SPATIAL AND MULTIVARIATE ANALYSIS OF TRACE ELEMENTS IN THE SURFACE WATER AND DEEP SEDIMENTS OF FRESH WATER AQUATIC ECOSYSTEM

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ABSTRACT

The aim of this study was to assess the levels of various trace metals present in water and sediment of fresh water aquatic ecosystem during the post monsoon season. The study was extended to identify the trace metal contamination in the water and sediment samples collected along the shores of Lambapur and Peddagattu the tribal villages in India using an Inductively Coupled Plasma Optical Emission Spectrometer (ICPMS). The trace metal contents in water samples were copper- 24.2 to 47.5, chromium- 4.4 to 8.2, cadmium- 0.1 to 0.3, lead- 2.1 to 3.8, Nickel- 5.9 to 9.7, Zinc- 4.6 to 9.7, Manganese- 10.8 to 13.2, Iron- 52.9 to 157.2 ($\mu g \ L^{-1}$) cobalt and arsenic were in BDL and the values were within the limits of Indian drinking water standards (BIS 10500: 1991). The trace metals concentration in the sediment samples ranged from ($mg \ kg^{-1}$): Copper- 61.5 to 113.7, chromium- 138.4 to 177.5, cobalt- 33.2 to 42.7, cadmium- 1.0 to 2.1, lead- 57.9 to 103.4, Nickel- 36.1 to 56.6, Zinc- 51.2 to 102.1, Manganese- 610.8 to 1301.7 and Iron- 2.5 to 2.9%. In our study, four reliable indices such as Enrichment factor, Contamination factor, Geoaccumulation Index and Pollution Load Index were applied to estimate metal pollution and the results comparison are discussed below. The data generated were used to determine the quality of the sediments based on the enrichment factor, contamination factor and degree of contamination, geochemical index and Pollution Load Index (PLI).

Keywords: Enrichment Factor, Pollution Load Index, Nagarjuna Sagar Dam, Contaminant Factor

1. INTRODUCTION

Sediments that enter a reservoir may contain materials from geological formations within the catchment area and organic substances originating from decomposed plant and animal remains (Karbassi *et al.*, 2011; Wang *et al.*, 2007; Zhang and Shao, 2013). Therefore, sediments within reservoirs can act as sensitive indicators for monitoring the contaminants in aquatic environments. Since sediments play a very important role in physicochemical and ecological dynamics, any change in toxic concentrations of heavy metal residues on the sediments will affect the natural aquatic life support systems (Orebiyi *et al.*, 2010). Sediments have polluted with various kinds of hazardous substances, including trace metals (Harikumar *et al.*, 2009). The study of sediment cores have shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments (Vinodhini and Narayanan, 2008; Wang *et al.*, 2007). The concentration of organic matter increases gradually within reservoirs, thereby affecting the quality of water and potentially changing the oxidation state into an anoxic condition. The conditions conducive to reduction together with low pH result in the mobilization of metals from the sediment to the water column (Biati *et al.*, 2010). This may lead to

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serious changes in water quality because of the continuous interactions that commonly occur at the sediment-water interface (Barreto *et al*., 2008; Comero *et al*., 2014; Garizi *et al*., 2011). Different natural and artificial sources of pollution can pollute the environment with heavy metals (Dobra *et al*., 2006).

Nagarjuna Sagar Dam (NS Dam) built on the river krishna is the tallest masonry dam globally, with a maximum height of 124.7 m at the deepest portion of the river valley. The dam spreads over five districts in the Andhra Pradesh state of India, namely Nalgonda, Mahaboobnagar, Kurnool, Prakasam and Guntur. The Krishna River flows through a Nature reserve over a distance of 130 km within the Andhra Pradesh state and is a major source for irrigation and domestic use. The Atomic Mineral Division (AMD) identified new deposits of uranium at Lambapur and Peddagattu located in Pedda Adsarlapalli Mandal of Nalgonda district at a distance of about 135 km from Hyderabad andhra Pradesh state, India (Reddy *et al*., 2003). The deposits are known to exist at the unconformity contact between granitic basement and overlaying srisailam quartzite at Lambapur (Jha *et al*., 2012; Sartandel *et al*., 2009). There is the potential for this area to develop into a future uranium mining center (Verma *et al*., 2011). The granitic rocks of the Lambapur area in Nalgonda district of Andhra Pradesh state, India, contain uranium in the range of 10.2-116 ppm with an average of 35 ppm and thorium in the range of 25.5-60: 7 ppm with an average of 50 ppm (Brindha *et al*., 2011; Raghavendra *et al*., 2013).

The area within Lambapur and Peddagattu containing the uranium deposits is drained by rivulets, which eventually flow into the Nagarjuna Sagar Dam (Reddy *et al*., 2003). The contribution of naturally occurring radionuclides and trace metals originating from the catchment of the dam would reflected in the sediment of Nagarjuna Sagar Dam. The sediment survey provides information on long term contamination trends and the environmental radionuclide concentration within different matrices. The trace metal concentrations within sediments are found to be higher because of the contribution of trace metals by rivulets draining into the reservoir. As a result, investigation of both water and sediment quality is required to assess the quality of reservoir water (Sartandel *et al*., 2009).

The main objective of this study was to determine the trace metal concentrations (Cd, Cr, Cu, Fe, Ni, Pb, Se, Co, As, Zn) in water and sediments within the shores of Peddagattu and Lambhapur the tribal village areas of nalgonda district andhra Pradesh, India. The results obtained from this study have value in providing information on background levels of metals in the water and sediment of the reservoir, contributing to the effective monitoring of both environmental quality and the health of the organisms inhabiting the reservoir ecosystem. The study was carried out during the pre-monsoon period, March 2010.

2. MATERIALS AND METHODS

2.1. Study Area

Nagarjuna Sagar, known in ancient days as Vijayapuri, is located 150 km from Hyderabad and is one of the most prominent Buddhist centers and tourist spots in Andhra Pradesh. Nagarjuna Sagar Dam is the world's largest masonry dam with a height of 124.7 m, creating a reservoir with a capacity of up to $11,472 \times 10^6$ m^3 of water. It is situated at 16° 50' N latitude and 79° 20' E longitude. The leaching of uranium deposits by rivulets occurs in the study area within Lambapur and Peddagattu which experience hot climate during summer (April and May) with ranging temperatures from 30 to 46.58°C and 16 and 29.8°C in winter. The average annual rainfall is ~500 mm occurring mostly during southwest monsoon (Raghavendra *et al*., 2013). Therefore, the sediment and water samples were collected from the shores of Lambapur and Peddagattu for our study.

Ten sampling points were selected based on the criteria that the sampling point should be around 500 m away from the shore and the sampling point should receive runoff from the shores of Lambapur and Peddagattu throughout the season. **Table 1** shows a list of the chosen sampling points with their position and **Fig. 1** shows the sampling locations within the map of the study area.

2.2. Sampling

Undisturbed surface sediment samples can provide an immediate assessment of the present levels of contamination in the area in relation to the textural and geo-chemical characteristics of the sediment. Triplicate sediment samples were collected from ten different locations as shown in **Fig. 1 and Table 1**. The depths at which sediment samples collected ranged from 49.5-138.6 feet. The sediment samples from deeper regions of the reservoir were collected using a Van Veen Grab Sampler (Norinco Pvt. Ltd., Chennai) and stored in precleaned and acid rinsed PVC covers under cold temperatures for further analysis (Abdel-Gawad *et al*., 2012). The surface water samples were collected from 10-15 cm below the water surface using acid washed PVC cans. The water samples were filtered through 0.45 μm PTFE filter and immediately acidified using 3 mL^{-1} of 70% nitric acid per liter of sample.
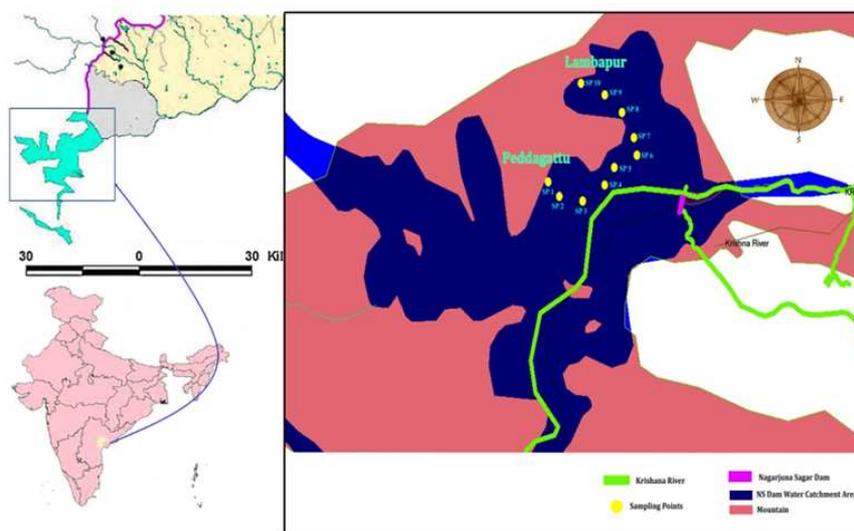
Fig. 1. Location of sampling sites within Nagarjuna Sagar Dam andhra Pradesh

Table 1. Sample coordinates from Nagarjuna Sagar dam

Sample station	Latitude	Longitude	Sampling depth (feet)
SP1	16°35'12.69"N	79°13'24.84"E	138.6
SP2	16°34'37.11"N	79°13'57.96"E	95.7
SP3	16°34'24.51"N	79°14'51.58"E	108.9
SP4	16°34'52.62"N	79°15'45.79"E	108.9
SP5	16°35'20.42"N	79°16'25.23"E	84.1
SP6	16°35'52.55"N	79°16'54.25"E	108.9
SP7	16°36'37.29"N	79°16'59.25"E	117.0
SP 8	16°37'12.05"N	79°16'28.89"E	49.5
SP 9	16°37'41.60"N	79°15'44.02"E	72.6
SP 10	16°37'59.14"N	79°14'47.33"E	26.4

In addition, 5 mL^{-1} of Chloroform was added per 10 liter of water sample in order to prevent microbial growth and the water samples were stored at 4°C until further analysis for its physio chemical and trace metal concentrations (Ong *et al*., 2009). All the collected samples cooled in ice soon after collection and then transported. Care is taken to avoid contamination of the sample during sampling, handling and transport to the laboratory.

2.3 Microwave Digestion of Sediment Samples

The sediment samples were dried in a hot air oven at 105°C for 2-3 days until a constant weight was obtained and subsequently ground to a powder using a glass mortar and stored in precleaned polythene zip lock bags (Jumbe and Nandini, 2009). 0.5 g of sediment samples were digested using a CEM MARS-5 microwave oven (CEM Corp., Matthews, NC) with a 12-position HP-1500

Plus vessel and rotor system. The sample was digested using 1600 w power with the ramp time of 10 min. After cooling to room temperature, all the digests were filtered through 0.45 µm PTFE filter and diluted to 50 mL^{-1} with ultrapure water and stored in polyethylene vials at 4°C untilanalysis in AAS and the blank was prepared without sample (Harzdorf *et al*., 1998; Muratli *et al*., 2012).

2.4. Analysis of Water Samples

About 2.5 liter of water sample was digested with 70% HNO$_3$ and 35% HCl on a hot plate at 105°C. The residue was dissolved by adding 0.5 M HCl and the contents were filtered through 0.45 µm PTFE filter.The filtered contents were made up to 50 mL^{-1} with 0.5 M HCl and analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) (Perkin Elmer Optima 5300 DV) at Sophisticated Analytical Instrument Facility (SAIF), the Indian Institute of Technology, Madras, Chennai. (Arunachalam *et al*., 2013).

2.5. Quality Assurance

The quality of chemical analysis and the accuracy of the data were monitored using the Sediment Reference Materials purchased from International Atomic Energy Agency, Austria. (IAEA-SL-1-Trace and Minor Elements in Lake Sediment). The analytical results of the trace metals of the samples showed a good agreement with the analytical values of the reference materials. In addition, the recoveries rates are shown in **Table 2** for the selected metals from the standard reference material were in the range of 95.91-115.73%.

Table 2. Quality assurance for analysis of sediment samples

Element	Certified reference value mg/kg)	Measured value (mg/kg)	Recovery (In %)
Copper	36.00	36.76	102.11
Chromium	104.00	102.72	98.77
Cobalt	21.30	24.65	115.73
Lead	37.70	38.13	101.14
Nickel	44.90	43.91	97.80
Zinc	223.00	213.79	95.87
Manganese	3460.00	3284.00	94.91
Iron	67400.00	64250.00	95.33

Two replicates of the homogenized filtered water samples were subjected to recovery studies by spiking samples using metal standards of about the same concentrations of the analytes of interest; the resulting mixtures were then subjected to the same digestion and analysis procedure (Oyoo-Okoth *et al.*, 2010). The metals recovery ranged from 82-94%. A blank was run for each digestion procedure to correct the measurements and to check all reagents and procedures for interferences and cross contamination.

2.6. Calculation of the Enrichment Factor (EF)

EF was calculated to determine whether the metal concentrations in the sediments collected from the shores of Peddagattu and Lambapur and the surrounding aquatic environment were of anthropogenic origins. To evaluate the magnitude of contaminants in the environment, the enrichment factors were computed relative to the abundance of species in source material to that found in the earth's crust (Zakir *et al.*, 2008). To identify the anomalous metal concentration, geochemical normalization of the trace metals data to a conservative element, such as Fe, was employed. Iron was selected because it is a major sorbent phase for trace metals and is a quasi-conservative tracer of the natural metal bearing phases in fluvial and coastal sediments (Hasan *et al.*, 2013). Several authors have successfully used iron to normalize trace metal contaminants (Hasan *et al.*, 2013; Martins *et al.*, 2012; Muñoz-Barbosa *et al.*, 2012). The following formula described in Equation 1 was used to calculate the EF value.

$$EF = \frac{\left(^{C_{metal}}/C_{Fe}\right)_{Sediment}}{\left(^{C_{metal}}/C_{Fe}\right)_{Control}} \tag{1}$$

Where:

$(C_{metal})_{Sediment}$ = Concentration of the particular metal in sediment

$(C_{Fe})_{Sediment}$ = Concentration of Iron in sediment

$(C_{metal})_{Control}$ = Control value concentration of the particular metal of the unpolluted environment in the Earth crust

$(C_{Fe})_{Control}$ = Control value concentration of iron of the unpolluted environment in the Earth crust

EF values were interpreted as suggested by (Taylor, 1964) where EF <1 suggests no enrichment, 1≤EF<3 is minor; 3≤EF<5 is moderate; 5≤EF<10 is moderately severe; 10≤EF<25 is severe; 25≤EF<50 is very severe; and 50≤EF is extremely severe. The EF calculation seeks to reduce the metal concentration viability associated with variations in sediment/sand ratios and is a convenient tool for plotting geochemical trends across large geographical areas.

2.7. Contamination Factor (CF) and Degree of Contamination (mC$_d$)

The contamination degree (C_d) aims to provide a measure of the degree of overall contamination within the surface layers in a particular sampling site. Hakanson (1980) had suggested an overall indicator of contamination based on interpreting the data by a contamination factor C_f^i of a given Trace metal as described in Equation 2 and the degree of contamination (mC$_d$) to describe the degree of contamination as described in Equation 3:

$$C_f^i = \frac{c_{0-1}^i}{C_n^i} \tag{2}$$

$$mC_d = \sum_{i=1}^{7} C_f^i / n \tag{3}$$

Where:

N = Number of analyzed elements and

I = i[th] element (or pollutant)

C_f^i = Contaminant Factor of specific metal

C_{0-1}^i = Mean value of the specific metal

C_n^i = Reference value for the metal

The Classification of contamination factor and contamination degree is given in **Table 3**.

2.8. Geo-Accumulation Index (I$_{geo}$)

The most common approach for estimating the enrichment of metal concentration above background is by the Geo-accumulation index (I$_{geo}$). This index was introduced by Müller (1981) in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels. The Geo-accumulation index (I$_{geo}$) is used by most of the researchers for trace element studies in soils and sediments (Hasan *et al.*, 2013; Hou *et al.*, 2013; Jumbe and Nandini, 2009; Zahra *et al.*, 2014), is defined in Equation 4:

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$$I_{geo} = Log_2 \frac{C_n}{1.5 \times B_n} \qquad (4)$$

where, C_n = measured concentration of the metal examined (mg kg^{-1}), B_n = geochemical background value (mg kg^{-1}) (Turekian and Wedepohl, 1961). The constant 1.5 = the background matrix correction factor owing to lithogenic variations in the sediment (Stoffers et al., 1986). This method assesses the degree of metal pollution in terms of seven enrichment classes based on the increased value of the index as $I_{geo} < 0$ is not contaminated, <1 is Not Contaminated to Moderately contaminated, <2 is Moderately contaminated, <3 is Moderately to highly contaminated, <4 is Highly contaminated, <5 is Highly to very highly contaminated, <6 is Very highly contaminated.

2.9. Pollution Load Index (PLI)

The Pollution Load Index (PLI) is an empirical index, which provides a simple method for assessing the level of trace metal pollution. Tomlinson et al. (1980) had employed a simple method based on the PLI to assess the extent of pollution by metals within estuarine sediments (Qiao et al., 2013; Varol, 2011). Sediment PLI was calculated using Equation 6 and the individual contamination factor for each metal is determined using Equation 5:

$$CF = \frac{C_{metal}}{C_{Background}} \qquad (5)$$

Sediment PLI is determined by:

$$PLI = \sqrt[n]{Cf_1 \times Cf_2 \times Cf_3 \times .... \times Cf_n} \qquad (6)$$

Where:
CF   = The contamination factor
C_{metal} = The concentration of pollutant in sediment
$C_{background}$ = The background value for the metal, the total number of metals is represented by n

Table 3. Classification of contamination factor and contamination degree

C_f^i	mC_d	Pollution status
$C_f^i < 1$	$mC_d < 1.5$	Very low degree of contamination
$1 \leq C_f^i < 3$	$1.5 \leq mC_d < 2$	Low degree of contamination
$3 \leq C_f^i < 6$	$2 \leq mC_d < 4$	Moderate degree of contamination
$C_f^i > 6$	$4 \leq mC_d < 8$	High degree of contamination
-	$C_d > 8$	Very high degree of contamination

The PLI value is interpreted as polluted where PLI>1 whereas PLI<1 indicates no pollution. This index allows comparison between the several estuary systems.

2.10. Spatial Analysis of Trace Metals

Magesh et al. (2011) has described the spatial analysis of trace element contamination in sediments. The geospatial distribution of trace element contents was accomplished by a spatial analysis module in ArcGIS. An Inverse Distance Weighted (IDW) algorithm was used to interpolate the data spatially and to estimate values between measurements. The Inverse Distance Weighting (IDW) is an algorithm for spatially interpolating, or estimating values between measurements and implemented in ARCGIS 10.2 GIS software. Each value estimated in an IDW interpolation is a weighted average of the surrounding sample points. Using concentrations of heavy metals or the factor scores produced by PCA as variables with spatial interpolation techniques to create various continuous surfaces to determine the pollution patterns influenced by each potential pollution source. Weights are computed by taking the inverse of the distance from an observation's location to the location of the point being estimated (Mathes and Rasmussen, 2006). Many researchers have reported that IDW with a squared distance term yielded results most consistent with the original input data (Acosta et al., 2011; Delgado et al., 2010; He et al., 1997; Li et al., 2013; Lima et al., 2003; Zamani-Ahmadmahmoodi et al., 2013).

2.11. PCA of Sediment and Water Samples

Principal components analysis (PCA) is robust with respect to multivariate data normality and as it is an exploratory technique it does not involve statistical significance testing. PCA is a statistical method used to decide components that are linear combinations of the original variables. The central idea of the PCA is to reduce the dimensionality of a data set consisting of a large number of interrelated variables, while retaining as much as possible of the variation present in the data set. The Principal Component Analysis was employed to infer the hypothetical source of trace metals (natural or anthropogenic). The components of the PCA were rotated by a varimax rotation. The PCA is a standard approach to explore the variability in multivariate data by converting the observations of possibly correlated variables into a set of linearly independent variables, namely Principal Components (PCs) and has been frequently used to investigate environmental pollution with respect to different factors, including major pollutants, influential factors, or possible sources (Nobi et al., 2010). A Varimax rotation

was applied to aid interpretation of the results, this works by loading variables more strongly on fewer factors, but should only be applied where correlations between the factors are not expected. In PCA, the first PC, is the linear combination of the variables with maximal variance and represents the largest variability of the original data set. The second component is the linear combination with the next largest variability that is orthogonal to the first components and so on (Garizi *et al.*, 2011).

2.12. Statistical Analysis

The data obtained from analytical methods were treated statistically using SPSS software (version 20.0 for windows). Descriptive data analysis was performed, including the calculation of mean, SD, maximum, minimum. Pearson correlation matrix was performed to identify the relationship between the trace metals.

3. RESULTS

3.1. Trace Elements in Sediment Samples

The concentrations of tracemetals in the deep sediment sections of the Dam given in **Table 4**. Showed wide variations among the sampling points. The trace metals concentration in the sediment samples ranged from (mg kg^{-1}): Copper- 61.5 to113.7, Chromium- 138.4 to 177.5, Cobalt- 33.2 to 42.7, Cadmium 1.0 to 2.1, Lead 57.9 to 103.4, Nickel 36.1 to 56.6, Zinc- 51.2 to 102.1, Manganese 610.8 to 1301.7, Iron 2.5-2.9%. Iron was the major element in the sediment followed by Manganese and the concentration of other trace elementsare in the order of Fe>Mn>Cr>Cu>Pb>Zn>Ni>Co> Cd. The concentrations for metallic trace elements bear the positive correlation coefficients among themselves.

Sartandel *et al.* (2009) have reported that the trace elements lead and chromium in the top sediment (0-10 cm) from Peddagattu ranged from 120 mg kg^{-1} and 211 mg kg^{-1} and the concentration gradient of lead and chromium suggested a change in geochemical characteristics of sediments and influence of fine particulates input through river in this area (Sartandel *et al.*, 2009). Similarly Krishna *et al.* (2011) has reported the chromium values in the range of 15.8 to 107.8 mg kg^{-1} (Krishna *et al.*, 2011) in the sediment samples of Wailpalli Watershed, Nalgonda District nearer to the Nagarjuna Sagar dam.

3.2 Trace Metals in the Water Samples

The trace metals concentrations in the surface water samples of Nagarjuna Sagar Dam given in **Table 5** are the mean value of the ten sampling points showed the values in (µg L^{-1}) copper- 24.2 to 47.5, chromium -4.4 to 8.2, cadmium-0.1 to 0.3, lead-2.1 to 3.8, Nickel-5.9 to 9.7, Zinc-4.6 to 9.7, Manganese-10.8 to 13.2, Iron- 52.9 to 157.2, cobalt and arsenic were in BDL.The average concentrations of the trace elements in the Dam water was within the permissible limits of the Bureau of Indian Standards (BIS 10500: 1991). In addition, the results were comparable to the previous reports clearly demonstrated that the Dam water has not been polluted with trace metals. Contaminants enter the reserviours through mainly two pathways. These are firstly point sources that are identifiable sources such as municipal, industrial wastewater effluents. The second patway is called diffuse sources which are closely related to meteorological factors. Major diffuse sources include: Surface run-off, erosion, atmospheric deposition.

The trace elements contents in river and reservoir sediments of the various locations around the world are discussed in the **Table 6**. (Förstner, 1981) has described the world average metal concentration in the sediment samples. The earth's crust content is used as background for different reliable sediment quality indices where no background or reference value is available. In our study, as described earlier four reliable indices such as Enrichment factor, Contamination factor, Geoaccumulation Index and Pollution Load Index were applied to estimate metal pollution and the results comparison are discussed below.

3.3. Enrichment Factor (EF) for the Sediment

The Enrichment Factor (EF) is a convenient measure of geochemical trends and is used for making comparisons between areas. The EF values were calculated from the mean concentrations of the trace metals within the sampling points of the study area. The unpolluted or background point sampling point was considered to be the control point. The normalizing element used in this study was iron (Fe) because of its occurrence of low variability. The Enrichment Factor (EF) for the deep bottom Damsediments was determined and interpreted as suggested by Birch 2003 and tabulated in **Table 7**.

A value of unity denotes neither enrichment nor depletion relative to the Earth's crust (Hasan *et al.*, 2013). From **Table 7** it is evident that Cadmium and nickel has shown no enrichment (EF<1) in all ten sampling locations indicated that these metals were derived from the natural sources, such as underlying geological material. The metals copper, chromium, cobalt are in minor enrichment (1≤EF<3) in all the sampling points whereas lead in the sampling points SPS1 to SPS3 is moderately severe enrichment while the other sampling (SPS4 to SPS10) locations showed moderate enrichment.

Table 4. Concentration and descriptive statistics of trace elements in fresh water dam sediments

	Concentration of trace elements in the deep sediment (mg kg^{-1})									
Sample code	Copper (Cu)	Chromium (Cr)	Cobalt (Co)	Cadmium (Cd)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)	Manganese (Mn)	Iron (Fe)	Arsenic (As)
SPS1	100.800	177.000	33.90	1.00	103.4	50.40	96.400	1187.90	29000.200	BDL
SPS2	75.400	169.800	40.70	2.00	96.9	56.60	98.200	1013.30	28360.900	BDL
SPS3	76.500	174.500	41.80	1.00	102.4	49.90	102.100	1301.70	28355.700	BDL
SPS4	65.400	138.400	33.20	2.00	82.1	49.90	88.100	1161.20	28406.400	BDL
SPS5	103.700	174.800	41.90	2.10	57.9	51.80	66.800	782.50	28902.400	BDL
SPS6	92.400	177.500	34.00	2.10	67.3	53.10	63.500	1059.10	29075.400	BDL
SPS7	66.200	140.800	42.20	2.10	72.8	43.40	54.200	919.30	29185.900	BDL
SPS8	99.400	142.400	42.70	2.10	69.6	43.90	58.200	610.80	28994.800	BDL
SPS9	61.500	139.500	33.40	2.10	59.4	36.60	51.200	741.20	28813.800	BDL
SPS10	68.200	146.800	35.30	2.10	65.0	36.10	65.500	628.60	25954.100	BDL
Arithmetic mean	81.000	158.200	37.90	1.90	77.7	47.20	74.400	940.60	28505.000	-
Geometric mean	79.500	157.300	37.70	1.80	76.0	46.70	72.100	911.20	28490.100	-
SD	16.400	17.700	4.20	0.50	17.5	6.90	19.600	242.90	947.900	-
Minimum	61.500	138.400	33.20	1.00	57.9	36.10	51.200	610.80	25954.100	-
Maximum	103.700	177.500	42.70	2.10	103.4	56.60	102.100	1301.70	29185.900	-
BDL Limits	0.008	0.075	0.01	0.01	0.1	0.01	0.042	0.01	0.015	0.005

*BDL- Below Detection Limit

Table 5. Concentration and descriptive statistics of trace elements in dam surface water

	Concentration of trace elements in dam surface water (mg/L)									
Sample code	Copper (Cu)	Chromium (Cr)	Cobalt (Co)	Cadmium (Cd)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)	Manganese (Mn)	Iron (Fe)	Arsenic (As)
SPW1	28.400	8.200	BDL	0.30	2.4	9.00	9.700	12.50	136.300	BDL
SPW2	29.400	6.500	BDL	0.20	2.4	8.80	8.600	12.70	123.500	BDL
SPW3	43.200	7.200	BDL	0.10	2.6	6.80	7.700	13.20	114.300	BDL
SPW4	43.700	5.600	BDL	0.30	2.5	8.10	6.300	11.20	52.900	BDL
SPW5	31.400	4.600	BDL	0.20	2.1	7.20	9.600	12.50	148.000	BDL
SPW6	38.000	4.400	BDL	0.30	2.8	7.80	8.600	11.60	146.500	BDL
SPW7	24.200	7.400	BDL	0.10	3.8	8.50	4.600	12.30	152.000	BDL
SPW8	33.500	5.800	BDL	0.30	3.7	6.30	6.900	10.80	155.800	BDL
SPW9	47.500	7.900	BDL	0.30	3.3	9.70	7.900	12.30	134.200	BDL
SPW10	36.100	6.400	BDL	0.20	2.4	5.90	6.400	11.90	157.200	BDL
Arithmetic mean	35.500	6.400	-	0.20	2.8	7.80	7.600	12.10	132.100	-
Geometric Mean	34.800	6.300	-	0.20	2.7	7.70	7.500	12.10	127.100	-
SD	7.600	1.300	-	0.10	0.6	1.20	1.600	0.70	31.200	-
Minimum	24.200	4.400	-	0.10	2.1	5.90	4.600	10.80	52.900	-
Maximum	47.500	8.200	-	0.30	3.8	9.70	9.700	13.20	157.200	-
BDL Limits	0.008	0.075	0.01	0.01	0.1	0.01	0.042	0.01	0.015	0.005

Table 6. Comparison of Trace element concentration in sediment samples of other rivers and reservoirs

Name of reservoir	Cu	Cr	Cd	Pb	Ni	Zn	Mn	Fe	References
Nagarjuna Sagar Dam	61.5-103.7	138.4-177.5	1.1-2.1	57.9-103.4	36.1-56.6	51.2-102.1	610.8-1301.7	25954-29185	Present study
Manwan dam, China (µg/g)	15.85-56.32	28.29-89.85	0.24-2.5	17.03-92.20	-	45.32-259.84	246.58-769.06	19,133-37,936	(Wang et al., 2012)
Rybnik Resevoir, Polland (µg/g)	16-1116	14.27-739.11	2.40-85.06	11-315	3-183	50-2441	246-4215	3982-98510	(Loska and Wiechuła, 2003)
Wadi Al-Arab dam, Jordan (mg\g)	0.022-0.186	-	0.0055-0.0125	-	-	0.172-0.964	0.201-0.806	7.77-15.75	(Ghrefat and Yusuf, 2006)
Ataturk dam, Turkey (mg/kg)	14.57	-	-	-	43.69	60.78	73.60	12587	Karadede and Unlu (2000)
Veeranam lake sediments, India (mg/kg)	65.44-125.64	39.84-150.41	0.20-3.90	20.11-41.0	34.32-95.60	68.8-598.8	-	-	(Suresh et al., 2012)
Bed sediments of Krishna River Basin (µg/g)	35	82	-	-	32	26	906	25000	(Ramesh et al., 1990)
Krishna mainstream sediments (mg/kg)	206-291	138-206	-	-	88-100	164-223	0.17-0.22%	13-17.4	(Das and Krishnaswami (2007)
World average (mg/kg)	20-90	20-190	0.1-1.5	10-100	30-250	50-250	-	-	(Förstner, 1981)

Where as, Zinc showed no enrichment (EF<1) in the sampling points SPS5 to SPS9 and showed minor enrichment in the sampling points SP1 to SP4 and SP 10.The EF value of nearly 1 suggests that a given metal may originate entirely from natural sources, such as crustal materials or natural weathering processes (Tang *et al*., 2013). When the EF value showed minor enrichment significant portion of the metal originated from anthropogenic processes only. So our study results for lead showed that lead is the only major metal which might have originated from the anthropogenic process. Anzali international wetland located in southwestern Caspian Seacoast is one of the most important wetlands of Iran have showed EFs greater than 10 for Cd. (Jamshidi-Zanjani and Saeedi, 2013).

3.4. Contamination Factor C_f^i and Modified Degree of Contamination (mC$_d$) for Sediment

The contamination factor and the degree of contamination calculated for the fresh water Dam sediment samples are tabulated in **Table 8**. The results of the modified Degree of Contamination clearly showed that Nickel and Zinc has the low Degree of Contamination, whereas Cu, Cr, Co were in Moderate Degree of Contamination in all the sampling locations. Lead and Cadmium showed high degree of Contamination to very high degree of contamination as classified by Hakanson (1980). Abrahim and Parker (2008) has reported that modified degree value of cadmium indicates a moderate to high degree of fine fraction sediment contamination in Tamaki Estuary.

3.5. Classification of Geo-Accumulation Index for Dam Sediment

The Geo accumulation indexes for the Dam sediment samples were calculated using Equation 4 are listed in **Table 9**. The I$_{geo}$ values <1 corresponds to Not Contaminated to moderately contaminated were observed for nickel and zinc. The elements chromium and cobalt

has I$_{geo}$ values <2 which is moderately contaminated whereas lead showed highly contaminated for sampling locations SPS1 to SPS3 with I$_{geo}$ values <4,I$_{geo}$values <3 was shown for SPS4, SPS6, SPS7, SPS8 and SPS10 while SPS5 and SPS9 showed I$_{geo}$ values <2.

Cadmium pollution observed in the Dam sediment is due to anthropogenic sources including fertilizers and pesticides used in the agricultural fields around the sampling points SPS8 to SPS10 in Lambhapur where agricultural activities are done by the tribal people. Similarly Cevik *et al*. (2009) had assessed the Cadmium as the only pollution element in the surface sediments of Seyhan dam where the anthropogenic sources were via fertilizers and pesticides. He has also pointed out that the usage volume of fertilizers is higher in the region than the national average (Cevik *et al*., 2009). According to the geo-accumulation index categorized by Magesh *et al*. (2011) in revealed that the sediments of Tamiraparani Estuary, southeast coast of India is extremely contaminated by Cd (Magesh *et al*., 2011). Similarly Hindon River sediments have also been reported for strong cadmium contamination range (Chabukdhara and Nema, 2012).

3.6. Pollution Load Index (PLI)

The Pollution load index is an integrated index which combines all trace metals to one index which allows comparison of pollution status of various sites so the priority contamination sites can be identified for remediation. **Table 10** clearly shows the analyzed Damsediment samples were not contaminated for Nickel and Zinc while Co, Cd, Cu, Cr, Pb contamination was observed. I$_{geo}$ and EF depend on the background data used, grain size and bonding forms of metals. The PLI calculated for every sampling point exceeds the background pollution and pointed to the anthropogenic load at each studied site. It can be assumed from our results that Lead and cadmium are the only major elements originated from the anthropogenic where as the PLI of the other elements showed that the area may be polluted but it is in the range of non polluted site.

Table 7. Trace metals enrichment factor for deep bottom dam sediments

Sample code	Copper (Cu)	Chromium (Cr)	Cobalt (Co)	Cadmium (Cd)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
SPS1	2.03	2.03	1.95	0.17	5.94	0.61	1.39
SPS2	1.55	1.99	2.39	0.36	5.69	0.70	1.44
SPS3	1.58	2.05	2.45	0.18	6.01	0.62	1.50
SPS4	1.35	1.62	1.95	0.36	4.81	0.62	1.29
SPS5	2.10	2.01	2.41	0.37	3.34	0.63	0.96
SPS6	1.86	2.03	1.95	0.36	3.85	0.64	0.91
SPS7	1.33	1.61	2.41	0.36	4.15	0.52	0.77
SPS8	2.00	1.64	2.45	0.37	4.00	0.53	0.84
SPS9	1.25	1.61	1.93	0.37	3.43	0.45	0.74
SPS10	1.54	1.88	2.26	0.41	4.17	0.49	1.05

Table 8. Contamination factor and modified degree of contamination for dam sediment

Sample code	Contamination factor C_f^i for fresh water dam sediments						
	Copper (Cu)	Chromium (Cr)	Cobalt (Co)	Cadmium (Cd)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
SPS1	1.77	1.77	1.78	5.0	5.17	0.74	1.01
SPS2	1.32	1.70	2.14	10.0	4.85	0.83	1.03
SPS3	1.34	1.75	2.20	5.0	5.12	0.73	1.07
SPS4	1.15	1.38	1.75	10.0	4.11	0.73	0.93
SPS5	1.82	1.75	2.21	10.5	2.90	0.76	0.70
SPS6	1.62	1.78	1.79	10.5	3.37	0.78	0.67
SPS7	1.16	1.41	2.22	10.5	3.64	0.64	0.57
SPS8	1.74	1.42	2.25	10.5	3.48	0.65	0.61
SPS9	1.08	1.40	1.76	10.5	2.97	0.54	0.54
SPS10	1.20	1.47	1.86	10.5	3.25	0.53	0.69
Modified degree of contamination (mC_d)	2.57	4.51	2.85	13.28	5.54	1.77	1.11

Table 9. Classification of geoaccumulation index for trace metals for dam sediment

Sample code	Copper (Cu)	Chromium (Cr)	Cobalt (Co)	Cadmium (Cd)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
SPS1	1.18	1.31	1.19	3.33	3.45	0.49	0.68
SPS2	0.88	1.26	1.43	6.67	3.23	0.55	0.69
SPS3	0.89	1.29	1.47	3.33	3.41	0.49	0.72
SPS4	0.76	1.03	1.16	6.67	2.74	0.49	0.62
SPS5	1.21	1.29	1.47	7.00	1.93	0.51	0.47
SPS6	1.08	1.31	1.19	7.00	2.24	0.52	0.45
SPS7	0.77	1.04	1.48	7.00	2.43	0.43	0.38
SPS8	1.16	1.05	1.50	7.00	2.32	0.43	0.41
SPS9	0.72	1.03	1.17	7.00	1.98	0.36	0.36
SPS10	0.80	1.09	1.24	7.00	2.17	0.35	0.46

Table 10. Pollution load index and the status of trace metal pollution in dam sediments

Trace metals	Pollution load index	Status
Copper (Cu)	1.39	Polluted
Chromium (Cr)	1.57	Polluted
Cobalt (Co)	1.98	Polluted
Cadmium (Cd)	8.96	Polluted
Lead (Pb)	3.79	Polluted
Nickel (Ni)	0.69	Not polluted
Zinc (Zn)	0.76	Not polluted

The PLI values for the studied Dam sediments ranged from 0.69 to 8.96 with an average of 2.73. Suresh *et al.* (2012) has reported that Veeranam lake sediments in India the PLI values are ranged from 1.18 to 4.09 with an average of 2.03. Qiao *et al.* (2013) has reported that Shantou Bay was slightly impacted by metal pollutants with PLI values ranging from 0.97 to 1.79 and a zonal PLI value of 1.22.

3.7. Spatial Analysis of Trace Metals in Dam

A GIS-based chemometric approach has proven to be useful in determining the spatial distribution patterns of trace metals in sediments and water samples to identify impacts of pollution at the sampling locations. The Spatial analysis of the sediment and the water samples are shown in the **Fig. 2 and 3**. By visualizing the degree of trace element contamination in sediments and water by spatial interpolation exposes the pollution status of the fresh water aquatic ecosystem. The spatial association and scaling are two different aspects of local structures and surfaces. Both should be taken into account in data interpolation and surface mapping of geochemical variables.
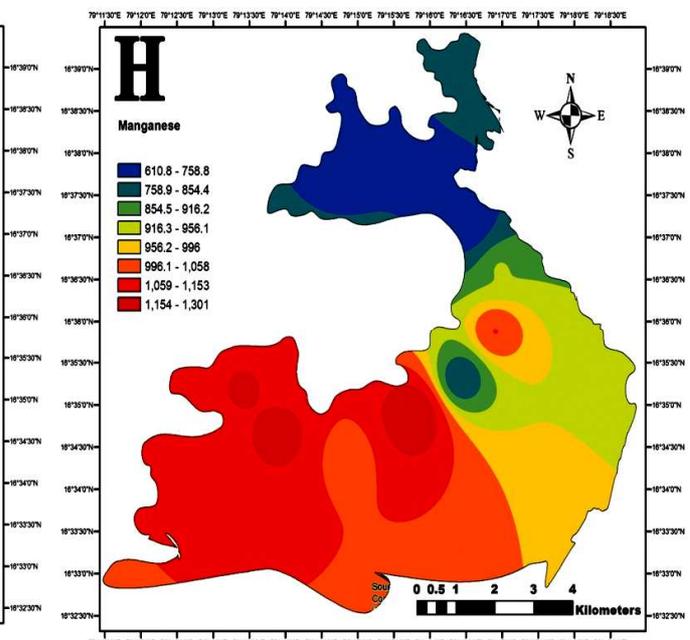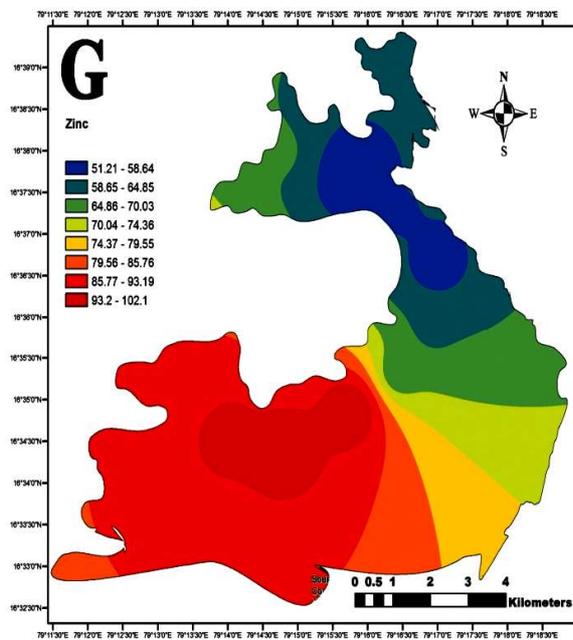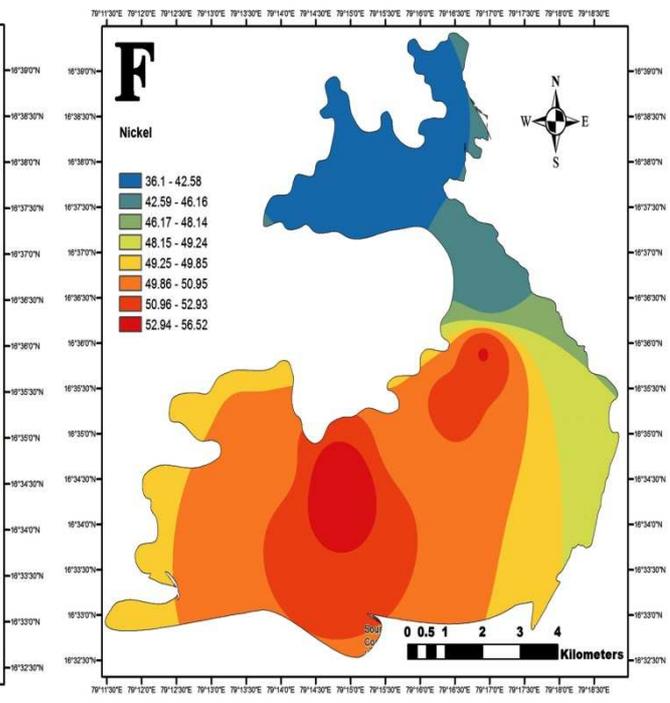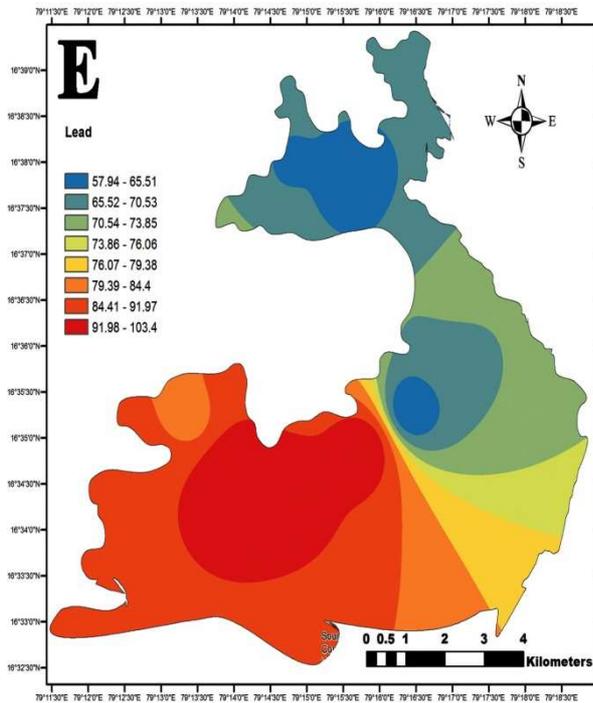
From **Fig. 2** the spatial distribution pattern of trace metals in deep bottom sediments of Nagarjuna Sagar dam, it is observed that copper (**Fig. 2A**), cobalt (**Fig. 2C**) and Iron (**Fig. 2I**) follow similar pattern of distribution; it is further confirmed by the principle component analysis (**Table 13** and **Fig. 4**). Chromium (**Fig. 2B**) and Nickel (**Fig. 2F**) follow the similar pattern of distribution, whereas Lead (**Fig. 2E**), Zinc (**Fig. 2G**) and Manganese (**Fig. 2H**) follow the quite different pattern from above metals. The trace metal Cadmium (**Fig. 2D**) does not follow any trend as compared with any other metal, since the cadmium is considered to have an anthropogenic origin of pollution from the fertilizers and pesticides used in agricultural activities around the sampling points. The

differential distribution of trace elements may indicate their different sources of origin and the controlling mechanism of distribution patterns, which can be clearly understood from the principle component analysis.

From **Fig. 3** the spatial distribution of trace metal in surface water samples of the reservoir showed the different distribution pattern among the analyzed metals. From the results it is observed that lead (**Fig. 3D**), copper (**Fig. 3A**) and Chromium (**Fig. 3B**), followed the similar geographical trends. The metal zinc (**Fig. 3F**), Nickel (**Fig. 3E**) andiron (**Fig. 3H**), follow different spatial distribution. The spatial surveys of trace metals in water samples is the key step in understanding the contamination in the freshwater aquatic ecosystem. The spatial trends of contaminated major elements like cadmium and lead showed similar trend of the spatial distribution of sediment and water samples from the reservoir.
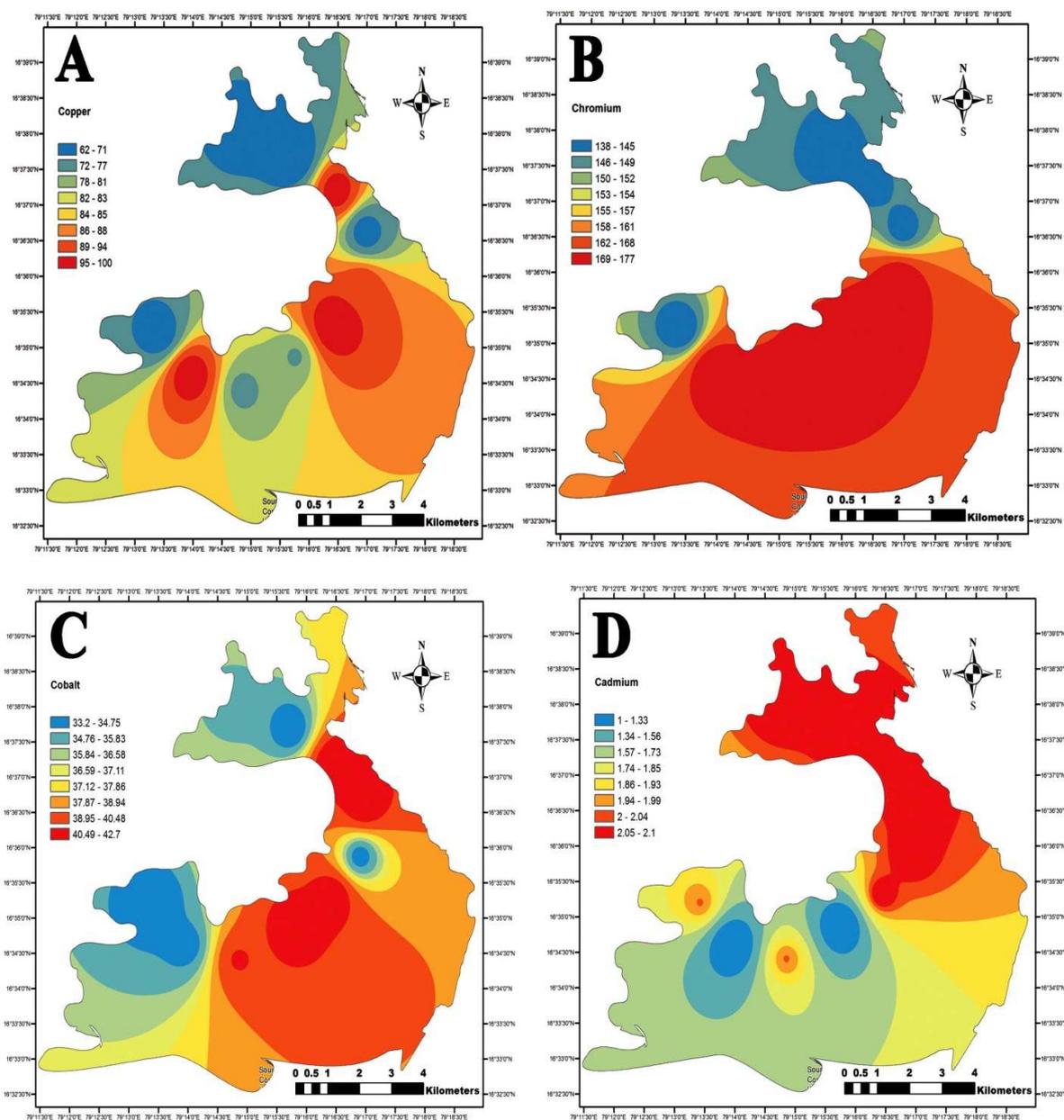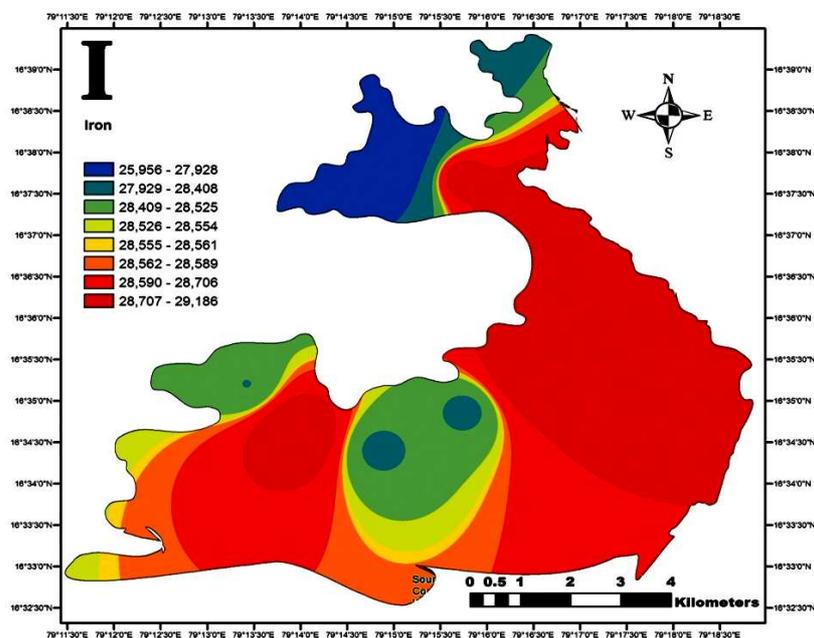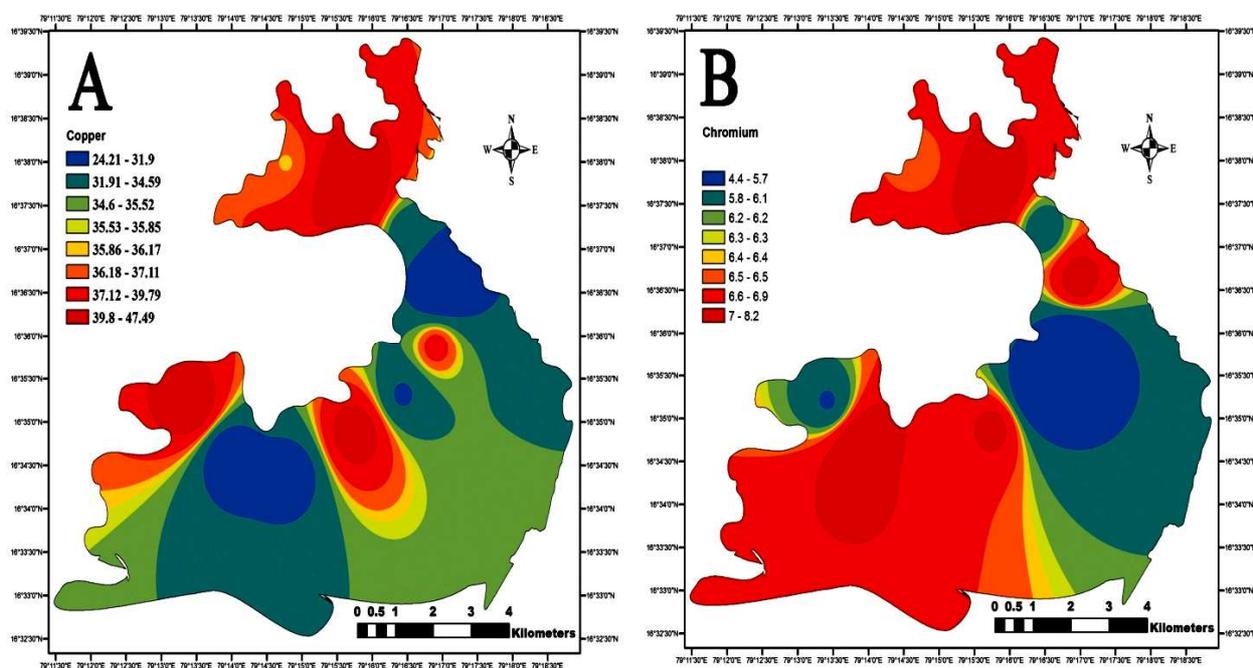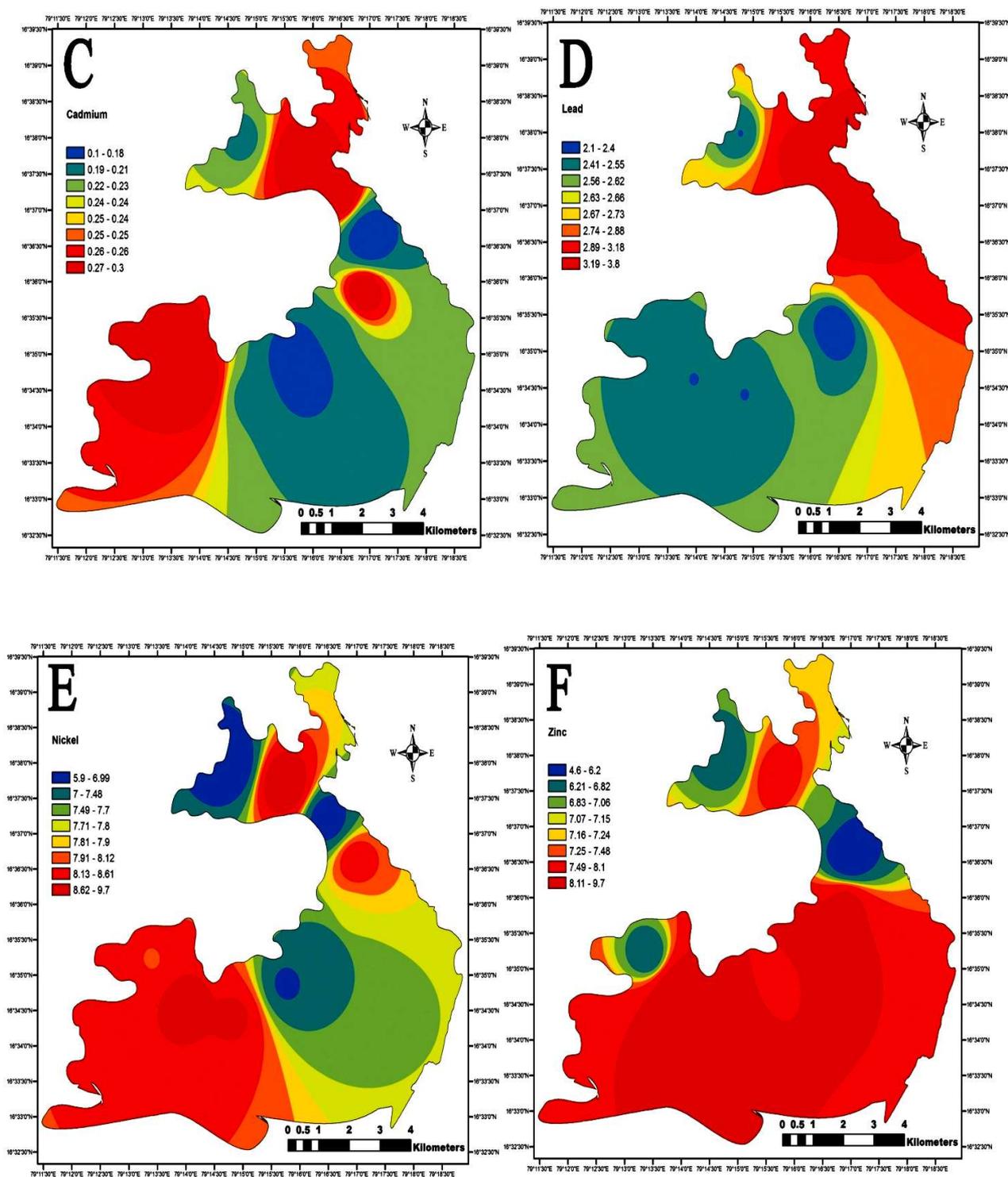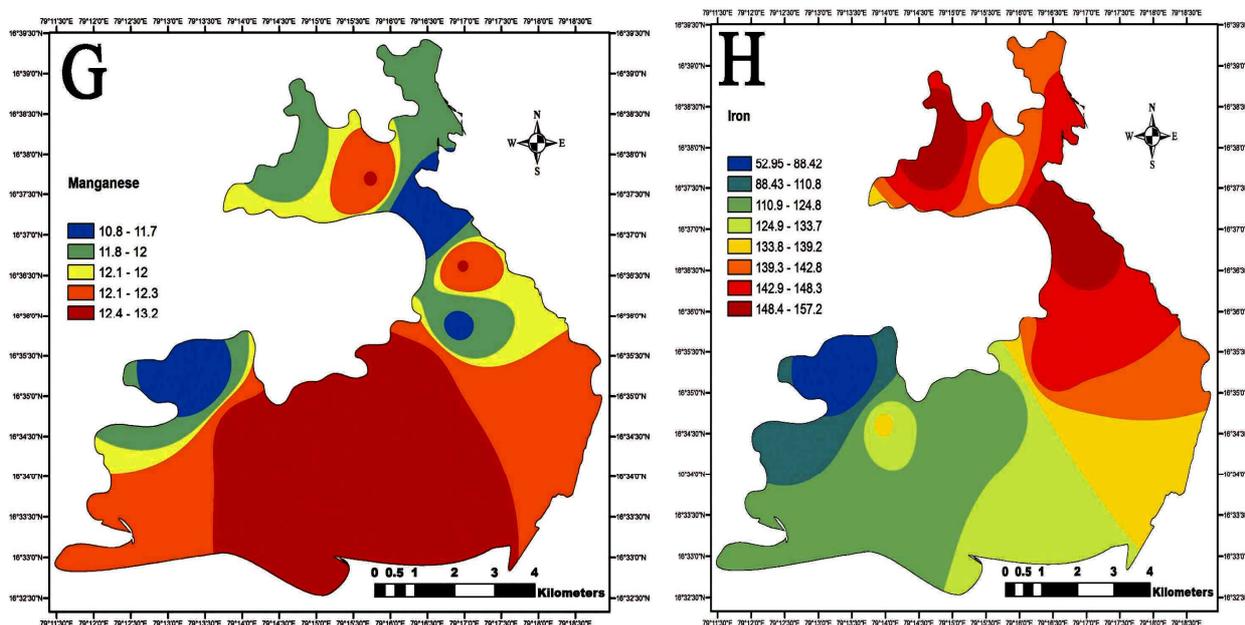
Fig 2. Spatial distribution pattern of trace metals in bottom sediments of Nagarjuna Sagar Dam (A) Copper (B) chromium (C) Cobalt (D) Cadmium (E) Lead (F) Nickel (G) Zinc (H) Manganese (I) Iron

Fig. 3. Spatial distribution of trace metal in surface water samples of Nagarjuna Sagar Dam (A) Copper (B) Chromium (C) Cadmium (D) Lead (E) Nickel (F) Zinc (G) Manganese (H) Iron

3.8. Pearson Correlation Analysis

Interrelation between metals can provide information on sources of contamination and heavy metal pathways The Pearson Correlation matrixes of trace metals in sediments presented in **Table 11**. established a positive correlation for few metals and the correlation is significant at p<0.01 level for zinc and lead(r = 0.907). Similarly manganese is positively Correlated at p<0.01 for lead (r = 0.784) and zinc(r = 0.775). Chromium is positively correlated to nickel (r = 0.719) at p<0.05 level of significance. Cadmium is the only trace element which exhibited the strong negative correlation at p<0.01 for lead (r = -0.809) and zinc (r = -0.726) and Manganese (r = -0.702) at p<0.05 level of significance suggesting that each paired elements have identical source or chemical phenomena, whereas the rest of the elemental pairs are not correlated with each other. Iron is the trace element which showed the positive correlation for all the metals except Cadmium and Zinc. Fe in sediment will strengthen the geochemistry of the other trace elements, which is more clearly visible from the correlation analysis. More positive correlation between metals indicated that they are probably derived from the same source. A simple correlation analysis was done to clarify the relationships between various metals. This correlation between metals synergies can exist, thus resulting in the potential compound in the field to explain the fate and transport of metals.

Correlation measures the linear relationship between random variables. The Pearson correlation matrix of trace metals in water sample (**Table 12**), it is observed that no significance was observed at p<0.01 or p<0.05 Level. Iron is positively correlated to lead, Zinc, Manganese and chromium and negatively correlated to copper, cadmium and Nickel. Manganese is also positively correlated to cr, Ni and Zn and negatively correlated to Cu, Cd and Pb. From our results the major contaminant as cadmium is positively correlated with Ni(r = 0.236), Zn(r = 0.354), Cu (r = 0.305) and negatively correlated with Mn(r = -0.631), Cr(r = -0.196), Fe(r = -0.159). The statistical analysis of the water data indicated that Fe is mostly of lithogenic origin.

The significant positive correlations observed between the heavy metals contents in sediment and water means that the metals in the two environmental media could have common sources. The metals probably originate from either same waste or parent material as the case may be. The metals adsorbed to the sediment are however desorbed (remobilized from the sediment) back to the water column due to changes in environmental conditions such as pH and redox potentials.

Table 11. Pearson correlation matrix of trace metals in dam sediment

	Copper	Chromium	Cobalt	Cadmium	Lead	Nickel	Zinc	Manganese	Iron
Copper	1	0.617	0.244	-0.22	0.037	0.462	0.081	-0.019	0.384
Chromium		1	0.101	-0.522	0.428	0.719*	0.535	0.505	0.188
Cobalt			1	0.019	0.065	0.194	-0.004	-0.16	0.205
Cadmium				1	-0.809**	-0.275	-0.726*	-0.702*	-0.092
Lead					1	0.524	0.907**	0.784**	0.077
Nickel						1	0.640*	0.646*	0.434
Zinc							1	0.775**	-0.08
Manganese								1	0.289
Iron									1

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed)

Table 12. Pearson correlation matrix of trace metals in dam water

	Copper	Chromium	Cadmium	Lead	Nickel	Zinc	Manganese	Iron
Copper	1	-0.04	0.305	-0.079	-0.008	0.014	-0.115	-0.484
Chromium		1.00	-0.196	0.257	0.463	-0.145	0.460	0.020
Cadmium			1.000	-0.023	0.236	0.354	-0.631	-0.159
Lead				1.000	0.107	-0.617	-0.366	0.302
Nickel					1.000	0.203	0.286	-0.243
Zinc						1.000	0.346	0.093
Manganese							1.000	0.078
Iron								1.000

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed)

Table 13. Total variance and component matrices for trace metals in dam sediments

	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
Component	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)
1	4.348	48.313	48.313	4.348	48.313	48.313	4.019	44.651	44.651
2	1.852	20.578	68.891	1.852	20.578	68.891	2.182	24.240	68.891
3	0.919	10.207	79.097						
4	0.883	9.811	88.908						
5	0.621	6.905	95.813						
6	0.255	2.837	98.650						
7	0.081	0.901	99.551						
8	0.040	0.449	100.000						
9	3.19E-05	0.000	100.000						

Extraction method: Principle component analysis

3.9. Principle Component Analysis

PCA was applied to the all the trace elements in sediment samples and described in **Table 13**. Due to the standardized data, the correlation matrix was used for the analysis. The principal components that have eigenvalues higher than one were extracted. The results indicate that there were two eigen values higher than one. The first and second principal component usually include a large portion of the total variance; therefore, the first two Principle Components (PC1 and PC2) are plotted against each other and clustering of samples is possible in the effects of all variables within the two dimensional plane as represented in **Fig. 4**.

The PCA analysis enabled us to find the sources of the tracemetals whether it is of natural or/and anthropogenic origin. The component plot shown in **Fig. 4** in rotated space for metal distribution of the sediments described that the metals lead, zinc and manganese were of natural origin and Fe can be from natural weathering of the earth's crust and rocks. The

metals chromium and nickel which are in elevated levels along with cobalt and copper in the sediment samples can be of anthropogenic sources such as domestic activities. These results were confirmed by the repeated sampling at various seasons in the same locations. The PCA plot in rotated space for metal distribution of the sediment clearly indicated that cadmium is the only major anthropogenic element.

From **Table 14** it is observed that only the first four components have eigenvalues greater than 1, which was confirmed by Scree plot. From **Fig. 5** the Component plot in rotated space for metal distribution in water sample, the metals copper, iron and zinc concentrations can be normalized together and relatively inert with respect to chemical weathering and has no significant anthropogenic source. Whereas the trace metals lead, chromium and nickel can be of migration process and are mainly lithogenous components, indicating that their metal concentrations might be controlled by external factors.

Table 14. Total variance and component matrices for trace metals in dam water

Component	Initial Eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)
1	2.079	25.985	25.985	2.079	25.985	25.985	1.887	23.587	23.587
2	1.978	24.724	50.710	1.978	24.724	50.710	1.738	21.726	45.313
3	1.611	20.132	70.842	1.611	20.132	70.842	1.691	21.140	66.453
4	1.227	15.337	86.179	1.227	15.337	86.179	1.578	19.727	86.179
5	0.637	7.964	94.143						
6	0.356	4.445	98.589						
7	0.113	1.408	99.997						
8	0.000	0.003	100.000						

Extraction method: Principle component analysis
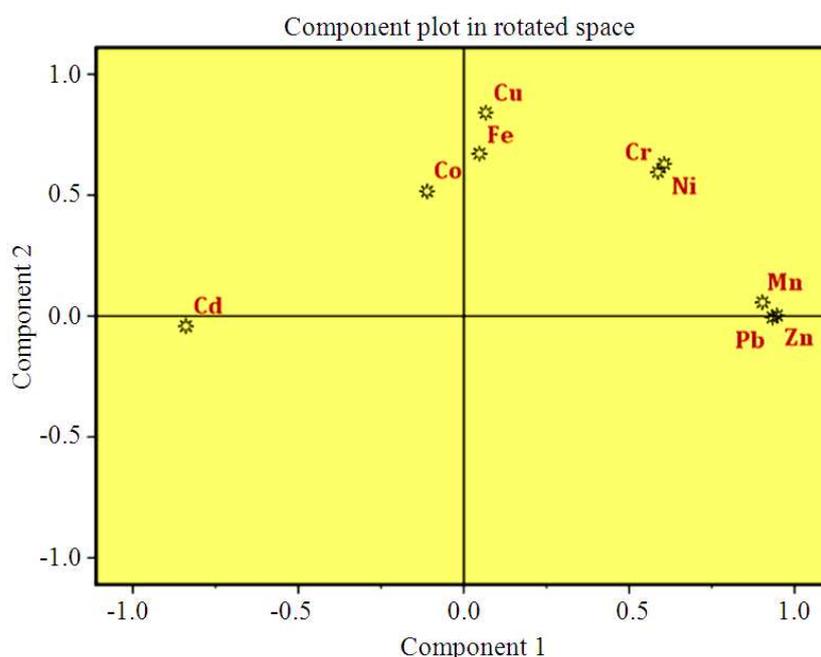
Fig. 4. Component plot in rotated space for metal distribution in the sediment
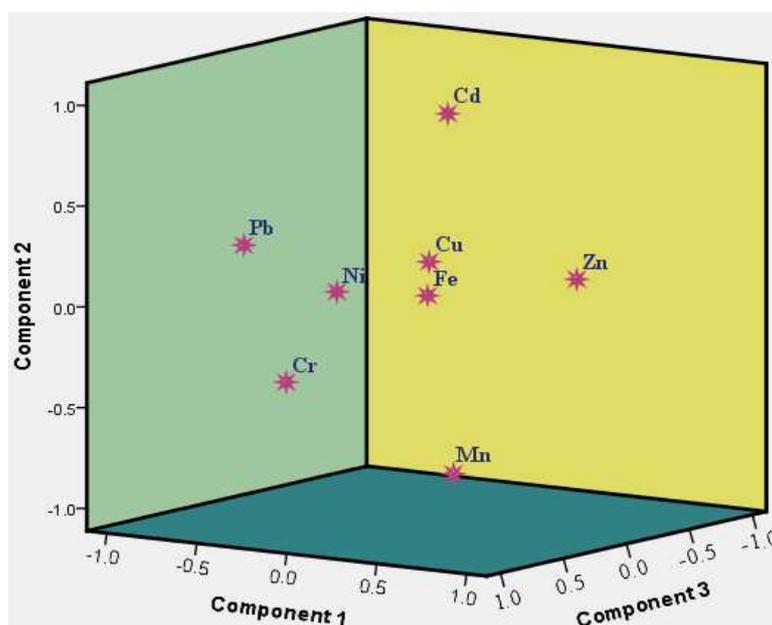
Fig. 5. Component plot in rotated space for metal distribution in the Water

4. CONCLUSION

The present study reveals that the water samples at different sampling positions within Nagarjuna Sagar Dam are not polluted by any of the studied Trace metals as per BIS 10500:1991 permissible limits. In addition, the deep sediment samples from Nagarjuna Sagar Dam show considerable amount of trace metal accumulation. The spatial distributions of trace elements in sediments in the estuarine environment are influenced by so many factors including geochemical and biogeochemical processes like sedimentation, precipitation and flocculation of particulate substances (Chatterjee *et al*., 2007). EF is widely used as an indicator to assess the status of environmental contamination. Yet, threshold values of the element enrichment have not been recognized.

The Degree of Contamination Index indicates that lead and Cadmium shows high degree of Contamination to very high degree of contamination within the dam. The Geo accumulation index classification indicates that the Trace metals chromium and cobalt is moderately contaminated and lead is highly contaminated. Considering all the criteria Cadmium is the trace elements in sediment samples is due to anthropogenic sources including fertilizers and pesticides used in agricultural activities around the sampling points SPS8

to SPS10, where agricultural activities are taking place in and around the region. GIS based spatial analysis by Inverse Distance Weighting (IDW) is an algorithm for spatially interpolating, have been proven a powerful tool to represent the distribution of trace element in sediment and water samples.

Considering all the assessment criteria, we can conclude that the sediment samples shown considerable amount of contamination of chromium, nickel, zinc and copper. The urban runoff from Srisailam to Nagarjuna Sagar Dam and the leaching effect of rivulets through areas in Lambapur and Peddagattu could be the possible reason for the Trace metal accumulation. This study is a preliminary observation of the metal concentrations within sediment and water of Nagarjuna Sagar Dam and further detailed study is required to trace the sources of contamination of these Trace metals.

5. ACKNOWLEDGMENT

5.1. Disclosure

The authors declare no conflicts of interest in this study.

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