International Journal of Research
Available at https://edupediapublications.org/journals
e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 05 Issue 12
April 2018

Distribution of Heavy metals in Sediments of Wailpalli watershed, Nalgonda District, Telangana, India

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Abstract

Monitoring of sediments is important for tracing the spreading and impact of pollution related changes as lakes/stream sediments act as sinks of pollution and accumulate heavy metals from the surrounding geogenic or anthropogenic sources. Environmental geochemical investigations were carried out in and around Wailpalli watershed located in between the latitudes 17^{0}20" to 17^{0}80", longitudes 78^{0}48" to 79^{0}00" of Nalgonda district to assess the distribution of heavy metals in the study area. Sediment samples were collected and analyzed for Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr concentrations by Philips PW 2440 X-ray fluorescence spectrometer (XRF). Sediment samples were collected along the streams (nalas/creek) from a depth of 0-10cms. The concentration ranges were Ba 929.4 mg/kg, Co 36.2 mg/kg, Cr 107.8 mg/kg, Cu 43.1 mg/kg, Ni 69.8 mg/kg, Pb 114.1 mg/kg, Rb 446.2 mg/kg, Sr 360.6 mg/kg, V 240.8 mg/kg, Zn 130.1 and Zr 2668 mg/kg. The visualization of spatial data is made by preparing distribution maps of heavy metal concentration in sediments using SURFER software. Using multivariate statistical analysis (PC, PCA), we evaluate the interrelationship of elements, and enrichment factor (EF) analysis was used for the differentiation of the metal source between anthropogenic and geogenic. These results indicate prevalent enrichment of Co, Cu, Ni, Pb, Rb, V and Zn which highlight the need for instituting a systematic and continuous monitoring of the study area for heavy metals as most of the area in Wailpalli watershed is under active irrigation and these elements may enter the food chain of the human beings and may be hazardous to human health.

Keywords: *Sediments; Heavy metals; Enrichment factor; Metal distribution; Wailpalli*

1. Introduction

Heavy metals may be natural constituents of the sediments. They come from rocks and soils via their geochemical mobility. They also can be anthropogenic sources, in which case they are incorporated into the sediments as artificial pollutants coming from industrial or urban releases and wastes (Benamar et al., 1999).

Sediment contamination possesses one of the worst environmental problems in marine ecosystems, acting as sinks and sources of contaminants in aquatic systems (Adams et al., 1992; Mucha et al., 2003). Sediments are preferable monitoring tools since contaminant concentrations are orders of magnitude higher and they show less variation in time and space, allowing more consistent assessment of spatial and temporal contamination (Tunear et al., 2001; Caccia et al., 2003). Heavy metals in water and sediments of the wailpalli watershed may have a substantial detrimental effect on the environment of alluvial plain and delta regions due to their toxicity and accumulation in microorganisms, plants, animals and humans. Hence, knowledge of heavy metal concentration and distribution in sediments is of fundamental importance in an environmental study of the Wailpalli watershed area.

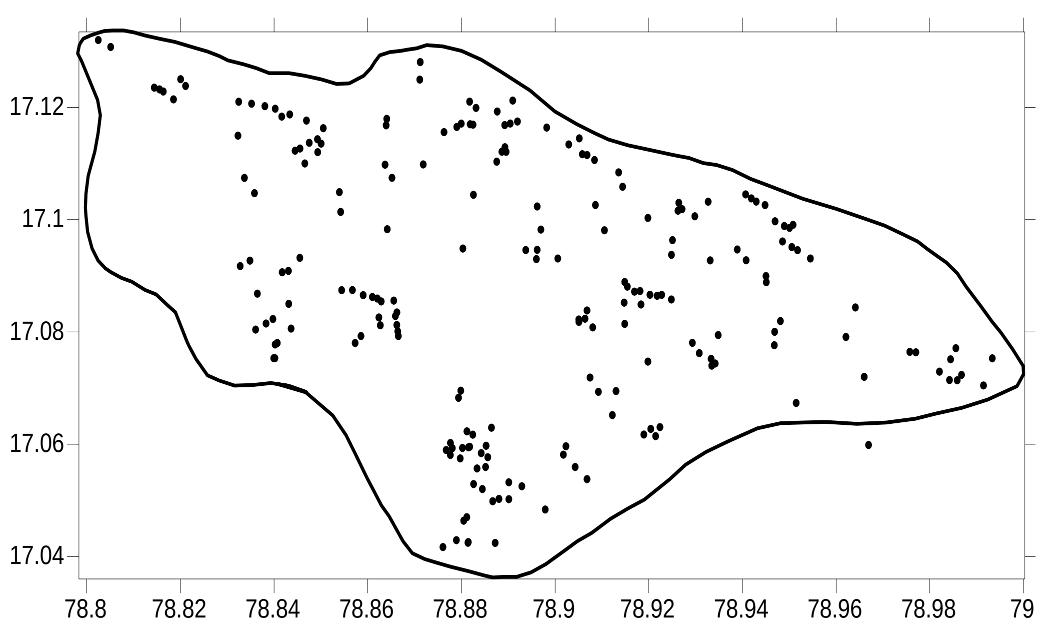
It is generally regarded that the bioavailability of heavy metals is closely related to their chemical forms, rather than the total concentration in sediments (Forstner, 1993). Heavy metals in sediments occur in different geochemical forms, which have distinct mobility, biological toxicity and chemical behaviors. It is essential to distinguish and quantify the various forms of metals to yield better understanding of the potential and actual environmental impacts of contaminated sediments. However, direct determination of specific chemical forms is generally impractical due to various binding phases of metals and their structural properties (Gonzalez et al., 2000). The concentrations of heavy metals will show exponential increase with time, because there is no activity to funnel out the sediments and dilute the effects of pollution. This increase will pose more threats as ultimately it will make its way laterally and vertically through the sediments, thereby polluting groundwater. The main aim of the present study which is the first comprehensive investigation of distribution of heavy metals in sediment in Wailpalli watershed, application of multivariate statistics, correlation matrix and to study the enrichment factor of the elements analyzed and to identify possible sources of sediment bound heavy metals.

2.0 Study area

2.1 Regional setting

Wailpalli watershed area is approximately 120 sq km extending in the east west direction ~ 15 km and NS direction about 8 km. Figure. 1 represents the location map of the study area. The area is structurally controlled and a major lineament passing through the center of the watershed. In the western side, with hillocks about 30m thick valley fills/weathered portion formed as potential groundwater sources. The area between Madhu Tanda and Radhanagar Tanda about 1 sq km groundwater being exploited through more than 100 bore wells with submersible pumps, there are of medium size and many small size tanks exist.

Location map of sediments samples - Wailpalli watershed



e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 05 Issue 12
April 2018

Fig: 1 Location map of the study area.

2.2 Physiography and drainage

The area is connected to Hyderabad- Nagarjunsagar state highway on the west and the Hyd-Vijaywada NH-7 on east taking off at Gunegal and Chowtuppal. Physiographically the area is represented by a series of low hill ranges with valleys filled up by alluvial deposits with generally rolling topography. The northwest and western parts are having ground surface elevation of 400m above mean sea level and above with gentle gradients in south eastern and eastern directions with lowest level and above with gentle gradients in southeastern directions with village. The drainage is dendritic in nature indicating no variations in resistance of the rocks to influence the stream pattern in the area.

2.3 Climate and rainfall

The area is served mostly by the south west and to a lesser extent by the Northeast monsoon. The normal annual rainfall of the area is 836.50 mm. The climate of the area is semi-arid to arid.

2.4 Hydrogeology

The investigated area is underlain by Archean group of rocks, mainly consisting of granites and gneisses. They are mostly pink and grey granites. These rocks are intruded by dolerite dykes. The textures of rocks observed were porphytic, medium to coarse grained. Pink granites are predominantly spread over the entire area with quartz and feldspars as essential minerals. Grey granites are also seen in Jangaon and Purlakunta surrounding villages. The pink granite patches are observed in Yelmakanna village.

Dolerite dykes are observed in Ghatt uppal, Lachnaguddam villages. The trend of the dyke is mainly East-West and in some places Northeast- Southwest. Occurrence of groundwater is controlled by dykes. The investigated area is covered by red sandy, loamy, clayey and black clayey soils of 1 to 2m thickness. Black cotton soils are occurring in grey granitic areas.

3. Material and methods

3.1 Sample collection and preparation

Surface sediment samples (0-10cms) were collected with augers. Sampling locations were chosen to provide good area coverage (Fig.1). After sampling, sediment samples were dried and kept in an oven for two days at 60^0C temperature. The dried sediments were then disaggregated with mortar and pestle and sieved through 2mm sieve and further these samples were ground in agate swing grinding mill to make the sample homogeneous and to get accurate analytical data, as it is essential that the surface layer should be representative of the bulk specimen. Weighing of sample is accomplished using analytical balance with precision as low as 0.0001g. Pressed pellet is prepared by using collapsible aluminum cups (Govil, 1985; Krishna et al, 2007). These cups are filled with boric acid and about 2 gms of the finely powdered sample is put on the top of the boric acid and pressed under a hydraulic press at 25 tons pressure to get a pellet.

3.2 Instrumentation

Elemental composition was determined using X-ray fluorescence spectrometer, type Philips MagiX PRO model PW2440 XRF with an Rh 4KW tube. Its high level performance enables a very sensitive and accurate determination of major & trace elements (Si, Al, Na, Mg, Ca, Fe, P, S, As, Ba, Co, Cd, Cu Mo, Ni, Pb, Rb, Sr, V, Zn & Zr). With the PW 2440 it is possible to scan the elements of interest from F to U. The MagiX PRO is a sequential instrument with single goniometer- based measuring channel covering the complete elemental range. The instrument is microprocessor controlled for maximum flexibility.

International soil and sediment reference materials from US Geological Survey, Canadian Certified reference materials (SO-1, 2, 3, 4; LKSD-1, 2, 3, 4). International working groups France & National Geophysical Research Institute, India were used to prepare the calibration curves for major and trace elements and to check the accuracy of the analytical data.

3.3 Statistical analysis

In present study the Pearsons coefficient (PC) and principal component analysis (PCA) were conducted using SPSS for windows 2.0 in order to study the interrelationship among the chemical elements. The varimax method was chosen as the rotation method for PCA. The distribution maps of all the elements are constructed using SURFER 8.0 version. The interpolation method used was kriging method. Descriptive statistics of the analyzed samples for the nine elements is given in Table1.

4. Results and discussion

4.1 Heavy metal concentrations

Some of the elements show a wide variation in elemental concentration as reflected by large standard deviation values. The descriptive statistical analysis data is shown in Table.1.

Element	Ba	Co	Cr	Cu	Ni	Pb	Rb	Sr	V	Zn	Zr
Minimum	128.5	0.4	15.8	1.6	0.2	2.3	8.0	73.0	7.9	24.5	108.4
Maximum	929.4	36.2	107.8	43.1	69.8	114.1	446.0	360.6	240.8	130.1	2668.9
Mean	539.9	12.7	60.6	19.0	26.3	39.5	232.1	160.9	87.3	56.8	786.2
Median	538.6	11.4	59.1	15.9	23.3	36.8	236.5	154.1	89.1	52.6	562.6
Mode	551.2	11.4	54.1	9.6	21.9	38.2	236.7	126.8	54.1	59.2	662.4
Standard Deviation (±)	108.0	7.4	14.8	9.6	14.0	15.7	76.1	52.1	40.4	20.9	733.2
Kurtosis	1.3	-0.6	0.4	-0.8	-0.1	2.9	0.7	1.5	0.6	0.1	12.7
Skewness	0.2	0.4	0.3	0.5	0.6	1.2	-0.3	1.1	0.5	0.7	2.8
Coef. Of Variation (%)	20.0	58.3	24.4	50.5	53.2	39.8	32.8	32.4	46.3	36.8	93.3

Table 1. Descriptive statistics of the determined elements in stream sediment samples (n=208), Wailpalli, Nalgonda District, Andhra Pradesh, India.

4.2 Principal Component Analysis (PCA)

In the analysis the first three principal components accounted for nearly 81.90% of the total variance, and the variances of F1, F2 & F3 is 48.97, 22.17, 10.76% respectively (Table.2). Apparently the result of PCA is well corresponded with coefficient correlation matrix. The first group includes chemical elements of Ba, Co, Cr, Ni, V and Zn. The scores of F1 for these elements are much higher than the other two factors, and relatively coefficient between these groups of parameters exceed 0.70. Elements Co, Ni, and Cr belong to siderophile element, and is main rock forming elements. It is easy for them catering into iron-magnesium silicate mineral for isomorphism with Fe and Mg; in natural environment; Cu and Zr always disperse in rock-forming minerals besides existing as independent minerals in shallow sea environment, Ba usually exists in detrital silicate minerals (Zwolsman, et al., 1996). This association represents lithological and natural input in the area, i.e, the elements in the group come from the terrigenious detrital matter taken by the run-off.

Element	Ba	Co	Cr	Cu	Ni	Pb	Rb	Sr	V	Zn	Zr
Ba	1.00										
Co	0.64	1.00									
Cr	0.35	0.63	1.00								
Cu	0.45	0.88	0.67	1.00							
Ni	0.34	0.73	0.72	0.79	1.00						
Pb	0.51	0.44	0.00	0.26	0.12	1.00					
Rb	-0.15	-0.36	-0.41	-0.44	-0.30	0.29	1.00				
Sr	-0.23	-0.14	0.14	0.00	0.08	-0.62	-0.54	1.00			
V	0.89	0.81	0.45	0.62	0.47	0.55	-0.20	-0.28	1.00		
Zn	0.63	0.90	0.48	0.86	0.66	0.58	-0.25	-0.19	0.75	1.00	
Zr	0.15	-0.24	-0.20	-0.43	-0.39	0.02	0.22	-0.17	0.09	-0.34	1.00

Table 2. Pearson's product moment linear correlation coefficients of determined metal elements in stream sediment samples (n=208).

F2 scores of Pb, Rb exceeds 0.65, beyond the other elements the scores of Ba, V, and Zr exceeds 0.35 but less than 0.5. From coefficient matrix, Table.2 Zn has much higher co-relation with Ba, Co, Cu, Pb and V. Zinc has quite similar geochemical character with Pb and always accretes with it, the Zn in waters can also be absorbed by organic matter during the migration. The trace elements Co, Cr, Cu, Ni and Ba always migrate in colloid form in aquatic environment and deposit to the bottom sediment. Therefore, the association of F2 is similarly related to local anthropogenic as well as natural inputs.

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The remaining elements Sr and Rb also confer the natural input from surrounding rocks. The element association obtained by correlation coefficient and principal component score can indicate different origin of heavy metals in the sediments. The feature of point sources lies in that the impact of heavy metals occur over a finite period of time and many have been effectively retained in the sediments near the sources, rather than re-suspended and distributed uniformly throughout the study area.

4.3 Enrichment Factor (EF)

The main component of elements in sediments is the aluminosilicate material. If there were no anthropogenic sources, concentration of elements should have been explained by this source (Table.3). However, contribution from various natural and anthropogenic sources, the degree of the modification in the chemical composition of sediments may be different at each sampling point due to different magnitude of source contributions at each station (Atgm et al., 2000). Generally EF values less than 10.0 are not considered significant, since such small enrichments may arise from differences in the composition of local soil material and reference soil used in EF calculation.

Element	Factor 1	Factor 2	Factor 3
Ba	0.718	0.379	0.425
Co	0.959	0.002	0.002
Cr	0.694	-0.376	0.118
Cu	0.905	-0.242	-0.159
Ni	0.782	-0.324	-0.187
Pb	0.478	0.728	-0.217
Rb	-0.370	0.669	-0.371
Sr	-0.138	-0.820	0.291
V	0.845	0.338	0.323
Zn	0.927	0.100	-0.170
Zr	-0.285	0.465	0.725
Eigen value	5.39	2.44	1.18
% variance explained	48.97	22.17	10.76
Cumulative % variance	48.97	71.14	81.90

Table 3. Factor loadings on elements in stream sediment samples (n=208).

Using the data obtained in the analysis, the EF of all the elements can be calculated by the following equation:

$$(EF) = \frac{(C_x / C_{Zr})_{Sample}}{(C_x / C_{Zr})_{Crust}}$$

Where $(C_x / C_{Zr})_{Sample}$ is the ratio of concentration of the element being tested (C_x) to that of Zr (C_{Zr}) in the sediment sample and $(C_x / C_{Zr})_{Crust}$ is the same ratio in unpolluted reference baseline. However, metal enrichment identification can be utilized as a sifting tool to assist cost-effective use of sediment toxicity tests. Therefore, only those with metal concentrations exceeding the expected natural background levels will be further studied on toxicity (Chapman and Wang, 2001).

The EF values are interpreted as suggested by Blaser et al., 2000 and Zhang and Liu, 2002: The EF<1 indicates enrichment depletion, EF.1 indicates enrichment and EF>1.5 is considered to indicate that an important proportion of trace metals is delivered from non-crustal materials or non-natural weathering processes. EF>2 means the significant enrichment. From Table.4 the minimum, median and maximum enrichment factors were calculated for all analyzed metals in this study area.

Statistical parameters	EF-Ba	EF-Co	EF-Cr	EF-Cu	EF-Ni	EF-Pb	EF-Rb	EF-Sr	EF-V	EF-Zn
Minimum	0.31	0.45	0.49	0.26	0.41	0.53	0.69	0.12	0.50	0.26
Maximum	1.67	3.59	3.88	2.47	3.99	4.03	2.43	0.94	3.09	2.24
Median	0.30	0.31	0.58	0.20	0.36	0.64	0.73	0.16	0.38	0.24

Table 4. Minimum, maximum and median values of Enrichment Factor (EF) for the determined elements in stream sediment samples (n=208).

4.4 Distribution maps of elements

The distribution of elements concentrations in sediment samples collected from wailpalli watershed are given as contour maps. The distribution patterns of 9 elements (Ba, Sr, Cu, Zn, Cr, Ni, Co, Pb and V) whose concentrations were measured by X-ray fluorescence spectrometer (XRF) were depicted through the interpolation of elemental concentrations by using SURFER 8.0 software. Distribution of Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr were skewed (the skewness coefficient exceeded 1.0). The highest skewness is found in Zr with the g1 value of 2.82. Skewness measures the asymmetry of the observations. The environmental geochemical phenomena including heavy metal concentrations in sediments, commonly correlated, are caused by the physico-chemical features of elements and geochemical processes (Zhang and Selinus, 1998).

The sediment samples in the study area contain concentrations in the range of 929.4 mg/kg for Ba, Co 36.2 mg/kg, Cr 107.8 mg/kg, Cu 43.1 mg/kg, Ni 69.8 mg/kg, Pb 114.1 mg/kg, Sr 446.0 mg/kg, V 360.0 mg/kg, Zn 130.1 mg/kg and Zr 5668.9 mg/kg. This high barium enrichment can be attributed to feldspar weathering in silicate rocks. High levels of Sr are commonly found in acidic rocks such as granite which is a common rock in the area. Therefore, the high levels of Ba and Sr may not be due to any anthropogenic source but due to erosion of granite surrounding the study area.

The abundance of Cu in basaltic rocks is greater than for granitic rocks, and is very low in carbonate rocks (Alloway, 1995). Gabbro & basalt rocks have higher Cu contents, and granite the lowest, which clearly indicates the geogenic source from surrounding rocks. The abundance of Cu in soil and plants is less than that of Zn unless the soil has been contaminated with an industrial source of Cu.

Concentration of Chromium and Nickel in granitic igneous rocks range from 2-90 mg/kg for Cr, and 2-20mg/kg for Ni. Depending on the origin of the soil and pedogenic processes, the surface or the subsoil may be relatively enriched, or have the same Ni concentrations. Distribution of Cobalt is normal throughout the area, the maximum value being approximately 36.2 mg/kg. Lead appears to accumulate naturally in surface horizons of soil and sediments. Most heavy metals, including Pb, remain in an insoluble or stable form in surface layers of sediments after application of sewage sludge.

Vanadium is ubiquitous in the lithosphere, with a mean crustal abundance of 150 mg/kg this is of the same order as Ni, Cu, Zn and Pb. V is largely associated with basic magmas, especially titaneferous magnatites, and may be present in elevated concentrations; in acidic and silicic igneous rocks, V content is much lower.

5. Conclusion

The concentration and spatial distribution of trace metals Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr has been observed at different points in the study area. These metals mainly come from the geogenic source from the surrounding rocks controlling the large scale distribution.

From the enrichment factor analysis the study area is prevalently enriched in Ba, Co, Cu, Cr, Rb and Zn. This suggests that these metals are not toxic and readily bioavailable at the measured concentrations. The peculiar high EF values of Pb and Ni suggest that point source input of some specific metal contamination may have caused significant sediment contamination in the local area. With further industrialization and economic development in the study area, greater attention should be paid to point source contamination around the area. Although additional work is required to examine this possibility in more detail, the present study has provided a fundamental understanding of the link between toxicity and bioavailability of metals in the sediments and valuable insight into the ecological responses to human-induced stresses.

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