

Spatial distribution and the extent of heavy metal and hexavalent chromium pollution in agricultural soils from Jajmau, India

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Abstract This study quantifies the extent of heavy metal pollution in the agricultural soils (57 samples) from Jajmau, Kanpur, India. Heavy metal concentrations (mg/kg) in agricultural soils, frequently irrigated with treated tannery effluent, are significantly higher: Cr 118–3142, Cr(VI): 2–87, Mn 341–821, Ni 24–47, Zn 78–427, V 73–110, Cd 2–13, Pb 15–69. Sludge embedded soil, mainly comprising of tannery sludge disposed in open ground, contains ~40,500 mg/kg Cr [and 1,400 mg/kg Cr(VI)], Zn (884), Cu (300), Cd (192), Pb (180) and Ni (68 mg/kg). Results show ~65 % of the total chromium is easily leachable from these soils under acidic conditions. Pollution assessment suggests that agricultural soils are highly polluted with Cr, Cu, Cd, Pb and Zn. Spatial distribution maps of heavy metals identifies specific areas that are heavily contaminated with Cr, Cu, Zn, Cd, Pb and Cr(VI), mostly along the length of the major canal constructed to distribute the treated tannery effluents. Principal component (PC) and cluster analysis suggest two principal components (or two clusters) that explain 83 % of data variability. PC1 positively correlates with Cr, Cu, Zn, Cr(VI), Pb, Cd and OM, which is attributed to anthropogenic activities, i.e. irrigation by treated tanneries effluent,

open dumping of Cr sludge. PC2 strongly correlates with Fe, Ni, Co, V and Mn, which is attributed to weathering of parental materials. This study clearly reveals significant metal pollution including Cr(VI) pollution in Jajmau, which can lead to widespread soil and groundwater contamination.

Keywords Hexavalent Chromium · Heavy metals · Soil pollution · Spatial distribution · Tannery effluent

Introduction

Several decades of negligence and anthropogenic indulgence with regards to waste disposal, particularly discharge of industrial and municipal-waste effluents containing heavy metal pollutants, have resulted in soil pollution in Kanpur city, India and elsewhere (Singh et al. 2004; Mapanda et al. 2005; Tariq et al. 2005; Sharma et al. 2006; Tiwari et al. 2011). Soil pollution becomes a threat to the environment and ultimately to humans. Leather tanning industries are known to have contributed to toxic heavy metal, predominantly chromium, pollution in soil. The tanning process widely uses chromium salts, particularly $\text{Cr}_2(\text{SO}_4)_3$, and during this process leather absorbs ~60–80 % of Cr, whereas the rest are usually discarded as waste effluent and released to the environment (Van-Greenstein et al. 2002; Leghouchi et al. 2009). Chromium exists in two stable oxidation states [Cr(III) and Cr(VI)], of which Cr(VI) in the form of mainly chromates and dichromates oxyanionic species is more soluble, mobile, and more bioavailable under alkaline to slightly acidic condition resulting in higher toxicity.

The Jajmau region in Kanpur, India is home to ~400 tanning factories (CPCB 2006; Sinha et al. 2006, 2008;

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Rawat et al. 2009; Gowd et al. 2010). Most of these use outdated chrome tanning technologies and do not have in-house chrome recovering plants (Apte et al. 2005). Since December 1994, a 36,000 m³/day (36 MLD) common effluent treatment plant (CETP) using upflow anaerobic sludge blanket (UASB) process has been operational in Jajmau, Kanpur, with an objective of removing excess Cr from the effluent before distributing the treated water for irrigation through a network of canals and eventually disposing into the Ganga river. Tare et al. (2003) reported very high Cr concentrations of $\sim 61.2 \pm 15.2$ mg/L (or ppm) and 7.9 ± 3.2 ppm in the tannery effluent reaching the UASB plant and treated water going out of the plants, respectively. The Cr content of treated water is higher than the permissible limit of 2 ppm recommended by the Indian standard for wastewater discharge (IS 10500 1992). The treated effluent (1:3 ratio of tannery to sewage water) still contains high concentrations of heavy metals, e.g. Fe, Cr, Zn, Mn, Cu and Ni, and has been extensively used to irrigate $\sim 2,100$ acres of agricultural land for more than two decades (Sinha et al. 2006, 2008).

Several studies have addressed various aspects of contamination of agricultural soil (Singh et al. 2004; Rawat et al. 2009; Gowd et al. 2010; Singh et al. 2006), surface and ground water (Singh et al. 2009), crops and edible vegetables (Sinha et al. 2006; Gupta and Sinha 2006), and genotoxic and mutagenic potential of agricultural soil (Alam et al. 2009) from Jajmau. Indiscriminate dumping of hazardous waste has led to heavy contamination of local soil in Jajmau and Unnao industrial areas (Gowd et al. 2010). A study on heavy metal contamination in industrial waste, roadside soil, and road dust samples, from Jajmau and Panki industrial areas reported high concentrations of Ni, Pb, and Cr (Rawat et al. 2009). Another study (Singh et al. 2009) on Cr mapping and groundwater contamination in an area close to Jajmau revealed a narrow zone ($26^{\circ}27.15'N$ and $80^{\circ}16.218'E$) having high Cr levels of ~ 16.3 ppm, located at ~ 35 – 40 m below surface. The study concluded that migration of this Cr plume is likely to magnify and further contaminate the local groundwater reservoirs. Gupta and Sinha (2006) studied Cr bioavailability and uptake by plants grown on Jajmau soil, and reported high daily intake of Cr by the local population and emphasized the need for Cr remediation measures, which were later supported by similar findings (Sinha et al. 2006, 2008).

Most of the studies on the Jajmau area are based on soil samples collected around 2005 or prior, and reveal wide range of variations in heavy metal concentrations. Further, Cr(VI) concentration in soil has rarely been reported, which is the major reason to initiate this study in Jajmau. The primary objectives of this study were to (1) assess extent of heavy metal [Fe, Ni, Mn, Co, Cr, Cu, V, Zn, Cd,

Pb and Cr(VI)] pollution in agricultural soil and treated effluent samples (2) assess spatial distribution of heavy metals and identify possible sources of contamination. In addition, Cr leaching potential, an important factor in spreading contamination to the local environment, was evaluated.

Materials and methods

Study area and sampling

Our study area, Jajmau ($26.467^{\circ}N$ and $80.35^{\circ}E$), is located in one of the industrial areas of Kanpur, Uttar Pradesh, India (Fig. 1). It is one of the tanneries hub in India as well as world, comprises of many large and small-scale tanneries. Jajmau, comprising of ~ 20 villages, is located in the western banks of Ganga river. It has a population of $\sim 650,000$, deriving their livelihood mainly from agriculture and animal husbandry. The climate is subtropical humid with an average annual rainfall of 82 cm (Indian Meteorological Department).

In total, 57 soil samples were collected in 2012 from different sites like agricultural land near village settlements and sludge disposal site, apart from treated water samples from the water treatment plant in Jajmau locality (Fig. 1). The sampling area was divided into four zones. Zone 1 (Z1) is a sludge dump site, close to the Central Effluent Treatment Plant (CEPT) and the Central Leather Research Institute (CLRI), where tannery sludge is disposed in open ground. Four samples (JS 54–57) were collected from the Z1 site. The agricultural soils samples were collected from three village settlements: 26 samples (JS 23–47 and JS 49) collected from zone 2 (Z2) that belongs to Pevondi and Sekhpur village; 16 samples (JS 1–6, JS 11–14, JS 21–22 and JS 50–53) collected from zone 3 (Z3) that is close to the Kanpur airport; and finally 11 samples (JS 7–10, JS 15–20 and JS 48) collected from zone 4 (Z4) toward the southern part of the study area that includes Motipur village. All samples were collected from a depth of 15 cm below surface as studies have shown that treated tannery effluent contaminants mostly pollute the top soil whereas this effect is negligible with increasing depth (García-Díaz and Prats-Montalbán 2005; Singh et al. 2006). Soil samples were collected in labeled polyethylene bags for transport to the laboratory and stored in freezer. Figure 1 also shows the major canal that carries the UASB plant treated tanneries effluent; there exists several functional outlets along the stretch of the major canal that are used to divert water for irrigation. Treated tanneries effluent samples were collected from two locations: WW1 from the UASB outlet, and WW2 from the leaking canal in Sekhpur village, 2 km far from the WW1 site.

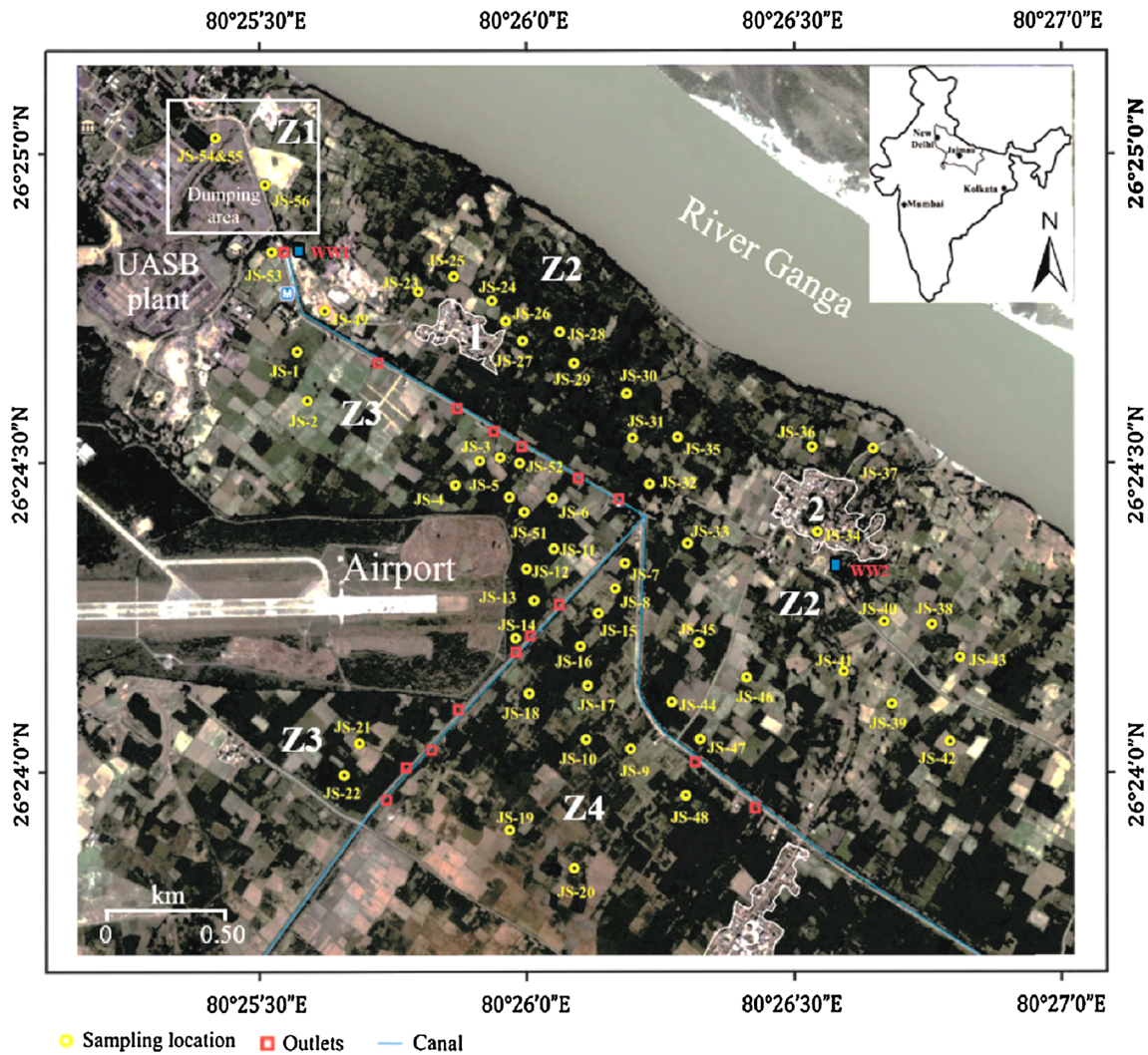


Fig. 1 Map of Jajmau, Kanpur showing the soil sampling locations. Sampling area is divided into four zones, which are discussed in detail in the text. Also shown are the upflow anaerobic sludge blanket

treatment plant (UASB) and the main canal used to route treated tannery effluent and distributed for irrigation by a local network of sub canals (shown by squares) along the length of the main canal

Physicochemical and mineralogical analysis

The soil pH and electrical conductivity (EC) were determined on a 1:5 ratio of sample to MilliQ water, using Eutech pHScan2 pH and Eutech TDSscan4 meter, respectively. The organic matter (OM) content was estimated following the loss on ignition method, in which soil was heated at 500 °C for 2 h. After removal of organic matter, XRD analyses of bulk soil and clay-sized fractions were performed to determine the bulk and clay mineralogy. All XRD analyses were conducted at Indian Institute of Technology Kanpur (IITK) using a Seifert (ISO-Debyflex 2002) Diffractometer run at 40 kV and 25 mA, Cu-K α source, 2 θ scan of 6°–70° for bulk mineralogy and 6°–30° for clay mineralogy, scan speed of 1° 2 θ /min and step size of 0.05°. Grain size distribution was determined from

relative abundances of sand (>64 μ m), silt (2–64 μ m) and clay-sized (<2 μ m) fractions, following the wet sieving method, to obtain soil textural class (Soil Survey Staff 2011).

Bulk and leachable heavy metal analysis

All soil samples were oven-dried at 35 °C for 2 days, and stones (>2 mm) and coarse plant roots/residues removed. About 5.0 g homogenized soil powder (<70 μ m) was heated at 500 °C for 2 h to remove organics, mixed with boric acid as binder and pressed at 12 ton to obtain 30 mm diameter pressed-powder pellets that were analyzed with Rigaku ZSX primus-II wave-length dispersive X-ray fluorescence (WD-XRF) spectrometer at IITK, having 4 KW Rh target and operated at 60 kV and 50 mA. Repeated

measurements of reference soil standards (TILL-3, STSD-2, and LKSD-4) indicate an accuracy of $\leq 10\%$ for all analyzed metals.

To determine the leachable fraction of Cr in soils, United States Environmental Protection Agency (USEPA) 3050B acid digestion method (USEPA 1996a) was followed. For this, ~ 1 g of selected agricultural soils (28 samples) from Z2 to Z4 zones were treated with concentrated HNO_3 , H_2O_2 and HCl in round bottom flasks and refluxed for 5 h at 95°C , filtered and analyzed by atomic absorption spectroscopy (AAS). A procedural blank was also prepared with each batch of soil samples. Subsequently, metal concentrations were analyzed using both inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP 6000 series) and flame atomic absorption spectroscopy (FAAS, AAnalyst 400, Perkin Elmer) at IITK. Note that the concentration of Cd and Pb in the leachate was also analyzed by AAS. The standard solutions used for calibration of analysis were prepared by successive dilution of standard stock solutions (NIST traceable multielement standard from Sigma-Aldrich and Merck, Germany) with MilliQ water. All chemicals used in this study were of analytical grade. Three Canadian Certified Reference Materials, namely geochemical soil (TILL-3), stream sediment (STSD-2) and lake sediment (LKSD-4) were used to estimate analytical accuracy. Good agreement was achieved between the measured and certified values (for the same method) of the standard reference materials, with recoveries of $\geq 95\%$. The total leachable amount of Cr(VI) in soil and water was determined following USEPA 3060A alkaline digestion method (USEPA 1996b) and subsequently measured colorimetrically by the USEPA 7196A diphenylcarbazide method (USEPA 1992). Check samples, prepared by adding 0.1 and 5 mg of Cr(VI) to uncontaminated soil and MQ water, and a reagent blank analyzed, produced desired results.

Pollution assessment

The extent of heavy metal pollution in the study area is assessed by evaluating enrichment factor (EF), contamination factor (CF), geoaccumulation index (I_{geo}), and pollution load index (PLI), and determining the pollution class using the respective classifications based on a range of parameter values. These are outlined below.

- (a) EF is defined as follows:

$$\text{EF} = \left(\frac{\text{M}}{\text{Fe}} \right)_{\text{soil}} / \left(\frac{\text{M}}{\text{Fe}} \right)_{\text{background}} \quad (1)$$

where $(\text{M}/\text{Fe})_{\text{soil}}$ corresponds to ratio of heavy metal of interest to the Fe content in the soil sample and $(\text{M}/\text{Fe})_{\text{background}}$ is the respective ratio in the

reference/background soil. Here, background soil is assumed to have similar composition as the average bulk crust (Rudnick and Gao 2003); Sutherland (2000) proposed five categories of pollution: $\text{EF} < 2$ for minimal, $\text{EF} 2\text{--}5$ for moderate, $\text{EF} 5\text{--}20$ for significant pollution, $\text{EF} 20\text{--}40$ for very, and $\text{EF} > 40$ for extreme pollution.

- (b) CF, a measure of soil contamination for individual metals, was defined by Hakanson (1980) as:

$$\text{CF} = \frac{C_0^i}{C_n^i} \quad (2)$$

where C_0^i is the mean concentration of metal i from at least five sampling sites, and C_n^i is the preindustrial reference concentration of metal i in soil. Following (Loska et al. 2004), C_n^i is assumed to represent average bulk crust (Rudnick and Gao 2003); Hakanson (1980) proposed four categories of contamination: $\text{CF} < 1$ for low, $1 \leq \text{CF} < 3$ for moderate, $3 \leq \text{CF} < 6$ for considerable, and $\text{CF} \geq 6$ for very high contamination.

- (c) I_{geo} , compares the heavy metal concentrations in the present soil sample with that of the preindustrial concentration. I_{geo} was estimated following Loska et al. (2004) that used slightly different assumptions than the original definition proposed by (Müller 1969):

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (3)$$

where C_n is the bulk concentration of an element in soil and B_n the average concentration of that element in the bulk continental crust (Rudnick and Gao 2003). The constant 1.5 is the correction factor accounting for fluctuations due to both natural and anthropogenic influences. I_{geo} values define six classes of soil heavy metal contamination (Müller 1981).

- (d) PLI, as defined by Tomlinson et al. (1980), was used to compare the overall pollution status amongst different sites of study area. The PLI for a site was estimated using the individual CF values of each metal at a specific site as follows:

$$\text{PLI} = \sqrt[n]{\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n} \quad (4)$$

where n is the number of contamination factors for a specific site. A value of $\text{PLI} \leq 1$ indicates no pollution, whereas $\text{PLI} > 1$ suggests high metal pollution.

Spatial distribution and multivariate statistical analysis

Spatial distribution maps showing heavy metal enrichment in the study area were prepared using the inverse distance

weighted (IDW) interpolation tool in ArcGIS 9.3. Principal component analysis (PCA) of the data (12×53 matrix) obtained in this study was performed to extract components to maximize the proportion of variability explained by each component subjected to the orthogonality constraint. Each principal component obtained from PCA method is a linear combination of original variables. Those components with eigen value greater than one were extracted as the primary factors. An orthogonal factor rotation was performed using the Kaiser Varimax rotation to remove loadings in the mid range 0.3–0.5 and to maximize the loadings for each variable for only one factor. This information was used to interpret sources of pollution for Jajmau soils. Hierarchical cluster analysis (CA) was performed on the same data set using Euclidean distance and nearest neighbor linkage method to generate dendrogram of different clusters having highest degree of similarity. All the statistical calculations were performed using SPSS Statistics 17.0.

Results and discussion

Physicochemical and mineralogical analysis

Various soil parameters like pH, EC, OM, grain size, and mineralogy play an important role in sorption–desorption of heavy metals in soil, thus controlling mobility and leaching of metals into groundwater (McClean et al. 1992; Robinson et al. 2005). The mean pH of Jajmau agricultural soil (Z2–Z4) varies in the range 6.8–8.2 (mildly alkaline). The reason behind this alkalinity is the use of basic salts in the tanning process leading to higher soil pH through the use of treated tanneries effluent for irrigation. The average OM content of Z2–Z4 varies in the range 2.8–3.8 %. Very high OM content (23.1 %) for Z1 soil may be attributed to the organic waste from tanneries used for land fill and hide dumping. A study on chromium leaching in soil columns simulated under laboratory conditions demonstrated that chromium transport is strongly affected by the OM content due to metal sorption onto the OM (Andjelkovic et al. 2012). It also showed humic substances in soil OM facilitated reduction of Cr(VI) in soil to Cr(III) under acidic leaching conditions. Also, Choppala et al. (2013) demonstrated that soils having high OC content with easily oxidizable functional groups facilitate reduction of Cr(VI) to immobile Cr(III), and Cr(VI) reduction decreases with increasing soil pH. Although OM or OC content is considered important for soil fertility (Reeves 1997), but presence of high concentration of toxic heavy metals in agricultural soil may reduce its fertility (Alvarez-Bernal et al. 2006). The EC values for agricultural soil (Z2–Z4) are in the range of 0.5–4.2 mS/cm which is due to presence of salts in soil originating from tanneries effluent.

One critical aspect of soil pollution and remediation is to understand the soil mineralogy and texture (grain size distribution) that affect porosity and permeability. Particle size plays a vital role in the retention of metals (Ljung et al. 2006); generally finer (<50 μm) particles have greater binding capacity. The finer particles can adversely affect the environment as these are easily transported by wind and water. Grain size analysis of several agricultural soil samples (sand 36–43 %, silt 38–44 %, clay 13–22 %) suggests these soils to be “loam” according to the soil textural triangle classification given by the United States Department of Agriculture (USDA). Lower clay and higher silt and sand contents in agricultural soil make them vulnerable to leaching and subsequent contamination of groundwater.

Mineralogy is important because soil mineralogy is dominated by aluminosilicate minerals, i.e. clay minerals such as kaolinite and smectite. Clay minerals typically have net negative charged surfaces, which serve as potential sites for cation adsorption or nutrient storage, hence play a vital role in soil fertility. Adsorption of metal onto the clay surface decreases in the order montmorillonite \rightarrow beidellite \rightarrow smectite \rightarrow illite (Helios-Rybacka and Kyziol 1991). X-ray diffraction data of Jajmau bulk soils reveal the presence of quartz, mica/illite, feldspar and calcite. XRD of clay-sized fractions show distinct peaks for illite, halloysite, and very little smectite, whereas kaolinite is minor or absent. Presence of moderately expansive clays in the soil matrix implies medium level of metal retention capacity of soils, and high leaching potential.

Bulk and leachable heavy metal analysis

The results of heavy metal analysis in bulk agricultural soils from Jajmau are given in Table 1. It is evident in Fig. 2 box plot that Z2–Z4 agricultural soils display a large variation in metal concentrations; in particular Cr, Cr(VI), Zn, Cu, Cd, and Pb contents vary considerably (Table 1). In contrast, Z1 sludge embedded soils are characterized with low Fe (17,500 mg/kg), Mn (380 mg/kg), Pb (183 mg/kg) and V (56 mg/kg) contents, extremely high Cr, Cr(VI) and Cd of 40,500 mg/kg, 1,400 mg/kg and 190 mg/kg respectively, and high Cu (300 mg/kg), Ni (70 mg/kg) and Zn (884 mg/kg) (Table 1). A comparison of Jajmau soil data with the maximum permissible concentrations of toxic elements in Chinese agricultural soils indicate that metal contents in Z2–Z4 agricultural soils largely exceed permissible limits for Cr, Zn, Cu and Cd. Our results are inconsistent with the study by Singh et al. (2006) that reported maximum concentrations of Fe (40,000 mg/kg), Cr (1,382), Zn (574), Mn (692), Cu (185), and Ni (73) in Jajmau agricultural soils. XRF analyses of soils from Jajmau and Unnao industrial areas, Uttar

Table 1 Statistics of heavy metal concentrations in the four zones of Jajmau soils ($n = 57$) and treated tanneries effluent analyzed in this study

	Fe (mg/kg)	Ni	Mn	Co	Cr	Cu	V	Zn	Cd	Pb	Cr(VI)
Z1 (N = 4)											
Mean \pm SD	17,461 \pm 8,810	68 \pm 19	380 \pm 232	7 \pm 3	40,529 \pm 14,100	304 \pm 37	56 \pm 25	884 \pm 222	192 \pm 12	183 \pm 28	1,385 \pm 528
Range	11,169–30,144	55–94	39–525	5–11	19,767–50,226	252–341	26–85	616–1,135	180–210	141–198	597–1,684
Skewness	1.6	1.6	-1.8	0.0	-1.8	-1.1	-0.1	-0.2	-0.5	-2.0	-2.0
Kurtosis	2.2	2.3	3.3	-1.2	3.2	2.1	0.4	-0.9	1.7	3.9	3.8
Z2 (N = 26)											
Mean \pm SD	34,216 \pm 4,459	36 \pm 7	567 \pm 86	13 \pm 2	847 \pm 727	56 \pm 28	91 \pm 9	173 \pm 92	5 \pm 3	35 \pm 13	18 \pm 19
Range	25,759–45,489	24–47	364–776	10–18	118–2,603	26–125	73–110	78–419	2–11	15–69	1–65
Skewness	1.0	0.5	0.2	1.2	1.0	1.3	0.6	1.2	1.3	1.2	1.3
Kurtosis	1.1	-1.0	1.0	0.7	-0.1	0.7	0.5	0.7	1.0	2.3	1.0
Z3 (N = 16)											
Mean \pm SD	30,557 \pm 2,099	34 \pm 5	439 \pm 49	12 \pm 1	1,118 \pm 706	77 \pm 29	88 \pm 5	259 \pm 91	5 \pm 2	43 \pm 13	30 \pm 27
Range	25,178–33,235	24–39	380–550	9–13	387–3,142	38–124	76–94	116–400	3–13	27–64	2–87
Skewness	-1.1	-0.4	0.9	-0.7	1.6	0.3	-1.2	0.2	3.2	0.2	0.9
Kurtosis	1.6	-0.5	0.3	0.3	3.6	-1.2	1.6	-1.3	11.8	-1.3	-0.1
Z4 (N = 11)											
Mean \pm SD	30,419 \pm 2,711	32 \pm 4	478 \pm 144	11 \pm 1	692 \pm 362	59 \pm 19	89 \pm 6	207 \pm 93	4 \pm 2	37 \pm 10	21 \pm 23
Range	26,318–34,655	24–39	341–821	10–13	238–1,399	39–103	80–96	105–427	3–8	25–57	2–82
Skewness	-0.1	0.2	1.6	0.2	0.7	1.3	-0.5	1.7	1.1	1.0	2.2
Kurtosis	-1.0	1.9	2.4	-1.5	-0.3	2.2	-1.1	2.6	0.4	0.7	5.5
Indian limit ^a	-	75–150	-	-	-	135–270	-	300–600	3–6	250–500	-
Chinese limit ^b	-	50	-	-	200	100	-	250	0.3	300	-
Published data ^c	1,000–180,000	6–72	165–692	-	18–6,228	12–185	1–30	43–574	3–15	9–142	141
Treated tanneries effluent											
WW1	1.3	0.2	0.2	ND	3.4	0.3	ND	0.2	ND	0.3	0.20
WW2	5.8	0.2	0.3	ND	3.7	0.5	ND	0.3	ND	0.5	0.18

For comparison data on Indian, Chinese agricultural soil standards along with already reported data on Jajmau soils are presented

Soil metal concentrations analyzed by WD-XRF except for Cd, Pb analyzed by AAS; Treated tanneries effluent analyzed by ICP-OES, and Cr(VI) by diphenylcarbazide method

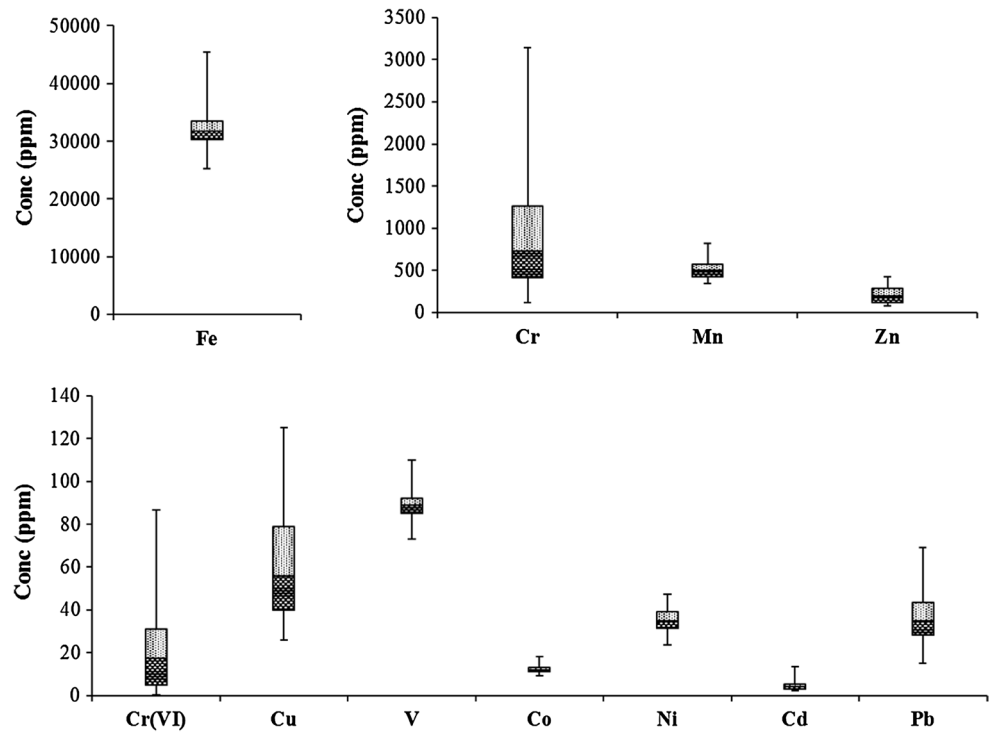
ND not detected

^a Awasthi (2000)

^b CEPA (1995)

^c Singh et al. (2004), (2006), Gupta et al. (2007), Gowd et al. (2010), Alam et al. (2009)

Fig. 2 Box plot of heavy metal concentrations in Z2-Z4 agricultural soil zones in Jajmau. The error bars show the minimum and maximum concentration of heavy metals, boxes show the range from 25th to 75th percentile. Metal concentrations in the sludge embedded soils (Z1 zone) are explained in the text



Pradesh by Gowd et al. (2010) showed high metal concentrations (Cr = $2,652 \pm 2,006$ (1σ), Cu = 43 ± 27 , Zn = 160 ± 128 , V = 54 ± 62 , and Pb = 38 ± 13), which are comparable to our Z2–Z4 agricultural soils. Gowd et al. (2010) concluded that significant soil contamination observed in areas nearby small-scale industries (tanneries, refractories, fertilizers, and paints) point to indiscriminate dumping of hazardous waste and open discharge of effluents by these local industries for many years. Rawat et al. (2009) reported Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni concentrations in industrial solid waste, soil, and road dust collected within 10–35 m radius from small-scale industries from Jajmau area. Their reported metal concentrations in soil (e.g. Cr = 393, Cu = 13, Zn = 77, Cd = 1.7 and Pb = 8.2 mg/kg) are 3–6 times lower than the respective metal averages in our agricultural soils. Sinha et al. (2006) also reported high levels of total Cr (up to 311 ± 72 mg/kg) in Jajmau soils collected in 2002–03, of which ~30–60 % was estimated to be bioavailable.

This study shows very high concentration of Cr(VI) in the range 1–87 mg/kg (av. 22 ± 22 mg/kg) in Jajmau agricultural soil, and much higher average of 1,385 mg/kg in the Z1 sludge embedded soil. A study at Rooma Usar site in Jajmau, particularly used for dumping Cr-rich sludge from the UASB plant, reported ~50,000 mg/kg Cr(III), ~2,500 mg/kg Cr(VI), and 600 mg/kg Mn in the fresh sludge (Verma 2003), similar to our Z1 site. To understand why Cr(VI) concentration in the surface runoff and aged sludge samples at the Rooma Usar site was very high,

despite having comparatively little Cr(VI) in the fresh sludge, Apte et al. (2005) performed thermodynamic equilibrium calculations for Cr oxidation under various environmental conditions. Their results showed that interaction of aqueous Cr(III) species with MnO₂ solid surface (dominant at pH 7 and aerobic condition) facilitated conversion of Cr(III) to Cr(VI), independent of total Mn concentration. Apte et al. (2005) also suggested that oxidation of Cr₂O₃–CrO₃ under natural aerobic conditions is thermodynamically feasible. These conclusions were supported by experimental data on conversion of Cr(III) to Cr(VI) under varied conditions (Apte et al. 2006) that showed up to 17 % oxidation occurring in sludge under aerobic conditions within a month. Heating of black sludge samples (similar to our Z1 samples) under aerobic conditions by Apte et al. (2006), at 100 °C for 24 h and 550 °C for 30 min, resulted in a 130 % increase in Cr(VI) from 2,500 to 5,800 mg/kg. These results suggest that even though the sludge from the UASB plants typically contain Cr(III) and no Cr(VI), subsequent conversion of Cr(III) to Cr(VI) is feasible under aerobic conditions in the presence of MnO₂. Therefore, the Z1 site has potential to become a source of Cr(VI) pollution in the study area. Higher concentrations of Cr(VI) in agricultural soil and dump site samples are potentially harmful to both the local surface and groundwater. Singh et al. (2009) reported 0.042–4.2 mg/kg Cr(VI) and 15–60 mg/kg total Cr in the aquifer sediments, and ≤16 ppm Cr(VI) in local groundwater, at a site in Nauriyakhera, Kanpur, India. They

identified a narrow zone (26°27.15'N, 80°16.218'E) polluted with Cr at a depth of 35–40 m below ground level and attributed it to indiscriminate dumping of Cr sludge by industries. In addition, the extent to which a certain metal is leachable from soil affects its bioavailability and potential for spreading contamination to both surface and ground water systems. The extent of leachable Cr estimated following the USEPA 3050B acid digestion method suggests that ~65 % of Cr can be readily leached from the agricultural soils under strong acidic conditions, which poses danger to the local ecosystem.

Further, previously reported Fe, Cr, Zn and Mn concentrations of 3.9, 3.2, 0.39, and 0.12 ppm, respectively in the treated effluent of Jajmau UASB plant by Sinha et al. (2006), (2008) are similar to the treated tanneries effluent composition measured in this study (Table 1). The levels of Cr in these tannery effluents are slightly higher than the recommended 2 ppm by the Indian standard for wastewater discharge (IS 10500 1992), but much higher than the Food and Agriculture Organization (FAO) recommended limit (0.1 ppm) for irrigation water (Ayers and Westcot 1985). The measured Cr(VI) in treated tanneries effluent is ~0.2 ppm (Table 1), whereas the recommended permissible limit in drinking water and wastewater discharge for irrigation is 0.05 mg/L (WHO) and 2 ppm (Indian standard for wastewater discharge, IS 10500 (1992), respectively.

Pollution assessment

The results of pollution assessment (EF, CF, I_{geo} , and PLI indices) are given in Fig. 3. EF estimates (Fig. 3a) for Z2–Z4 agricultural soils show extremely high enrichment for Cd (95 ± 49), significant enrichment for Cr (11 ± 8), Zn (5 ± 2), Pb (6 ± 2), and moderate for Cu (4 ± 2). The remaining heavy metals (Ni, Mn, Co, and V) from all zones show minimal enrichment. In contrast, Z1 soils are characterized with extremely high enrichment factor (EF > 40) for Cr ($1,135 \pm 640$), Cd ($8,473 \pm 3,109$), Pb (60 ± 28) and Zn (41 ± 14), and very high enrichment for Cu (EF = 38 ± 12) (not shown in Fig. 3a).

The estimated I_{geo} for Z1 soils also suggests extreme contamination for Cr and Cd, and moderate to heavy contamination for Cu, Pb and Zn as shown in Fig. 3b. Further, I_{geo} values for Z2–Z4 agricultural soil samples show extreme contamination for Cd, moderate to heavy contamination for Cr, moderate contamination for Pb, and negligible contamination for Cu and Zn. Note that although both EF and I_{geo} values suggest moderate to heavy contamination for Pb, the Pb contents are below the permissible limits suggested by both the Indian and Chinese soil standards (Table 1). Further, both EF and I_{geo} results also suggest that agricultural soil is practically uncontaminated with respect to Ni, Mn, Co, and V. Results for PLI

calculated for Z1–Z4 soils, considering all 10 metals analyzed in this study (Fig. 3c), indicate significant metal pollution load for the Jajmau site.

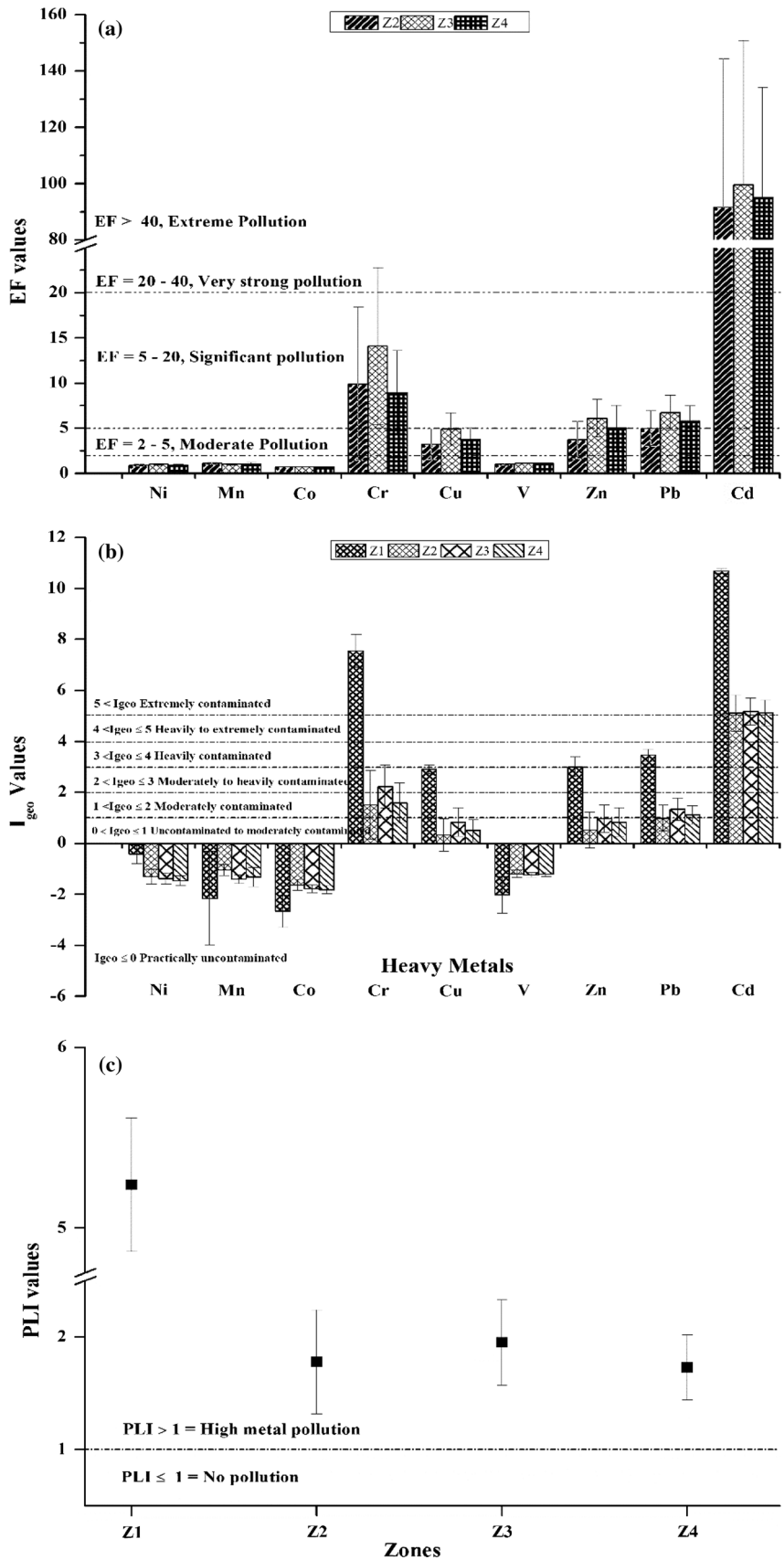
Spatial distribution of heavy metals in the soils

Spatial distribution maps of Cr, Cu, Zn, Cd, Pb, and Cr(VI) in Jajmau locality are shown in Fig. 4, in which polluted areas are identified on the basis of enrichment factors (EF) except for Cr(VI). Note that pollution assessment also revealed Jajmau soils are moderate to heavily contaminated with these metals (Fig. 3a, b). As stated earlier, Z1 is a sludge dump site, close to the UASB plant and the Central Leather Research Institute, where tannery sludge is disposed in open ground (Fig. 1). It is evident from Fig. 4 that Z1 is a 'hot spot' that is extremely polluted with respect to Cr (EF = 250–1,730) and Cd (EF > 4,000), highly polluted with Cu (EF = 22–44), Pb (EF = 22–82) and Zn (EF = 27–40). Figure 3 also shows that zones Z2–Z4 are extremely contaminated with Cd (EF > 40), which also correlates positively with Cr contaminated areas. Further, ≥ 50 % of area belonging to Z3 and Z4 sites is significantly polluted with Cr and Pb, whereas the Z2 site shows moderate to significant pollution. The Z3 site is significantly polluted with Cu and Zn compared to the Z2 and Z4 sites that show moderate pollution. The Z1 soils are characterized with extremely high Cr(VI) content in the range 597–1,684 mg/kg. Further, ~50 % area of Z2–Z4 zones has Cr(VI) contents in the range 4–43 mg/kg, with values of ~80 mg/kg at few sampling sites. It is concluded that Jajmau agricultural soils comprise of very high concentration of leachable Cr(VI), which has the potential to contaminate surface and groundwater. Further, the leachable Cr will also be available for plant uptake. It is also evident that majority of the polluted areas are aligned along the length of the major canal which distributes treated tanneries effluent also used to irrigate these agricultural lands. Spatial distribution patterns and associated high-value areas with respect to Cr, Cd, Cu, and Zn suggest that topsoil of Jajmau is affected by anthropogenic activity.

Principal component analysis and source identification

PCA was performed to identify the sources of heavy metals in the top soil. The results of PCA analysis of 12×53 matrix comprising of twelve variables are presented in Table 2 and Fig. 5. Two principal components, PC1 and PC2 having eigen values >1, together explaining 83 % of variance in the data set were extracted. The first component PC1 explains 52 % of variance and has high positive factor loadings for Cr, Cu, Zn, Cr(VI), Pb, Cd and OM (Table 2). The second component PC2 explains 31 % of variance and has high positive loadings for Fe, Ni, Mn, Co, and V.

Fig. 3 a Metal enrichment factor (EF) estimates in the Z2–Z4 agricultural soil zones. EF values for Z1 are several orders magnitude higher which are discussed in the text. **b** I_{geo} estimates for Z1–Z4 agricultural soil zones. **c** Pollution load index (PLI) estimated for the entire study area. Also shown for comparison are the respective classifications based on specific range of assessment parameters



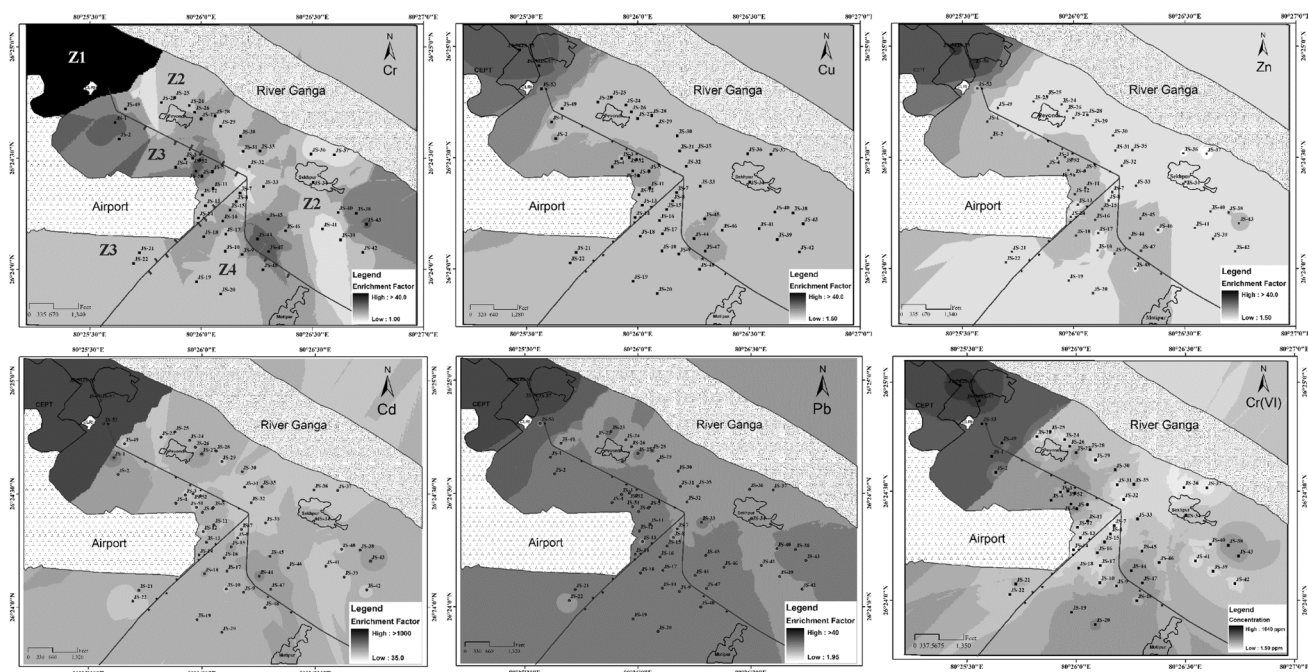


Fig. 4 Spatial distribution maps of Cr, Cu, Zn, Cd, Pb, and Cr(VI) in Jajmau top soil. Polluted areas are identified on the basis of Enrichment Factors (EF) except for Cr(VI), which is based on the

measured concentrations (mg/kg) as no background value is available for natural/uncontaminated soil

Table 2 Factor loadings for rotated principal components, eigen values obtained from principal component analysis

Element	Component	
	PC1	PC2
Fe	-0.137	0.969
Ni	0.428	0.828
Mn	-0.537	0.567
Co	-0.182	0.933
Cr	0.935	-0.061
Cu	0.949	-0.008
V	-0.051	0.927
Zn	0.943	-0.102
Cr(VI)	0.805	-0.040
Cd	0.936	-0.060
Pb	0.949	-0.011
OM	0.800	-0.084
Eigen values	6.26	3.70
% Total variance	52	31
Cumulative %	52	83

Further, Ni is affected more by PC1, whereas Mn is affected equally by both the components (Fig. 5). We assign PC1 to the Cr-embedded sludge in Z1 site along with contributions from the UASB treated tannery effluent utilized for irrigation of Jajmau soils. Leaching of Z1 soils that are rich in Cr, Cu, Zn, Pb, Cd, and OM content

(Tables 1) is likely to spread these contaminants to the nearby agricultural fields. This may explain extreme and significant to moderate enrichment in Cr, Cd, Cu, Pb and Zn (Fig. 3) in the agricultural soils. During field visits, we observed that tannery sludge and waste products were being processed openly in the agricultural fields, dried and often used as fertilizer (personal communication with the on-site contractor). This may also be attributed to the PC1 component. Figure 4 shows that majority of the polluted areas are aligned along the length of the major canal, which suggest some contributions from UASB treated tanneries effluent also used to irrigate these agricultural lands. A report by the Central Pollution Control Board (CPCB), India highlighted that the poorly maintained UASB plant operates at <70 % efficiency and frequently shut down due to regular power cuts (CPCB 2006). Our visit to the treatment facility also revealed that due to various logistic issues, the plant always operates at significant under load conditions. Therefore, significantly high metal contents in the treated tanneries effluent at times cannot be ruled out, which if used for irrigation will lead to contamination. Further, PC2 shows positive factor loadings in Fe, Ni, Co, and V, however, the estimated EF values for these metals in the agricultural soils (≤ 1 , Fig. 3a) suggest no to minimal pollution. Spatial distribution maps for these elements showed no significant enrichment in these metals in the study area (not shown in figure). Therefore, PC2 is attributed to weathering of natural soils.

The result of hierarchical CA comprising of nine heavy metals plus OM in 53 agricultural soil samples is illustrated using a dendrogram (Fig. 6). All the parameters were merged to two distinct clusters in the dendrogram with a rescaled distance of 25. Cluster 1 comprises of Fe, Co, Ni, V and Mn, which also show no significant enrichment in spatial distribution maps of the study area. Cluster 1 may be associated with weathering of parental materials. Cluster 2 comprises of Cr, Cu, Zn, Cr(VI), Cd, Pb and OM, which is attributed to anthropogenic activities like utilization of treated tanneries effluent for irrigation, sludge dumping/processing in the agricultural fields. The PCA results agree with CA analysis confirming the two principal sources for heavy metal distribution in the study area.

Conclusions

This study evaluates both the extent and sources of heavy metal pollution including Cr(VI) in the jajmau locality, India, which is a major hub of leather tanning industries and several small-scale industries that have been operating for several decades. The effluent from these industries, mainly tanneries, contains significant levels of heavy metals, more often higher than the prescribed standards, which has been inferred by others to be the major source of soil pollution. Our results suggest very high concentrations of heavy metals (e.g., ~40,500 mg/kg Cr, ~900 mg/kg Zn, ~300 mg/kg Cu, ~200 mg/kg Cd) in the sludge embedded soils located in Z1 area, where tannery sludge is disposed in open ground. Heavy metal concentrations in agricultural soils irrigated with UASB plant treated tannery effluent, particularly Cr (118–3,142 mg/kg), Cu (26–125 mg/kg), Zn (78–427 mg/kg), Cd (2–13 mg/kg) contents are also significantly higher. The concentration of Cr(VI) varies in the range 1–87 mg/kg in the agricultural soils and even higher in the Z1 dump site (1,385 ± 528 mg/kg). Results also suggest that on average ~65 % of Cr is leachable from these samples. The spatial distribution maps show similar patterns for Cr, Cu, Zn, Cd, Pb and Cr(VI), highlighting the contributions from the sludge dump site (Z1) as a “hot spot”. Another likely source for these metals is attributed to the UASB treated tanneries effluent that flows in the main canal and used for irrigation through a network of canal outlets. Both PCA and CA reveal two principal components that explain ~83 % of variability in metal concentrations. First principal component positively correlated with Cr, Cu, Zn, Cd, Pb, Cr(VI) and OM, is attributed to anthropogenic activities, i.e. irrigation by treated tanneries effluent, open dumping of Cr sludge. The second principal component is strongly correlated with Fe, Ni, Co, V and Mn, which is

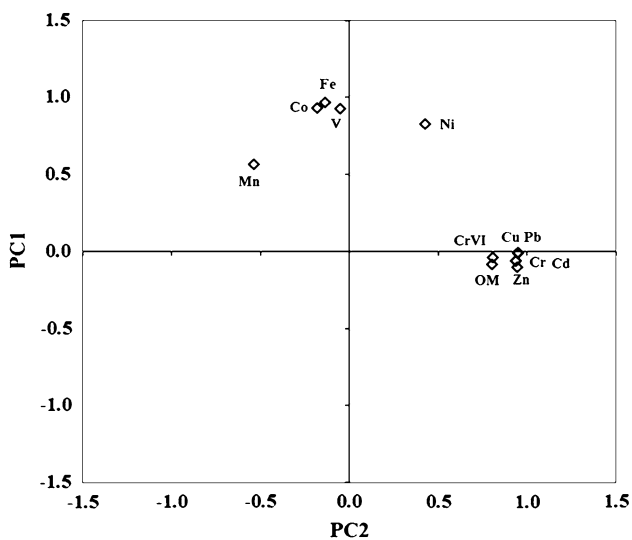
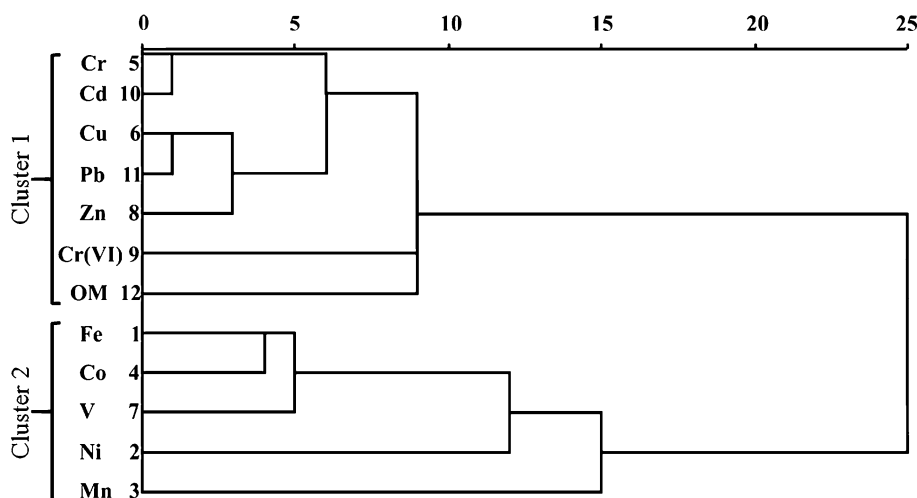


Fig. 5 Factor loadings for two principal components obtained from data set comprising of 12 × 53 matrix

Fig. 6 Dendrogram showing hierarchical cluster analysis results with a rescaled distance of 25. Two clusters are identified



attributed to weathering of parental materials. Pollution assessment using EF, I_{geo} , and PLI indices also suggests significant metal pollution in the study area. It is concluded that significant soil contamination can occur due to random dumping of tannery or UASB plant treated products such as raw waste and sludge. Leakage of leachate from sludge dump areas will lead to widespread soil contamination. This study clearly reveals the urgent need to evaluate the operation of the UASB plant which treats the tanneries influent, waste management of the sludge from these tanneries for safe disposal, and most importantly to remediate the already contaminated agricultural soil to prevent contamination of local groundwater and agricultural resources.

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