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An assessment of heavy metals in red sand dunes near Bhimili of Visakhapatnam

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ABSTRACT

The contamination levels of the thirteen elements Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, V, Y, Zn and Zr have been assayed in the Red sand dunes on the basis of geoaccumalation index, enrichment factor, contamination factor and degree of contamination. The tests reveal that the degree of contamination value obtained is 20.41, which is indicating the considerable degree of contamination in the study area. The mean soil P^H is 6.38 indicating slightly acidic. Acidic P^H increases the mobility of toxic metals results the toxic metals may enter the food chain and causes hazard to the health of life forms and by leaching their content also increase in ground water too.

Keywords: Red Sand Dunes, Index of Geo-accumulation, Enrichment Factor, Degree of contamination.

INTRODUCTION

Visakhapatnam city is situated on east coast of A.P, India. The area of experimental region is in between Nerellavalasa and Bhimunipatnam with latitudes 17°52ʹ-53ʹ N, longitudes 83°25ʹ-27ʹ E as shown in the Map.(fig.1). From some of the Hills of Eastern Ghats, the top soil had been carried and deposited at the bottom of hills which are popularly known as Red Sand Dunes. The red sand dunes of 'ErraMattiDibbalu' in general terms, near Bhimili with the occasional patches of vegetation is attracting tourists. Scientists believe that the red sand dunes had formed during the quarternary era, i.e. 1.8 million years ago, during which sea level oscillations and subsequent rapid climatic and geomorphological changes involving multiple cycles of depositions thereby formation of the dunes. These laterite ferruginous red loamy soils are derived from Kondalite suite of rocks and deposited as dunes which are hard and compact when dry. The geographical extent of this area is about 600 hectares.

More than a century back W. King (1886) recorded the Red Sand Dunes near Bhimili and described them as 'badlands' to represent the denudational remnants of great sand banks or isolated banks formed around the sunken hills. Until 1940s the Red Sand Dunes could not draw the attention of the scientific community, but the publication of Mahadevan and Satpathi (1949) generated interest among the earth scientists of Andhra University. The topographical and geophysical characters of the Red Sand Dunes are systematically analysed and they are variously known as 'highlands' [17]'red sediments' [16]. The mineralogical studies with compactness and composition characteristics indicate the original derivation of Red Sand Dunes from the local Khondalite formations.

Theoccurance of heavy meatls in the environment at some high concentrations is hazard to the health of humans and wildlife[8]. Heavy metals in high concentrations reflect the contamination of soil in the study area. Heavy metals on the soil surface undergo downward transportation, or metal interaction with associated waste matrix enhances mobility[5, 9].

The toxicity and accumulation of the elements causes leaching into the groundwater, taken up by plants, released as gases into the atmosphere, or bond semi-permanently by soil components such as clay or organic matter, which later affect human health[1,13].This study aimed to estimate the levels of heavy metals contamination by using the geoaccumulatio, enrichment factor, contamination factor and degree of contamination[6].

MATERIALS AND METHODS

Depending on the area, the total number of soil samples collected was 24. Most of the soil samples were collected from the outer surface, i.e., 5-15 cm depth to study the contamination. The samples were collected in self-locking polythene bags and were sealed in double bags. Use of metal tools was avoided and a plastic spatula was used for sample collection. Figure 1shows the location of soil sample collection in the study area. Soil samples were dried for two days at 60^{o}C. The dry soil sample was finely powdered to –250 mesh size (US Standard) using a swing grinding mill. Sample pellets were prepared for analysis by X-ray fluorescence spectrometry (XRF), using a backing of boric acid and pressing it at 25 tons of pressure. A hydraulic press was used to prepare pellets for XRF analysis to determine trace elements. To monitor the quality of chemical analysis and examine the accuracy of the data, soil reference materials, ***SO-2*** issued by Canadian reference materials were analyzed with the soil samples during the course of analysis.

Index of geoaccumulation

The index of geoaccumulation (I_{geo}) is used to assess the contamination[10].

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

Where, C_n is the measured concentration of the element in the pelitic sediment fraction (<2 *l*m) and B_n is the geochemical background value in fossil argillaceous sediment (‘‘average shale’’).

The constant 1.5 is to analyze natural fluctuations in the content of a given substance in the environment.

Enrichment factor

The value of EF is calculated by using the modified formula Krzysztof et al. (2003) based on the equation by Buat-Menard and Cherselet (1979). Reference element is characterized by low occurrence variability[12]. Strontium was used as a reference element. It is one of the main components of the Earth’s crust, and its concentration in soil is connected mainly with matrix. Similar to I_{geo}, the reference environment adopted was the average concentration of elements in the earth’s crust. This is to enable a comparison of the two factors I_{geo} and EF.

$$EF = \frac{\dfrac{C_n(sample)}{C_{ref}(sample)}}{\dfrac{B_n(background)}{B_{ref}(background)}}$$

Where C_n (sample) is the content of the examined element in the examined environment, C_{ref} (sample) is the content of the reference element in the examined environment, B_n (background) is the content of examined element in the reference environment and B_{ref} (background) is the content of the reference element in the reference environment.

Contamination factor and degree of contamination

As suggested by Hakanson (1980), they enable an assessment of soil contamination through the reference value of the concentration in Earth’s crust.

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

Where C_{0-1}^i is the mean content of metals from at least five sampling sites and C_n^i is the concentration of individual metal.

RESULTS AND DISCUSSION

To examine the accuracy of the data, soil reference materials, ***SO-2*** issued by Canadian reference materials were analyzed with the soil samples during the course of analysis. The analytical concentrations of the metals are listed in (Table.1). It seems that our analytical values are within the range of the certified values of the reference materials as shown in the (Table.1).

(Table.2) gives the contents of the metals in the soil. The individual results obtained for each metal are shown in (Table.2&3), and (Table.3) shows descriptive statistical data contents of the metals in the soil and also contains contents of the metals in Earth's crust, which served as reference values (Taylor and McLennan. 1995).High levels of some elements are observed in some pockets only.

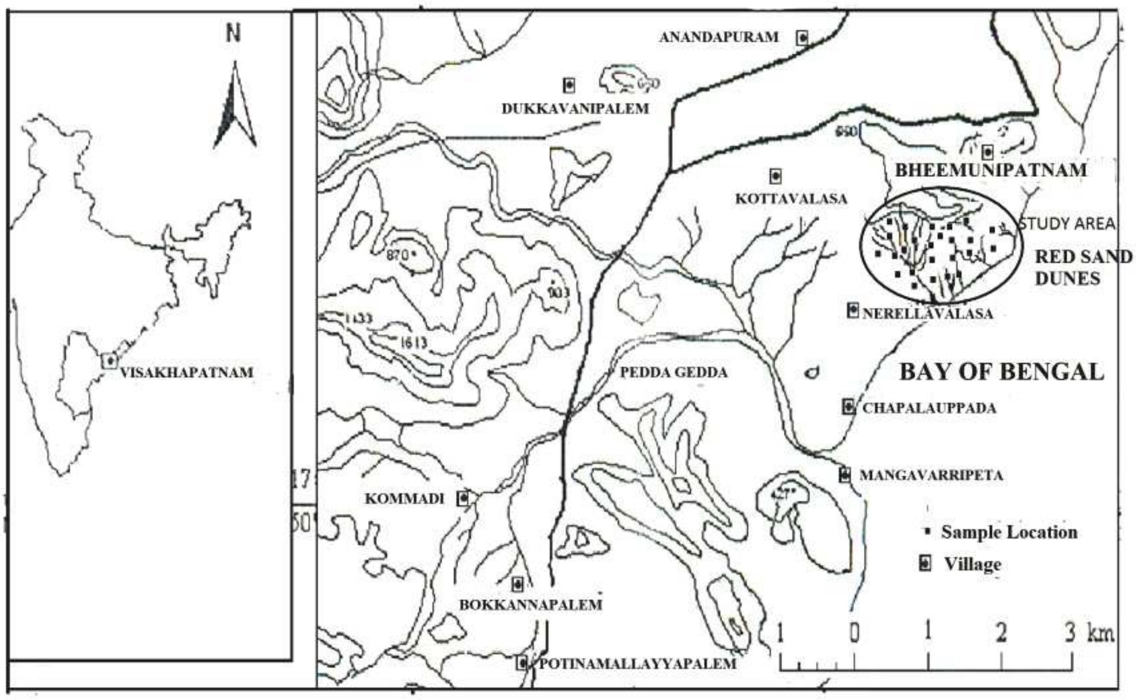

Fig.1. Showing the Study Area

Barium

The mean barium content of 553.31 mg/kg ranging from 208.3 to 904.2 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.72) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with barium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.42 to 1.76 (Fig.3) and the mean EF of barium is 1.08 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.38 to 1.64 and the mean contamination factor is 1.01(Fig.4) which is moderately contaminated with Ba [3].

Cobalt

The mean cobalt content of 16.17 mg/kg ranging from 0 to 33.7 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.25) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with cobalt as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0 to 3.56 (Fig.3) and the mean EF of cobalt is 1.73 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0 to 3.37 and the mean contamination factor is 1.62 (Fig.4), which is moderately contaminated with Co [3].

Chromium

The mean Chromium content of 73.72 mg/kg ranging from 19.5 to 136.7 mg/kg has been found in study area (Table.3). The mean I_{geo} (0.39) obtained reveal that the sample examined fell into class 1, which is uncontaminated to moderately contaminated with Chromium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.59 to 4.13 (Fig.3) and the mean EF of Cr is 2.26 confirming the moderate enrichment [14]. The contamination factor is ranging from 0.56 to 3.91 and the mean contamination factor is 2.11(Fig.4), which is moderately contaminated with Cr [3].

Table1: Results of analytical values of the soil standard reference materials SO-2 (podzalic B horizon soil) in comparison with the certified values.

CRM	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
SO-2	935.5	14	17.7	ND	1.2	10.6	25.6	57.8	330	177.2	20.9	115.2	407.8
	1000	7.6	12.3	8	2	8	20	77	331	57	40	115	760

First row indicates measured values; Second row indicates certified values

Table 2.Heavy metal XRF data (mg/Kg)

sample	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
SB 1	835.5	6.6	88.1	ND	ND	16.5	21.7	49.4	330.8	614.2	43	85.5	2069.3
SB 2	816.4	2.7	54.7	21.6	0.9	33.1	19.3	46.2	331.7	512.8	14.2	99.1	524.8
SB 3	769.2	8.6	93.1	ND	2.1	21.6	16.1	37.4	330	215.1	26.5	86.3	314.2
SB 4	612.1	16.4	47.3	16.9	0.4	17.4	18.5	76.7	332.1	119.7	12.4	129.5	442.5
SB 5	896.1	21.5	68.4	ND	0.7	53.4	28.4	38.1	333.2	37.3	20.6	112.7	334.1
SB 6	475.9	14.1	19.5	ND	1.7	11.7	22	59.3	331.4	274.2	35.9	141.6	473.8
SB 7	310.5	5.7	81.2	22.1	ND	61.2	31.8	27	312.8	57.3	14.5	85.9	342.4
SB 8	273.4	11.4	63.2	ND	0.4	1.7	26.2	131.6	329.1	ND	27.3	132.5	531.7
SB 9	864.1	0.9	56.3	0.7	1.6	41.3	31.7	43.1	314.7	163.1	36.1	94.7	414.2
SB 10	297.5	17.3	93.4	29.1	1.3	18.5	16.3	93.7	333.1	219.5	19.2	86.1	381.5
SB 11	375.4	1.7	52.2	ND	2.7	20.8	18.5	40.3	332.6	25.1	15.4	148.8	424.4
SB 12	529.8	19.6	61.1	ND	2.7	47.2	19.4	64.2	317.2	241.2	42.8	121.3	374.6
SB 13	359.2	26.1	58.7	ND	4.1	59.3	23.8	26.1	319.4	603.4	25.4	107.1	392.1
SB 14	802.5	16.5	76.3	12.1	0.2	61.4	21.1	38.6	321.9	524.7	16.2	125.2	421.3
SB 15	208.3	18.3	119.8	ND	4.7	32.7	32.5	74.7	316.4	ND	47.1	141.9	473.6
SB 16	381.7	32.4	82.3	1.7	3.2	15.8	32	98.1	331.2	243.1	32.4	143.5	512
SB 17	280	0	52.3	ND	3.2	10	20.2	26.5	333	ND	12.2	136.8	311.7
SB 18	904.2	31.8	52.4	24.5	1.9	12.6	19.6	62.8	327.5	73.4	48.6	138.2	497.2
SB 19	520.1	22.2	95.8	1.4	0.3	63.7	17.1	112.7	327.1	512.9	27.3	87.3	315.1
SB 20	371.7	15.8	121.6	ND	0.7	24.8	21.6	61.9	315.4	271.5	16.9	96.7	342.5
SB 21	614.8	29.5	56.9	ND	1.4	30.3	27.3	87.1	328.7	61.7	21.7	93.4	373.8
SB 22	235.3	12.6	64.2	ND	3.4	44.7	34.3	51	327.5	194.1	14.3	117.1	361.4
SB 23	817.2	22.7	73.8	19.7	0.7	16.1	18.2	73.4	333.1	83.6	12.1	140.7	395.7
SB 24	728.5	33.7	136.7	30.5	0.7	68.3	35.1	150.2	331.3	227.6	42.7	111.4	403.4

Copper

The mean Copper content of 16.39 mg/kg ranging from 0.7 to 30.5 mg/kg has been found in study area(Table.3). The mean I_{geo} (-1.95) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Copper as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.03 to 1.29 (Fig.3) and the mean EF of copper is 0.70 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.03 to 1.22 and the mean contamination factor is 0.66 (Fig.4), which is indicating low contamination factor with Cu [3].

Table 3: Metal content in Red sand dunes and reference value (Taylor and McLennan, 1965) mg/kg

	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
minimum	208.3	0	19.5	0.7	0.2	1.7	16.1	26.1	312.8	25.1	12.1	85.5	311.7
maximum	904.2	33.7	136.7	30.5	4.7	68.3	35.1	150.2	333.2	614.2	48.6	148.8	2069.3
average	553.31	16.17	73.72	16.39	1.77	32.67	23.86	65.42	326.72	251.21	26.03	115.14	476.14
skewness	0.11	0.07	0.63	-0.44	0.71	0.42	0.56	1.04	-0.93	0.78	0.55	-0.02	4.60
kurtosis	-1.61	-0.88	0.52	-1.25	-0.51	-1.20	-1.17	0.66	-0.71	-0.60	-1.09	-1.58	21.97
STDEV	241.31	10.22	26.83	10.97	1.32	20.15	6.20	33.12	6.89	191.04	12.18	22.28	345.96
median	524.95	16.45	66.3	19.7	1.5	27.55	21.65	60.6	329.55	219.5	23.55	114.9	399.55

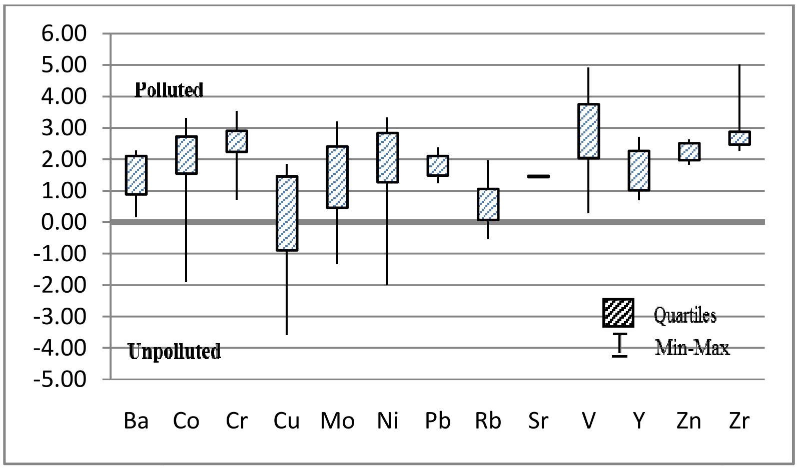

Fig.2. Geo-accumulation chart.

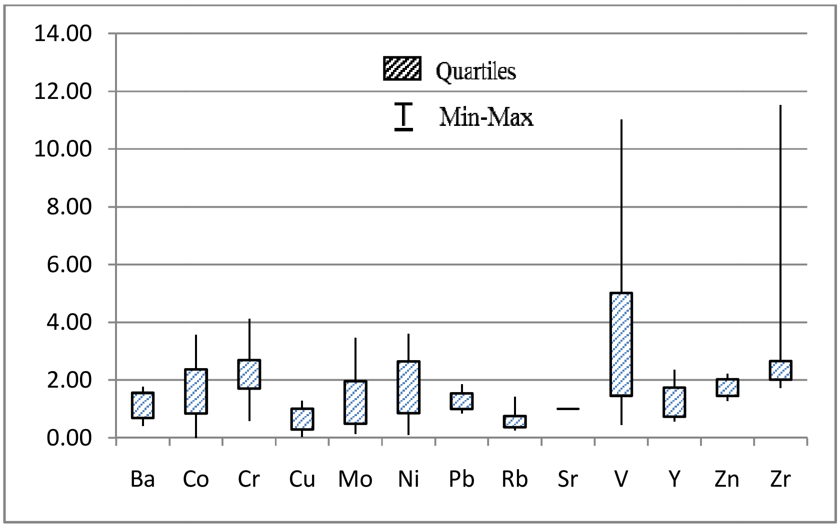

Fig.3.Enrichment Factor chart

Molybdenum

The mean Molybdenum content of 1.77 mg/kg ranging from 0.2 to 4.7 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.82) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Molybdenum as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.14 to 3.47 (Fig.3) and the mean EF of Molybdenum is 1.27 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.13 to 3.13 and the mean contamination factor is 1.18 (Fig.4), which is moderately contaminated with Mo [3].

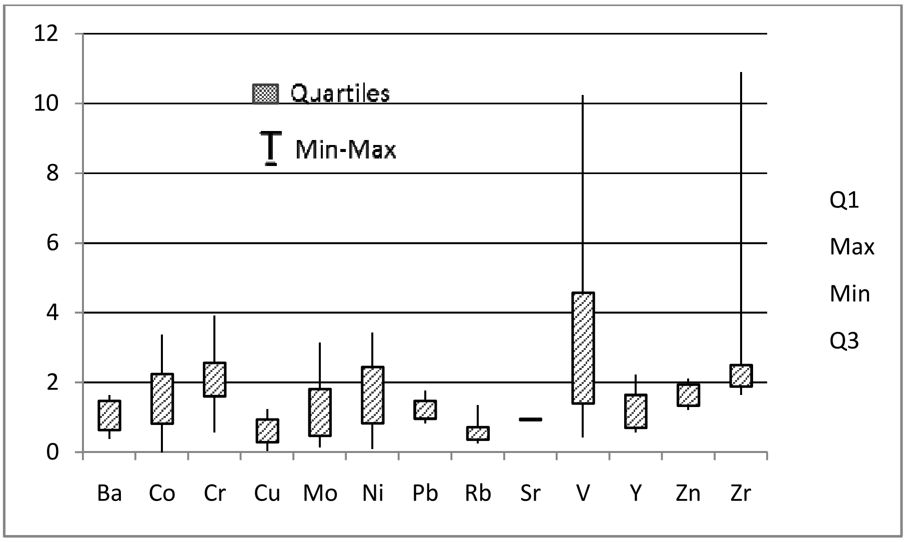

Fig.4. Contamination Factor chart

Table.4. Degree of contamination:

	minimum	Maximum	Mean
Ba	0.38	1.64	1.01
Co	0.00	3.37	1.62
Cr	0.56	3.91	2.11
Cu	0.03	1.22	0.66
Mo	0.13	3.13	1.18
Ni	0.09	3.42	1.63
Pb	0.81	1.76	1.19
Rb	0.23	1.34	0.58
Sr	0.89	0.95	0.93
V	0.42	10.24	4.19
Y	0.55	2.21	1.18
Zn	1.20	2.10	1.62
Zr	1.64	10.89	2.51
Deg. Of Contamination	6.93	46.17	20.41

Table.5. Correlation coefficient

	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
Ba	1												
Co	0.117	1											
Cr	-0.087	0.271	1										
Cu	0.001	0.148	0.248	1									
Mo	-0.534	-0.044	-0.052	-0.234	1								
Ni	0.117	0.209	0.328	-0.086	-0.060	1							
Pb	-0.198	0.191	0.253	-0.127	0.297	0.359	1						
Rb	-0.103	0.542	0.411	0.129	-0.358	-0.051	0.183	1					
Sr	0.205	0.087	-0.230	0.323	-0.275	-0.446	-0.319	0.258	1				
V	0.039	-0.075	0.154	-0.306	0.023	0.253	-0.217	-0.057	-0.107	1			
Y	0.185	0.355	0.211	-0.054	0.287	0.009	0.244	0.310	-0.210	0.147	1		
Zn	-0.187	0.150	-0.336	-0.045	0.309	-0.391	0.041	0.069	0.242	-0.311	0.081	1	
Zr	0.253	-0.173	0.062	0.033	0.020	-0.246	-0.049	-0.044	0.151	0.444	0.354	-0.180	1

Nickel

The mean Nickel content of 32.67 mg/kg ranging from 1.7 to 68.3 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.24) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Nickel as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.09 to

3.61 (Fig.3) and the mean EF of Nickel is 1.76 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.09 to 3.42 and the mean contamination factor is 1.63 (Fig.4), which means moderate contamination factor with Ni [3].

Lead

The mean lead content of 23.86 mg/kg ranging from 16.1 to 35.1 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.38) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with lead as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.85 to 1.85 (Fig.3) and the mean EF of lead is 1.28 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.81 to 1.76 and the mean contamination factor is 1.19 (Fig.4), which means moderate contamination factor with Pb[3].

Rubidium

The mean Rubidium content of 65.42 mg/kg ranging from 26.1 to 150.2 mg/kg has been found in study area (Table.3). The mean I_{geo} (-1.53) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Rubidium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.25 to 1.42 (Fig.3) and the mean EF of Rubidium is 0.62 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.23 to 1.34 and the mean contamination factor is 0.58 (Fig.4), which means low contamination factor indicating low contamination with Rb[3].

Strontium

The mean Strontium content of 326.72 mg/kg ranging from 312.8 to 333.2 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.68) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Strontium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). Strontium used as a reference element. A reference element is the one characterized by low occurrence variability[12]. This work uses Strontium as reference element. Strontium is one of the main components of the Earth's crust, and its concentration in soil is connected mainly with matrix.

Vanadium

The mean vanadium content of 251.21 mg/kg ranging from 25.1 to 614.2 mg/kg has been found in study area (Table.3). The mean I_{geo} (0.99) obtained reveal that the sample examined fell into class 1, which is uncontaminated to moderately contaminated with vanadium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.44 to 11.02 (Fig.3) and the mean EF of cobalt is 4.49 confirming the moderate enrichment [14]. The contamination factor is ranging from 0.42 to 10.24 and the mean contamination factor is 4.19 (Fig.4), which show the considerable range of contamination factor with V [3].

Yttrium

The mean Yttrium content of 26.03 mg/kg ranging from 12.1 to 48.6 mg/kg has been found in study area (Table.3). The mean I_{geo} (-0.49) obtained reveal that the sample examined fell into class 0, which is practically uncontaminated with Yttrium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 0.58 to 2.37 (Fig.3) and the mean EF of Yttrium is 1.27 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 0.55 to 2.21 and the mean contamination factor is 1.18 (Fig.4), which means moderate contamination factor with Y [3].

Zinc

The mean zinc content of 115.14 mg/kg ranging from 85.5 to 148.8 mg/kg has been found in study area (Table.3). The mean I_{geo} (0.09) obtained reveal that the sample examined fell into class 1, which is uncontaminated to moderately contaminated with zinc as per Muller's (1981) six classes of the geoaccumulation index (Fig.2). The EF ranged from 1.27 to 2.21 (Fig.3) and the mean EF of Zinc is 1.74 confirming the deficiency to minimal enrichment [14]. The contamination factor is ranging from 1.20 to 2.10 and the mean contamination factor is 1.62 (Fig.4), which means moderate contamination factor with Zn [3].

Zirconium

The mean Zirconium content of 476.14 mg/kg ranging from 311.7 to 2069.3 mg/kg has been found in study area (Table.3). The mean I_{geo} (0.59) obtained reveal that the sample examined fell into class 1, which is uncontaminated to moderately contaminated with Zirconium as per Muller's (1981) six classes of the geoaccumulation index (Fig.2).

The EF ranged from 1.72 to 11.52 (Fig.3) and the mean EF of cobalt is 2.68 confirming the moderate enrichment [14]. The contamination factor is ranging from 1.64 to 10.89 and the mean contamination factor is 2.51 (Fig.4), which means moderate contamination factor with Zr[3].

The mean Igeo value of Ba, Co, Cu, Mo, Ni, Pb, Rb, Sr and Y indicates that these elements fell into class '0', which is practically uncontaminated. Uncontaminated to moderately contaminate with Cr, V, Zn and Zr these elements fell into class '1' as per Muller (1981) six class index of geoaccumulation(Fig.2).

Deficiency to minimal enrichment with the Ba, Co, Cu, Mo, Ni, Pb, Rb , Sr, Y and Zn. Moderate enrichment with the Cr, V and Zr according to Hakanson (1980) five contamination categories of Enrichment factor (Fig.3).

The mean Contamination Factor values indicating that, low contamination factor with Cu, Rb and Sr. Moderate contamination factor with Ba, Co, Cr, Mo, Ni, Pb , Y, Zn and Zr. Considerable contamination factor with V according to Hakanson (1980) four categories index of contamination factor (Fig.4).

According to the Degree of Contamination the metals are in the order of V>Zr>Cr>Ni>(Co & Zn)>Pb>(Mo & Y)>Ba>Sr>Cu>Rb (Table.4). All most all metals showing the negative correlation except Co with Rb observed (Table.5).

CONCLUSION

On the whole, the degree of contamination value 20.41 representing the considerable degree of contamination in the study area. Correlation matrix of the metal data reveals the strong positive correlation between Co withRb, and rest of all metals representing the weak correlation. That does indicating the metals are fromgeogenic, supporting the study area is having the sediment dunes formed as a result of rapid climatic and geomorphological changes involving multiple cycles of deposition from millions of years.The study area is very closer and slopes to the Bay of Bengal, it is under severe erosion during rainy season. As a result of rapid erosion these metals are ending up into the sea, causes hazard to the aquatic environment. Metal depletion in the soil of mean EF<1 was observed for most elements is indispensable to the proper growth of the plants.

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