination by multivariate statistical analysis methods in Pondicherry mangroves, India

P. Satheeshkumar[1*], D. Senthilkumar [2]

1. Department of Ecology and Environmental Sciences, Pondicherry University, Puducherry, India-605014

2. Kandaswamy Kandar Arts and Science College, Department of Zoology,

Paramathy-Velur, Tamilnadu, India-638181

*Email of the corresponding author: indianscientsathish@gmail.com

Abstract

Pondicherry mangroves received a heavy influx of sewage, industrial effluents; domestic and agricultural waste which consists of varying hazardous chemical and causing deleterious effects on fish and other aquatic organisms. Surface water and sediments (0-5 cm) were collected in two locations from the Pondicherry mangroves, India. Fractionation of the metals in Zn, Cu, Fe, Mn, Cd & Hg was investigated. Cluster analysis, principal componenent analysis and multidimensional scale plot were employed to evaluate tropic status of pollution for monitoring the present study stations. This study confirmed that source of water and sediment heavy metals concentration followed the hierarchy; Fe>Zn>Mn>Cu>Cd>Hg in estuary. An important observation is that, in general lowest heavy metal concentrations are found during summer, compared Post, pre and monsoon. Enrichment factor values of station 2; sediments reveal unpolluted nature and the positive correlation among Fe, Mn and other heavy metals indicate the influence of early diagnostic process.

Keywords: correlation, estuary, heavy metal, Pondicherry, sediment, water

1. Introduction

Pollution of the natural environment by heavy metals is a worldwide problem because these metals are permanent and most of them have toxic effects on living organisms when they exceed a certain concentration (Chakraborty *et al.* 2009). In coastal environments and estuaries, which are often characterized by large industrial settlements and urban areas, the impact of effluent discharges leads to the accumulation of contaminants such as heavy metals and organometallic and persistent organic pollutants (Ridgway & Shimmield 2002). Heavy metals are introduced anthropogenically as pollutants into lotic and lenthic aquatic ecosystems from industrial, agricultural and domestic wastewater / effluents (Ho *et al.* 2003). Concentration of metals in sediment of the Indian waters has been documented by (Mitra *et al.* 1996; Hema Achyuthan *et al.* 2002; Agoramoorthy *et al.* 2008). Discharge of greater quantity pollutants into the aquatic environment may result into deterioration of ecological imbalance, changes the physical and chemical nature of the water and aquatic biota (Mitra *et al.*1996).

Mangrove environment of Pondicherry is important as supports the local fishing activities, nursery grounds for many fish and shellfish species, and as well as being central ecotourism activities. Pondicherry coastal area is polluted due to discharge of industrial, domestic and agricultural wastes through small tributaries and channels in to the Bay of Bengal. Ariyankuppam estuary is regarded as one of the most polluted estuaries in Pondicherry, due to a long history of contamination, and as a result sediments are seriously affected by metal pollution (Ananthan *et al.* 2004). It is difficult to quantify anthropogenic input of heavy metals into many polluted environments as frequently no direct evidence of heavy metal content in sediments from pre-industrial periods (De Groot *et al.* 1976). Marine sediments are very important accumulation site of metals in the coastal areas; therefore analyses of these metals are important to assess the degree of pollution in the marine environment. Hence, the present study has been made to survey metals composition of mangroves in relation to their surrounding water and sediment. The primary objectives of the present study was to obtain a preliminary assessment about the levels and spatial distribution of these selected elements, to estimate the total concentrations of the heavy metals in the water and sediments at Pondicherry mangroves and to evaluate the grain size effect on metal levels in the sediments.

2. Materials and Method

2.1 Study site

The Pondicherry mangrove is located between latitudes 11°46'03" to 11°53'40" N and longitudes 79°49'45" to 79°48'00" E (Figure 1). Mangrove exists as fringing vegetation over 168 ha distributed along the sides of Ariankuppam estuary, which is seasonally bar-built and semi diurnal type that flows eastwards and empties into the Bay of Bengal at Veerampatinam, carrying wastes from adjacent agriculture lands and industries in addition to domestic municipal and distillery effluents. These estuaries with their wetlands, lagoons, mangroves and sea-grass beds are rich in natural resources including fisheries. They also offer tremendous potential for recreation, aquaculture, and extraction of freshwater and transport and play a dominant role in the economy of coastal population. Our present investigation was carried out in two stations: 1 Ariyankuppam, 2 Veerampattinam. Triplicate samples were collected every month for one year from October 2008 to September 2009, For the sake of interpreting the data, a calendar year wise divided into four main seasons, viz pre monsoon (July-September), monsoon (October-December), post monsoon (January-March), summer (April-June).

2.2 Sampling and analysis

Water samples collected from two stations in mangrove (three sites from each station). All water samples were kept in clean polyethylene bottles. Finally samples were acidified with 10 % HNO3, placed in an ice box and then brought back to the laboratory for analysis. Dissolved oxygen was estimated by the modified Winkler's methods and sulphide by (Strickland and Parsons 1972), salinity with hand Refractometer (ERMA), water pH and temperature (hand water pH meter pH scan-2), electrical conductivity (EC) was measured using an electrical conductivity instrument (Elico). Sediment texture (Krumbein and Pettijhon 1983) was determined by pipette analysis method. Organic matter (OM) of the sediment was determined by wet oxidation method (Elwakeel and Riley 1957).

Sediment samples were collected from each a clean and dried corer and samples were transformed to clean polyethylene covers. Samples were stored frozen until analysis. Sediment samples were separated in to fine and coarse material by sieving in the laboratory, prior to analysis of 63 < μm dry fraction by microwave *2.3* digestion using nitric acid, this dissolution of the biological material after freeze drying. Determination of metal concentration was undertaken using ICP-AES (Inductive Coupled Plasma- Atomic Emission Spectroscopy).

2.3 Estimation of heavy metal enrichment

A common approach to estimating anthropogenic impact on water and sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Salomons and Forstner 1984). The EF measured in heavy metal content with respect to a sample reference metal such as Fe or Al (Ravichandran *et al.*1995). Due to the lack of geochemical background value of the study areas an alternative of the average crustal concentrations as reference material. In this approach Fe or Al is considered to act as a "proxy" for the clay content (Windom *et al.*1989; Din 1992). Deely and Fergusson (1994) proposed Fe as an acceptable normalization element to be used in the calculation of the enrichment factor since they consider the Fe distribution which was not related to other heavy metals (Table 1). In the present study EF values were applied to evaluate the dominant source of sediment and as indicator for pollution effects.

The EF is calculated according to the following equation:

$EF = Mx / Feb \div Mb / Fex$

Where Mx and Fex are the sediment sample concentrations of the heavy metal and Fe (or other normalizing element), while Mb and Feb are their concentrations in a suitable background or baseline reference material (Salomons and Forstner 1984).

2.4 Statistical analysis

Co- efficient of correlation (r) was calculated in order to understand relationship among variables. Significant of the models was also tested using correlation co efficient. Mean and standard deviation were calculated for each parameter. All these statistical analyses were performed using SPSS statistics (Version 7.5 for Windows XP, SPSS, and Chicago, IL, USA). The multivariate statistical techniques such as Cluster analysis (CA), Non- Multidimensional scale plot (MDS) and Principal Component analysis (PCA) have widely been used as unbiased methods in analysis of water quality data for drawing meaningful conclusions (Simenov *et al.* 2003; Yongming *et al.* 2006). CA was applied to heavy metals in water and sediment data using a wards method. Cluster analysis was again used to find homogeneous groups of samples on the basis of their geochemical and granulometric compositions.

Multivariate analysis was performed using PAST (statistical Version 1.93 for Windows XP). In the present study, the efficiency of different multivariate statistical techniques (CA, PCA and MDS) is applied to evaluate heavy metal pollution status of Pondicherry Coast. Cluster analysis was used to identify similar groups of temporal and spatial variations of water quality; the temporal and spatial patterns of trophic status were also determined by principal component analysis.

3. Results

3.1 Physico- chemical characteristics of water

This study showed that in general physical properties of water and ancillary parameters such as grain size and total organic matter were also determined. The results of physico-chemical parameters of water and sediment characteristics in the study area are shown in (Table 2). Surface water temperature ranged between 16.66 ℃ - 37.91 ℃ maximum during summer and minimum during monsoon. The salinity distribution indicated strongly mixed estuarine characteristics with the salinity increasing in the summer. Salinity showed wide variations in the ranges 6.36 - 36.77 ppt. Generally, changes in the salinity of the brackish water habitats such as estuaries, backwaters and mangrove are due to the influx of freshwater from land run off, caused by monsoon or by tidal variations.

The dissolved oxygen concentration in the surface water were generally high (5.17 ml/l) during monsoon and low (3. 94 mg/L.) during summer. Season-wise observation of dissolved oxygen showed an inverse trend against temperature and salinity, it is well known that temperature and salinity affect the dissolution of oxygen. pH in surface waters remained alkaline throughout the study period, they varied from 7.26 to 8.31, Whereas maximum during summer and minimum in monsoon. EC at two stations varied from 26.65-52 mS/cm with maximum EC (52 mS/cm) recorded at station 2. Seasonal mean fluctuations recorded in the sulphide concentration varied from 2.76 - 47.16 mg/l respectively with maximum during pre and post monsoon. In the present investigation maximum content of sulphide (47.16 mg/l) was recorded at station 1 on September. Significant negative correlation between sulphide and DO ($r = -0.601$; $P<0.05$) at station 1 indicates that DO is largely influenced by sulphide at this station.

3.2 Sediment characteristics

Seasonal variations in sediment components and OM are detailed here below (Table 3).The substratum was mainly composed of sand with an admixture of silt and clay. Sand fraction ranged between (67.60 - 87.31 %) followed by silt (9.89-24.21 %) and clay (3.06-10.49 %). Seasonally, station 1 recorded higher fractions of sand during monsoon and summer, silt content during post monsoon and pre monsoon period and clay during summer season. Such differed combinations of sediment observed were mainly due to the transport of sediments from one place to another and back associations with tidal currents. Soil texture, sand, silt and clay showed significant correlations at $P<0.01$. In general sand is dominating in the upper estuarine region i.e. at station 1 whereas silt, clay and OM are mostly enriched in the lower part of the mangrove sediments. Organic matter distribution is associated with estuary and hydrodynamic factors, and its levels explain the black color and H_2S odor of the sediments.

3.3 Heavy metal distributions in water and sediments

The average concentration of surface water was shown in Table 4. Monthly variation of different heavy metal concentrations were observed, correlation revealed that both spatial and temporal variations of all metals were significant. The magnitude of different heavy metals followed hierarchy, Fe>Zn>Mn>Cu>Cd>Hg. In this present study, Fe varied from 3-133.2 µg/g followed by Zn 2.95-69.9 µg/g ;Mn 1.8-14.7 µg/g ; Cu 0.72-7 µg/g; Cd 0.03-3.01 µg/g and Hg 0.1-3.01 µg/g. However, the seasonal variation was remarkable and the maximum discharges occur consistently during monsoon and the minimum in summer. The concentration of Mn in this study positively correlated to the concentration of Cu and Fe ($p < 0.01$), respectively the concentration of Zn was positively correlated with Fe and Cu ($p < 0.01$).

Heavy metal concentrations in sediments are shown in Table 5. The hierarchy of heavy metals are as follows, Fe>Zn>Mn>Cu>Cd>Hg. In this present study, Fe ranged from 360-1440 µg/g; Mn 105-787 µg/g; Zn 310-1140 µg/g; Cu 25-482µg/g; Cd 0.39-9.02 µg/g and Hg 0.21-6.93 respectively. Maximum concentrations of heavy metals were observed during monsoon and their concentrations were gradually decreased from onset of post monsoon and they reach as minimum in summer. Comparisons of the metal levels in the sediments from different areas of estuary indicate that there is a detectable anthropogenic input into the Pondicherry mangroves. The concentration of Hg in this study positively correlated to the concentration of Zn ($p < 0.05$), respectively the concentration of Mn and Cu was positively correlated with Fe ($p < 0.01$) Table 7.

3.4 Correlation of heavy metals with environmental parameters

The correlation of heavy metals concentration in water and sediment samples from Pondicherry coast were examined and given in Table 6 and 7. Correlation analysis also revealed close relationships between individual elements, Fe and Zn (r = 0.957), Mn and Zn (r = 0.859), Cu and Fe (r =0.960), Cd and Hg (r = 0.734) these results could suggest Fe and Mn compounds in the surface sediments are very effective scavengers of other metals. Mn showed positive correlation with Fe in all the sites and this may be explained as redox cycling of Mn that mainly controls Fe in the study area. The Physico- chemical parameters of water indicated high positive correlation that exist between DO with Mn (r= 0.913; $P<0.01$), Fe (r = 0.738; $P<0.05$), Zn (r = 0.711; $P<0.05$), Cu (r = 0.708; $P<0.05$) and also a positive correlation was observed between sulphide and Fe (r = 0.789; $P<0.05$). A high negative correlation was observed between salinity and Cd (r = -0.920; $P<0.01$), salinity and Hg (r = -0.732; $P<0.05$), temperature and Cd (r = -0.918; $P<0.01$), temperature and Hg (r = -0.771; $P<0.05$), pH and Hg (r = -0.732; $P<0.05$) respectively. Among sediments clay has been exhibit positive correlation with Cd (r = 0.722; $P<0.05$) and Hg (r = 0.891; $P<0.01$), negative correlation were observed between sand and Hg (r = -0.732; $P<0.05$), OM and Fe (r = -0.840; $P<0.01$), OM and Zn (r = -0.759; $P<0.05$). This suggests that these metals are significantly associated with clay and silt, clay-sized constituents of the surface sediments. Results showed that municipal and domestic discharges to the river through the populated urban area contained high concentrations of heavy metals.

3.5 Enrichment factor

Sediment Enrichment of Mn and Zn was lower in comparison, reflecting their ability to be efficiently regulated. The EF varied from a low of 0.001 for Mn (Pre monsoon) to a high of 947.5 for Fe in Monsoon season. Enrichment of water low in Zn (0.001) on summer and to a high of Fe (87.66) in monsoon and Hg in during Pre monsoon; In contrast high EF values of Fe and Cu indicate anthropogenic source for this metal. In particular very high EF values of Fe from this anthropogenic source of metal. Very high positive correlation of Zn and Cu in water (0.970) and sediment (0.979) clearly indicates that these elements were derived from weathering materials of upper crust and associated with high organic contents, is indicative of the influence of organic wastes from municipal sewage entering the mangrove environment at Pondicherry.

3.6 Multivariate statistical analysis

Cluster analysis (CA) was used to detect similar groups between the sampling sites in four seasons. Bray-Curtis similarities were calculated on (root transformed) between the physico-chemical parameters of water and sediment characteristics and heavy metals at two stations and result is depicted, based on which two distinct community groupings could be distinguished that apparently reflected differences in sediment /habitat types with in Pondicherry coast. The achieved dendogram is displayed in water and sediments heavy metal (Figure 2, 3). Group A included MS1, PRM1, PMS1 and SS1 (all the sampling station 1) and Group B included MS2, PRM2, PMS2 and SS2 (all the sampling station 2) correspond to a relatively low pollution, high pollution regions, respectively. From the resulting dendrogram, it is possible to grade the results according to season and stations. The station 1 showed separation from the remaining station 2, except monsoon season in water strongly influenced by season, with the monsoon season being associated with much higher levels of nutrients and sediments than the dry season.

The results from temporal PCA suggested that most of the variations in mangrove water quality are explained by the soluble salts (natural), toxic metals (industrial), nutrients (non-point) and organic pollutants (anthropogenic). However, PCA served as a means to identify those parameters, which have greatest contribution to temporal variation in the mangrove water quality and suggested possible sets of pollution sources in each of the catchments regions of the Pondicherry coast. The data were distributed in a limited region of space spanned by the PCA well-defined axes (Figure 4, 5). Group A included MS1, PRM1, PMS1 and SS1 and Group B included MS2, PRM2, PMS2 and SS2. Station 2 had positive values in group 2, they had higher concentration of sulphide and OM. Similar approach based on PCA for evaluation of temporal and spatial variations in water quality has earlier been used (Vega *et al.* 1998). However, from the PCA results, it may convincingly be presumed that in all the four regions under study, pollution is mainly from agricultural run-off, leaching from solid waste disposal sites, domestic and industrial wastewater disposal. It can be concluded for the MDS (Figure 6 and 7), it was found that all the station 1 were ordinate separately from the station 2 which conform to the dendogram. From the above discussion, we can say that CA, MDS and PCA are a useful tool to analyze the pollution source and monitoring sites. It can offer information to identify polluted sites and help in the decision making on controlling of water pollution.

4. Discussion

Estuaries are highly dynamic systems from both a chemical and physical point of view. Sharp gradients in parameters such as salinity, temperature, pH, dissolved oxygen induce considerable biogeochemical reactivity and model the behaviour of trace elements in the system (Murray *et al.* 1999; Wang *et al.* 2007). Dissolved heavy metals Cu and Zn presented a maximum at relatively high salinity and decreased seawards, following the same behavior observed for Cd. Higher values of Cu and Zn profiles have also been observed in upper estuary (Owens and Balls, 1993). In most cases metal concentrations were lowest near the mouth of estuary. This is to be expected, since Adyar estuary acts as a sink for trace metals supplied by rivers and storm water canals that feed the estuary (Hema Achyuthan *et al.* 2002). EC variations were not random. In estuaries, EC is highly influenced by the mixing of river and seawater. The volume ratio of each source will control the salinity, Hence EC may not be a factor controlling the seasonal variation of the studied metals, these similar results corroborate with (Papafilippaki *et al.* 2008). This ratio is obviously controlled by the tidal coefficient recorded during samplings. Besides, EC hardly ever controls metal contents in natural water; this role is played by pH and redox conditions that possibly enhanced metal speciation.

Concentrations of heavy metals increase in the estuarine mud due to decrease of grain size, and increase an OM, pH and input of anthropogenic metals from industrial pollution. In addition to the heavy metal inputs, sediment grain size plays a significant role in the accumulation of heavy metals in tidal flats (Xu *et al.* 1997). The high concentrations of heavy metals at station 1 correspond well to an increase in the clay fractions in these sediments, although samples from station 2 have low heavy metal concentration due to the fact that they are relatively coarse compared to their counter parts at station1. The high concentrations of heavy metals at station 1 have considerable significance in terms of sewage discharge in the Pondicherry coast; these similar results were reported by (Zhang *et al.* 2001) at Yangtze Estuary, China. Atkins (1953) noticed adsorption consequent settlement by particulate matter is another reason for low concentration of metals in waters.

Concentrations of available and total particulate Fe maximum in the uppermost estuary mean while Mn has significantly high concentrations in the lower estuary. Zwolsman and van Eck (1999) found similar distributions of particulate Fe and Mn concentrations in estuaries elsewhere. The maximum seasonal averages of the dissolved Fe found in monsoon, possibly reflect the higher amounts of river runoff input in this season. An elevated concentration of Fe was observed in sampling station 1 where the domestic sewage and industrial waste water and medical hospital waste were discharged directly into the river. On the other hand, concentrations of Mn in the estuarine sediments were lower than the background level, 400±850 mg g^{-1} as quoted by Deely and Fergusson (1994). Pollution of aquatic environment by man directly or indirectly results in impairment of water quality with respect to its use in agricultural, industrial, and recreational activities. Results showed that municipal and domestic discharges to the river through the populated urban area contained high concentrations of heavy metals.

It is well established that OM contents are important controlling factors in the abundance of trace metals (Rubio *et al.* 2000). The organic matter content of the sediments showed negatively correlated with Fe and Zn (Table 7). The statistical analysis of intermetallic relationship revealed that the high degree correlation among metals indicate the identical behavior of metals during its transport in the estuarine environment. In the present study, poor associations of Mn with other metals (Cu and Hg) suggest that Mn – oxide may be only a minor host phase for these elements in the Pondicherry estuarine environment.

Zn shows strong positive correlations with Fe and Mn and significant correlation with Cu. Donazzolo *et al.* (1984) suggested that abnormally Zn concentrations found in samples collected offshore are related to industrial tailing and wastes. The correlation of Zn with Fe is ($r = 0.73$, $P< 0.05$), Mn ($r = 0.68$, $P< 0.05$); so, it can be clearly confirmed that high levels of this element are related to the presence of diffuse anthropogenic activities (e.g., residential effluents, city runoff). There are significant correlations between Fe and Cu with Mn, positive correlations are also revealed for Mn with Hg. The WHO (1996) recommended value for Zn in water for domestic supply is 3 mg/l and should not be a problem if the water is used for domestic purpose. Hence the significant amount of Zn present in the most available fraction is likely to be due the presence of anthropogenic sources, and Zn cans in garbage moulds, rusty and unwanted galvanized scars. The maximum seasonal average of the dissolved Cu found in monsoon, inspite of higher amounts of riverine input in this season. Inspite of the lowest river discharge, the summer average value of the dissolved Cu was lower than those in the pre and post monsoon in the studied area. High concentrations of these metals occurred in the sampling station 1, Cu contents ranged from water 1.6-7 µg/g and sediment 80-482µg/g; with the highest value found in station 1 (482 µg/g). This element is well correlated with OM ($r = 0.844$, $P < 0.05$), thus suggesting that organic matter contributes in controlling its distribution. Decomposition of OM and ion-exchange controlled the release of about one-third of the Cu bound to large particles reported by Sung (1995).

Cd is one of the most dangerous pollutants due to its high-potential toxic effects. Cadmium is extremely toxic and the primary use of water high in Cd could cause adverse health effect to consumers such as renal disease and cancer (Fatoki *et al.* 2002 and Passos *et al.* 2010). The WHO and EPA has established a human health based guideline of 0.003 mg/l for drinking water (USEPA 1996 and WHO 1996). These guidelines were exceeded at all the sampling sites. In view of the fact that major use of the water is domestic, high levels of Cd in the estuary is of great concern. The probable sources of Cd in the estuary are from natural sources due to the catchment soils and runoffs from agricultural soils where phosphate fertilizers have often been used since Cd is a common impurity in phosphate fertilizers. Other probable sources include leachates from disused nickel–cadmium based batteries and cadmium-plated items that are disposed at refuse dumps by the communities. Hg is highly toxic metal and these high concentrations need to be investigated further to assess the present sources and pathways of this metal in Ariyankuppam estuary. Among heavy metals, mercury deserves particular attention due to its high toxicity and tendency to bioaccumulation and biomagnifying in aquatic organisms. The low correlation between sand and Hg ($r= 0.327$, $P<0.05$), this indicates that Hg must not be common on sandy sediments. Similar studies conducted by Jain (2004), using sediment from the Yamuna river (India), highly polluted by contaminants contained in domestic and industrial effluents, resulting in a high risk to environment.

Cluster analysis was used to identify the similarity groups between the sampling sites. It implies that for rapid assessment of heavy metals only one site in each group may serve as good in spatial assessment of the heavy metals as the whole network. It is evident that the CA technique is useful in affording reliable classification of heavy metals in the whole region and will make possible to design a future spatial sampling strategy in an optimal manner. It can be concluded from the CA, PCA and MDS results shows station 1 highly polluted by anthropogenic sources and industrial effluents in Pondicherry estuarine environment. The anthropogenic source is probably the major mechanism, However from the enrichment factor values, it is obvious that along the south east coast of India, sediments are depleted Fe, Mn, Zn and Cu; Enriched with Fe and Cu in the midst of respect to upper crustal composition. On the other hand, Zn is very close to upper crustal value in all the seasons are depleted when comparing to UCC. Higher EF values of Fe, Cu and Hg in all the locations clearly suggest the influence of anthropogenic sources/ industry effluents of these three heavy metals. Therefore, the study area is assumed to be heavily affected by industry and sewage run-offs. The enrichment factor analysis is used to differentiate between anthropogenic and naturally occurring metal source and also to assess the anthropogenic influence in sediment samples (Wang *et al.* 2007).

Conclusions

It is observed that, in general, lowest heavy metal concentration are found during the summer and compared to post, pre and monsoon. Relatively high seasonal averages of dissolved Fe and Zn were found in monsoon, and those Cd and Hg were found in post monsoon. The relative variability followed the order Fe>Zn>Mn>Cu>Cd>Hg water and sediment. Our results clearly indicate that Fe>Zn> Cu >Cd>Hg high in station1. The sediment heavy metal contamination of these mangroves is a cause for concern as these metals may undergo bioaccumulation and affect the benthic organisms.

The seasonal variation of the studied heavy metals may be related to the variations of DO, pH, salinity, temperature and sulphide with sediment characteristics such as sand, clay and OM. Correlation with organic matter have allowed to understand the distribution of metals and its association within the sediments. Correlation between the studied metals and DO were satisfying, but with EC was observed no remarkable relationship. Clay rich sediments together with a downstream location relative to the sewage outlets result in elevated concentration of heavy metals at station 1. This implies that the accumulation of heavy metals is not dependent only on the closeness to contaminant sources, but also on the pattern of sediment transport and sedimentation with estuarine hydrodynamics.

In this case study, different multivariate statistical techniques were used an assessment of heavy metal pollution status in Pondicherry estuarine water and sediment. Based on the results multivariate analyses CA, PCA and MDS can be used as available tool to provide information of pollution status of heavy metal in the Pondicherry Mangroves. The estuary is exposed to sewage waste water from industries, urban waste water and agricultural runoff all contributing to the current condition of the sources contaminating the Pondicherry coast. In addition, H_2S pollution from both agricultural and industrial inputs deteriorates the water quality of estuary ecosystem at station 1 and 2. It can be recommended that accumulation of heavy metals in the region should be stopped. As a result it is essential that Pondicherry estuary and mangrove health in coastal environment monitoring is urgently required.

Acknowledgements
Authors thank the University Grants Commission, Government of India for the financial support. The authors thank the authorities of Pondicherry University for providing necessary facilities.

References

Agoramoorthy, Fu-An Chen, Minna J. & Hsu. (2008), "Threat of heavy metal pollution in halophytic and mangrove plants of Tamilnadu, India" *Environmental Pollution* **155,** 320-326.

Ananthan, G.A., Sampathkumar, P. Soundarapandian, P. & Kannan, L. (2005), "Observation on environmental characteristics of Ariyankuppam estuary and Veerampattinam coast of Pondicherry, India" *Journal of Aquatic Biology* **19,** 67-72.

Atkins, W.R.G. (1953), "Seasonal variations in the copper content of sea water" *Journal of Marine Biological Association of UK* **31,** 493-494.

Chakra borty, R. Zaman, S. Mukhopadhyay, N. Banerjee, K. & Mitra, A. (2009), "Seasonal variation of Zn, Cu and Pb in the estuarine stretch of west Bengal" *Indian Journal of Marine Science* **38**(1), 104-109.

De Groot, A.J., Salomons, W. & Allersma, E. (1976), "Processes affecting heavy metals in estuarine sediments" In: Burton, J.D., Liss, P.S. (Eds.), Estuarine Chemistry. Academic Press, London, pp. 131-157.

Deely, J.M., & Fergusson, J.E. (1994), "Heavy metal and organic matter concentration and distributions in dated sediments of a small estuary adjacent to a small urban area" *Science and Total Environment* **153**, 97–111.

Din, T.B. (1992), "Use of aluminum to normalize heavy metal data from estuarine and coastal sediments of straits of Melaka" *Marine Pollution Bulletin* **24**, 484–491.

El Wakeel, S.K., & Riley, J.P. (1957), "The determination of organic carbon in marine muds" *Conseil Per Inter Exp J* **22,** 180-183.

Fatoki, O.S., Lujiza, N. & Ogunfowokon, A.O. (2002), "Trace metal pollution in Umtata River" Water SA, vol. 28, No. 2. Pretoria. pp. 183–189.

Hema Achyuthan, D. Richardmohan, S. Srinivasalu, & Selavaraj, K. (2002), "Trace metals concentrations in the sediment cores of estuary and tidal zones between Chennai and Pondicherry, along the east coast of India" *Indian Journal of Marine Science* **21**, 141-149.

Ho, S.T., Tsai, L.J. & Yu, K.C. (2003), "Correlations among aqua- regia extractable heavy metals in vertical river sediments" Diffuse Pollution Conférence, Dublin. pp. 12-18.

Jain, C.K. (2004), "Metal fractionation study on bed sediments of River Yamuna, India" *Water Research* **38**, 569 – 578.

Krumbein, W.C., & Petttijohn, F.J. (1983), "Manual of sedimentary Petrography Appleton Century-Crafts Inc" New York.

Mitra, A.S., Trivedi, A. Gupta, Abhijit Choudhury, Amalesh Choudhury. (1996), "Distribution of trace metals in the sediments from Hooghly estuary, India" *Pollution Research* **15**, 137-141.

Murray, K.S., Cauvent, D. Lybeer, M. & Thomas, J.C. (1999), "Particle size and chemical control of heavy metals in bed sediment from the Rouge River, southeast Michigan" *Environment Science and Technology* **33**, 397–404.

Owens, R.E., & Balls, P.W. (1993), "Dissolved trace metals in the Tay estuary" *Estuarine, Coastal and Shelf Science* **44**, 421–434.

Papafilippaki, A.K., Kotti, M.E. & Stavroulakis, G.G. (2008), "Seasonal variations in dissolved heavy metals in the Keritis River, chania, Greece" *Global NEST Journal* **3**, 320-325.

Passos, E.A., Jeferson, C. Alves, Izaias, S. dos Santos, Patrocínio, H. Alves, Carlos Alexandre, B. Garcia, Antonio, & Spinola Costa, C. (2010), "Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis" *Micro Chemistry* **96**, 50–57.

Ravichandran, M. Baskaran, M. Santschi, P.H. & Bianchi (1995), "History of trace metal pollution in Sabine- Neches Estuary, Beaumont, Texas" *Environment Science and Technology* **29**, 1495–1503.

Ridgway, J. & Shimmield, G. (2002), "Estuaries as repositories of historical contamination and their impact on shelf areas" *Estuarine, Coastal and Shelf Science* **55**, 903–928.

Rubio, B. Nombela, M.A. & Vilas, F. (2000), “Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution” *Marine Pollution Bulletin* **40**, 968-980.

Salomons, W. & Forstner, U. (1984), “Metals in the hydro cycle” Springer, Berlin Heidelberg Tokyo.

Simeonov, V. Stratis, J.A. Samara, C. Zachariadis, G. Voutsa, D. Anthemidis, A. *et al.* (2003), “Assessment of the surface water quality in Northern Greece” *Water Research* **37**, 4119–4124.

Strickland, J.D.H, & Parsons, T.R. (1972), “A practical hand book of seawater analysis” Bulletin Fisheries Research Board, Canada.

Sung, W. (1995), “Some observation on surface partitioning of Cd, Cu and Zn in estuaries” *Environment Science and Technology* **29**, 1303–1312.

Vega, M. Pardo, R. Barrato, E. & Deban, L. (1998), “Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis” *Water Research* **32**, 3581–3592.

USEPA (1996), “Drinking water regulations and health advisories” EPA 822-R-96-001.

Wang, S. Cao, Z. Lan, D. Zheng, Z. & Li, G. (2007), “Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River estuary” *Environmental Geology* **55**(5), 963–975.

WHO (1996), “Health criteria and other supporting information” 2nd ed. Guidelines for drinking water, vol. 2, Geneva.

Windom, H.L., Smith, R.G. & Rawlinson, C. (1989), “Particulate trace metal composition and flux across the south eastern US continental shelf” *Marine Chemistry* **27**, 283–297.

Xu, S, Tao, J. & Chen, Z. (1997), “Dynamic accumulation of heavy metals in tidal flat sediments of Shanghai” *Oceanography and Limnology Sinca* **28**(5), 509-515.

Yongming, H. Peixuan, D. Junji, C. & Posmentier, E.S. (2006), “Multivariate analysis of heavy metal contamination in urban dusts of Xi’an, Central China” *Science and Total Environment* **355**, 176-118.

Zhang, W. Yu, L. & Hutchinson, S.M. (2001), “China’s Yangtze Estuary: I. Geomorphic influence on heavy metal accumulation in intertidal sediments” *Geomorphology* **41**, 195-205.

Zwolsman, J.J.G., & van Eck, G.T.M. (1999), “Geochemistry of major elements and trace metals in suspended matter of the Scheldt Estuary, southwest Netherlands” *Marine Chemistry* **66**, 91–111.

Table 1 Selected concentration in average continental crust

Element	Average continental Crust $_a$ (mg/kg)
Cu	45
Fe	46,000
Zn	95
Cd	0.3
Mn	800
Hg	0.5

Source: (Salomons and Forstner 1984)

Table 2. Seasonal variation of physico chemical parameters of water and sediments grain size composition at stations 1 and 2

Seasons	Salinity	T ℃	pH	DO	EC	Sulphide
Monsoon						
Station 1	15.67±3.92	22.55±4.82	7.26±0.17	4.86±0.16	36.48±4.53	13.75±11.6
Station 2	14.31±6.91	22.89±4.53	7.29±0.07	5.17±0.22	33.20±3.984	5.01±1.65
Post monsoon						
Station 1	21.77±2.50	23.39±0.81	8.02±0.43	5.02±0.41	39.19±6.71	17.64±4.26
Station 2	25.77±4.33	25.59±0.95	7.44±0.21	4.09±0.05	41.33±4.26	5.89±1.50
Summer						
Station 1	31.68±1.56	32.31±0.36	7.61±0.42	4.2±0.25	39.44±11.19	13.80±0.22
Station 2	35.20±2.34	35.85±0.09	8.31±0.14	3.94±0.27	34.83±9.07	4.19±1.28
Pre monsoon						
Station 1	27.85±2.64	28.45±2.59	7.56±0.12	4.28±0.24	36.51±8.54	26.25±6.88
Station 2	29.95±1.34	29.55±1.85	7.8±0.23	4.64±0.09	39.59±5.40	5.65±0.54

T ℃: temperature; DO: Dissolved oxygen; EC: Electrical conductivity, OM: Organic matter

Table 3. Seasonal variation of sediment composition and organic matter at stations 1-2.

Season	Sand (%)	Silt (%)	Clay (%)	OM (%)
Monsoon				
Station 1	82.38±3.64	13.12±11.81	4.5±1.59	0.94±0.31
Station 2	73.24±17.20	21.60±12.94	5.81±3.18	3.21±0.88
Post monsoon				
Station 1	72.40±16.31	16.66±14.41	10.01±0.84	1.58±0.31
Station 2	67.60±22.37	26.06±24.07	6.23±1.91	3.13±0.86
Summer				
Station 1	87.31±9.74	9.89±11.46	3.06±1.59	1.74±0.51
Station 2	75±11.48	15.31±8.64	10.49±10.23	3.64±0.45
Pre monsoon				
Station 1	71.83±21.02	24.21±20.75	4.04±0.42	1.12±0.30
Station 2	77.87±10.06	18.02±8.69	4.07±2.05	3.82±0.74

OM=Organic matter

Table 4. Seasonal variations of heavy metals in water recorded at stations 1 and 2.

Season	Cu (µg/g)	Fe (µg/g)	Zn (µg/g)	Mn (µg/g)	Hg (µg/g)	Cd(µg/g)
Monsoon						
Station 1	6.1 ±0.77	121.1 ±9.79	43.23 ±12.63	11.36 ±2.46	1.12 ±0.07	1.123 ±0.29
Station 2	1.21 ±0.08	4.96 ±0.23	3.72 ±0.094	2.36 ±0.04	2.41 ±0.427	2.08 ±0.73
Post monsoon						
Station 1	3.3 ±0.57	36.93 ±17.62	24.43 ±10.51	5.7 ±1.55	0.89 ±0.08	1.12 ±0.071
Station 2	1.03 ±0.72	4.47 ±0.38	3.21 ±0.14	2.204 ±0.065	1.08 ±0.14	1.71 ±0.35
Summer						
Station 1	2.6 ±0.09	11.3 ±6.92	6.6 ±2.66	2.86 ±0.99	0.44 ±0.25	0.82 ±0.91
Station 2	0.826 ±0.37	3.58 ±0.417	3.19 ±0.30	2.17 ±0.13	1.01 ±0.164	0.703 ±0.46
Pre monsoon						
Station 1	3.7 ±0.06	43.23 ±20.82	24.93 ±3.39	7.73 ±0.30	0.89 ±0.05	0.85 ±0.96
Station 2	1.01 ±0.04	4.12 ±0.105	3.62 ±0.07	2.31 ±0.07	1.2 ±0.2	1.49 ±0.49

Table 5. Seasonal variations of heavy metals in sediment recorded at stations 1 and 2.

Season	Cu (µg/g)	Fe (µg/g)	Zn (µg/g)	Mn (µg/g)	Hg (µg/g)	Cd (µg/g)
Monsoon						
Station 1	441.33 ±52.54	1395 ±14.57	1048 ±82.9	623 ±82.92	3.42 ±0.06	6.88 ±0.14
Station 2	46.66 ±2.08	476.66 ±163.77	455.33 ±25.48	260 ±25.48	6.13 ±0.73	8.01 ±1.04
Post monsoon						
Station 1	159.33 ±27.68	991 ±74.70	586.6 ±100.16	526.33 ±100.16	3.03 ±0.12	5.49 ±0.59
Station 2	37.66 ±3.05	441 ±127.57	344 ±21.16	138.33 ±21.16	4.88 ±0.14	5.27 ±0.82
Summer						
Station 1	98.66 ±22.05	765 ±30.89	520 ±100.37	201.66 ±100.37	1.55 ±1.30	2.26 ±2.22
Station 2	27 ±2.021	387 ±100	344.33 ±36.11	111.66 ±36.11	3.28 ±0.63	2.17 ±1.66
Pre monsoon						
Station 1	268 ±46.35	1119.33 ±44.44	901.33 ±117.85	403 ±117.85	3.04 ±0.10	2.93 ±2.53
Station 2	36 ±3.021	445 ±21.35	401.66 ±10.40	158.33 ±10.40	3.623 ±0.49	4.3 ±1.76

Journal of Environment and Earth Science www.iiste.org
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol 1, No.1, 2011

Table 6. Correlation of water heavy metals between physico-chemical parameters of water and sediment characteristics

	Cu	Fe	Mn	Zn	Hg	Cd	Salinity	pH	DO	EC	Sulphide	Sand	Silt	Clay	OM
Cu	1														
Fe	0.953	1													
Mn	0.966	0.968	1												
Zn	0.97	0.961	0.983	1											
Hg	-0.381	-0.21	-0.229	-0.298	1										
Cd	-0.147	-0.112	-0.093	-0.077	0.675	1									
Salinity	-0.262	-0.465	-0.385	-0.349	-0.737	-0.543	1								
pH	0.057	-0.21	-0.139	-0.056	-0.783	-0.34	0.844	1							
DO	0.736	0.721	0.771	0.779	0.165	0.534	-0.596	-0.2	1						
EC	-0.368	-0.421	-0.292	-0.212	-0.02	0.027	0.291	0.229	-0.196	1					
Sulphide	0.677	0.473	0.648	0.657	-0.535	-0.243	0.285	0.493	0.452	0.18	1				
Sand	0.414	0.2951	0.346	0.447	-0.805	-0.428	0.515	0.562	0.03	0.347	0.638	1			
Silt	-0.474	-0.432	-0.425	-0.554	0.292	-0.005	0.085	-0.185	-0.362	-0.368	-0.464	-0.703	1		
Clay	-0.279	-0.163	-0.188	-0.267	0.931	0.565	-0.705	-0.65	0.177	-0.173	-0.467	-0.897	0.356	1	
OM	-0.78	-0.561	-0.663	-0.675	0.647	0.253	-0.293	-0.589	-0.477	0.1869	-0.897	-0.557	0.358	0.488	1

DO: Dissolved oxygen; EC: Electrical conductivity, OM: Organic matter

Table 7. Correlation of sediment heavy metals between physic-chemical parameters of water and sediment charactersitcs

	Cu	Fe	Mn	Zn	Hg	Cd	Salinity	pH	DO	EC	Sulphide	Sand	Silt	Clay	OM
Cu	1														
Fe	0.960	1													
Mn	0.883	0.924	1												
Zn	0.979	0.957	0.859	1											
Hg	-0.274	-0.406	-0.161	-0.275	1										
Cd	0.229	0.153	0.432	0.183	0.734	1									
Salinity	-0.337	-0.177	-0.409	-0.261	-0.74	-0.92	1								
pH	-0.097	0.143	-0.021	-0.047	-0.81	-0.661	0.844	1							
DO	0.708	0.738	0.912	0.711	0.153	0.698	-0.596	-0.2	1						
EC	-0.364	-0.241	-0.135	-0.335	0.068	-0.252	0.291	0.229	-0.19	1					
Sulphide	0.646	0.789	0.644	0.736	-0.51	-0.219	0.285	0.493	0.452	0.18	1				
Sand	0.361	0.485	0.359	0.346	-0.73	-0.501	0.515	0.562	0.03	0.347	0.638	1			
Silt	-0.418	-0.515	-0.568	-0.336	0.211	-0.137	0.085	-0.18	-0.36	-0.36	-0.465	-0.70	1		
Clay	-0.219	-0.324	-0.146	-0.212	0.89	0.721	-0.705	-0.65	0.177	-0.17	-0.467	-0.89	0.356	1	
OM	-0.696	-0.84	-0.661	-0.759	0.672	0.193	-0.294	-0.59	-0.47	0.187	-0.898	-0.55	0.3581	0.488	1

DO: Dissolved oxygen; EC: Electrical conductivity, OM: Organic matter

Table 8.Enriched metal concentrations in Pondicherry estuary water and fraction sediments at seasonal wise

Water	Cu	Fe	Mn	Zn	Hg	Cd
Monsoon						
Station 1	0.04	87.66	0.043	0.13	0.588	0.011
Station 2	0.027	1.12	0.03	0.04	0.52	0.007
Post monsoon						
Station 1	0.015	17.43	0.015	0.005	1.429	0.03
Station 2	0.22	0.93	0.026	0.032	0.326	0.005
Summer						
Station 1	0.009	4.08	0.005	0.001	0.214	0.004
Station 2	0.015	0.65	0.022	0.28	0.158	0.0019
Pre monsoon						
Station 1	0.019	22.9	0.023	0.006	1.678	0.006
Station 2	0.22	0.86	0.027	0.036	0.214	0.004
Sediment						
Monsoon						
Station 1	2.97	947.5	0.0236	0.003	0.0661	0.0006
Station 2	0.1	107.9	0.033	0.004	0.0841	0.0002
Post monsoon						
Station 1	0.76	468.26	0.0141	0.00013	0.042	0.00003
Station 2	0.78	92.12	0.0016	0.0003	0.0222	0.00002
Summer						
Station 1	0.36	277.16	0.443	0.0009	0.004	0.00001
Station 2	0.5	71.41	0.0001	0.0003	0.002	0.00006
Pre monsoon						
Station 1	1.44	591.17	0.012	0.0002	0.334	0.00002
Station 2	0.77	93.88	0.019	0.00004	0.019	0.00001

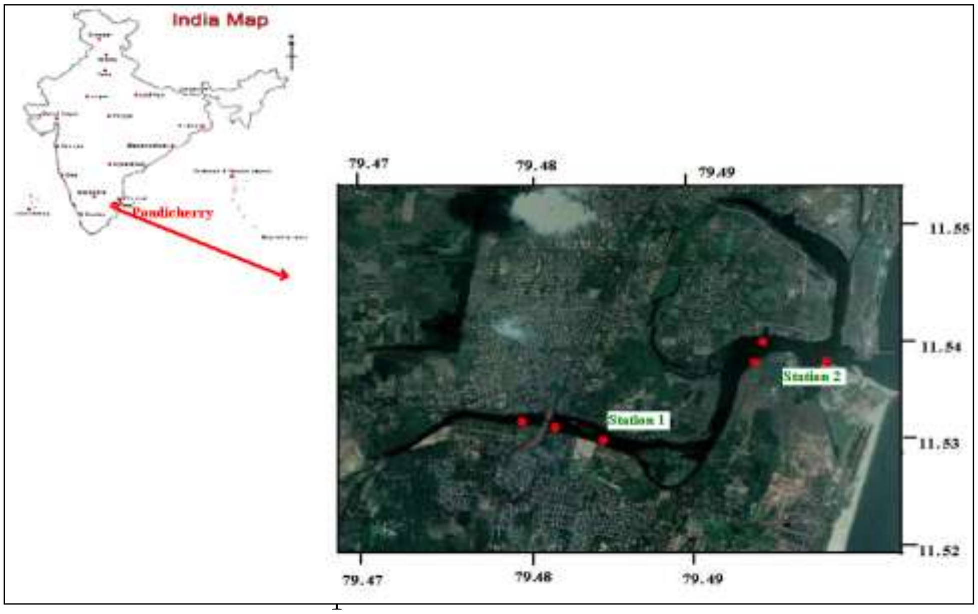

Figure 1. Study site from Pondicherry coast

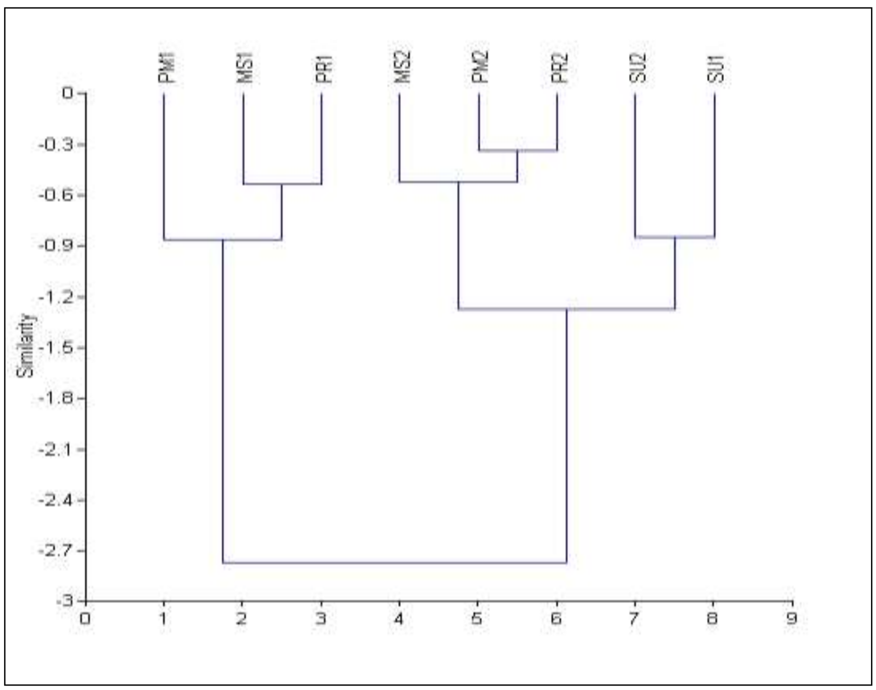

Figure 2. Dendrogram showing Bray-Curtis similarity of water heavy metals,

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2

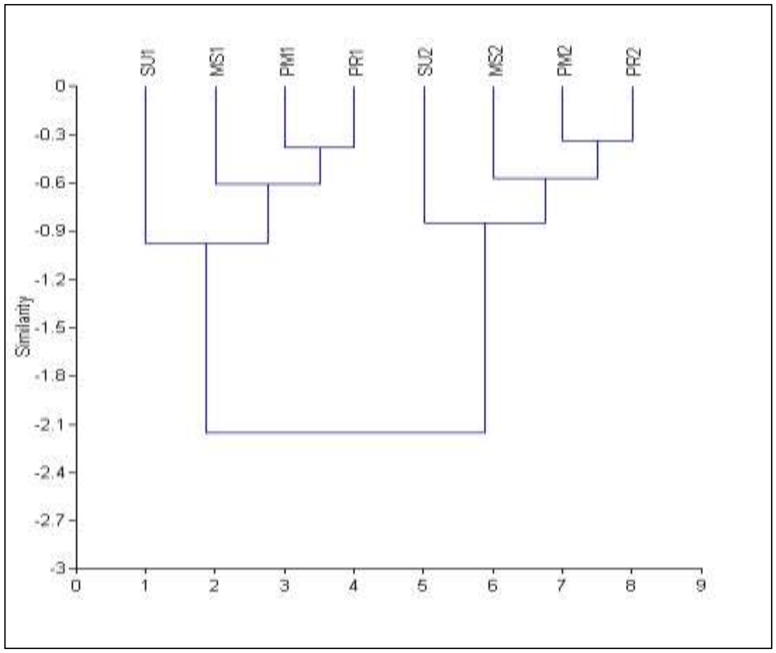

Figure 3. Dendrogram showing Bray-Curtis similarity with sediment heavy metals

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2

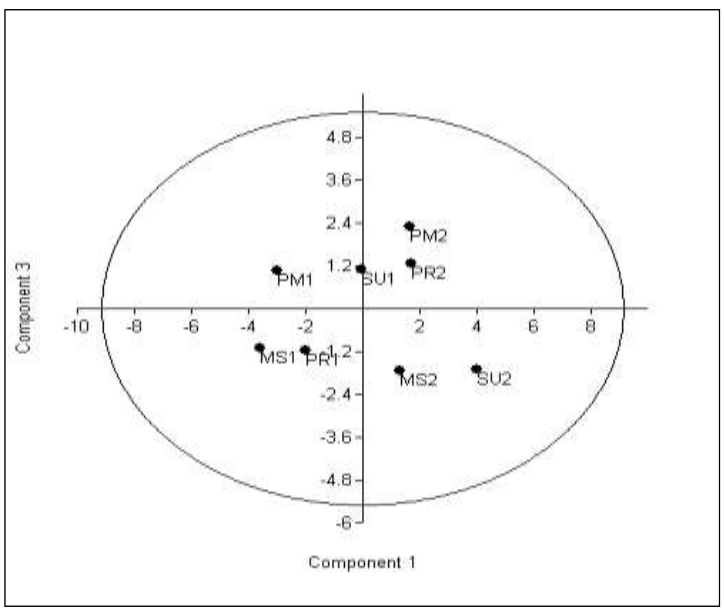

Figure 4. Principal Component analysis showing similarity with water heavy metal

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2

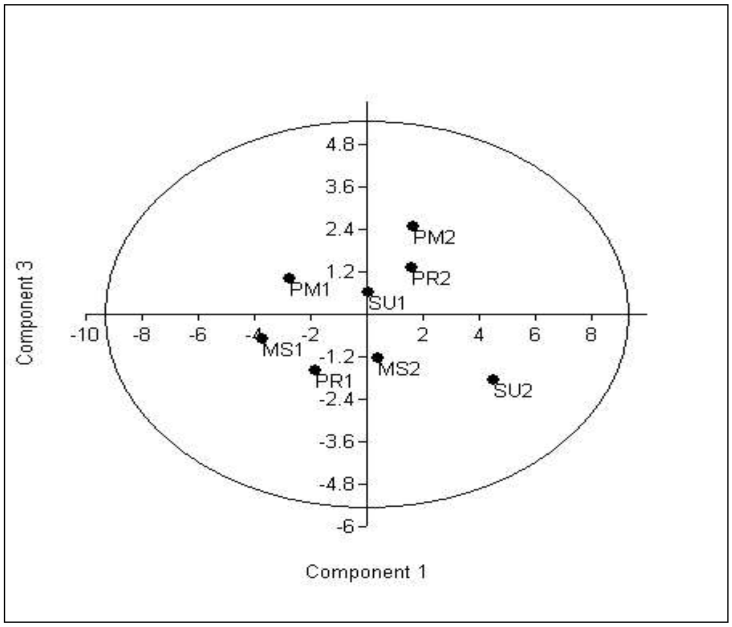

Figure 5. Principal Component analysis similarity showing similarity with sediment heavy metal

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2

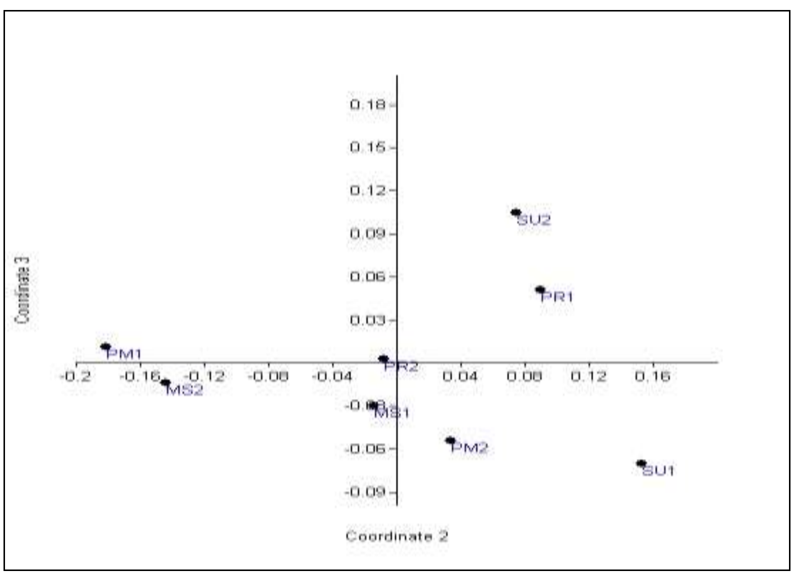

Figure 6. N- MDS plot analysis showing similarity with water heavy metal

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2

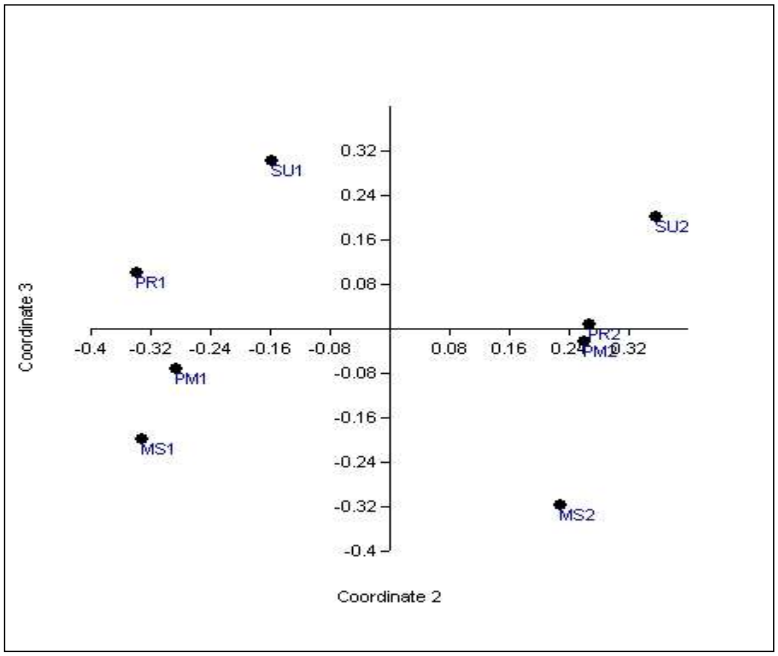

Figure 7. N- MDS plot analysis showing similarity with sediment heavy metal

MS1= Monsoon station 1; MS2 = Monsoon station 2; PM1= Post monsoon station 1; PM2 = Post monsoon station 2; SU1 = summer station 1; SU2 = summer station 2; PR1 = Premonsoon station 1; PR2 = Premonsoon station 2