A Multivariate Statistical Approach for Monitoring of Heavy Metals in Sediments: A Case Study from Wailpalli Watershed, Nalgonda District, Andhra Pradesh, India

A. Keshav Krishna, K. Rama Mohan and N.N. Murthy
Environmental Geochemistry Group, National Geophysical Research Institute, (Council of Scientific and Industrial Research), Hyderabad, India

Abstract: The aim of the present study, focuses on investigation of heavy metal distribution in sediments of the Wailpalli watershed located in Nalgonda district of Andhra Pradesh, India, and to study different causes of enrichment by applying multivariate statistics on the studied elements, including correlation and factor analyses, and to identify possible sources of sediment bound heavy metals. Sediment samples were collected along the streams from a depth of 0-10 cm and were analyzed for Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr by using Philips PW 2440 X-ray fluorescence spectrometer (XRF). The concentration ranges were Ba 128.5 to 929.4 mg/kg, Co 0.4 to 36.2 mg/kg, Cr 15.8 to 107.8 mg/kg, Cu 1.6 to 43.1 mg/kg, Ni 0.2 to 69.8 mg/kg, Pb 2.3 to 14.1 mg/kg, Rb 8.0 to 446.2 mg/kg, Sr 73.0 to 360.6 mg/kg, V 7.9 to 240.8 mg/kg, Zn 24.5 to 130.1 mg/kg, and Zr 108.4 to 2668 mg/kg. Distribution maps metal concentrations in sediments were plotted by using Golden Software’s SURFER program. Using multivariate statistical analysis (correlation coefficients, factor analysis), the interrelationships among elements, and Enrichment Factor (EF) was calculated to differentiate the origin of metals between anthropogenic and geogenic sources. The results of median EF indicate no significant enrichment of the metals (Co, Cu, Ni, Pb, Rb, V and Zn) except for high Pb and Ni possibly indicating some point source input to the stream sediments. However, systematic and continuous monitoring of the study area for heavy metals is necessary as most of the area in Wailpalli watershed is under active irrigation and these elements may enter the food chain, and could be hazardous to human health.

Key words: Enrichment factor, India, metal distribution, heavy metals, sediments, wailpalli

INTRODUCTION

Heavy metals are natural constituents of sediments. They come from rocks and soils through the processes of erosion, transport and deposition. They can also be derived from anthropogenic sources, in which case they are incorporated into sediments as artificial pollutants from industrial or urban releases and wastes (Benamar et al., 1999).

Sediment contamination constitutes 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 preferred monitoring tools, since contaminant concentrations are orders of magnitude higher than in water, and they show less variation in time and space, allowing more consistent assessment of spatial and temporal contamination (Thornton and Webb, 1979; Howarth and Thornton, 1983; Tuncer et al., 2001; Caccia et al., 2003). Heavy metal concentrations in water and sediments of the Wailpalli watershed, if their abundance is above normal, they 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 speciation, rather than the total concentration in sediments. Heavy metals in sediments occur in different geochemical forms, which have distinct mobility, biological toxicity and chemical behaviours. It is essential, therefore, to distinguish and quantify the various molecular and ionic species of metals in order to understand 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 an increase with time, because there is no activity to funnel out the sediments and dilute the effects of pollution. This
potential increase in heavy metal concentrations will pose more threats, due to their lateral and vertical movement 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 the Wailpalli watershed, is to study different causes of enrichment by applying multivariate statistics on the studied elements, including correlation and factor analyses, and to identify possible sources of sediment bound heavy metals.

Study area:
Regional setting: The Wailpalli watershed area is approximately 120 km² extending for ~15 km in an E-W direction, and 8 km in a N-S direction (Fig. 1). The area is structurally controlled by a major lineament passing through the centre of the watershed. The IRS-ID satellite image, studied by Seshunarayana et al. (2008), shows clearly two sets of lineaments in this region oriented (i) N-S to NE-SW and (ii) ESE-WNW. These lineaments express themselves as narrow linear valleys forming one of the main drainage systems in the Wailpalli watershed area. These lineaments cut across the granite massifs and probably underlie the alluvial cover. Ground structural analysis points to shear zones, fractures and dykes.

Physiography and drainage: The area is connected to the Hyderabad-Nagarjunsagar State highway in the west, and the Hyd-Vijaywada NH-7 in the east, which branches at Gunegal and Chowtuppal. Physiographically the area is made up of a series of low hill ranges with valleys filled up by alluvial deposits with generally rolling topography. The north-west and western parts have a ground surface elevation of up to 400 m above mean sea level, with gentle slopes to the SE and E. The drainage is dendritic, indicating no variations in resistance of the rocks to erosion.

Climate and rainfall: The climate of the area is semi-arid to arid. It is affected mostly by the south-west and to a lesser extent by the north-east monsoon. The average annual rainfall is 836.50 mm.

Geology: Figure 2 shows the simplified geological map of the study area. The investigated area is underlain by Archaean rocks, mainly consisting of pink and grey granite and gneiss. These rocks are intruded by dolerite dykes. The texture of “these granite” rocks observed were porphyritic, medium to coarse grained. Pink granite with quartz and feldspars as the major minerals is predominantly found over the entire area, and in patches near the Yelmarkanna village. Grey granite is seen in the
vicinity of the villages of Jangaon and Purlakunta. Dolerite dykes occur in the vicinity of the villages of Ghatt uppal and Lachnaguddam. The trend of the dyke is mainly E-W, and in some places NE-SW. The investigated area is covered by red sandy, loamy, clayey and black clayey soil of 1 to 2 m thickness. Black cotton soils which do not absorb much water and are extremely prone to water logging occur over grey granitic areas.

The study area is devoid of major strike features, like folds and faults. Many mafic dykes, which are basically fine grained dolerite, traverse the granite. Groundwater is controlled by the dolerite dykes, and occurs in shallow-weathered gneiss. The depth of water level varies from a few metres to about 26 m below ground level (Saxena et al., 2005). Groundwater is mostly extracted through dug wells and bore wells for irrigation, and domestic purposes. The main source of groundwater is precipitation, and to a lesser extent infiltration of water from tanks and surface water during the monsoon periods.

**MATERIALS AND METHODS**

**Sample collection and preparation:** Active surface sediment samples (n = 208) were collected from 0-10 cm depth. Sampling locations were chosen to provide good area coverage (Fig. 1). After sampling, sediment samples were dried in a thermostatically controlled oven for two days at 60°C temperature. The dried sediments were then disaggregated in a porcelain mortar with a pestle, and sieved through a 2 mm nylon mesh. The samples were subsequently ground in agate swing grinding mill to fine powder for better homogenisation of the sample, in order to obtain a representative aliquot for precise analytical results.

Two grams of each powdered sample was weighed using an analytical balance with a precision as low as 0.0001 g. Pressed pellets were afterwards prepared by using collapsible aluminium cups (Krishna et al., 2007). These cups are filled at the bottom with ~2.5 g of boric acid, and the 2 g of the fine powdered sample is placed on the top, and “then” pressed under a hydraulic pressure of 25 tons to obtain the pellet of each sample.

**Instrumentation:** Elemental composition was determined using an X-ray fluorescence spectrometer, type Philips MagiX PRO model PW2440 XRF with Rh 4KW tube. The MagiX PRO is a sequential instrument with a single goniometer-based measuring channel covering the element range from F to U. The instrument is microprocessor controlled for maximum flexibility. Its high level performance enables, therefore, a sensitive and accurate determination of major and trace elements (Si, Al, Na, Mg, Ca, Fe, P, S, As, Ba, Co, Cd, Cu Mo, Ni, Pb, Rb, Sr, V, Zn and Zr). The accuracy of analytical results was evaluated by comparison with certified values of the analyzed reference materials. Results of certified reference materials were within the quoted confidence limits.

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

**Statistical analysis:** For the study of interrelationships among the chemical elements determined, the Pearson’s product moment linear correlation coefficient (PC) and principal component analysis (PCA) were calculated using version 2 of the SPSS package for Windows. The varimax method was chosen as the rotation method for
RESULTS AND DISCUSSION

Heavy metal concentrations: The multiple box and whisker plots show the statistical distribution of heavy metal concentrations in the Wailpalli stream sediments. The rectangular part of the plot extends from the 1st quartile to the 3rd quartile, which cover the central half of the concentrations of each element, representing 50% of the values. The central line within each box shows the location of the median concentration of each element. The whiskers extend on either side of the box up to 1.5 times the interquartile range; outliers are plotted as individual points (+).

All studied elements have a wide variation in their concentrations, and the greatest is shown by Co, Cu, Ni, V and Zr (Fig. 3, Table 1).

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Minimum</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Rb</th>
<th>Sr</th>
<th>V</th>
<th>Zn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>128.5</td>
<td>0.4</td>
<td>15.8</td>
<td>1.6</td>
<td>0.2</td>
<td>2.3</td>
<td>8.0</td>
<td>73.0</td>
<td>7.9</td>
<td>24.5</td>
<td>108.4</td>
</tr>
<tr>
<td>Maximum</td>
<td>929.4</td>
<td>36.2</td>
<td>167.8</td>
<td>43.1</td>
<td>69.8</td>
<td>114.1</td>
<td>466.0</td>
<td>360.6</td>
<td>240.8</td>
<td>103.0</td>
<td>2668.9</td>
</tr>
<tr>
<td>Mean</td>
<td>539.9</td>
<td>12.7</td>
<td>60.6</td>
<td>19.0</td>
<td>26.3</td>
<td>39.5</td>
<td>223.1</td>
<td>160.9</td>
<td>87.3</td>
<td>56.8</td>
<td>786.2</td>
</tr>
<tr>
<td>Median</td>
<td>538.6</td>
<td>11.4</td>
<td>59.1</td>
<td>15.9</td>
<td>23.3</td>
<td>36.8</td>
<td>236.5</td>
<td>154.1</td>
<td>89.1</td>
<td>52.6</td>
<td>562.6</td>
</tr>
<tr>
<td>Mode</td>
<td>551.2</td>
<td>11.4</td>
<td>54.1</td>
<td>9.6</td>
<td>21.9</td>
<td>38.2</td>
<td>236.7</td>
<td>126.8</td>
<td>54.1</td>
<td>59.2</td>
<td>662.4</td>
</tr>
<tr>
<td>Standard Deviation (±)</td>
<td>108.0</td>
<td>7.4</td>
<td>14.8</td>
<td>9.6</td>
<td>14.0</td>
<td>15.7</td>
<td>76.1</td>
<td>52.1</td>
<td>40.4</td>
<td>20.9</td>
<td>733.2</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>1.3</td>
<td>-0.6</td>
<td>0.4</td>
<td>-0.8</td>
<td>-0.1</td>
<td>2.9</td>
<td>0.7</td>
<td>1.5</td>
<td>0.6</td>
<td>0.1</td>
<td>12.7</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.5</td>
<td>0.6</td>
<td>1.2</td>
<td>-0.3</td>
<td>1.1</td>
<td>0.5</td>
<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Coef. of variation (%)</td>
<td>20.0</td>
<td>58.3</td>
<td>24.4</td>
<td>50.5</td>
<td>53.2</td>
<td>39.8</td>
<td>32.8</td>
<td>32.4</td>
<td>46.3</td>
<td>36.8</td>
<td>93.3</td>
</tr>
</tbody>
</table>

Fig. 3: Boxplots showing the variation of total heavy metal concentrations (mg/kg) in stream sediment samples (n = 208)

PCA. The distribution maps of all elements were prepared with version 8 of Golden Software’s SURFER program using linear kriging method. Descriptive statistics of the analyzed samples for the nine elements determined are tabulated in Table 1.

Element distribution maps: The distribution of nine elements concentrations in stream sediment samples (Ba, Sr, Cu, Zn, Cr, Ni, Co, Pb and V), collected from Wailpalli watershed are given as contour maps (Fig. 4 to 13). Environmental geochemical phenomena, including heavy metal concentrations in stream sediments, commonly correlated, are caused by the physico-chemical features of elements and geochemical processes (Zhang et al., 1998).

The sediment samples in the study area contain maximum concentrations for Ba 929.4, Co 36.2, Cr 107.8, Cu 43.1, Ni 69.8, Pb 114.1, Sr 446.0, V 360.0, Zn 130.1 and Zr 5668.9 mg/kg. Barium (Fig. 4) and Sr (Fig. 5) contents were found to be high in most stream sediment samples. This high Ba 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 to the erosion of granite occurring in the study area.

Distribution of copper in the study area ranged from 1.6 to 43.1 mg/kg with an average value of 19.0 mg/kg and zinc ranged from 24.5 to 130.1 mg/kg with an average value of 56.8 mg/kg. Figure 6 and 7 shows the distribution of Cu and Zn, respectively. The abundance of Cu in dolerite is greater than for granite rocks (Alloway, 1995). Data reveals that there is no considerable enrichment and pollution due to Cu and Zn which were within the threshold limits.

Chromium values in the study area ranged from 15.8 to 107.8 mg/kg (Fig. 8), with an average of 60.6 mg/kg and is considerably little higher in the area surrounded by granitic rocks, where normally Cr concentration is always below 50 mg/kg in granites. Whereas Ni values ranged from 0.2 to 69.8 mg/kg (Fig. 9) with average 26.3 mg/kg. The levels of Cr and Ni in sediments are within permissible levels which indicate its normal concentration and reflect the background value in sediments. The source appears to be the geogenic contribution of Cr and Ni in sediments. In general concentration of Cr and Ni in granitic igneous rocks range from 2-90 mg/kg for Cr and 2-20 mg/kg for Ni.

Distribution of Cobalt (Fig. 10) is normal throughout the area, the maximum value being 36.2 mg/kg. Lead...
Fig. 4: Distribution of Barium (mg/kg) in stream sediment samples (n = 208)

Fig. 5: Distribution of Strontium (mg/kg) in stream sediment samples (n = 208)

Fig. 6: Distribution of Copper (mg/kg) in stream sediment samples (n = 208)

appears to accumulate naturally in surface horizons of soil and sediments. Figure 11 shows the distribution of lead, there is little evidence that Pb is readily lost from soil profiles by leaching. Most heavy metals, including Pb, remain in an insoluble or stable form in surface layers of sediments after application of sewage sludge. Since there was no much coefficient of variation in the lead concentrations which ranged from 2.3 to 114.1 mg/kg with a mean value of 39.5 mg/kg in the study area the source would be geogenic from the run of sediments.

Figure 12 shows the distribution of Vanadium in the study area ranging from 7.9 to 240.8 mg/kg with an average value of 87.3 mg/kg. 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
Fig. 7: Distribution of Zinc (mg/kg) in stream sediment samples (n = 208)

Fig. 8: Distribution of Chromium (mg/kg) in stream sediment samples (n = 208)

Fig. 9: Distribution of Nickel (mg/kg) in stream sediment samples (n = 208)

Fig. 10: Distribution of Cobalt (mg/kg) in stream sediment samples (n = 208)
Fig. 11: Distribution of Lead (mg/kg) in stream sediment samples (n = 208)

Fig. 12: Distribution of Vanadium (mg/kg) in stream sediment samples (n = 208)

Fig. 13: Distribution of Zirconium (mg/kg) in stream sediment samples (n = 208)

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Ba</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Rb</th>
<th>Sr</th>
<th>V</th>
<th>Zn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.64</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.35</td>
<td>0.63</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.45</td>
<td>0.88</td>
<td>0.67</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.34</td>
<td>0.73</td>
<td>0.72</td>
<td>0.79</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.51</td>
<td>0.44</td>
<td>0.00</td>
<td>0.26</td>
<td>0.12</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>-0.15</td>
<td>-0.36</td>
<td>-0.41</td>
<td>-0.44</td>
<td>-0.30</td>
<td>0.29</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>-0.23</td>
<td>-0.14</td>
<td>0.14</td>
<td>0.00</td>
<td>0.08</td>
<td>-0.62</td>
<td>-0.54</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.89</td>
<td>0.81</td>
<td>0.45</td>
<td>0.62</td>
<td>0.47</td>
<td>0.55</td>
<td>-0.20</td>
<td>-0.28</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.63</td>
<td>0.90</td>
<td>0.48</td>
<td>0.86</td>
<td>0.66</td>
<td>0.58</td>
<td>-0.25</td>
<td>-0.19</td>
<td>0.75</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.15</td>
<td>-0.24</td>
<td>-0.20</td>
<td>-0.43</td>
<td>-0.39</td>
<td>0.02</td>
<td>0.22</td>
<td>-0.17</td>
<td>0.09</td>
<td>-0.34</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Principal Component Analysis (PCA): The results of the Pearson’s product moment linear correlation coefficients are shown in Table 2 and those of the Principal Component Analysis (PCA) in Table 3 and after varimax rotation in Table 4. Principal component analysis is one of the multivariate statistical analytical tools used to assess metal behaviour in sediments (Zhou et al., 2004; Liu et al., 2003), and it is applied to detect the hidden structure and associations of elements in the data set, in an attempt to explain the influence of latent factors on the data distribution (Simeonov et al., 2000).

The first three principal components account for 81.90% of total variance, and the variances of F1, F2 and F3 are 48.97, 22.17, 10.76%, respectively (Table 3). Apparently the result of PCA corresponds well with the correlation coefficients. Factor 1 has strong loadings of Co, Zn, Cu, V, Ni, Ba and Cr; correlation coefficients among this group of elements exceed 0.60. Cobalt, Ni and Cr belong to the siderophile elements, and are main rock forming elements. It is easy for them to enter into iron-magnesium silicate minerals, because of their similar ionic radius. Copper and Zr always disperse in rock-forming minerals, besides their occurrence as independent minerals; Ba usually exists in detrital silicate minerals (Zwolsman et al., 1996). This element association is considered to represent the lithology of the study area, and a natural input, i.e., they are derived from terrigenous detrital material transported by surface run-off.

Factor 2 loadings on Pb and Rb exceed 0.65, while those on Ba, V and Zr vary between 0.35 and 0.5 (Table 4). Zinc has a higher correlation with Co, Cu, V, Ni, Ba and Pb. Zinc has quite similar geochemical character with Pb. The association of Pb and Rb points to felsic rocks in the NW area, which occur in the basement and have been exposed by erosion. Factor 2 showing strong negative loading of -0.82 for Sr can be explained by the fact that Sr in stream sediment is contained in lithic fragments and detrital feldspars, also the distribution of Sr is affected both by strong adsorption on clay minerals as it can be seen from the study area covered by clayey soil. Therefore, the association of elements in F2 is considered to be related to geogenic inputs.

Factors 3 is dominated by the strong loading on Zr. Zircons are resistant to weathering and are invariably present in soil/sediment samples. The strong loading on Zr, and its association with Ba, V and Sr, suggests a geogenic source.

The impact of heavy metals occurs over a finite period of time, and many have been effectively retained in the sediments near their sources, rather than resuspended and distributed uniformly through out the study area.

Enrichment Factor (EF): The main geochemical component in sediments is the aluminosilicate material. If there are no influences by anthropogenic sources, the concentration of the elements should be explained by this source. However, because of the contribution from various natural and anthropogenic sources, the chemical composition of the sediments may be affected at each sampling point, due to different source contributions at each sampling location (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.

To assess the enrichment or depletion of trace elements in a stream sediment sample, the trace element concentration can be normalized to an element, which is relatively inert with respect to chemical weathering, and has no significant anthropogenic source. Zircon belongs to the lithophile elements, and always occurs as an oxide...
or a silicate; in addition, it has a high chemical stability during weathering. So, most of the Zr minerals accumulate in placer deposits, a small quantity takes part in sedimentation circulation and is absorbed by clay minerals (Shanshan et al., 2007). Zircon has been used widely in geochemical studies of mineral weathering as a stable lithogenic element or to assess the depletion of more reactive heavy metals in sediments (Rubio et al., 2000; Zhang et al., 2006; Cobela-Garcia and Prego, 2003), and to reduce the scatter of data and to allow a precise definition of background value as a normaliser. So, in this study Zr was chosen as the reference element.

The EF of all studied elements can be calculated by the following equation:

\[
EF = \frac{(C_x/C_{Zr})_{\text{sample}}}{(C_x/C_{Zr})_{\text{crust}}}
\]

where \((C_x/C_{Zr})_{\text{sample}}\) is the ratio of concentration of the element being tested \((C_x)\) to that of Zr \((C_{Zr})\) in the sediment sample, and \((C_x/C_{Zr})_{\text{crust}}\) is the same ratio in an unpolluted reference crustal baseline; the crustal Zr value used is 240 mg/kg (Taylor and Macleannan, 1995). However, metal enrichment identification can be utilized as a shifting tool to assist cost-effective use of sediment toxicity tests. Therefore, only the metals with concentrations exceeding the expected natural background levels should be studied with respect to toxicity (Chapman and Wang, 2001).

The minimum, median and maximum enrichment factors we calculated for all analysed metals in this study are given in Table 5 and Fig. 14. Elements can be divided into three major groups with respect to their corresponding median enrichment factors: elements without enrichment \((EF<10)\), elements with medium level enrichment \((10<EF<100)\) and finally highly enriched elements \((EF>100)\) (Hakan, 2006). For comparison purposes, the median EF values of elements are considered. All median EF values are below 10, indicating, therefore, that there is no significant metal enrichment. The area is dominated by granite and gneiss, which govern the distribution patterns of all elements. Consequently, the natural lithology is the dominant factor influencing the distribution of elements, and not anthropogenic sources.

**CONCLUSION**

The concentrations and spatial distribution of Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr are directly related to geogenic sources. There does not seem to be a significant enrichment of these metals in the stream sediment samples, as indicated by the median EF values. It can be safely assumed that these metals are not toxic and readily bioavailable at the measured concentrations. However, the high maximum EF values of Pb (4.03) and Ni (3.99) possibly suggests that there is locally some point source input of these metals, contaminating the stream sediment. As most of the study area is under active irrigation and the source of enrichment of these elements Pb and Ni would be from anthropogenic activity due to application of pesticides in agricultural activities. With further industrialization and economic development in the study area, greater attention should be paid to point source contamination.

This study was carried out under the CSIR Network project for the development of techniques and methodologies for exploration, assessment and management of groundwater in hard rock areas. Further, the findings in this study were significant because it has provided crucial information to decision makers, and regulatory agency staff, working on the protection of aquatic habitats, restoration, enhancement and dredging projects in the study area.
ACKNOWLEDGMENT

The present study was carried out as part of the CSIR Network Project COR-0005. The authors are thankful to Dr. Y.J. Bhaskar Rao, Director of the National Geophysical Research Institute in Hyderabad for his continuous support, encouragement and his permission to publish this paper. Thanks are also due to Mr. B.V. Ramana and Mr. Vittal Babu for their continuous support in the field.

REFERENCES
