Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India

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ABSTRACT

Environmental geochemical studies were carried out in and around Jajmau (Kanpur) and Unnao industrial areas (80°15′–80°34′E longitude and 26°24′–26°35′N latitude), of Uttar Pradesh to find out the extent of chemical pollution in soil due to industrial waste. Jajmau and Unnao are prominent centers for leather processing clusters of tannery industries (about 450) along the banks of river Ganga, besides other industries. Geologically the study area is beset with alluvium of Quaternary age consisting of older alluvium of middle to upper Pleistocene and newer alluvium of Holocene. The climate of the study area is semi-arid type. Fifty-three soil samples were collected from Jajmau and Unnao industrial areas from top 15 cm layer of the soil and were analyzed for heavy metals by using Philips MagiX PRO-PW 2440 X-ray fluorescence spectrometer. The data reveals that the soil in the area is significantly contaminated with heavy metals such as chromium varies from 161.8 to 6227.8 mg/kg (average of 2652.3 mg/kg), Ba varies from 44.1 to 780.9 mg/kg (average of 295.7 mg/kg), Cu varies from 1.7 to 126.1 mg/kg (average of 42.9 mg/kg), Pb varies from 10.1 to 67.8 mg/kg (average of 38.3 mg/kg), Sr varies from 46.6 to 150.6 mg/kg (average of 105.3 mg/kg), V varies from 1.3 to 208.6 mg/kg (average of 54.4 mg/kg) and Zn varies from 43.5 to 687.6 mg/kg (average of 159.9 mg/kg). Soil contamination was assessed on the basis of geoaccumulation index, enrichment factor (EF), contamination factor and degree of contamination. Indiscriminate dumping of hazardous waste in the study area could be the main cause of the soil contamination, spreading by rainwater and wind. Distribution and correlation of heavy metals in soil along with possible remedial measures are discussed.

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1. Introduction

Soil is considered contaminated when chemicals are present or other alterations have been made to its natural environment. This is often caused by accidental releases of chemicals or the improper disposal of hazardous waste. Increased inputs of metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in the developing country like India, has led to large-scale pollution of the environment. These chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters and human health [1,26,58,60]. Heavy metal content of soil is of major significance in relation to their fertility and nutrient status. Many metals such as Zn, Cu, and Se are essential elements for normal growth of plants and living organisms. However, high concentrations of these metals become toxic. Other metals, which are not included in the group of essential elements, such as Pb or Cr, may be tolerated by the ecosystem in low concentration, but become harmful in higher concentrations [3,42]. Soluble metal compounds and metals held in exchange complexes are considered to be available to vegetation uptake. The bioavailability of metal compounds is influenced by the pH, temperature, redox potential, cation exchange capacity of the solid phase, competition with other metal ions, ligation by anions and composition and quality of the soil solution [36,38,51].

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. 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 remains as Cr(VI) [2,4,6,12,35,52,53,54].

The Ganga Plain is one of the most densely populated regions and one of the largest groundwater repositories of the Earth. The alarming population growth rate, unplanned urbanization and

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industrialization in the plain have brought about various geo-environmental hazards such as sediment, water, and soil pollution, lowering of groundwater level in certain parts, flooding, water logging, formation of alkaline soils and improper management of the agricultural areas [15,50,57]. Kanpur (Jajmau) and Unnao, the eighth largest metropolis of India, is a centre of multinational leather industries and is considered to be the hot spot region of pollution in the Ganga Plain [6,50].

The main objective of the study was 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. 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 [34,40]. 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. In this work, the soil contamination was assessed using various indices, including index of geoaccumulation, normalized enrichment factor (EF), contamination factor and degree of contamination.

2. Materials and methods

2.1. Index of geoaccumulation

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments [39], it can also be applied to the assessment of soil contamination. It is computed using the following Eq. (1):

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \tag{1}$$

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 allowed to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. In the present paper the modified calculation based on the equation given in [34] was applied, where C_n denoted the concentration of a given element in the soil tested, while B_n denoted the concentration of elements in the Earth's crust [56,59]. 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 [39] 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.

2.2. Enrichment factor

The value of EF was calculated using the modified formula given by [34] based on the equation (2) suggested by [10]. 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 [44,46,55]. In this study strontium was used 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.

$$EF = \frac{C_n(\text{sample})/C_{ref}(\text{sample})}{B_n(\text{background})/B_{ref}(\text{background})} \tag{2}$$

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, based on the Eq. (3). The c_f^i 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 [24], 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).

$$c_f^i = \frac{c_{0-1}^i}{c_n^i} \tag{3}$$

where c_{0-1}^i is the mean content of metals from at least five sampling sites and c_n^i is the pre-industrial concentration of individual metal. In the present study a modification was made for the factor as applied by [34] that used the concentration of elements in the Earth's crust as a reference value, similar to the other factors.

2.4. Study area

Jajmau and Unnao industrial areas are parts of Kanpur and Unnao Districts of Uttar Pradesh, located in 80°15′–80°34′E longitude and 26°24′–26°35′N latitude and is a chronic polluted area and one of the biggest exporting centers of tanned leather. It is situated on the right bank of the Ganga River and the left bank of its tributary, the Pandu River as shown in Fig. 1. The Ganga River enters the town from NW and leaves it in SE direction. The Pandu River enters the city from the west and joins the Ganga River at a distance of 156 km downstream of Kanpur city. The Kanpur–Unnao region is one of the largest industrial complexes of the Ganga Plain, in which a number of industries such as cotton and wool textile mills, tanning and leather manufacturing industries, large fertilizer factories and several arms factories are situated. In addition to this, light engineering factories for rerolling and casting, and the manufacture of chemicals, paints, plastics, and other miscellaneous items dominate Kanpur's small- and medium-scale industries are producing a large amount of industrial waste, which is indiscriminately spread in the region. Further, with a population of about 2.4 million in Kanpur city and 0.2 million in Unnao city, a large amount of untreated municipal waste is also discharged in this region. The area is traversed by the Ganga River and there are a number of smaller rivers of varying channel characters. The region shows a marked micro geomorphic variability and polluting industries are located in different geomorphic settings [6].

2.5. Geology and climate

Geologically the study area is underlain by the alluvium of Quaternary age consisting of older alluvium of middle to upper
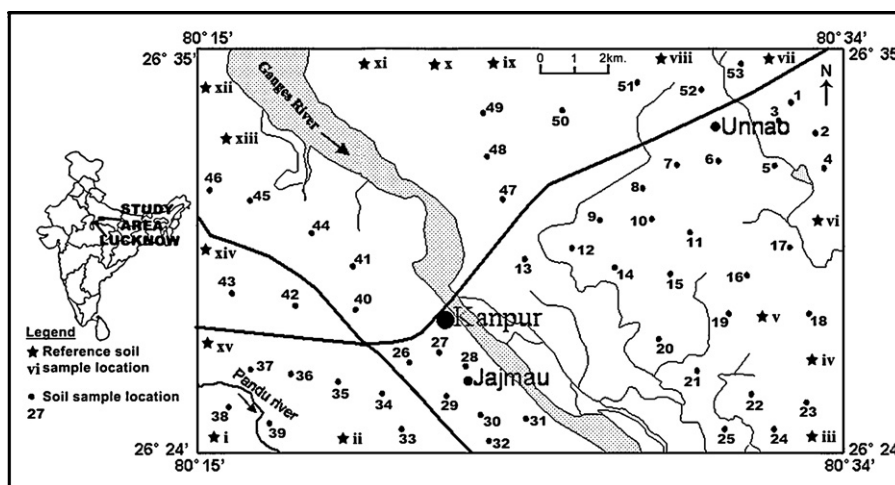
Fig. 1. Location map of the study area showing soil sample and reference soil sampling points.

Pleistocene and newer alluvium of Holocene. The Ganga Plain is a large alluvial system formed in response to the development of the Himalaya [31,43,47,48]. Because of its setting in front of the rising Himalayan chain, huge sediment loads are brought into the plain by the rivers and redistributed by the fluvial processes. The central part of the plain drained by the Ganga River system is known as the Ganga Plain. The Kanpur–Unnao region is a part of the Central Ganga Plain with its characteristic landforms. The area under study is traversed by the Ganga, Pandu and Loni rivers as shown in Fig. 2. The alluvial deposits of the Gangetic Plain are mainly composed of sand, silt and clay. The sediments are micaceous and show varying colour from unoxidised grey to oxidized yellowish brown. The grain size varies from 2.2φ to 3.5φ, moderately to well sorted, very coarse to finely skewed and polykurtic to leptokurtic in nature. The heavy mineral assemblage is characterized by kyanite, sillimanite, garnet, epidote, hornblende, tremolite, chlorite and opaques suggesting metamorphic provenance [31,41,49]. The main constituents (sand, silt and clay) of alluvium occur in variable proportions in different sections. The three types of soil have been identified pertaining to three distinct physiographic units of the basin which are sandy loam, sandy loam to loam, and loam to clay loam. The soils are alkaline in nature and the pH ranges from 8.05 to 8.35.

The study area is situated in the zone of humid subtropical climate and the year is divided into three seasons: the cold season (November–February), the hot season (March–June) and the monsoon season (July–October). Heavy rainfall occurs during the monsoon season in the months of July, August and September. Generally 70–80% of the total rainfall occurs during this period [13].

2.6. Sampling and analysis

The total number of soil samples is 53 and were collected from the top soil i.e., 5–15 cm depth ('A' horizon of soil), which is usually contaminated, 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 sites has been determined. 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 by swing-grinding mill and then sieved to −250 mesh size (US Standard). Sample pellets were prepared for analysis by X-ray fluorescence spectrometry (XRF), using a hydraulic press and in collapsible aluminum cups. These cups were filled with boric acid and 1 g of the finely powdered sample was put on the top of the boric acid and pressed under a hydraulic press at 25-ton pressure to get a pellet (Hydraulic Press, Herzog, Germany). To monitor the quality of chemical analysis data and examine the accuracy of the data, soil reference materials, SO-1 and SO-4 issued by Canadian Council of Ministers of the Environment [11] were analyzed along with the soil samples during the course of analysis as unknown samples. The analytical concentrations of the metals in reference samples are listed in Table 1. It is seen that the analytical values are
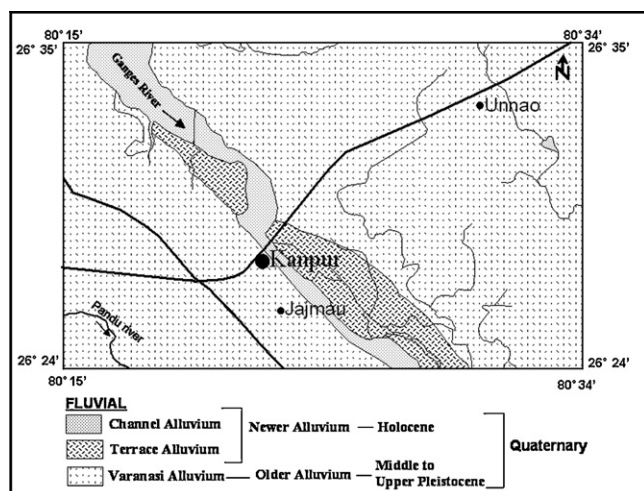

Fig. 2. Geology map of the study area.

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.

Table 2
Natural background values in the alluvial soil in the Jajmau and Unnao 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

within the range of certified values of reference materials.

2.7. 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 was 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 materials from the US Geological Survey, Canadian Geological Survey (SO-1, SO-2, SO-3, SO-4), International Working Group, France [22], and National Geophysical Research Institute, India (NGRI-D and NGRI-U) [17,18] were used to prepare the calibration curves for major and trace elements and to check the accuracy of the analytical data [16,21]. Precision and accuracy of the data were assured through repeated analysis of National Institute of Standards and Technology and the results were found to be within ±2% of the certified values. Average values of three replicates were taken for each determination.

2.8. 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 the parent material and by redistribution in the profile due to pedogenesis during the process of soil formation is given in Table 2 [5,23,29,50]. Out of 15 samples 5 were discarded for possibly anthropogenic contamination according to statistical analysis (Fig. 1). 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 (Fig. 1).

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. The analysis is done for eleven elements but, as other elements like As, Co, Ni, Mo are below contamination level and hence not discussed. Descriptive statistics of the analyzed samples for seven elements and reference value of metal concentrations in the continental crust [56,59] are tabulated in Table 4. Chromium, barium, copper, lead, strontium, vanadium, and zinc showed enrichment levels exceeding the normally expected distribution in soil giving rise to concern over suitability of soils in the study area [5,19,20,45,52,62]. High levels of these elements are observed in some pockets, very close to industries like tanneries, refractories, fertilizers, paints, which indicate that the source of these elements could be the industrial effluents. Table 5 shows that the soils of the study area are enriched in relation to the natu-

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

S.No.	Ba	Cr	Cu	Pb	Sr	V	Zn
1	173	1819	90	52	96	25	79
2	132	2758	46	46	124	20	51
3	128	2474	47	46	121	17	51
4	514	326	23	38	104	74	58
5	582	210	24	32	130	77	60
6	602	328	26	38	137	79	71
7	48	2356	2	20	47	51	115
8	616	4000	47	40	142	142	230
9	591	328	25	40	134	79	78
10	585	454	25	38	131	79	77
11	160	3146	97	56	135	14	75
12	153	3473	102	65	135	15	80
13	189	3802	126	68	142	24	80
14	137	4480	64	57	134	8	70
15	729	922	37	46	137	103	96
16	696	930	41	48	106	109	103
17	691	973	41	50	110	108	104
18	743	1089	39	46	132	107	105
19	725	1185	39	48	133	106	104
20	679	918	44	46	104	109	103
21	49	4885	35	22	73	2	181
22	59	5573	33	32	76	2	180
23	69	3049	28	40	94	5	164
24	77	5397	42	32	93	4	251
25	81	5939	37	29	90	2	229
26	56	6034	41	28	73	2	220
27	57	6228	31	28	74	1	144
28	73	5657	33	30	93	3	139
29	72	2882	26	30	91	5	181
30	54	4290	33	23	89	2	169
31	282	1615	44	34	118	30	240
32	63	255	25	29	95	4	50
33	63	898	32	36	97	2	118
34	260	1749	42	32	94	35	236
35	58	975	32	31	94	2	128
36	67	162	22	31	95	5	44
37	135	2861	108	57	115	10	628
38	64	221	26	23	93	5	45
39	83	465	33	34	79	6	242
40	68	216	24	29	94	4	45
41	47	315	28	27	75	4	44
42	58	257	25	22	76	5	44
43	144	3024	113	60	116	12	688
44	657	5634	60	51	112	192	299
45	44	2216	3	10	49	50	114
46	527.7	4125.0	51.0	57.1	118.3	147.6	242.6
47	625.8	4657.0	54.8	48.4	140.5	160.2	282.7
48	56.4	2165.0	2.3	10.6	48.1	50.1	114.7
49	46.9	2424.0	2.4	10.9	57.4	51.7	110.3
50	687.7	4570.0	59.0	53.8	150.6	179.0	283.4
51	745.9	6081.0	62.9	47.9	141.9	195.6	315.9
52	780.9	5557.0	59.2	45.7	135.2	208.6	278.9
53	589.2	4227.0	47.0	40.9	112.2	151.2	234.6

Table 4
Statistics of the determined elements in soil samples ($n = 53$), and reference value of element concentrations in the continental crust [59].

	Ba	Cr	Cu	Pb	Sr	V	Zn
Minimum	44.1	161.8	1.7	10.1	46.6	1.3	43.5
Maximum	780.9	6227.8	126.1	67.8	150.6	208.6	687.6
Mean	295.7	2652.3	42.9	38.3	105.3	54.4	159.9
SD	276.1	2006.1	27.1	13.5	27.1	61.8	127.9
Reference value	584.0	126.0	25.0	15.0	333.0	98.0	65.0

Table 5
Minimum, maximum and median values of enrichment factor (EF) for the determined elements in soil samples ($n = 53$).

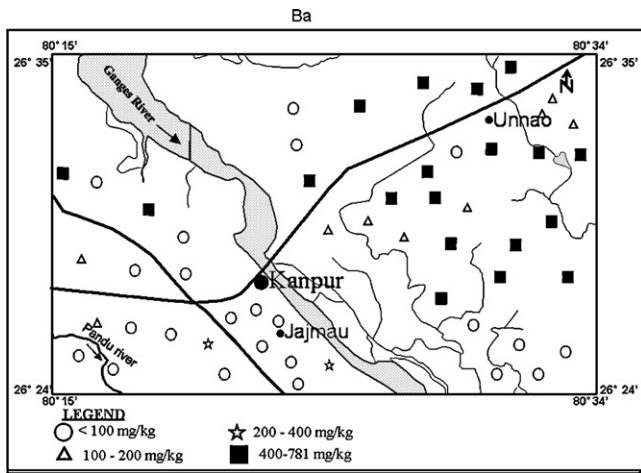| Statistical parameters	EF-Ba	EF-Cr	EF-Cu	EF-Pb	EF-V	EF-Zn
Minimum	0.35	4.27	0.49	4.22	0.06	2.10
Maximum	3.78	222.73	12.96	11.98	5.82	30.47
Mean	1.43	72.12	5.20	7.97	1.65	8.16
SD	1.20	60.20	2.82	1.78	1.72	5.99

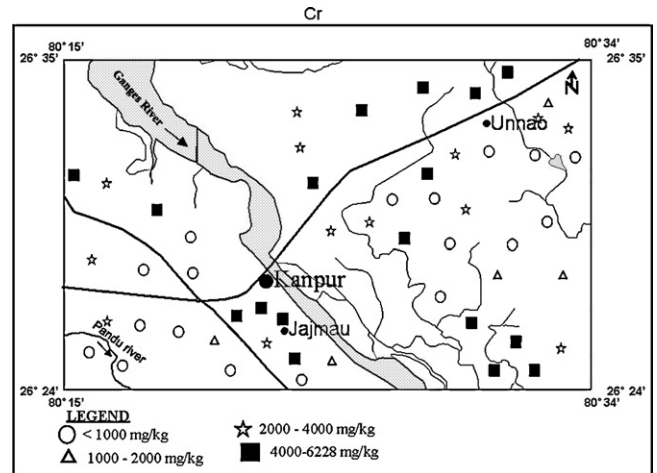**Fig. 3.** Distribution of barium (mg/kg) in soil.

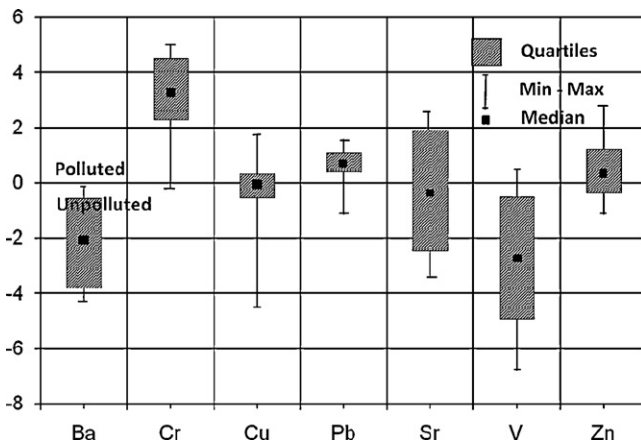**Fig. 6.** Distribution of chromium (mg/kg) in soil.

Fig. 4. Indexes of geoaccumulation for metals in soil of Kanpur–Unnao.

ral background values with factors of 1.43 for Ba; 72.12 for Cr; 5.20 for Cu; 7.97 for Pb; 1.65 for V, and 8.16 for Zn.

3.2. Barium

Barium is released into the air during the process of manufacturing of barium chemicals [8] in the study area. Barium levels in the study area ranged from 44.1 to 780.9 mg/kg, with an average of 295.7 mg/kg as shown in Fig. 3. Thirty-six per cent of the samples exceed the [14] value of 300 mg/kg. The mean I_{geo} (−2.33) obtained revealed that nearly all the samples examined fell into class 0 practically uncontaminated with barium as per Muller's six classes
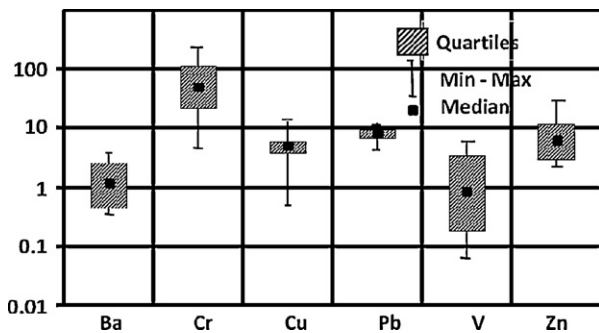
Fig. 5. Enrichment factors for metals in the soil of Kanpur–Unnao.

of the geoaccumulation index (Fig. 4). The EF was also low and ranged from 0.35 to 3.78, showing moderate enrichment with barium as shown in Fig. 5. 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.

3.3. Chromium

Chromium is a low mobility element, especially under moderately oxidizing and reducing conditions and near-neutral pH values. Cr^{6+} adsorption decreases with increasing pH, and Cr^{3+} adsorption increases with increasing pH. On the other hand, Cr(VI) is toxic for biological systems [27]. Chromium levels in the study area ranged from 162 to 6228 mg/kg, with an average of 2652 mg/kg as shown in Fig. 6. The data is cross checked by putting International reference materials as unknown samples. The I_{geo} showing heavily contaminated with a mean of 3.14, revealed that nearly all the samples examined fell into class 4, ranging from −0.22 to 5.04. The EF obtained for Cr ranged from 4.27 to 222.73, which falls under the class of extremely high enrichment [55]. Therefore, the source of Cr appears to be anthropogenic from the existing tannery industries, where they are using chromium and its compounds. The normal range of chromium in soil is 100 mg/kg [59] and all the samples are exceeding the normal value.

3.4. Copper

Copper values were found to be high in the study area. The copper levels in soil samples ranged from 1.7 to 126 mg/kg with an average value of 42.9 mg/kg (Fig. 7). The mean I_{geo} obtained for copper was −0.18 pointing to practically uncontaminated and the values ranged from minimum of −4.46 to maximum of 1.75. The EF for Cu was ranging from 0.49 to 12.96. The normal threshold value prescribed in soil is 30 mg/kg and copper normally accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources [28]. 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.
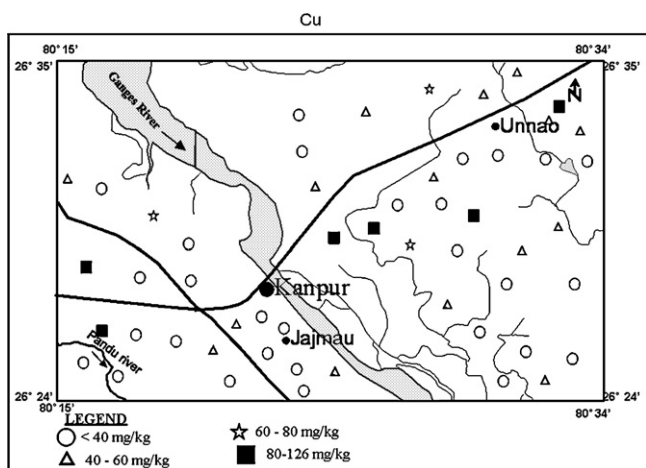
Fig. 7. Distribution of copper (mg/kg) in soil.

Fig. 9. Distribution of strontium (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 [27,61]. However, in the study area Pb content in soil was falling in class 2 showing moderately contaminated with I_{geo} ranging from −1.16 to 1.59 with a mean of 0.66. Similarly in the case of EF it showed significant enrichment in most of the samples ranging from 4.22 to 11.98 with a mean of 7.97.

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 [25,32]. The average concentration of lead in soil samples of the study area is 38.3 mg/kg and ranges from 10.1 to 68 mg/kg as shown in Fig. 8.

3.6. Strontium

The Ganga River is characterized by high Sr concentrations and gravel bed essentially made up of calcified kanker is seen at right bank of Ganga Ri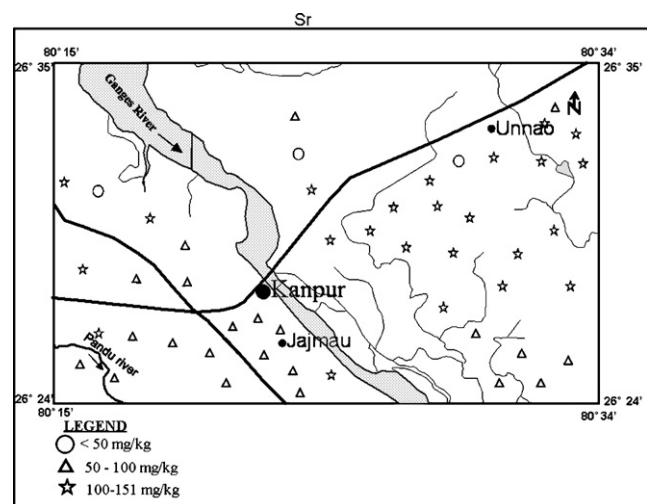ver in the study area [30,31]. Strontium is strongly associated with calcium and is indicative of calcareous rocks, especially in association with Sr, Mg and Ba. Where Ca and other elements indicate calcareous rocks, and other elements (e.g., REEs) indicate felsic intrusives, bedrock geology may be favorable for skarn mineralization. Strontium is easily mobilized during weathering, especially in oxidizing acid environments, and is incorporated in clay minerals and strongly fixed by organic matter [27,37]. The average strontium concentration in the study area is 105.3 mg/kg, ranges from 47 to 151 mg/kg (Fig. 9). Moreover the concentration of Sr in soil is within permissible levels, which indicate its normal concentration and reflect the background value in soil. However, in the study area Sr content in soil was falling in class 1 showing uncontaminated to moderately contaminated with I_{geo} ranging from −3.42 to 1.73 with a mean of −2.30. The source appears to be the geogenic contribution of Sr in soil.

3.7. Vanadium

Vanadium levels ranged from 1.3 to 209 mg/kg in the study area with a soil average of 54.4 mg/kg (Fig. 10). The I_{geo} indicated that the soils in the area fall under class 0 and class 1 ranging from minimum of −4.94 practically uncontaminated and maximum of 0.50 showing uncontaminated to moderately contaminated with a mean of −2.89. The EF indicated moderate contamination with a
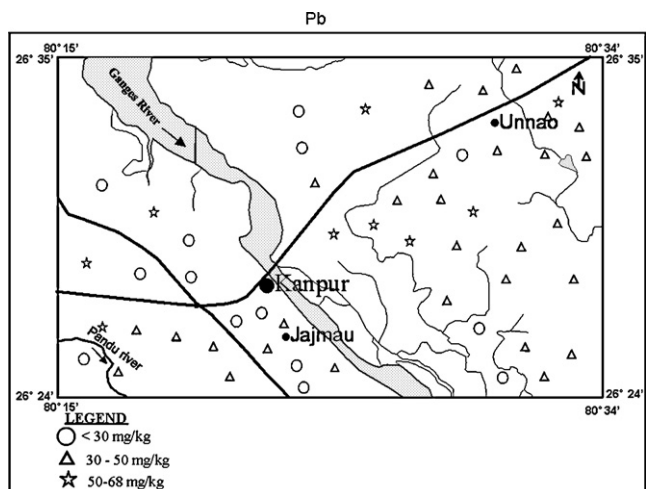

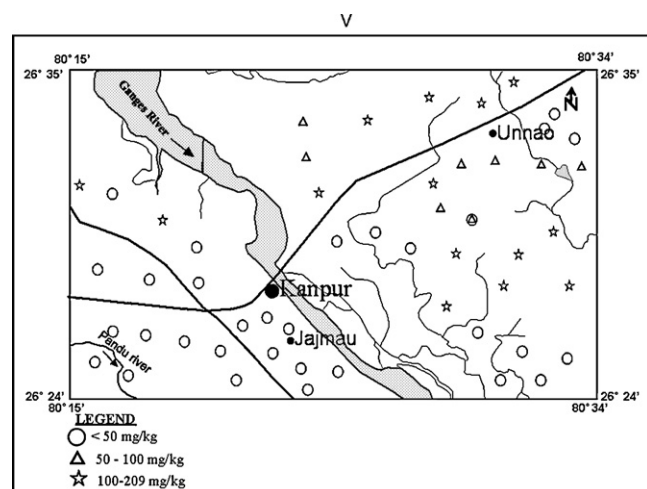**Fig. 8.** Distribution of lead (mg/kg) in soil.
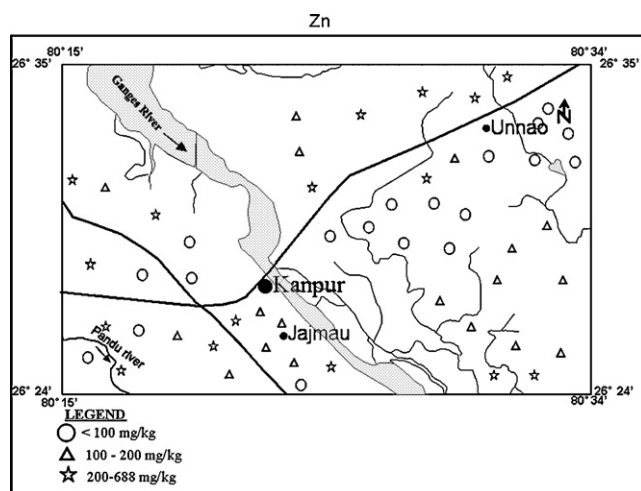

Fig. 10. Distribution of vanadium (mg/kg) in soil.

Fig. 11. Distribution of zinc (mg/kg) in soil.

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

Metal	Minimum	Maximum	Mean
Ba	0.08	1.34	0.51
Cr	1.29	49.43	21.01
Cu	0.07	5.04	1.72
Pb	0.67	4.52	2.55
Sr	0.14	0.45	0.32
V	0.01	2.13	0.55
Zn	0.67	10.58	2.46
Degree of contamination	2.93	73.49	29.12

Table 7
Pearson's product moment linear correlation coefficients of determined metal elements in soil samples ($n = 53$).

	Ba	Cr	Cu	Pb	Sr	V	Zn
Ba	1.00						
Cr	−0.05	1.00					
Cu	0.11	0.32	1.00				
Pb	0.47	0.15	**0.84**	1.00			
Sr	**0.68**	0.04	**0.56**	**0.80**	1.00		
V	**0.89**	0.17	0.07	0.35	**0.51**	1.00	
Zn	0.08	**0.45**	**0.47**	0.29	0.12	0.19	1.00

Bold values are showing positive correlation.

mean content of 1.65 ranging from 0.6 to 5.82. Normal threshold value for vanadium in soils is 100 mg/kg [33]. 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 is anthropogenic from industries in the area.

3.8. 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 [45]. The average zinc concentration in the study area is 159.9 mg/kg, ranges from 44 to 688 mg/kg, which is high (Fig. 11). The I_{geo} indicated that the soils in the study area fall under class 0 and class 1 ranging from minimum of −1.16 practically uncontaminated and maximum of 2.82 showing moderately to heavily contaminated with a mean of 0.36. The EF indicated moderate contamination with a mean content of 8.16 ranging from 2.10 to 30.47. The normal threshold value prescribed in soil is 200 mg/kg [9]. 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 [7].

3.9. Contribution of particular metals to the contamination of soil in Kanpur–Unnao 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_f^i) [34] the soil was classified as slightly contaminated with Ba and Va, moderately contaminated with Cu, 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).

The C_{deg} for the mean metal contents in the soil was 29 and indicated considerable contamination [24]. 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, 72.15%. Copper accounted for 6.01%, Pb, 8.76%,

and Zn, 8.45%. The remaining metals negligibly influenced the soil contamination, not exceeding 2% and decreased in the following order: Sr > Ba > V.

3.10. Correlation of heavy metals

Correlation matrix (Table 7) of the trace metal data indicates strong positive correlations ($r^2 > 0.5$) among Ba–Sr–V and Cu–Pb–Sr, and weak positive correlation ($r^2 \leq 0.5$) among Cr–Cu–Zn. The significant positive correlations within these metals reveal their common source viz., industrial contamination, and sinks in soils of the study area. The presence of Sr in the soils has a bearing on the accumulation of heavy metals in the study area, and has influenced the adsorption characteristics of V, Cu and Pb. The association of Sr and Ba is well known, which is reflected in relatively strong positive correlation coefficient ($r^2 = 0.68$). Thus, it is observed that Sr plays an important role in the enrichment of heavy metals, particularly Cu, Pb and V, in the study area. The geochemical association of Cr–Cu–Zn in the soil shows that these metals are deposited from anthropogenic sources, since there is no known geogenic source which can contribute to this type of association in the study area.

4. Conclusion 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 number of industries like cotton and wool textile mills, tanning and leather manufacturing industries, large fertilizer factories and several arms factories. 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 samples were found to exceed international threshold values. 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.

Acknowledgements

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