International Journal of
Recent Innovations in Academic Research
Open Access, Peer Reviewed, Abstracted and Indexed Journal

E-ISSN: 2635-3040; P-ISSN: 2659-1561
Homepage: https://www.ijriar.com/
Volume-5, Issue-6, June-2021: 38-53

Research Article

Heavy Metal Distribution and Contamination in Soils of Ranipet Industrial Area, Tamil Nadu, India

Srinivasa Gowd, S.

Dept. of Geology, Yogi Vemana University, Kadapa–516 005, India
Email: ssgowd@gmail.com

Received: June 8, 2021 **Accepted:** June 21, 2021 **Published:** June 29, 2021

Abstract: Environmental geochemical studies were carried out in and around Ranipet industrial area, Tamil Nadu, India (79º19'–79º22' E longitude and 12º53'–12º57' N latitude) to find out the extent of chemical pollution in soils due to industrial waste, which covers 90 km^2. The total number of industrial units located in and around the town is 400, among them 240 is tanning industries along with ceramic, boiler auxiliaries' plant, light engineering factories for rerolling and casting, manufacturers of chromium chemicals, fertilizers, paints, and plastics. Forty-nine soil samples were collected from the study area from top 10 cm layer of the soil and were analyzed for heavy metals by using Philips MagiX PRO-PW 2440 X-ray fluorescence spectrometer. Study reveals trace element enrichment in the soils showing very high concentrations of some of the toxic metals, such as Cr ranges 65.8-2258.3 mg/kg, Ba ranges 54.3-1028.6 mg/kg, Cu 11.9-287.2 mg/kg, Pb 12.5-118.4 mg/kg, Sr 62.7-1669.1 mg/kg, V 0.1-1140.3 mg/kg, and Zn 40.9-4540.4 mg/kg. The concentrations of the other elements were similar to the levels in the Earth's crust in the soil (EF<1). Soil contamination was assessed on the basis of geoaccumulation index, enrichment factor (EF), contamination factor and degree of contamination. The indiscriminate dumping of hazardous waste could be the main cause of the soil and surface water contamination and it may result in ecotoxicological effect on groundwater and aquatic ecosystems. High concentrations of these toxic elements are responsible for the degradation of human health in the study area and people suffer from occupational diseases such as asthma, chromium ulcers and skin diseases. Spatial distribution of heavy metals, which are potentially harmful to human health and ecosystem, and determination of natural background levels of trace elements for future pollution monitoring along with the possible remedial measures are discussed in this paper.

Keywords: Heavy metal pollution, Geo accumulation Index, Enrichment factor, Ranipet industrial area, India.

1. Introduction

Soil pollution is a major problem related to the economic/industrial growth of any country. The number of industries in India, during the last decade, has grown more than ten times and accordingly the problems related to environmental degradation have increased many folds. There is a need for sustainable development of economic growth and industries. Some of the industries release their effluents either on the open land on in surrounding surface water bodies contaminating the soil, surface water and ultimately groundwater. Government of India is aware of these problems and has started looking into the remedial measures to clean some of the highly contaminated surface water bodies. Involvement of very high costs of remediation will make this process slow and therefore, it is essential that the contamination of water bodies is controlled rather than remediation. In recent years, contamination of the environment by Cr, especially Cr (VI), has become a major concern (Farmer *et al.,* 1999; Shtiza *et al.,* 2005).

Leather production is a major industry in India, which makes significant contribution to the country's foreign exchange earning and provides employment opportunities to about three million people. Dissolved chromium reaches concentration levels of some g /kg $^{-1}$ due to anthropogenic pollution from tanneries, which is generally linked to the use of Cr (VI) compounds in several industries applications such as plating, metallurgy, pigments, and leather tanning (Nriagu 1988; Naidu *et al.,* 2003; Saadia *et al.,* 2006; Tariq *et al.,* 2006; Yefang *et al.,* 2006).

During the process of leather manufacturing, several chemicals like Cr $(SO_4)_3$, NaCl, Ca $(OH)_2$, H_2SO_4 etc. are extensively used. Therefore, the resultant effluent is enriched with chromium and sodium salts. The tannery waste is characterized by its strong color (reddish dull-brown), high BOD, high pH, and high total dissolved solids. Groundwater is the main source of water supply for domestic use and drinking purpose in rural areas. It is established that a single tannery can cause the pollution of groundwater around the radius of 7-8 km (CLRI 1990; Ansari *et al.,* 2000). Chromium present in effluent is primarily in the less toxic trivalent form (Cr (III) but when this effluent is discharged into the soil, due to varying environmental conditions, Cr (III) is oxidized to toxic hexavalent form, which seldom remains as Cr (VI) (Parthasarathy *et al.,* 2003; Hooda and Naidu 2004; Srinivasa Gowd 2008).

In Tamil Nadu state, where more than 60% of India's economically important tanning industry is located, tannery waste containing chromium and sodium compounds has, over many years, contaminated 55000 ha of agricultural land. Thousands of farmers lost their farms, or part of their earning capacity because of this contamination. Incidence of respiratory diseases among workers exposed to occupational and environmental risks of tannery industry at Ranipet industrial area is reported (Mahimairaja *et al.,* 2000). In many areas of Tamil Nadu, groundwater is not suitable for domestic use, forcing villagers to travel 4-5 km for water. Much of the groundwater is unsuitable for irrigation, and hundreds of wells in the region can no longer be used. This is one of the contaminated sites identified by Central pollution control board, India.

The objectives of the study were to assess the levels of soil contamination in respect to average concentrations of toxic metals in the region, to determine the associations between the different toxic elements and their spatial distribution and to identify possible sources of contamination that can explain the spatial patterns of soil pollution in the area. Second objective of the present study is to make a systematic assessment and evaluation of soil contamination under the influence of a high influx of metal pollutants from the anthropogenic activities and to control the dispersion of the contaminants.

The bioavailable metal content in soils exerts a decisive impact on soil quality and its use in food production. Hence, the assessment of metal contamination is of vital importance in industrial areas. Contaminants at large contaminated sites often share critical properties such as high acute and/or chronic toxicity, high environmental persistence, often high mobility leading to contamination of groundwater and high lipophilicity leading to bioaccumulation in food web. With a view to understand the heavy metal dynamics the present study was carried out on soil contamination using various indices, including index of geoaccumulation, normalized enrichment factor (EF), contamination factor and degree of contamination.

1.1 Study area

Ranipet industrial area is a part of Vellore District of Tamil Nadu, located in $79^0 19'$–$79^0 22'$ E longitude and $12^0 53'$–$12^0 57'$ N latitude is a medium-sized community, having population about 50,000 with the area of 75 km^2, and is a chronic polluted area and one of the biggest exporting centers of tanned leather (Figure 1). Many small-scale tanneries are processing leather in the study area and discharging their effluents on the open land and surrounding water bodies (Srinivasa Gowd and Govil, 2008). The total numbers of tannery industrial units located in and around this town are 240 besides other industries like ceramic, boiler auxiliaries' plant, light engineering factories for rerolling and casting, manufacturers of chromium chemicals, fertilizers, paints, and plastics. Industries located in Ranipet are discharging effluents into Puliathengal, Vanapadi, and Thandalam lakes and it is a matter of increasing concern, as these industries are located in Palar river basin. Studies of groundwater also indicated the high concentrations of chromium in Palar river basin, which is much more than the permissible limit in drinking water. These tanneries are polluting the Palar River, causing ecological degradation and health hazards.

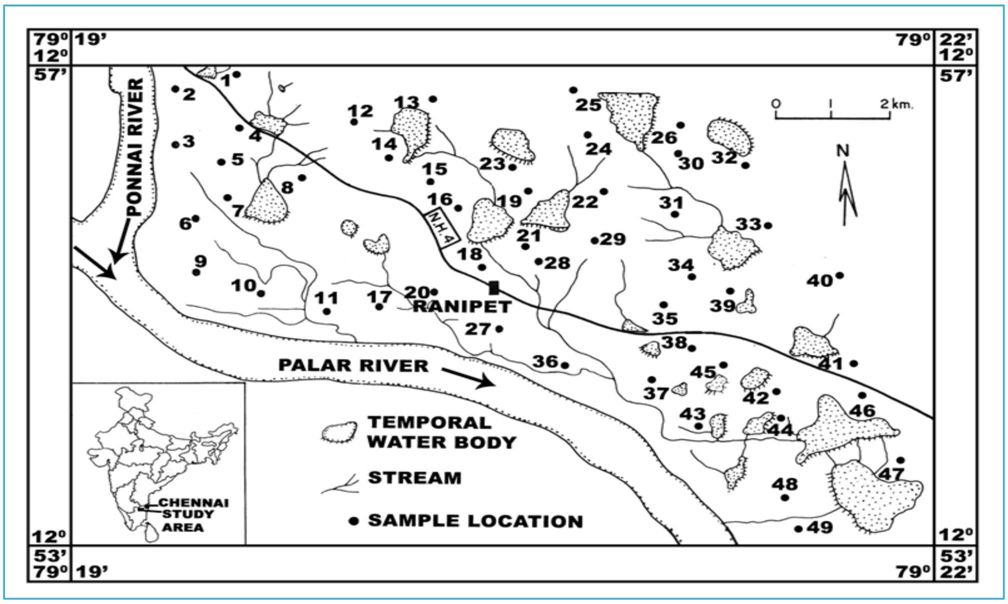

Figure 1. Location of soil sample collection in the vicinity of Ranipet industrial area

1.2 Geology

Geologically the study area is beset with Archaean Granite with highly metamorphosed gneissic complex as basement (Figure 2). The alluvium consisting of fine to coarse sand and clay occurring in the area is of a fluviatile origin and restricted to the course of Palar river and major streams The northern and northeastern portion of the study area is underlain by Granite and Gneissic terrain and southern and southwest portion show sedimentary environment caused by river action and the regional slope is towards south and southeast and the climate of the study area is semi-arid type (Subramanian and Selvan, 2001).

2. Materials and methods

2.1 Sample collection

The total number of soil samples is 49 and most of the soil samples were collected from the outer surface, i.e., 5–15 cm depth to study the anthropogenic sources of pollutants. The precise locations of the sampling points were determined in the field through the development of the GARMIN 12 Channel Instrument, based on the principles of Global Positioning System (GPS), the exact longitude and latitude of the sampling. The location of the sampling points is shown in Fig. 1. 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. Soil samples were dried for two days at 60°C. The dry soil sample was finely powdered and sieved 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-1 and SO-4 issued by Canadian reference materials were analyzed along with the soil samples during the course of analysis. The analytical concentrations of the metals in reference samples are listed in Table 1. It is seen that our analytical values are within the range of the certified values of the reference materials.

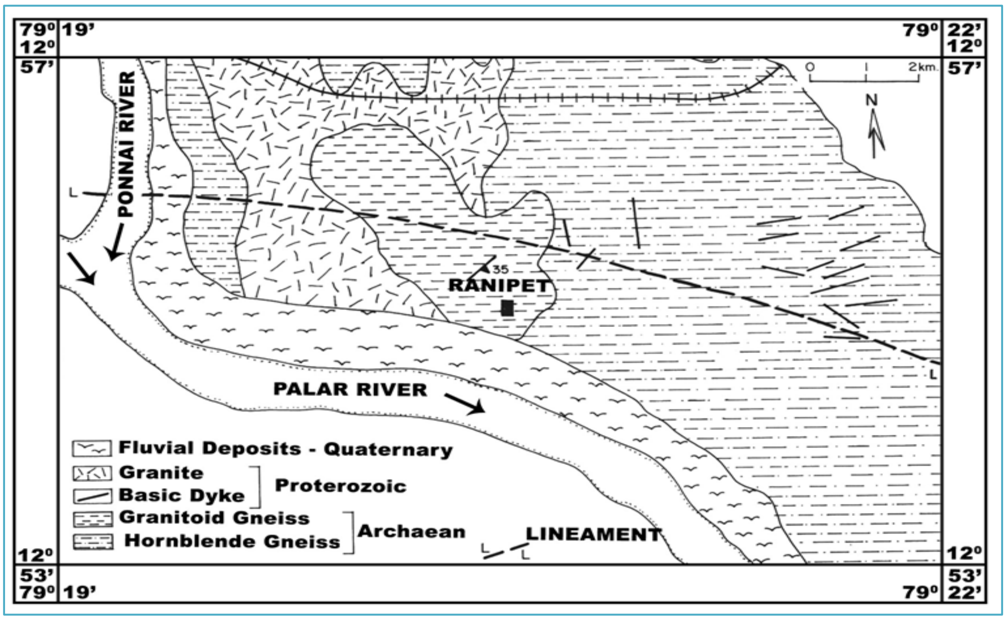

Figure 2. Geology map of the study area

2.1. Index of Geoaccumulation

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and preindustrial concentrations originally used with bottom sediments (Muller, 1969); it can also be applied to the assessment of soil contamination. It is computed using the following equation:

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

where C_n is the measured concentration of the element in the pelitic sediment fraction (<2 μm) and B_n is the geochemical background value in fossil argillaceous sediment (''average shale''). The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. In the present paper we applied the modified calculation as based on the equation given in Loska *et al.,* (2004), where C_n denoted the concentration of a given element in the soil tested, while Bn denoted the concentration of elements in the earth's crust (Taylor and Mclennan, 1995).

For some elements like As, Hg and Sb the average concentration in the Earth's crust is much higher than the average concentration in the shale accepted by Muller (1969) as a reference value. Here the focus is between the concentration obtained and the concentration of elements in the Earth's crust, because soil is a part of the layer of Earth's crust and its chemical composition is related to the one of the crust.

Table. 1. Results of analytical values of the soil standard reference materials SO-1 (regosolic clay soil) and SO-4 (chermozemic a horizon soil) in comparison with the certified reference values

CRM	Ba	Cr	Cu	Pb	Sr	V	Zn
SO-1	867	167.2	60.4	19.5	328	130.1	138.6
	(870)	(170)	(61)	(20)	(331)	(133)	(140)
SO-4	691.8	63.5	20.8	12.9	167.9	84.6	93.1
	(700)	(64)	(21)	(14)	(168)	(85)	(94)

First row indicates measured value (*n* = 3)
Second row in brackets indicate certified values

2.2. Enrichment factor

The value of EF was calculated using the modified formula given by Loska *et al.,* (2004) based on the equation suggested by Buat-Menard and Cherselet (1979). The EF was based on the standardization of a tested element against a reference one. A reference element is the one characterized by low occurrence variability (Reimann and de caritat, 2000; Sutherland, 2000; Saur and Juste, 1994). In this study we used Strontium as reference element due to its low occurrence. Strontium is also one of the main components of the Earth's crust and its concentration in soil is also connected with some matrix. Similar to I_{geo}, the reference environment adopted was the average concentration of elements in the earth's crust. This aimed to enable a comparison of the two factors I_{geo} and EF.

$$\text{EF}=\frac{\dfrac{\text{C}_{\text{n}}\,(\text{sample})}{\text{C}_{\text{ref}}\,(\text{sample})}}{\dfrac{\text{B}_{\text{n}}\,(\text{background})}{\text{B}_{\text{ref}}\,(\text{background})}}$$

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.

2.3 Contamination factor and degree of contamination

The assessment of soil contamination was also carried out using the contamination factor and degree. The $\text{C}^{\text{i}}_{\text{f}}$ is the single element index, the sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment and all four classes are recognized. In the version suggested by Hakanson (1980), they enable an assessment of soil contamination through the reference of the concentration in the surface layer of bottom sediments to pre-industrial levels (average shale).

$$C^{i}{}_{f}=\frac{C^{i}{}_{0-1}}{C^{i}{}_{n}}$$

Where $\text{C}^{\text{i}}_{0\text{–}1}$ is the mean content of metals from at least five sampling sites and $\text{C}^{\text{i}}_{\text{n}}$ is the pre-industrial concentration of individual metal. In the present study we applied a modification of the factor as applied by Loska *et al.,* (2004) that used the concentration of elements in the earth's crust as a reference value, similar to the other factors.

2.4 Instrumentation

A Philips MagiX PRO- PW2440 fully automatic, microprocessor controlled, 168-position automatic sample changer, wavelength dispersive X-ray Spectrometer was used for the determination of heavy metals (As, Ba, Co, Cr, Cu, Ni, Mo, Pb, Sr, V and Zn) in soil samples. The MagiX PRO is a sequential instrument with a single goniometer based measuring channel covering the complete elemental range.

A Rhodium anode X-ray tube is used, which may be operated at up to 60 kV and current up to 125 mA, at a maximum power level of 4 KW. Suitable software ''Super Q'' was used to take care of dead time correction and inter-element matrix effects. International Soil Reference samples from US Geological Survey, Canadian Geological Survey, International working group, France and NGRI, India were used to prepare calibration curves for trace metals (Govil, 1985).

2.5 Background (reference Data)

Geochemical baseline maps are not yet available in India though work is initiated under Global Geochemical Baselines Programme. The background levels of heavy metals in soils were determined by the levels that existed in parent material and by redistribution in the profile due to pedogenesis during the process of soil formation is given in Table 2. Out of 20 samples 5 were discarded for possibly anthropogenic contamination according to statistical analysis. The soil samples are sampled, prepared and analyzed in the same manner as the rest of the soil samples. The location of the background samples is in the surrounding areas of the study area.

Table 2. Natural background values in the soil at Ranipet industrial area

	Ba	Cr	Cu	Pb	Sr	V	Zn
Local natural background values	867	114	51	144	328	130	114
Soil Quality Guidelines, Res.* (Canadian)	500	64	63	140	200	130	200

3. Results and discussion

3.1. Heavy metal concentrations

Concentrations of various heavy metals in soils of the study area are given in Table 3. Table 4 gives the maximum, minimum and mean values of heavy metal concentrations and reference value of metal concentrations in the continental crust (Wedepohl, 1995). Chromium (501.2 mg/kg average), Barium (343.1 mg/kg average), Copper (48.0 mg/kg average), Lead (45.3 mg/kg), Vanadium (115.0 mg/kg average), and Zinc (329.6 mg/kg) data showed enrichment levels exceeding the normally expected distribution in soil giving rise to concern over suitability of soils in the study area (Alloway, 1995; Govil *et al.,* 2001, 2008; Callender 2003; Romic and Romic, 2003; Skordas and Kelepertsis, 2005; Srinivasa Gowd *et al.,* 2007; Srinivasa Gowd and Govil, 2008).

A comparison of the results with the Canadian Soil Quality Guidelines (CSoQGs, 2007) show that most of the industrial area is heavily contaminated by Cr, Pb, Sr, and Zn. High levels of these elements are observed in some pockets, very close to industries, which indicate that the source of these elements could be the industrial effluents. Tables 5 shows that the soils of the study area are enriched in relation to the natural background values with factors of 76.13 for Cr; 4.66 for Pb; 161.24 for V, and 12.09 for Zn.

Table 3. Heavy metal concentration (mg/kg) in soil samples-XRF data

Sample	Ba	Cr	Cu	Pb	Sr	V	Zn
TSS-1	64.8	85.1	23	12.5	211.1	182.6	72.1
TSS-2	631.3	220.6	23.9	42.7	159.4	85.4	80.3
TSS-3	56.4	73.0	17.8	44.4	138.6	35.9	46.5
TSS-4	64.5	118.9	32.1	33.4	270.3	69.3	69
TSS-5	227.1	355.4	33.3	48.6	334.9	37.7	106.7
TSS-6	218.1	383.5	32.4	47	307.7	36.4	101.6
TSS-7	202.2	174.0	40.6	48.2	420	160.4	147.2
TSS-8	202.8	349.6	38.8	45.7	424.7	163.2	136.8
TSS-9	355.7	149.2	11.9	39.2	245.2	38.9	42.5
TSS-10	118.1	289.9	156.3	46	150.6	185	610.4
TSS-11	197.2	259.1	287.2	38	171.1	501.9	863.6
TSS-12	327.3	190	37.8	52.5	254.4	180.1	195.4
TSS-13	170.2	344	258.5	23	137	244.7	4540
TSS-14	201.4	210.8	35.1	46	166.7	0.1	99.9
TSS-15	69.6	65.8	28.2	38.8	172.2	45.2	70.9
TSS-16	64.3	303.1	29	28.1	170.6	80.2	116.3
TSS-17	54.3	393.6	20.4	29.8	294	43.8	97.4
TSS-18	122.5	265.1	26.7	34.5	186	77.9	101.8

TSS-19	278.5	310.1	31.8	34.1	184.1	66.1	87.8
TSS-20	311.6	407.2	28.5	32.5	287.7	55.3	80
TSS-21	410.8	111.9	36.5	35.2	217	61.3	87.8
TSS-22	533.8	122.9	24.6	28	215.5	52.4	64
TSS-23	322.8	142.3	20.3	34.5	218.1	41.7	83.4
TSS-24	217.8	172.9	30.3	29	193.9	61.8	115.8
TSS-25	127.2	189.4	58.1	75.2	160.5	45.4	3309
TSS-26	460.8	308.1	22.5	46.2	234.8	25	664.6
TSS-27	324.9	1487.0	24.5	33.6	270.4	37.2	186.9
TSS-28	469.4	215.9	16	34.6	174.3	37.8	122
TSS-29	380.8	274.6	18.4	37.7	186.1	41.5	104.9
TSS-30	492.9	344.5	41.8	41.7	168.5	77	169
TSS-31	308.4	317.7	23.2	44.2	149.1	77.2	143.8
TSS-32	430.7	155.5	22.4	42.6	158.5	61.8	62.5
TSS-33	381.8	369.3	22	33.4	228.7	57.2	88.2
TSS-34	375.9	102.7	19.8	32	259	59.9	59.7
TSS-35	423.9	480.4	53.2	55.5	202.9	91.3	139.4
TSS-36	512.8	1781	52.1	50.5	235	95.2	133.1
TSS-37	312.9	1466.0	34.6	36.5	284.4	68.2	68.6
TSS-38	712.4	603.6	36.7	31.7	376.4	54.6	322.9
TSS-39	191.3	318.1	69.1	95.2	88.1	708.8	130.6
TSS-40	138.8	160.9	118.1	55.5	62.7	13.6	1098
TSS-41	272.7	363.6	51.5	46.7	172.9	1140	69
TSS-42	211.5	1194	42.6	70.8	1420	0.1	41.6
TSS-43	194.7	1335	44	65.4	1669.1	0.1	40.9
TSS-44	652.6	643.2	21.4	33.9	240.7	48.7	97.5
TSS-45	514.6	1764	78.1	109.5	256.2	84.1	294
TSS-46	693.3	813.2	84.5	118.4	252.9	80.5	256.8
TSS-47	931	617.3	27.3	48.5	159.4	84.8	227.5
TSS-48	1028.6	1499	22.5	42.4	158.9	71.7	197.8
TSS-49	847.6	2258.3	31.4	44.4	127.7	65.8	106.2

Table 4. Descriptive statistics of the determined elements in soil samples (n=49), and reference value of element concentrations in the continental crust (Wedepohl, 1995).

	Ba	**Cr**	**Cu**	**Pb**	**Sr**	**V**	**Zn**
Minimum	54.3	65.8	11.9	12.5	62.7	0.1	40.9
Maximum	1028.6	2258.3	287.2	118.4	1669.1	1140.3	4540.4
Mean	343.16	501.2	47.8	45.3	269.9	115.0	329.6
Median	311.6	310.1	31.8	42.4	211.1	61.8	106.2
SD	231.4	527.9	53.7	19.8	277.1	191.5	787.7
Kurtosis	0.99	2.46	12.28	5.25	19.19	18.81	20.95
Skewness	1.08	1.83	3.42	2.09	4.31	4.13	4.50
Reference value	584	126	25	14.8	333	98	65

Table 5. Minimum, maximum and median values of Enrichment factor (EF) for the determined elements in soil samples (n=49)

Statistical parameters	**EF-Ba**	**EF-Cr**	**EF-Cu**	**EF-Pb**	**EF-Sr**	**EF-V**	**EF-Zn**
Minimum	0.07	1.06	0.37	0.68	2.64	0.01	0.13
Maximum	13.81	100.09	26.41	18.91	771.59	28.73	178.45
Mean	3.23	19.69	3.92	4.09	51.68	2.46	11.78
SD	2.56	24.00	6.06	3.24	139.11	5.24	31.70

3.2. Barium

Barium waste may be released to air, soil and water during industrial operations. Barium is released into the air during the process of manufacturing of Barium chemicals (ATSDR. 2007) in the study area. Ceramic industry is using abundantly Barium hydroxide to make ceramics and discharging its effluents into the surrounding areas. The mean I_{geo} (0.02) obtained revealed that all the samples examined fell into class 0 practically uncontaminated with barium as per Muller's six classes of the geoaccumulation index (Figure 3). The EF was also low and ranged from 0.07 to 13.81, confirming the lack of contamination with barium (Figure 4). Barium levels in the study area ranged from 54.3 to 1028.6 mg/kg, with an average of 343.1 mg/kg (Figure 5). The normal range of Barium in soil is 300 mg/kg (USEPA, 2003).

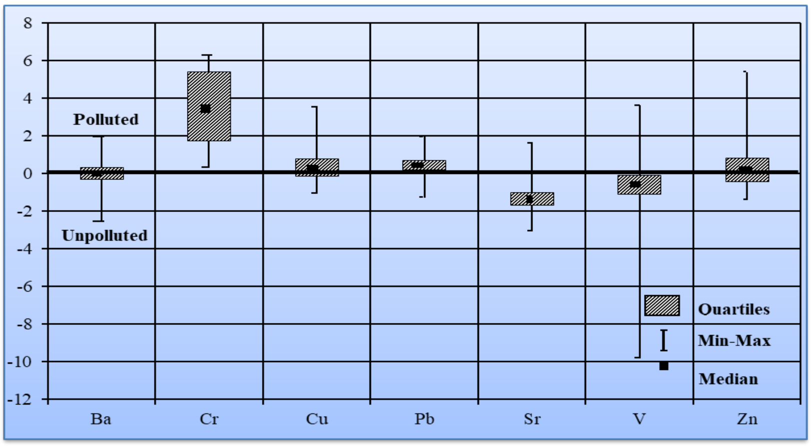

Figure 3. Indexes of geoaccumulation for metals in soil of Ranipet

Barium released from weathered rocks is not very mobile since it is easily precipitated as sulphate and carbonate, strongly adsorbed by clays, concentrated in Mn and P concretions, and specifically sorbed onto oxides and hydroxides (Kabata-Pendias, 2001). Barium easily displaces other sorbed alkaline earth metals from some oxides, *e.g.,* MnO_2 and TiO_2, but is displaced from Al_2O_3 by alkaline earth metals such as Be and Sr. In soil of temperate humid climatic zones, Ba is likely to be fixed by Fe-oxides and becomes immobile. Barium in soil may be easily mobilized under different physico-chemical conditions. Barium is essential for some organisms at low concentrations but, at higher concentrations, soluble Ba compounds are toxic to humans, animals and plants, *e.g.,* $BaCl_2$ is used as a rat poison and insecticide. Barium is an undesirable impurity in drinking water, and high levels of Ba in potable water have been associated with gastroenteritis and muscular paralysis (International Programme on Chemical Safety 1990). Small amounts of water-soluble barium may cause a person to experience breathing difficulties, increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, changes in nerve reflexes, swelling of brains and liver, kidney and heart damage.

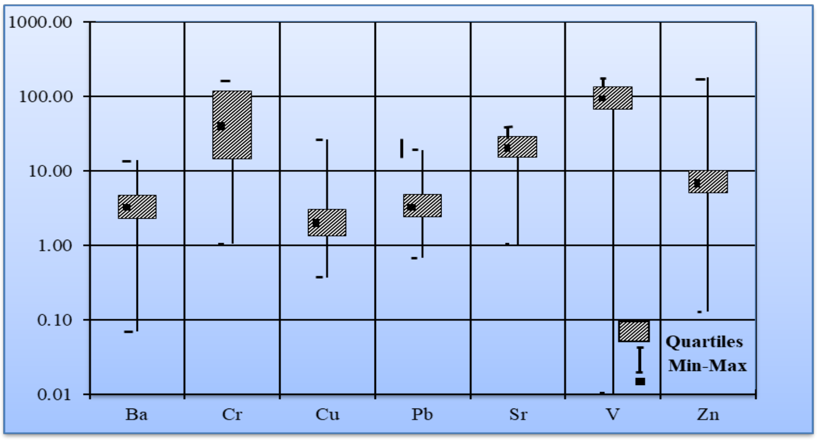

Figure 4. Enrichment factors for metals in the soil of Ranipet

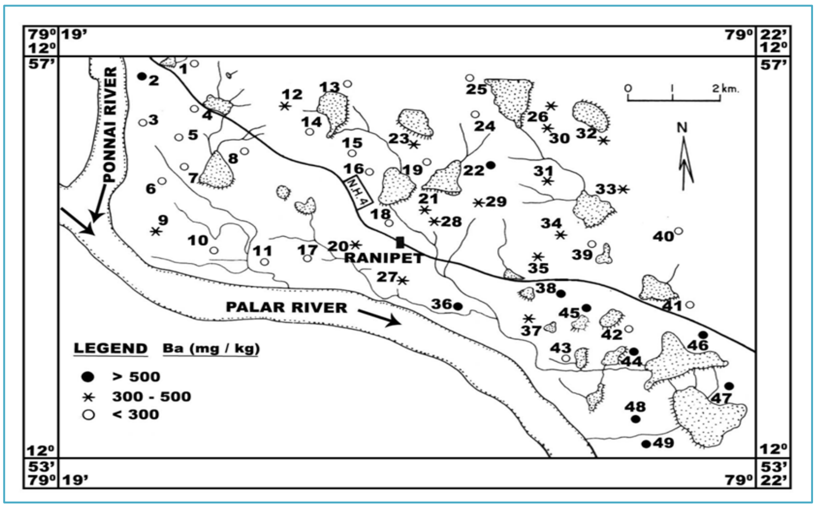

Figure 5. Distribution of Barium (mg/kg) in soil

3.3. Chromium

Chromium is a low mobility element, especially under moderately oxidizing and reducing conditions and near-neutral pH values. In soil, Cr behavior is governed by pH, Eh and organic matter. Its adsorption by clay is also highly dependent on pH; Cr^{6+} adsorption decreases with increasing pH, and Cr^{3+} adsorption increases with increasing pH. The dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} to Cr^{3+}, the rate of which increases with soil acidity (Kabata-Pendias, 2001). On the other hand, Cr (VI) is toxic for biological systems. Chromium is water soluble and extremely irritating and toxic to human body tissue owing to its oxidizing potential and permeability of biological membranes (Anderson, 1999). Chromium levels in the study area ranged from 65.8 to 2258 mg/kg, with an average of 501.2 mg/kg (Figure 6).

The normal range of chromium in soil is 100 mg/kg (USEPA, 2003) and all the samples are exceeding the normal value. The I_{geo} revealed that nearly all the samples examined fell into class 2, moderately contaminated ranging from 0.33 to 6.28. The EF obtained for Cr ranged from 1.06 to 100.09, which falls under the class of extremely high enrichment (Sutherland, 2000). Therefore, the source of Cr appears to be anthropogenic from the existing tannery industries, where they are using chromium and its compounds (Gupta and Sinha, 2006).

Chromium is an essential trace element, required for the metabolism of lipids and proteins and to maintain a normal glucose tolerance factor. High doses of chromium cause liver and kidney damage and chromate dust is carcinogenic (SEGH, 2001; Mugica *et al.,* 2002).

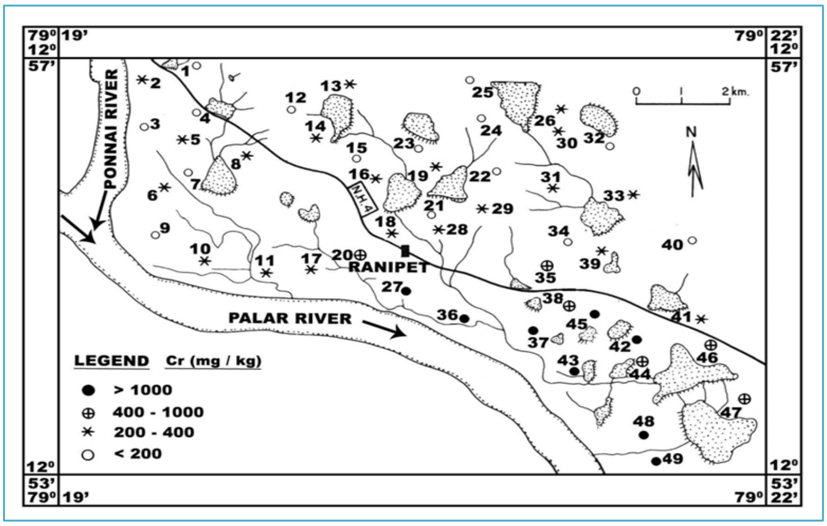

Figure 6. Distribution of Chromium (mg/kg) in soil

3.4. Copper

Copper values were found to be abnormally high in the study area. The soil samples in the area contain in the range of 11.9-287.2 mg/kg with an average value of 48 mg/kg (Figure 7). The normal threshold value prescribed in soil is 30 mg/kg. The mean I_{geo} obtained for copper is 0.52 pointing to uncontaminated to moderately contaminated. The values ranged from minimum of –1.07 to maximum of 3.52. The EF for Cu was high compared to other elements in almost all samples ranging from 0.37 to 26.41; there was a significant enrichment to extremely high enrichment of Cu in Ranipet soils. The I_{geo} and EF may be due to some input through industrial effluents on to the surface soil where by the normal copper value as in the earth's crust could have got enriched to maximum of 50.91 indicating heavy contamination due to accumulation over a period of time. Copper normally accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources (Kabata-Pendias, 2004). Copper accumulation in the soil of the study area is due to the industries like steel manufacture, blast furnace, and application of agrochemicals in the agro-based industry. Copper is however, characterized by the so called point sources of contamination, namely uncontrolled, active or untended waste dumps, present in large number in the study area. Such places imply great contamination risks for water (Romic *et al.,* 2001; Salminen, 2005). Copper is an essential trace element for all organisms, and humans can tolerate levels up to 12 mg per day (WHO, 2004), although the element can be toxic at extremely high levels. For example, Reimann and de Caritat (1998, 2005) report examples of kidney failure in small children resulting from drinking water from new copper pipes in low pH environments containing high concentrations of Cu up to about 1 mg l^{-1}. Overdoses of copper may also lead to neurological complications, hypertension, liver, and kidney dysfunctions (Larocque and Rasmussen, 1998; Rao *et al.,* 2001; Krishna and Govil, 2004).

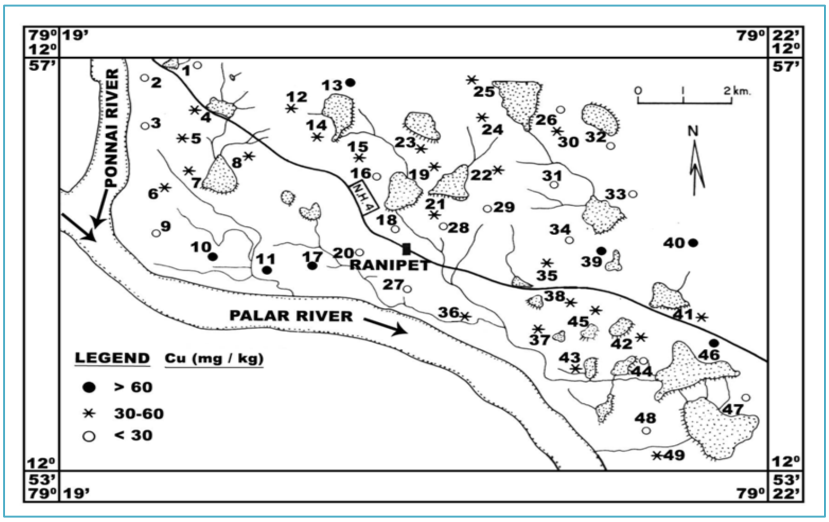

Figure 7. Distribution of Copper (mg/kg) in soil

3.5. Lead

The species of Pb vary considerably with soil type; it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations and a baseline Pb value for surface soil on the global scale has been estimated to be 25 mg/kg levels above this suggest an anthropogenic influence (Kabata-Pendias, 2001). Lead is released from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipe work. Lead solubility is controlled principally by $PbCO_3$ and low-alkalinity and low-pH waters can have higher Pb concentrations (Hem, 1989; Kumar *et al.,* 2005). The average concentration of lead in soil samples of the study area is 45.3 mg/kg and ranges from 12.5 to 118.4 mg/kg (Figure 8). However, in the study area Pb content in soil was falling in class 1 showing uncontaminated to moderately contaminated with I_{geo} ranging from –1.26 to 1.98. Similarly in the case of EF it showed deficiency to minimal enrichment (Sutherland, 2000) in most of the samples ranging from 0.68 to 18.91 with a mean of 4.09. The WHO maximum recommended concentration for Pb has recently been reduced from 50 mg/kg to 10 mg/kg because of concerns about chronic toxicity, although its concentration rarely exceeds in natural waters. Lead is a cumulative poison, initiating hypertension, tiredness, irritability, anemia, behavioral changes and impairment of intellectual functions in affected patients (Wong and Li, 2004). Long term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can affect adversely to nervous system and kidneys (Mugica *et al.,* 2002). Thus, lead pollution is a worldwide issue.

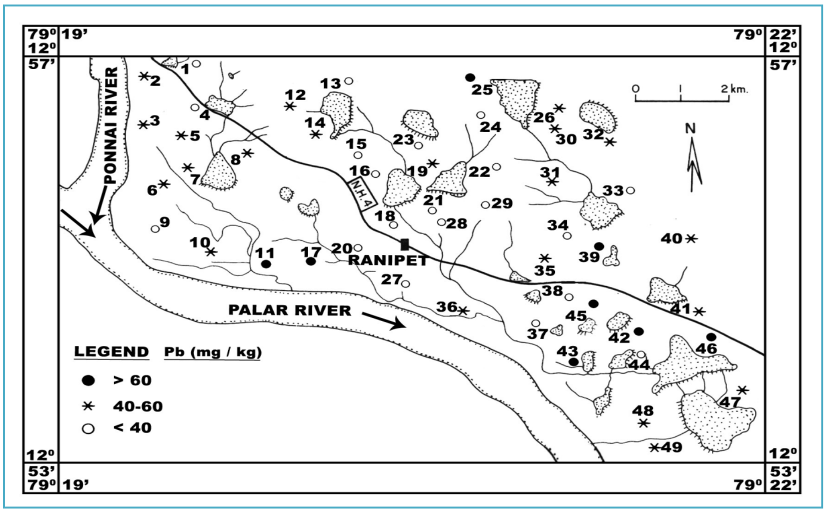

Figure 8. Distribution of Lead (mg/kg) in soil

3.6. Vanadium

Vanadium levels ranged from 0.1 to 1140.3 mg/kg in the study area with a soil average of 115 mg/kg (Figure 9). The I_{geo} indicated that the soils in Ranipet area fall under class 0 and class 1 ranging from minimum of –9.81 practically uncontaminated and maximum of 3.66 showing uncontaminated to moderately contaminated with a mean of –0.83. The EF indicated moderate contamination with a mean content of 2.46 ranging from 0.01 to 28.73. Normal threshold value for vanadium in soils is 100 mg/kg (Larocque and Rasmussen, 1998). Vanadium content of soil depends upon the parent material and the pedogenic process associated with its development. Composition of the parent material has less bearing on V content of mature, developed soils. Vanadium usually has a wide and varied industrial usage in dyeing, textile, metallurgy and electronics. As majority of the industries are textile and petroleum products, which clearly indicates that the source of Vanadium is anthropogenic in the study area. An intake of over 10 mg Vanadium per day can be toxic for adults, and the source is airborne anthropogenic Vanadium (WHO, 2004) in the study area. In severe cases, toxic levels of Vanadium causes the inhibition of certain enzymes with animals, which has several neurological effects, and can cause breathing disorders, paralyses and negative effects on the liver and kidneys.

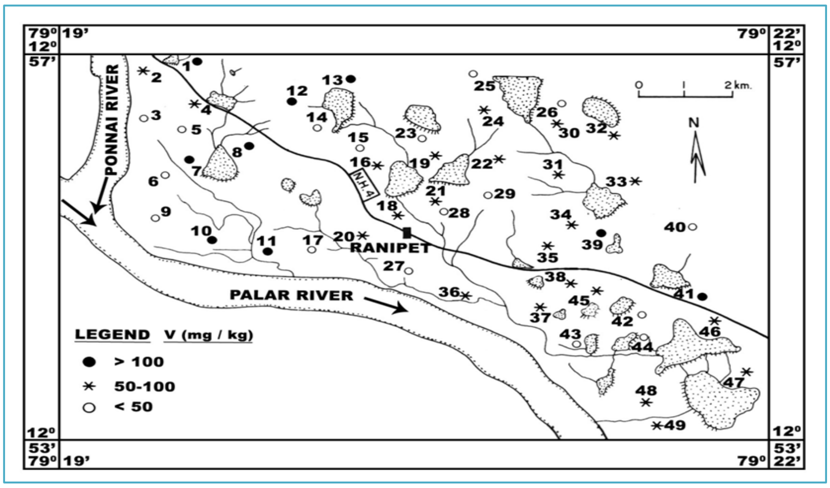

Figure 9. Distribution of Vanadium (mg/kg) in soil

3.7. Zinc

Zinc belongs to a group of trace metals, which are essential for the growth of humans, animals and plants and are potentially dangerous for the biosphere when present in high concentrations. The main sources of pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture (Romic and Romic, 2003). The average Zinc concentration in the study area is 329.6 mg/kg, ranges from 40.9-4540.4 mg/kg, which is very high (Figure 10). The I_{geo} indicated that the soils in the study area fall under class 0 and class 1 ranging from minimum of –1.38 practically uncontaminated and maximum of 5.41 showing uncontaminated to moderately contaminated with a mean of 0.41. The EF's indicated moderate contamination with a mean content of 11.78 ranging from 0.13 to 178.45.

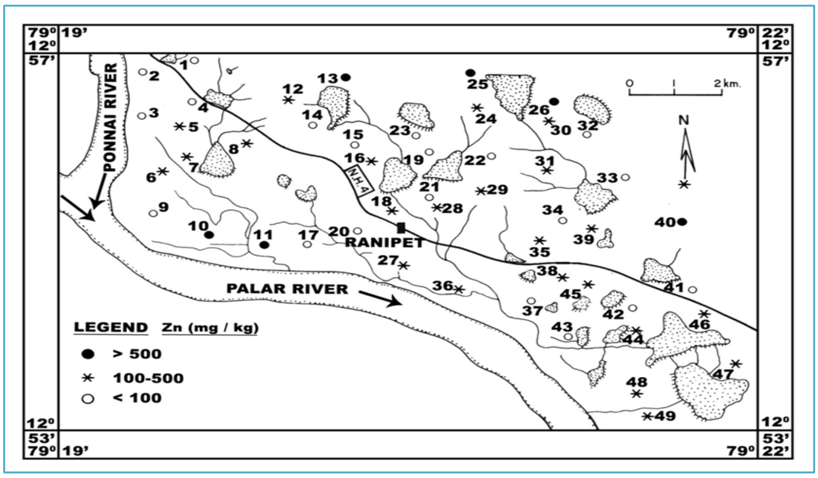

Figure 10. Distribution of Zinc (mg/kg) in soil

The normal threshold value prescribed in soil is 200 mg/kg (BIS, 1991) and in India 47% of soils are depleted in Zinc, however the high concentration of Zn are found in the nearby industrial areas, which clearly represents the source to be anthropogenic and not natural (Aswathanarayana, 1995). A recommended intake of 11.4 mg per day is suggested for adults (WHO, 2004). Symptoms of deficiency include growth retardation, dermatitis and slow wound healing, defective immune system and, in extreme cases, birth defects. In general, Zn toxicity is not so much a problem as deficiency, although excess Zn can still cause health problems such as stomach cramps, skin irritations, vomiting, nausea and pancreas damage. Higher contamination of Zn causes hematological disorders and deteriorates human metabolism.

3.8. Contribution of particular metals to the contamination of soil in Ranipet industrial area

The assessment of the overall contamination of soil was based on the degree of contamination (C_{deg}). On the basis of the contamination factor (C^i_f) (Loska *et al.,* 2004), moderately contaminated with Ba, Cu, V, considerably contaminated with Pb, and Zn and heavily contaminated with Cr. On the whole, the contamination factors confirmed the results achieved applying the I_{geo} and EF indices (Table 6).

Table. 6. Contamination factors and degree of contamination in the soil

Metal	Min	Max	Mean
Ba	0.25	5.95	1.84
Cr	1.88	116.35	38.11
Cu	0.48	11.49	1.91
Pb	0.63	5.92	2.26
Sr	0.18	4.77	0.77
V	0.00	19.01	1.92
Zn	0.58	63.95	4.64
Deg. Contam.	**3.99**	**227.44**	**51.45**

The C_{deg} for the mean metal contents in the soil was 51 and indicated very high degree of contamination (Hakanson 1980). The maximum values of the contamination degree denoted high contamination. It was found that Cr contributed most to the degree of contamination index of the soil, 75%. Copper accounted for 3.8%, Pb 4.4%, V 3.8%, and Zn, 9.1%.

4. Conclusions and recommendations

The results of the study show the impact of anthropogenic agents on abundances of heavy metals in soils of the study area and it is extremely contaminated due to many years of random dumping of hazardous waste and free discharge of effluents by the number of industries like ceramic, tanning and leather manufacturing industries, boiler auxiliaries' plant, manufacturers of chromium chemicals, fertilizers, paints, and plastics. The high content of toxic metals in the environment induces an increase in their content in ground waters as a result of leaching.

The detected levels of total metal contamination in many of the samples were found to exceed international threshold values. High concentration of Cr values confirms the contamination originating from the tannery waste. Pb and Zn showed a strong anthropogenic influence. However, it has been assumed that the anomalous concentrations of Lead in the vicinity of the highway and industry are of anthropogenic input. Copper is characterized by strongly scattered anthropogenic influence. This particularly relates to the uncontrolled waste dumps and liquid waste from industries.

High concentration of Cr and Zn obtained in the soil of the study area indicated that the pollution of these heavy metals in the area originated mainly from the industries in the area, either from dumping of industrial waste or from release of uncontrolled effluents on to the ground which contaminate the water bodies and streams present in the study area. There is an urgent need to measure toxic metals in industrial effluents before dumping them in Common Effluent treatment Plant (CETP). It is also desirable to check the outlet water of CETP after treatment to ensure that these toxic metals are not released into the adjoining water bodies. Alternatively, a pipeline can be laid in the area, which would carry the effluents to a safer place for treatment.

A considerable amount of surface soil/waste from dumping sites and heavily contaminated areas must be excavated and transported to a landfill site for hazardous waste. This study clearly highlights the necessity of immediate control measures for the exceptionally severe heavy metal pollution in the study area and the soils in the area require various remediation technologies like bioremediation, phyto-remediation by growing certain plants in the area should be carried out to minimize the rate of contamination, and extent of future pollution problems.

Conflicts of interest

The authors declare no conflicts of interest.

References

1. Alloway, B.J. 1995. Heavy metals in soils. Blackie and Son, Glasgow, Scotland, 22–151 pp.
2. Anderson, R.A. 1999. Chromium as an essential nutrient. The Chromium File no. 6. Intl. Chromium Development Association.
3. Ansari, A.A., Singh, I.B. and Tobschall, H.J. 2000. Importance of geomorphology and sedimentation processes for metal dispersion in sediments and soils of the Ganga Plain: identification of geochemical domains, Chemical Geology, 162: 245–266.
4. Aswathanarayana, U. 1995. Geoenvironment: an introduction. The Netherlands, Balkema, A.A. Rotterdam, 270 pp.
5. ATSDR. 2004. Toxicological profile for Strontium, U.S. Department of Health and Human Services. Atlanta, G.A: Public Health Service.

6. ATSDR. 2007. Toxicological profile for Barium, U.S. Department of Health and Human Services. Atlanta, G.A: Public Health Service,
7. BIS. 1991. Indian standard drinking water specifications, IS: 10500, Bureau of Indian Standards, New Delhi.
8. Buat-Menard, P. and Chesselet, R. 1979. Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth and Planetary Science Letters, 42(3): 399-411.
9. Callender, E. 2003. Heavy metals in the environment-Historical trends. In: Holland, H.D. and Turekian, K.K. (Eds.) Environmental Geochemistry, 9 Treatise on Geochemistry, Oxford: Elsevier-Pergamon.
10. CSoQgs. 2007. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Canadian Soil Quality Guidelines Summary Tables, 6 pp.
11. CLRI. 1990. Report on capacity utilization and scope for modernization in Indian tanning industry. Central Leather Research Institute, Madras, 12 p.
12. Farmer, J.G., Graham, M.C., Thomas, R.P., Licona-Manzur, C., Paterson, E., Campbell, C.D., Geelhoed, J.S., Lumsdon, D.G., Meeussen, J.C.L., Roe, M.J., Conner, A., Fallick, A.E. and Bewley, R.J.F. 1999. Assessment and modelling of the environmental chemistry and potential for remediative treatment of chromium contaminated land. Environ Geochem Health, 21: 331–337.
13. Govil, P.K.1985. X-ray fluorescence analysis of major, minor and selected trace elements in new IWG reference rock samples. Journal of Geological Society of India, 26: 38-42.
14. Govil, P., Reddy, G. and Krishna, A. 2001. Contamination of soil due to heavy metals in the Patancheru industrial development area, Andhra Pradesh, India. Environmental Geology, 41(3): 461-469.
15. Govil, P.K., Sorlie, J.E., Murthy, N.N., Sujatha, D., Reddy, G.L.N., Rudolph-Lund, K. and Mohan, K.R. 2008. Soil contamination of heavy metals in the Katedan industrial development area, Hyderabad, India. Environmental Monitoring and Assessment, 140(1): 313-323.
16. Gupta, A.K. and Sinha, S. 2006. Chromium levels in vegetables and grains grown on tannery effluent irrigated area of Jajmau, Kanpur, India: influence on dietary intake. Bulletin of Environmental Contamination and Toxicology, 77(5): 658-664.
17. Hakanson, L. 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research, 14(8): 975-1001.
18. Hem, J.D. 1989. Study and interpretation of the chemical characteristics of natural water: USGS Water-Supply Paper 2254, 264 pp.
19. Hooda, P.S. and Naidu, R. 2004. Speciation, bioavailability and toxicity relationships of contaminants in the terrestrial environment. Proc. International Contaminated site remediation conference, Adelaide, South Australia.
20. International programme on chemical safety. 1990. Environmental health criteria, 105 pp.
21. Kabata-Pendias. 2001. Trace elements in soils and plants. 3rd Edition, CRC Press, Boca Raton (FL), 432 pp.
22. Kabata-Pendias, A. 2004. Soil–plant transfer of trace elements—an environmental issue. Geoderma, 122(2-4): 143-149.
23. Krishna, A.K. and Govil, P.K. 2004. Heavy metal contamination of soil around Pali industrial area, Rajasthan, India. Environmental Geology, 47(1): 38-44.

24. Krishnaswami, S., Trivedi, J.R., Sarin, M.M., Ramesh, R. and Sharma, K.K. 1992. Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic87Sr/86Sr. Earth and Planetary Science Letters, 109(1-2): 243-253.

25. Kumar, M.P., Reddy, T.M., Nithila, P. and Reddy, S.J. 2005. Distribution of toxic trace metals Zn, Cd, Pb, and Cu in Tirupati soils, India. Soil & Sediment Contamination, 14(6): 471-478.

26. Larocque, A.C. and Rasmussen, P.E. 1998. An overview of trace metals in the environment, from mobilization to remediation. Environmental Geology, 33(2-3): 85-91.

27. Loska, K., Wiechuła, D. and Korus, I. 2004. Metal contamination of farming soils affected by industry. Environment International, 30(2): 159-165.

28. Mahimairajah, S., Sakthivel, S., Divakaran, J., Naidu, R. and Ramasamy, K. 2000. Extent and severity of contamination around tanning industries in Vellore district. In ACIAR PROCEEDINGS (pp. 75-82). ACIAR; 1998.

29. Muller, G. 1969. Index of geoaccumulation in sediments of the Rhine River. Geojournal, 2: 108-118.

30. Mugica, V., Maubert, M., Torres, M., Muñoz, J. and Rico, E. 2002. Temporal and spatial variations of metal content in TSP and PM10 in Mexico City during 1996–1998. Journal of Aerosol Science, 33(1): 91-102.

31. Naidu, S.R., Pollard, A., Juhasz, A.L., Megharaj, M., Smith, E., Owens, G. and Chen, Z.L. 2003. Risk based management of contaminated sites: a cost effective solution to managing contamination. Risk based Management of Contaminated Sites: Developing Cost Effective Strategies for Remediating Contaminated sites, Rydges, North Sydney, 29 September.

32. Nriagu, J.O. 1988. Production and uses of Chromiu. In: Nriagu, J.O., Nieboer, E., (Eds.), Chromium in the natural and human environment, Wiley & Sons, New York, 81-104.

33. Parthasarathy, G., Choudary, B.M., Sreedhar, B., Kunwar, A.C. and Srinivasan, R. 2003. Ferrous saponite from the Deccan Trap, India, and its application in adsorption and reduction of hexavalent chromium. American Mineralogist, 88(11-12): 1983-1988.

34. Rao, M.S., Gopalkrishnan, R. and Venkatesh, B.R. 2001. Medical geology—an emerging field in environmental science. In National symposium on role of earth sciences (pp. 213-222).

35. Reimann, C. and De Caritat, P. 1998. Chemical Elements in the Environment—Fact sheets for the Geochemist and Environmental Scientist. ISBN 3-540-63670-6. Springer–Verlag, Berlin, Germany, 398 pp.

36. Reimann, C. and Caritat, P.D. 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environmental Science and Technology, 34(24): 5084-5091.

37. Reimann, C. and de Caritat, P. 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Science of the Total Environment, 337(1-3): 91-107.

38. Romic, M. and Romic, D. 2003. Heavy metals distribution in agricultural topsoils in urban area. Environmental Geology, 43(7): 795-805.

39. Romic, M., Romic, D. and Kraljickovic, J. 2001. Copper in Vinyard soils. In: Proceedings 9th congress of Croatian society of soil science, Land Management and Soil protection for future generations, 3–7 July, 2001, Brijumi, Croatia.

40. Salminen, R., *et al.,* 2005. Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps. Espoo, Geological Survey of Finland, 526 pp.

41. Saur, E. and Juste, C. 1994. Enrichment of trace elements from long-range aerosol transport in sandy podzolic soils of southwest France. Water, Air, and Soil Pollution, 73(1): 235-246.
42. SEGH. 2001. Environmental Geochemistry and Health Special Issue. 18th European Conference. 23: No.3.
43. Shtiza, A., Swennen, R. and Tashko, A. 2005. Chromium and nickel distribution in soils, active river, overbank sediments and dust around the Burrel chromium smelter (Albania). Journal of Geochemical Exploration, 87(3): 92-108.
44. Skordas, K. and Kelepertsis, A. 2005. Soil contamination by toxic metals in the cultivated region of Agia, Thessaly, Greece. Identification of sources of contamination. Environmental Geology, 48(4-5): 615-624.
45. Srinivasa Gowd, S., Murthy, N.N. and Govil, P.K. 2007. Soil contamination due to heavy metals from tannery industries: A case study of Jajmau (Kanpur) and Unnao industrial areas, Uttar Pradesh, India. Geochimica et Cosmochimica Acta, 71(15): 1:A 964.
46. Gowd, S.S. and Govil, P.K. 2008. Distribution of heavy metals in surface water of Ranipet industrial area in Tamil Nadu, India. Environmental Monitoring and Assessment, 136(1): 197-207.
47. Subramanian, K.S. and Selvan, T.A. 2001. Geology of Tamil Nadu and Pondicherry, Geological Society of India Publication Bangalore, 192 pp.
48. Sutherland, R.A. 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environmental Geology, 39(6): 611-627.
49. Tariq, S.R., Shah, M.H., Shaheen, N., Khalique, A., Manzoor, S. and Jaffar, M. 2006. Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water: A case study from Peshawar, Pakistan. Journal of Environmental Management, 79(1): 20-29.
50. Taylor, S.R. and McLennan, S.M. 1995. The geochemical evolution of the continental crust. Reviews of Geophysics, 33(2): 241-265.
51. USEPA. 2003. Drinking water contaminants. National primary drinking water regulations. EPA 816-F-03-016, 6 pp.
52. Wedepohl, K.H. 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta, 59(7): 1217-1232.
53. WHO. 2004. Guidelines for drinking water quality. 3rd Edition. (ISBN 9241546387). Retrieved from http://www.who.int/water_sanitation_health/dwq/guidelines/en/.2004.
54. Wong, C.S.C. and Li, X.D. 2004. Pb contamination and isotopic composition of urban soils in Hong Kong. Science of the Total Environment, 319(1-3): 185-195.
55. Sun, Y., Xie, Z., Li, J., Xu, J., Chen, Z. and Naidu, R. 2006. Assessment of toxicity of heavy metal contaminated soils by the toxicity characteristic leaching procedure. Environmental Geochemistry and Health, 28(1-2): 73-78.

Citation: Srinivasa Gowd, S. 2021. Heavy Metal Distribution and Contamination in Soils of Ranipet Industrial Area, Tamil Nadu, India. International Journal of Recent Innovations in Academic Research, 5(6): 38-53.