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ORIGINAL ARTICLE

Soil contamination due to heavy metals from an industrial area of Surat, Gujarat, Western India

A. K. Krishna · P. K. Govil

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Abstract The pollution of soil is a source of danger to the health of people, even to those living in cities. The anthropogenic pollution caused by heavy industries enters plants then goes through the food chain and ultimately endangers human health. In the context, the knowledge of the regional variability, the background values and anthropogenic vs. natural origin of potentially harmful elements in soils is of critical importance to assess human impact. The present study was undertaken on soil contamination in Surat, Gujarat (India). The aims of the study were: i) to determine extent and distribution of heavy metals (Ba, Cu, Cr, Co, Ni, Sr, V and Zn) ii) to find out the large scale variability, iii) to delineate the source as geogenic or anthropogenic based on the distribution maps and correlation of metals in soils.

Soil samples were collected from the industrial area of Surat from top 10 cm layer of the soil. These samples were analysed for heavy metals by using Philips PW 2440 X-ray fluorescence spectrometer. The data reveal that soils in the area are significantly contaminated, showing higher levels of toxic elements than normal distribution. The heavy metal loads of the soils in the study area are 471.7 mg/kg for Ba, 137.5 mg/kg for Cu, 305.2 mg/kg for Cr, 51.3 mg/kg for Co, 79.0 mg/kg for Ni, 317.9 mg/kg for Sr, 380.6 mg/kg for V and 139.0 mg/kg for Zn. The higher concentrations of these toxic metals in soils need to be monitored regularly for heavy metal enrichment.

Keywords Soil contamination · Heavy metals · Surat · India

A. K. Krishna · P. K. Govil (✉)
National Geophysical Research Institute, Hyderabad, India
e-mail: govilpk@rediffmail.com

1 Introduction

Heavy metals are natural constituents of the earth crust. A number of these elements are biologically essential and are introduced into aquatic enrichments by various anthropogenic activities (Omar *et al.*, 2004). Main anthropogenic sources of heavy metals exist in various industrial point sources e.g., present and former mining activities, foundries, smelters and diffuse sources such as piping, constituents of products, combustion of by products, traffic industrial and human activities (Nilgun *et al.*, 2004).

Heavy metals at trace levels present in natural water, air, dusts, soils and sediments play an important role in human life (Isaac *et al.*, 2004). Soils are critical environment where rock, air and water interface. Consequently, they are subjected to a number of pollutants due to different anthropogenic activities (Industrial, agricultural, transport etc.) (Facchinelli *et al.*, 2001; Jonathan *et al.*, 2004). The chemical composition of soil, particularly its metal content is environmentally important, because toxic metals concentration can reduce soil fertility, can increase input to food chain, which leads to accumulate toxic metals in food stuffs, and ultimately can endanger human health. Because of its environmental significance, studies to determine risk caused by metal levels in soil on human health and forest ecosystem have attracted attention in recent years (Denti *et al.*, 1998; Sandaa *et al.*, 1999; Arantzazu *et al.*, 2000; Krzyztof Losk *et al.*, 2004).

Heavy metals may be derived from many different sources to the urbanized area. One of the most important heavy metals sources is vehicle emission. Three main factors known to influence the levels in soil samples, which have been reported, are traffic, industry and weathered materials. Topsoil and dusts in urban areas are indicators of heavy metal contamination from atmospheric deposition. It has been noted that location close to roads are severally polluted by heavy metals such as Pb, Zn, Cu, Cd etc, from traffic (Wilson *et al.*, 2005; Omar, 2004). These metals are toxic to human beings. Generally, the distribution of these metals is influenced by the nature of parent materials, climate and their relative mobility depending on soil parameter, such as mineralogy, texture and classification of soil. With a view to understand the heavy metal dynamics in soil, the present study was carried out on soil contamination in an industrial area, Surat in Gujarat (Western India).

In this study, spatial variations in elemental composition of soil is investigated by collecting and analyzing 25 surface soil samples in Surat. Distribution maps of heavy metals and correlation diagrams were prepared to investigate the source of contamination.

2 Materials and methods

Surat industrial area is one of the polluted industrialized area identified by Central Pollution Control Board, New Delhi (India). It is situated in south Gujarat, 250 km north of Mumbai, on the banks of river Tapi. Tapi is one of the major rivers flowing westward through the state of Gujarat and draining into the Gulf of Khambat of Arabian sea. Average annual rainfall in the study area is 1900 mm (Shah *et al.*, 1997) The middle and lower reaches of the Tapi basin in Surat are fairly industrialized. There are several large and medium scale textile industrial units besides large number of small-scale units. The city is also one of the largest centers in India for production of synthetic fiber and fabrics (nylon and polyester). Some of the major industries that have come up in and around Surat are textiles, petrochemical, refinery, natural gas, cement, steel plant etc.

2.1 Geology of the area

The study area is covered primarily with quarternary deposits, which genetically represent sand, silt and clay with gravel bed, and the Deccan trap formation includes basaltic rocks belonging to its three sub-provinces, i.e, Suarasthtra Plateau, Malwa Plateau and Deccan proper. The entire terrain of the study area, which falls under the Saurashtra plateau, is occupied by basaltic rocks. The study area shows an interesting assemblage of basaltic differentiates and alkaline derivatives from an important volcanic sub-province. The constituent rocks are thoelite and alkalic variation (Fig. 1). The soil type formation is mostly black cotton soil. These soils are mainly clayey soils and are neutral to alkaline in reaction (Merh, 1995).

2.2 Sampling and analysis

The total number of soil sampled was 25. Most of the soil samples were collected from the outer surface i.e., 5–15 cm depth to study the anthropogenic sources of pollutants as normally industrial pollutants contaminate the upper layer of the soil (0–40 cm). In case of natural abundance, the entire soil at all depths shows high metal enrichment. The samples were collected in self locking polythene bags and were sealed in double bags. Use of metal tools was avoided and a plastic spatula was used for sample collection. Figure 1 shows the location of soil sample collection in the study area.

Soil samples were dried for two days at 60°C. The dry soil sample was disaggregated with mortar pestle. The sample was finely powdered to –250 mesh size (US standard) using a swing grinding mill. Sample pellets were prepared for analysis by X-ray fluorescence spectrometry (XRF), using a backing of boric acid and pressing it at 25 tons of pressure. A hydraulic press was used to prepare the pellets for XRF analysis to determine trace elements.

2.3 Instrumentation

A Philips MagiX-PRO PW2440 fully automatic, microprocessor controlled, 168-position automatic PW 2540 vrc sample changer X-ray spectrometer was used

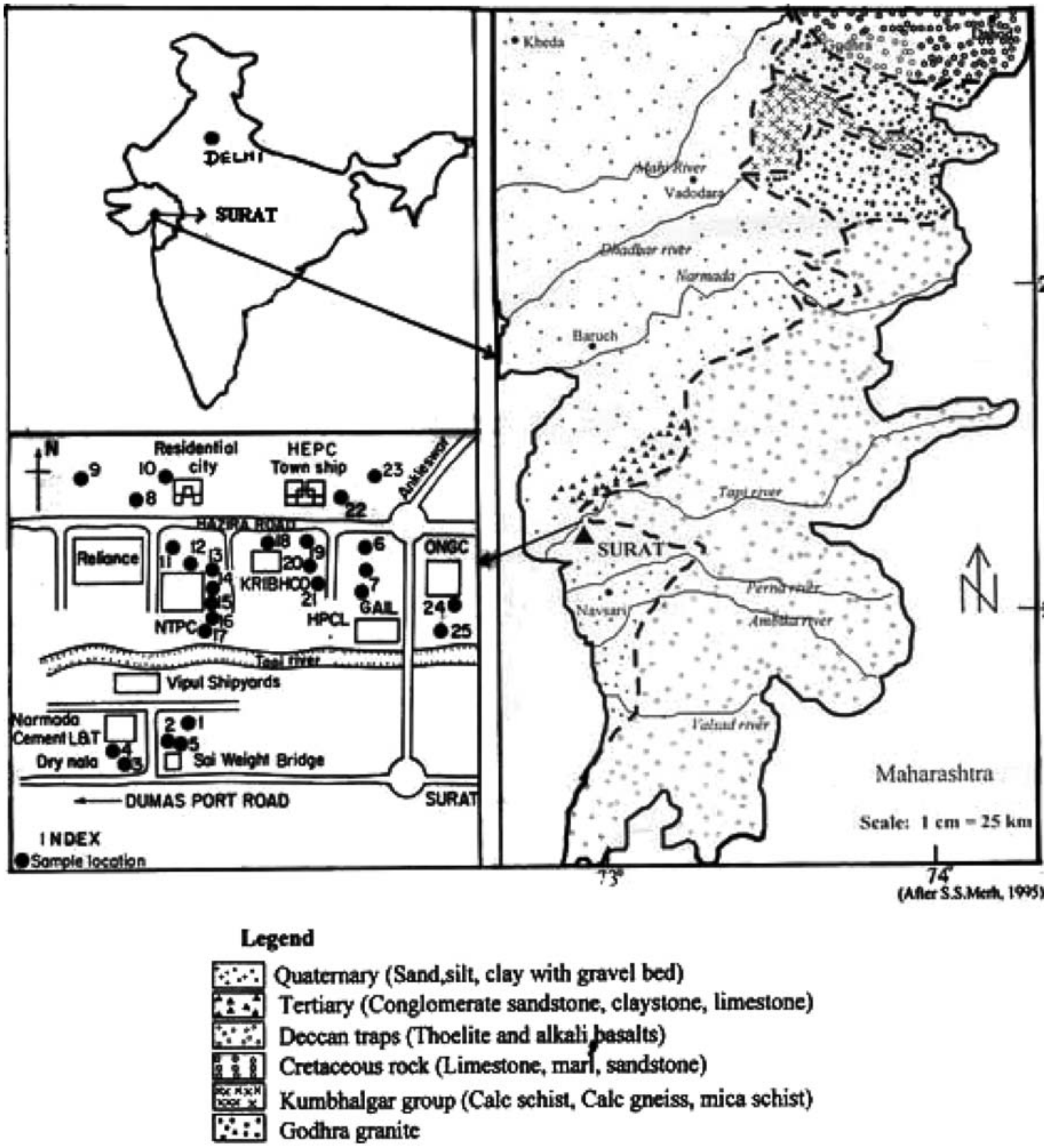


Fig. 1 Sample location and geology map of the study area

along with a 4 KW X-ray generator for the determination of heavy metals (Ba, Cu, Cr, Co, Sr, V, Zn and Zr) in soil samples. The MagiX PRO is a sequential instrument with a single goniometer based measuring channel covering the complete elemental range. A Rhodium (Rh) anode is used in the X-ray tube, which may be operated at upto 60 kV and current upto 125 mA, at 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 the US Geological Survey, Canadian Geological Survey, International working group, France and NGRI, India (Govil and Narayana, 1999; Govil, 1993) were used to prepare

Table 1 Heavy metal XRF data in soils (mg/kg)

Sample	Ba	Cu	Cr	Co	Ni	Sr	V	Zn
SU-1	302.3	125.7	222.7	47.5	79.0	246.9	228.6	139.0
SU-2	318.3	95.3	171.0	42.2	39.6	317.9	207.9	123.2
SU-3	367.1	102.0	197.7	42.3	56.2	216.0	232.5	106.9
SU-4	386.6	101.3	181.9	43.1	61.1	202.8	241.4	108.5
SU-5	266.3	77.1	100.4	24.4	53.4	125.3	141.9	91.0
SU-6	406.7	116.1	189.2	45.9	43.8	208.7	292.5	107.8
SU-7	399.7	122.1	169.6	48.5	44.2	175.4	278.9	104.5
SU-8	360.5	123.6	166.9	49.8	60.1	91.4	247.8	106.6
SU-9	401.5	101.8	213.4	46.0	44.1	220.5	295.1	121.3
SU-10	381.0	112.7	190.2	47.9	52.1	156.0	271.5	114.0
SU-11	471.7	107.4	279.1	46.7	43.7	158.5	374.7	112.4
SU-12	393.8	110.7	209.0	47.4	46.3	192.0	296.4	106.3
SU-13	389.6	109.6	203.1	45.7	49.3	163.1	291.0	103.8
SU-14	316.9	91.9	172.2	42.5	33.7	241.4	262.9	96.7
SU-15	421.8	95.0	305.2	45.4	34.6	221.1	380.6	104.4
SU-16	383.8	113.3	181.8	46.2	59.4	118.7	263.1	106.4
SU-17	392.1	111.1	179.5	47.2	54.3	137.6	266.5	109.6
SU-18	424.5	110.1	250.1	48.1	46.2	146.6	336.9	110.7
SU-19	391.9	119.1	174.4	46.4	41.9	208.2	299.7	102.3
SU-20	434.5	117.8	198.3	48.5	38.5	198.4	339.8	108.1
SU-21	426.6	119.6	195.1	46.4	42.0	187.0	328.1	107.2
SU-22	368.7	137.5	176.1	51.3	50.7	155.6	294.4	115.7
SU-23	396.6	130.4	183.8	50.9	44.8	200.4	300.2	116.2
SU-24	430.2	111.9	209.8	47.8	38.6	216.7	330.3	107.6
SU-25	422.2	112.0	198.7	45.5	41.3	206.2	318.2	104.3

Table 2 Statistical summary of metal concentration in soil (mg/kg)

	Ba	Cu	Cr	Co	Ni	Sr	V	Zn
Mean	386.2	111.0	196.8	45.7	48.0	188.5	284.8	109.4
Median	392.1	111.9	190.2	46.4	44.8	198.4	292.5	107.6
St. Dev	45.9	13.1	39.2	5.0	10.0	47.7	52.4	9.2
Max	471.7	137.5	305.2	51.3	79.0	317.9	380.6	139.0
Min	266.3	77.1	100.4	24.4	33.7	91.4	141.9	91.0
Skewness	−0.91	−0.45	0.76	−3.31	1.26	0.34	−0.54	1.27
Threshold value*	300.0	30.0	100.0	17.0	80.0	200.0	100.0	200.0
Mean(log10)	2.59	2.05	2.29	1.66	1.68	2.28	2.45	2.04
Median(log10)	2.59	2.05	2.28	1.67	1.65	2.30	2.47	2.03
SD(log10)	1.66	1.12	1.59	0.70	1.00	1.68	1.72	0.96

*Maximum permissible concentrations as defined by government regulations

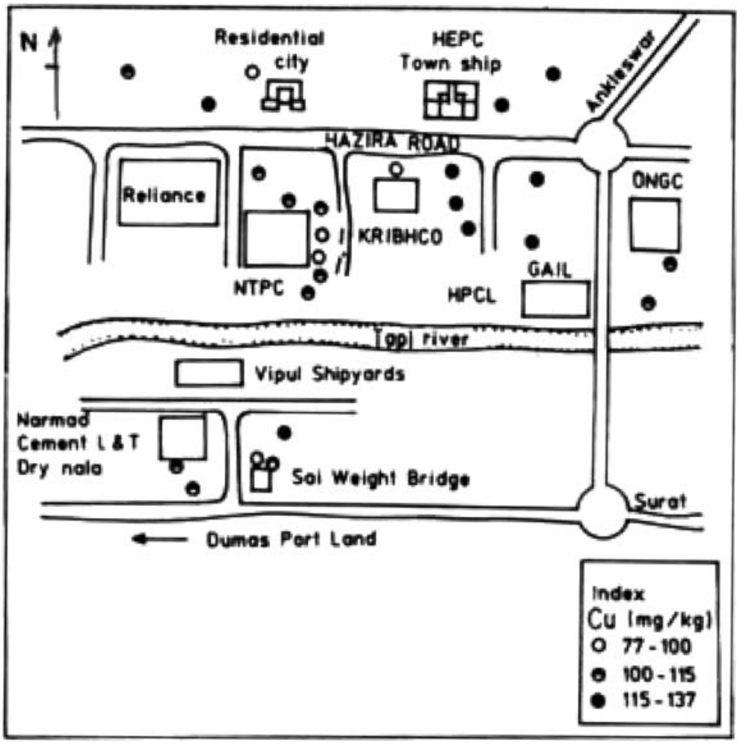
calibration curves for trace metals (Govil, 1985; Rao and Govil, 1995). Trace element data are given in Table 1.

3 Results

3.1 Heavy metal concentrations

The individual results obtained for each metal are shown in Table 1. To simplify the above results. Table 2 summarizes the statistics of the data. Maximal permitted threshold soil concentrations of potentially toxic metals prescribed by WHO guidelines (WHO, 1996) are also given. High levels of these elements are observed in some pockets only Fig. 1 close to some of the industries manufacturing textiles, petro-chemical, refinery, natural gas, cement and steel plant. Especially, Cu (137.5 mg/kg), Cr (305.2 mg/kg) Co (51.3 mg/kg) and V (380.6 mg/kg) data showed enrichment levels exceeding the normally expected distribution in soil

Fig. 2 Distribution of Copper in soils



giving rise to concern over suitability of soils in the study area. Such extremely high levels of pollutants in soils can be found in many industrial sites and waste disposal dumps, which result from very localized additions or accidental spillages of highly concentrated pollutant materials (Govil *et al.*, 1998). These elements can be leached into the surface water or ground water, taken up by plants, which later effect the human health (Acero P *et al.*, 2003; Saether OM *et al.*, 1997; Gough *et al.*, 1994). The study also showed that the concentrations of the metals are to a large extent linearly correlated; Table 4 is the correlation matrix, which shows good correlation between V and Ba ($r = 0.90$), Cu and Co ($r = 0.81$), Cr and V ($r = 0.78$), Co and Ba ($r = 0.59$).

3.2 Copper and Cobalt

Copper and Cobalt values were found to be high in almost all the samples. The soil samples in the study area contain copper in the range of 77.1 mg/kg to 137.5 mg/kg (Fig. 2) with average value of 111.0 mg/kg and Cobalt ranged from 24.4 mg/kg to 51.3 mg/kg (Fig. 3) with an average value of 45.7 mg/kg. The normal threshold value of Cu in soil is 30 mg/kg. The levels of Copper in soil normally reflect the concentration in parent rocks, like Cu in igneous basaltic rocks (90 mg/kg). High levels of Cu in the area, which is covered by major assemblage of basaltic differentiates and alkaline derivatives, the soils in the area being neutral to alkaline, such abnormal values of Cu may not be from any anthropogenic source but could be attributed to a geogenic activity in the study area. Whereas normal distribution of Co in soil ranges from 1 mg/kg to 17 mg/kg. Cobalt usually occurs in association with other metals such as Cu, Ni, and As. One of the most important properties of Co is soil acidity. The more acidic the soil is the greater the potential of cobalt toxicity (Romic *et al.*, 2001; Casas *et al.*, 2003). As the soil in the study area is neutral to alkaline in reaction and it is not possible to derive high value from natural soil and the source indicates to be anthropogenic activity from a metal manufacturing and its compounds. Cobalt is usually present in traces associated with many other sulfides and gets released during processing of sulfides, thus turning harmful to the environment. (Onianwa, 2001; Krishna *et al.*, 2004).

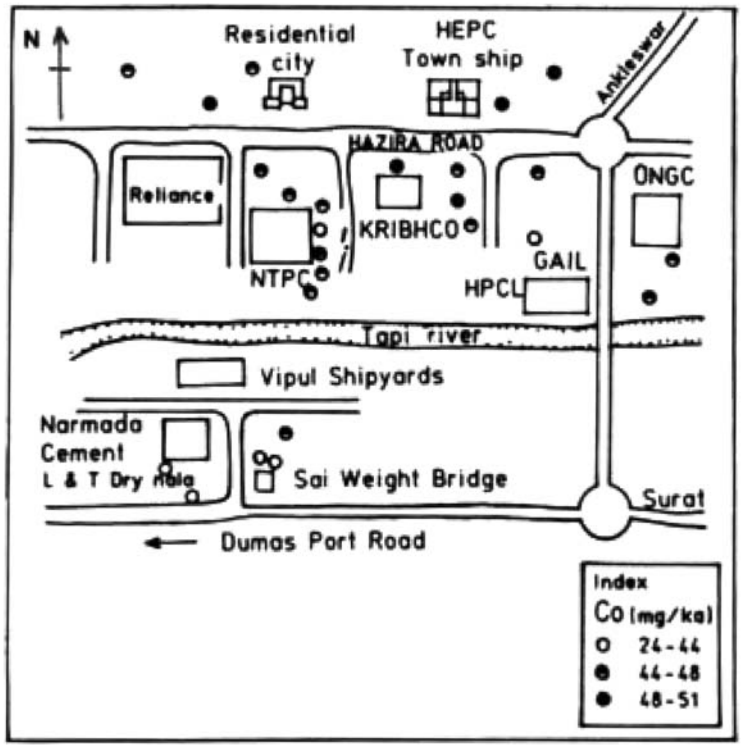


Fig. 3 Distribution of Cobalt in soils

3.3 Chromium and Nickel

Distribution of Chromium and Nickel levels (Figs. 4 and 5) in the study area ranged from 100.4 to 305.2 mg/kg and 33.7 to 79 mg/kg respectively with an average of 196.8 mg/kg for Cr and 48.0 mg/kg for Ni. Normal range of Cr and Ni in soils is 100 mg/kg and 80 mg/kg. The study area is mostly dominated by petrochemicals and refineries. Disposal of Fly ash on land is the largest single input of both Cr and Ni to soils. Table 3, Shows the average concentration of Cr and Ni in coal and fly ash. Fly ash is enriched in Cr and as a result, soils around coal-fired electricity generators may be slightly enriched with Cr. The dumping of large amounts of pulverized fuel ash on soil leads to background soils. Emission of Ni from smelters and Cr in the waste from chromate smelters bring about large increase in soil (Adriano *et al.*, 1980). Therefore, the source of Cr and Ni contamination in the study area appears to be anthropogenic from industries producing coal products, steel and some smelting activity. Ansari *et al.* (1999) obtained very high Cr levels in soil i.e., upto 1220 mg/kg in some industrial areas of India.

Table 3 Concentration of Cr, Ni in coal and fly-ashes (mg/kg) from Adriano *et al.* 1980

	Cr	Ni
Coal	15	15
Fly ash		
Bituminous	172	11
Sub-bituminous	50	18
Lignite	43	13

3.4 Vanadium and Barium

Vanadium and Barium levels ranged from 141.9 to 380.6 mg/kg and 266.3 to 471.7 mg/kg in the study area with a soil average of 284.8 mg/kg for Vanadium and 386.2 mg/kg for Barium. Distribution of Vanadium and Barium are shown in Figs. 6 and 7. Vanadium is the major trace metal in petroleum products, especially in the heavier fractions. An average V content of crude oil is 50 mg/kg, with a range from 0.6 to 1400 mg/kg (Alloway, 1995). Also the vanadium content of soil depends upon the parent material and the pedogenic process associated with its development. Composition of

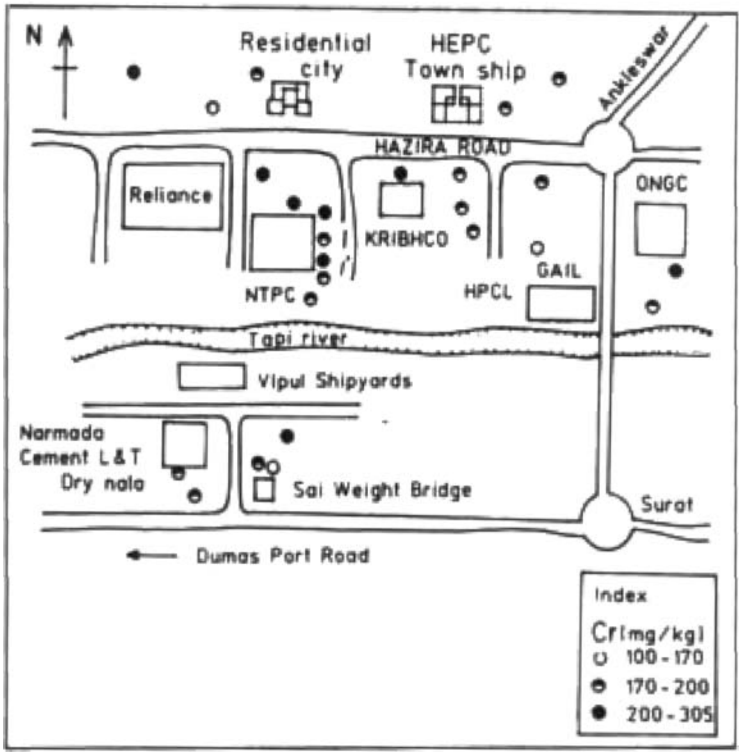


Fig. 4 Distribution of Chromium in soils

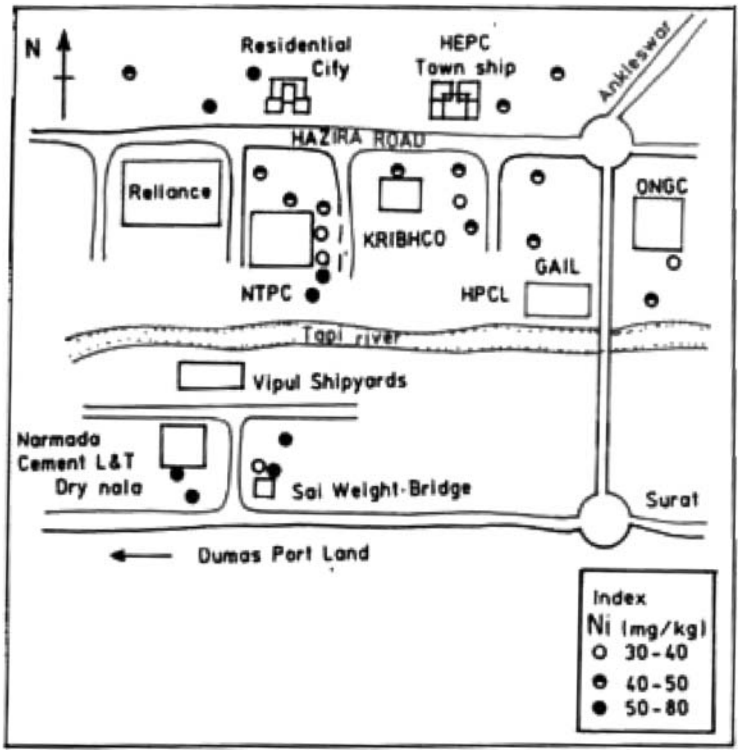


Fig. 5 Distribution of Nickel in soils

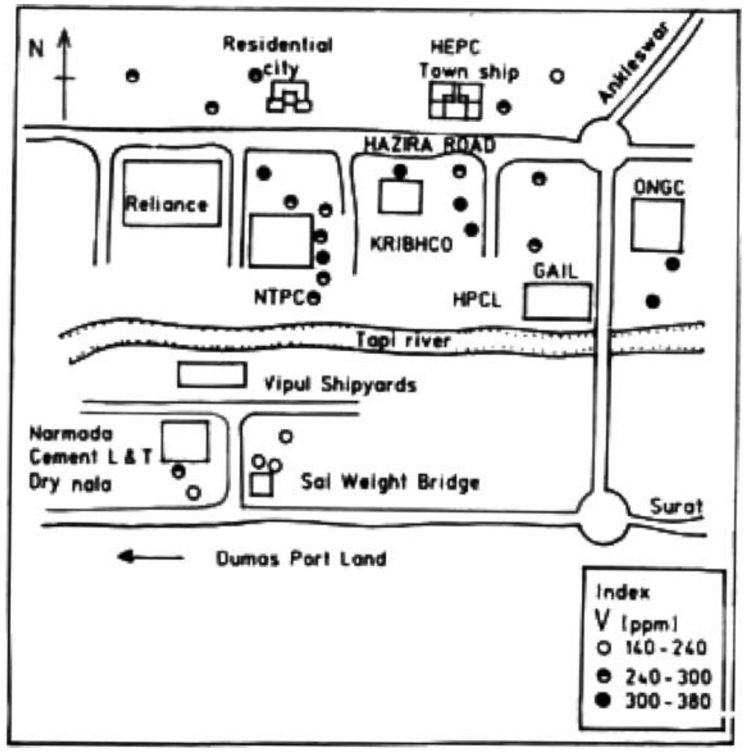


Fig. 6 Distribution of Vanadium in soils

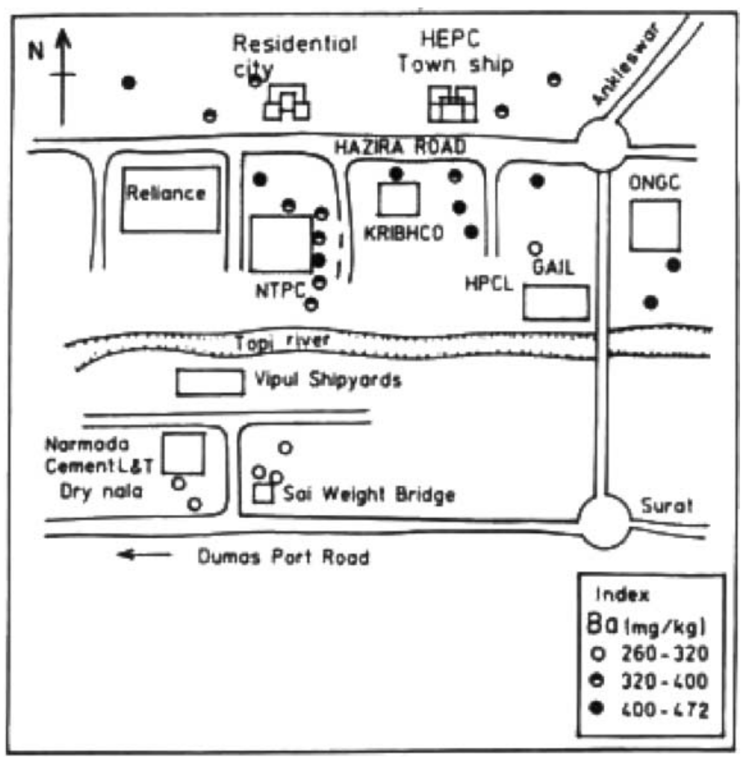


Fig. 7 Distribution of Barium in soils

the parent material has less bearing on V content of mature, developed soils. Normal threshold value for vanadium in soils is 100 mg/kg (Larocque and Rasmussen, 1998; Krishna *et al.*, 2004). 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 the source to be anthropogenic from industries in the area. Whereas, the highest amount of barium found in soils is about 100 to 3000 mg/kg. Barium waste may be released to air, soil and water during industrial operations. Barium is released into the air during the mining and processing of ore and during manufacturing operations (ATSDR, 2000). The contribution of industrial activity in the study area seem to be the source of contamination.

3.5 Strontium and Zinc

The average concentration of Strontium and Zinc in the investigated area equals 188.5 mg/kg and 109.4 mg/kg ranging from 91.4 to 317.9 mg/kg for Sr and 91.0 to 139.0 mg/kg for Zn. Figures 8 and 9 show the distribution of Strontium and Zinc in soil. The soil in the study area is basically derived from silt, kankar, claystone, sandstone, limestone and conglomerate sand stone (Merh, 1995). Kankar and limestone are enriched in Sr and this is suspended to have contributed the same in soil. Threshold value of distribution of Sr and Zn in soil is 200 mg/kg (Aswathanarayana, 1995; Krishna, 2004). Zinc is readily adsorbed by clay minerals, carbonates. Moreover the levels of Sr and Zn in soil are within permissible levels, which indicate its normal concentration and reflect the background value in soil. The source appears to be the geogenic contribution of Sr and Zn in soil.

4 Discussion

The area along the up-stream of River Tapi in Surat is urbanized and industrialized. The cumulative influence on the pollution of the River Tapi was increasing in Surat industrial area, since all industrial and domestic effluent was discharged directly into the river.

Also well elaborated in the scientific literature is the contribution of anthropogenic deposition of particles from urban sources (industrial emission, traffic,

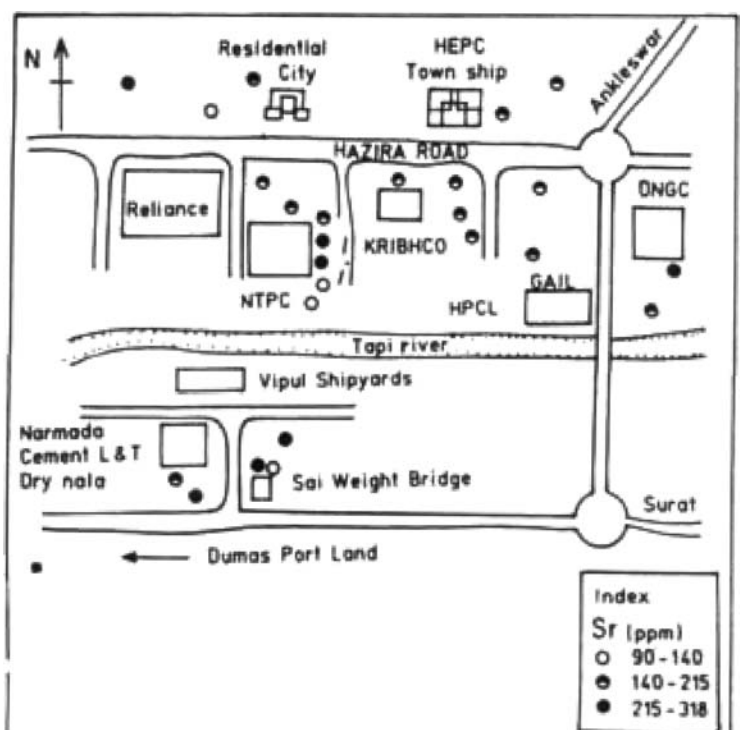


Fig. 8 Distribution of Strontium in soils

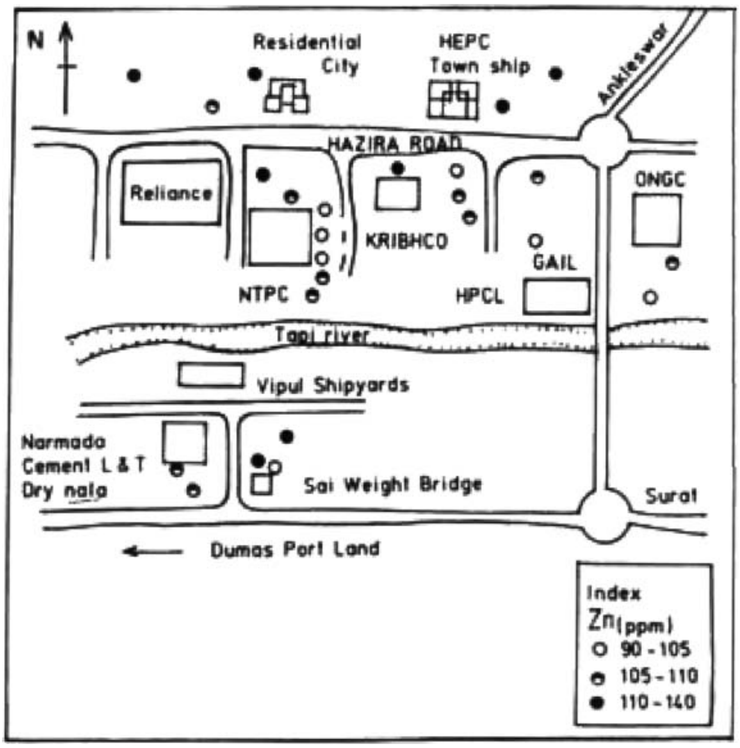


Fig. 9 Distribution of Zinc in soils

Table 4 Correlation matrix table, lower triangle for Surat soils

	Ba	Cu	Cr	Co	Ni	Sr	V	Zn
Ba	1.00							
Cu	0.33	1.00						
Cr	0.63	0.06	1.00					
Co	0.59	0.81	0.44	1.00				
Ni	−0.43	0.22	−0.20	−0.04	1.00			
Sr	−0.13	−0.20	0.17	−0.01	−0.31	1.00		
V	0.90	0.33	0.78	0.62	−0.54	0.00	1.00	
Zn	−0.05	0.41	0.30	0.44	0.43	0.39	0.00	1.00

waste disposal etc.,) to the load of heavy metals in soils (De Miguel *et al.*, 1999; Chen *et al.*, 1999). Although no individual element can be used as a specific 'tracer' of atmospheric deposition, the contribution from these sources can be evaluated by determining the difference between anthropogenic anomalies and natural concentrations. The area is intersected by very busy ring roads, while NTPC, HPCL, Pharmaceutical and chemical industries are located in the vicinity. However contribution of these sources can be approximately estimated by distinguishing anthropogenic anomalies from natural background. Table 4 and Fig. 10 showing scatter diagrams indicate correlation (Huisman *et al.*, 1997; Machin, 2002) of Copper with Zinc, Cobalt; Vanadium with Barium, Chromium as shown in Fig. 10. In general, there is a good correlation between V-Ba, Cr; Co-Cu, Ba and Cu-Zn. Positive correlation between V vs Ba showing a straight line indicates a common anthropogenic source from surrounding industries (petroleum and mining activity). The overall geochemical behavior of Ba, Cr, Co, Cu, V, Sr and Zn shows similarity and these elements seem to migrate together and percolate into groundwater thereby contaminating the groundwater table.

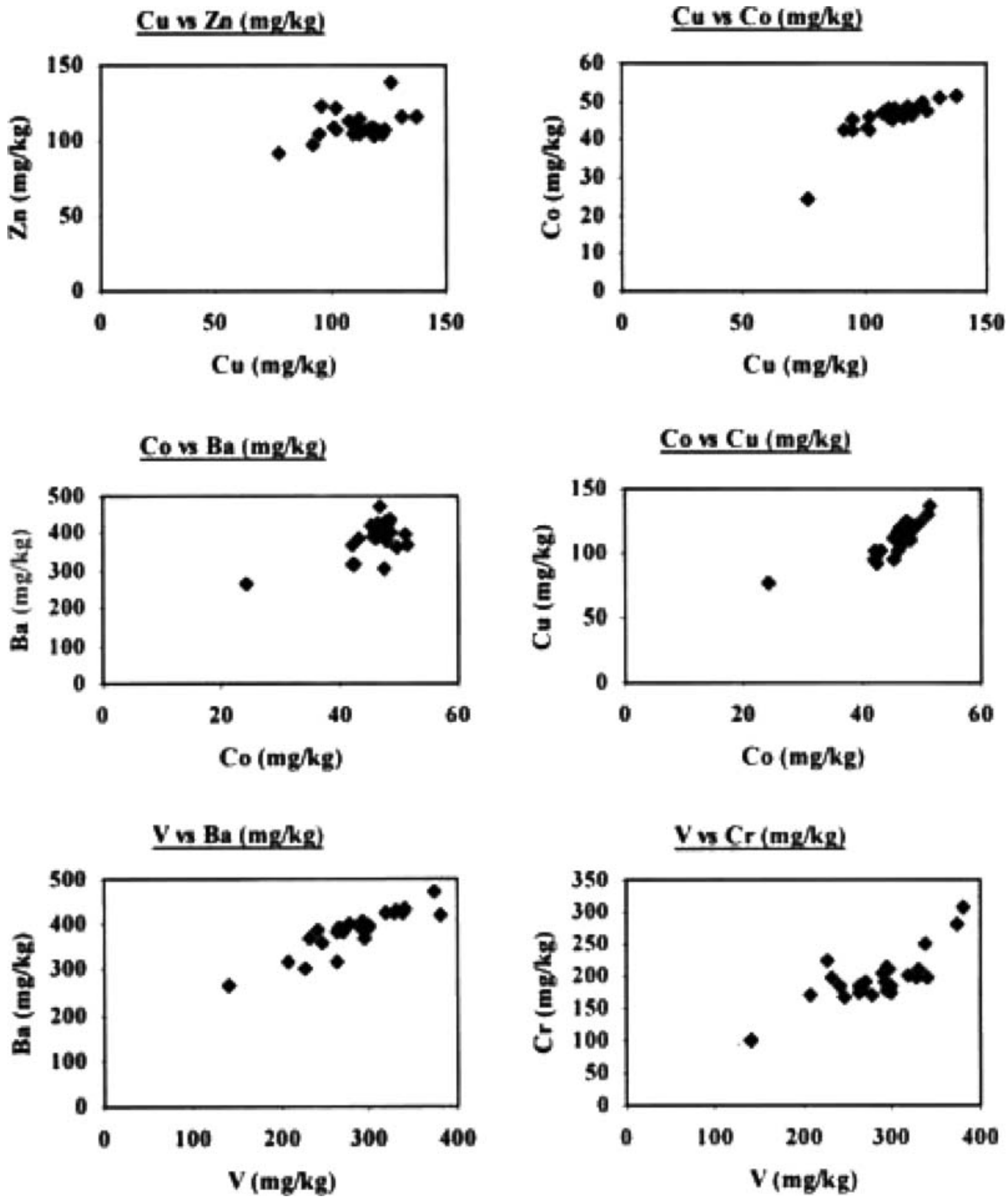


Fig. 10 Scatter plots showing correlation between Cu vs Zn, Co; Co vs Ba, Cu; V vs Ba, Cr

5 Conclusions

The results of the study, show that soils in the vicinity of Surat industrial area were found to be significantly contaminated with metals like Cu, Cr, Co, V and Zn at levels far above the background concentration in soil, which may give rise to various health hazards. There should be a provision to measure toxic metals in industrial effluents before dumping them on open land. A common effluent treatment plant should be installed to treat the industrial effluents before releasing the effluents on to the ground.

In general, the results confirm the source of contamination to be anthropogenic from industrial activity in surrounding Surat soils which has lead to the contamination of soil in the study area. Also the regular monitoring of heavy metal pollution and certain steps (like phyto-remediation by growing some plants in the area) should be taken up in the study area as soon as possible to minimize the rate, and extent of future pollution problems.

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