Sources apportionment and spatio-temporal changes in metal pollution in surface and sub-surface soils of a mixed type industrial area in India

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A B S T R A C T

Metals in the urban soils of industrial townships adversely affect human health and ecosystem. In the present work, surface and sub-surface soils collected at 0–10 cm and 10–20 cm depth, respectively, in pre and post monsoon seasons from twenty sites in an urban industrial area adjoining New Delhi are studied for the total metal concentrations (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) seasonal changes and pollution sources. Both surface and sub-surface soils are affected by high metal pollution with the contamination factor (CF) > 2 and the average pollution load index (PLI) of 2.77. The geo-accumulation index values of 6.6–8.2 (pre and post monsoon samples) for Zn, 6.7–8.2 for Cr and 5.6–5.1 for Cd in surface soils indicate extreme levels of pollution in the region. A total four metal sources, industrial emissions for Fe, Mn, Cu, Ni, Co and Cd, electroplating industry for Zn and Cr, geogenic for Al and V, and vehicular and biomass burning for Ba and Pb in the surface soils were identified using the principal component analysis. Industrial emissions, explaining 46% of data variance, are the major source of metals. Surface soils around small scale industries are more polluted with Zn, Cr and Cd (CFs = 25–31), and Cu and Pb (CFs = 7–11) and have high PLI (range: 3.28–8.77) compared to other sampling sites. Higher geo-accumulation indices and pollution load of metals in the urban soils are expected to have long term impact on human health, plants and crop productivity in this area.

1. Introduction

The surface soils, an important part of terrestrial ecosystems, receive pollutants from a variety of sources including industries in urban areas. Soil quality in the urban area is deteriorating rapidly due the ongoing rapid urbanization and industrialization and the changes in land use patterns (Cheng et al., 2014; Tume et al., 2011). The metal contaminated surface soils adversely affect the human health and ecosystem in the towns and cities (Cheng et al., 2014). In addition, the metal enriched surface soils contaminate atmosphere through re-suspension (Cyrys et al., 2003; Tandon et al., 2008) and surface/ground water via leaching (Bhuiyan et al., 2010; Chen et al., 2005; Liu et al., 2011). Metals like Pb, Cu, Zn, Ni, Cr and Cd cause serious environmental and health hazards due to their mobility in the environmental compartments (soil, air and water) (Dao et al., 2010; Nagajyoti et al., 2010; Wei and Yang, 2010). These potentially toxic metals enter into the food chain through plant uptake (Liu et al., 2011; Nagajyoti et al., 2010; Sharma et al., 2007) and can also accumulate in the human body via direct ingestion, inhalation and hand to mouth pathways (De Miguel et al., 1998, 2007; Madrid et al., 2002; Simon et al., 2013; Velea et al., 2009). Metals, unlike organic compounds, are non-biodegradable in nature and persist for years in the environment (Bailey et al., 1999). Thus, there is a need for the studies on

metal pollution/accumulation in urban soils in order to safe guard human health, particularly children and old age persons and ecosystems (Dao et al., 2010; De Kimple and Morel, 2000; Wei and Yang, 2010).

Industrial and vehicular emissions are the potential sources of metals in urban soils (Bhuiyan et al., 2010; Dao et al., 2010; Li et al., 2001, 2008; Moller et al., 2005; Nagajyoti et al., 2010; Wei and Yang 2010; Zhang et al., 2009; Zheng et al., 2002). The urban soils are also affected by the direct dumping of urban and industrial waste, open discharge of untreated effluents, agricultural runoff and atmospheric depositions (Chen et al., 2005; Nriagu 1989; Nriagu and Pacyna, 1988; Wei and Yang, 2010). These sources and pathways of metal contamination in the urban soils are very common and frequently observed in India (Nagajyoti et al., 2010; Rawat et al., 2009). In some cities, the vegetables and crops grown on the urban soils carry high amounts of potentially toxic metals and therefore, are not safe for consumption (Sharma et al., 2007, 2008; Khillare et al., 2012). In the Faridabad township, located adjacent to New Delhi, small and medium scale industries like electroplating, metal coating, tyre, tractor, and power plants are being run in the residential parts of the city without any effluent treatment facility. Pathak et al. (2013) have reported high levels of potentially toxic metals in the surface dust collected from this area. However, the surface soils are good proxy for assessing the metal pollution levels in urban areas (Dao et al., 2010; Manta et al., 2002), urban environmental quality (Cheng et al., 2014) as the metal contamination/ accumulation in urban soils takes place in surface layers (De Miguel et al., 1998). In this study,

we examined the total metal content in the surface and sub-surface soils collected at 0–10 cm and 10–20 cm depth, respectively, in pre and post monsoon season from twenty sites in Faridabad city adjoining the national capital of India. The data are discussed to understand the sources and the levels of metal pollution in surface and sub-surface soils and associated spatio-temporal changes. The geo-accumulation index and pollution load index of metals in urban soils are also discussed.

2. Study area

Present work on metal pollution of urban surface and sub-surface soils was undertaken in Faridabad Industrial Township, located in state of Haryana, adjoining New Delhi (Fig. 1). This township has emerged as the ninth largest industrial hub in Asia during last decade after Honorable Supreme Court of India's order to shift very large numbers of industries from New Delhi to nearby areas. At present about 15,000 small, medium and large scale industrial units are functional in Faridabad employing half a million people and generating 1500 billion rupees revenue per year (http://www.faridabad.nic.in/industri1.html). As per Haryana government directives, industrial units having capital value of 1–10 million, 10–50 million and more than 50 million Indian rupees are considered as small, medium and large scale industries, respectively. The large scale industries are situated in industry specific zones and have pollution control devices in place, but small scale industries, which includes motor winding, metal alloy, metal electro-plating and many more, are operating in the residential areas in an unorganized manner with no means for pollution control. Dumping of solid industrial discards on empty and open places, including roadsides, is a prevalent practice in this area. Effluents are drained directly into small channels which finally enter into river Yamuna flowing along eastern side of the city. Detailed description of the study area and industries with their respective products is reported elsewhere (Pathak et al., 2013).

3. Experimental

3.1. Materials and methods

Surface and sub-surface soil samples were taken from 0–10 cm and 10–20 cm depths, respectively, (Dao et al., 2010; Velea et al., 2009) during pre and post monsoon season from twenty sites in the study area. Nature and scale (small to large) of industries were seriously taken into consideration before selecting a sampling site. A general description of the industries around each sampling site is provided in Table 1. At each sampling site, three samples of surface and sub-surface soils from 30 X 30 cm size surface area were taken and mixed thoroughly to get a representative composite sample. All such samples were stored
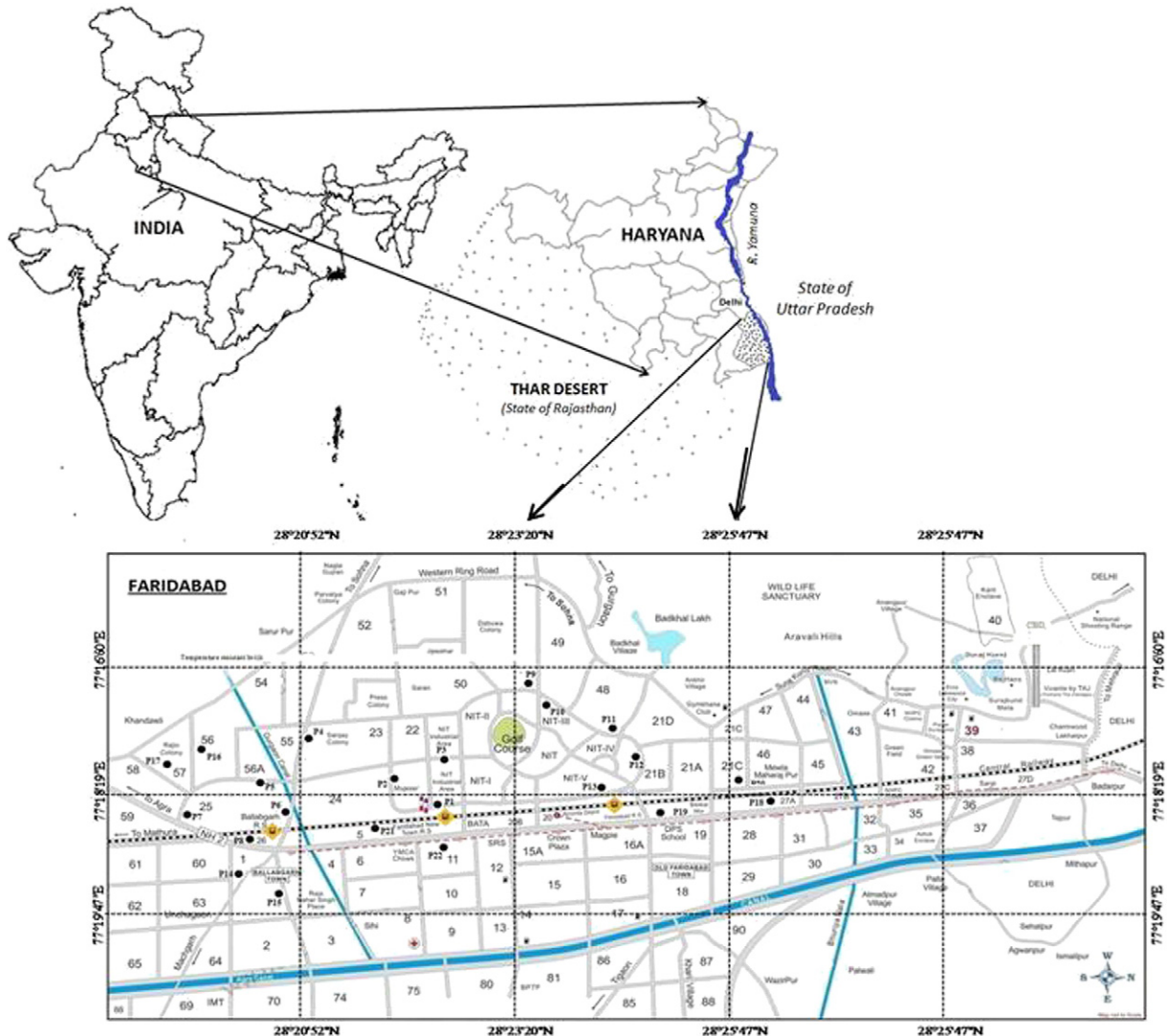

Fig. 1. Map of the study area showing Faridabad industrial area amidst the high population density residential areas. Numbers indicate residential pockets. Surface and sub-surface samples were collected near the small, medium and large scale industry in this area and are indicated by dark black dotes.

Table 1
Sampling locations of surface and sub-surface soil samples collected from the Faridabad industrial area adjoining Delhi.

Serial No.	Sample name	Nature of industry	Scale of Industry
1	P 1	Thermal power plant area	Large***
2	P 2	Thermal power plant area plus other metal related	Large
3	P 3	Thermal power plant area	Large
4	P 4	Metal alloy casting factory area	Medium**
5	P 5	Metal alloy casting factory area	Medium
6	P 6	Metal alloy casting factory area	Medium
7	P 7	Village with a number of small metal industries	Small*
8	P 8	Village with a number of small metal industries	Small
9	P 9	Temperature resistant brick manufacturing factory area	Small
10	P 10	Temperature resistant brick manufacturing factory area	Small
11	P 11	Electroplating factory area	Small
12	P 12	Electroplating factory area	Small
13	P 13	Electroplating factory area	Small
14	P 14	Village with a number of small metal industries, electric motor binding industries, lathe machine etc.	Small
15	P 15	Village with a number of small metal industries, electric motor binding industries	Small
16	P 16	Metal alloy casting factory area	Small
17	P 17	Centrifuge casting factory area	Small
18	P 18	Beside a very busy highway near steel factory	Small
19	P 19	Dying and printing factory area	Small
20	P 20	Dying factory and auto industry area	Small
21	P 21	Metal alloy casting factory area	Medium
22	P 22	Vehicle service station area	Small

* Small scale industry: annual turnover up to 10 million.
** Medium scale industry: annual turnover up to 50 million.
*** Large scale industry: annual turnover up to 500 million.

in the pre-labeled polythene zip bags and brought to the laboratory. Appropriate care was taken in the field to avoid collection of any obvious contaminants like plant leaves, pebbles etc. All samples were sun-dried for 4–5 days in plastic trays to drive out moisture and were passed through 2 mm sieve. Nearly 20–30 g of each sample was taken from the homogenized bulk sun dried sample by following coning and quartering method. All such samples were grounded to −200 mesh size (<63 μm) using agate mortar and pestle, and stored in pre-labeled plastic vials for chemical analysis. The processed soil samples were digested using combination of concentrated mineral acids i.e. HNO_3, HF and $HClO_4$ in three steps for determination of total metal content (Pruseth et al., 2005; Yadav and Rajamani, 2004). Silica a major interfering element during analysis was completely removed as volatile silicon fluoride using HF. Concentrated nitric acid (15.4 N) was used to decompose carbonates and sulfides, and to oxidize many metals of variable valency including iron into higher valence state. Perchloric acid was used to oxidize organic matter present in the samples.

Digested sample solutions were analyzed for different metals using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) model Ultima 2 (Jobin Yvon, France) and Atomic Absorption Spectrometer (AAS) model M6 (Thermo Electron Corporation, USA) installed at School of Environmental Sciences (SES), Jawaharlal Nehru University, New Delhi. The ICP-OES was calibrated using United States Geological Survey (USGS) standards namely BHVO-2, RGM, SGR and internal soil standard (21–6) digested along with samples. Error and precision of the data was checked by analyzing a separately digested BHVO-2 standard. Atomic Absorption Spectrometer was calibrated using serially diluted multi-element and single element standard stock solutions procured from E-Merck, Germany. Data precision and instrument stability was observed by analyzing the control standard at regular intervals during sample analysis. Closeness of analyzed value and reported values of BHVO-2 indicated good efficiency of the digestion method and metal analysis. Whole analytical work was carried out in a metal free positive pressure clean environmental chemistry laboratory at SES, JNU, New Delhi.

Total organic carbon (TOC) was determined by following Walkely (1947) method modified by Okalebo et al. (2002) and later modified in our laboratory. A portion (0.1–0.5 g) of each processed sample was taken in a 250 ml conical flask and 5 ml of 1 M $K_2Cr_2O_7$ solution was added. A quantity of 10 ml concentrated H_2SO_4 was added gently into the flask. The mixture was then allowed to cool and left undisturbed for 2–3 h. A volume of 50 ml of water was added and again allowed to cool. Then 0.3 ml of the Ferroin indicator ($[Fe(o\text{-hen})_3]^{2+}$ ion, a chromophore, that can be oxidized to the ferric derivative $[Fe(o\text{-phen})_3]^{3+}$) was added and the sample solution was titrated against 0.2 M ferrous ammonium sulfate solution; the end point was the color change from greenish to brown. The titrate value was recorded and corrected for the mean of two reagent blanks (T). Total organic carbon (TOC) was calculated according to the following equation:

$$\text{Total Organic Carbon } (\%) = \left[T_*(0.2)_*(0.3) \right] / \text{Sample weight}$$

where T is the titrate value.

3.2. Data analysis and pollution indices

Descriptive statistical analysis, including the mean, range (minimum-maximum), standard deviation (SD) and coefficient of variation (CV), were performed on the metal concentration data of surface and sub-surface soil samples. The SD and CV were determined to reflect the degree of dispersion distribution and variability of different metals in the examined environment of the study area (Mouli et al., 2006).

To understand the levels of metal contamination in the surface and sub-surface soils, the geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI) were calculated. The calculation of these indices requires concentrations of the metals in the background samples that are unaffected by the anthropogenic activities. The changing land use patterns, and variations in the surface soil chemistry and metal contamination, caused by anthropogenic sources and atmospheric depositions, made it difficult to define a true background soil sample for reference. Therefore, the local surface sediments (LSS), deposited on the Delhi ridge, are taken as background sample to assess pollution levels, and to calculate the CF and the I_{geo} of metals in this study. These sediments were away from the urban area and were unaffected by any anthropogenic inputs. Their homogenous chemical composition and similarity with the average chemical composition of upper continental crust (Tripathi and Rajamani, 1999; Yadav and Rajamani, 2004) indicated their uncontaminated nature.

3.2.1. Calculations of the contamination factor (CF)

The contamination factor (CF) was utilized to assess the degree of metal pollution (Caeiro et al., 2005; Hakanson, 1980). The CF is defined mathematically as:

$$CF = C_{sample}/C_{LSS}$$

Where $(C)_{sample}$ and $(C)_{LSS}$ are the concentration of metal in the soil sample and the local surface sediments, respectively. The contamination factor CF < 1 indicates low contamination; $1 \leq CF < 3$ refers to moderate contamination; $3 \leq CF \leq 6$ means considerable contamination and CF > 6 indicates very high contamination.

3.2.2. Calculations of the Pollution Load Index (PLI)

Pollution Load Index (PLI) has been proposed by Thomilson et al. (1980) for evaluating a particular sampling site for soil metal pollution levels. This index expressed as:

$$PLI = (CF_1 X CF_2 X CF_3 ---- X CF_n)^{1/n}$$

Where n is the number of metals and CF is the contamination factor as calculated above. The PLI values are used as a comparative means for assessing the sampling site quality for the soil metal pollution levels (Bhuiyan et al., 2010), where a value of one is considered as baseline level of pollution and a value of greater than one would indicate deterioration of sampling site quality (Thomilson et al., 1980).

3.2.3. Calculations of the geo-accumulation index (I_{geo})

The geo-accumulation index (I_{geo}) was computed by the following equation

$$I_{geo} = Log_2\{(C_n)/1.5(B_n)\}$$

where C_n and B_n represents the concentration of metal in the sample and the selected background (LSS) respectively. Multiplication factor of 1.5 is correction factor for inherent natural lithogenic variations in metal concentrations (Muller, 1971). The I_{geo} is partitioned in seven classes depending on its numerical value, each one representing different level of pollution: 1) unpolluted ($I_{geo} \leq 0$); 2) unpolluted to moderately polluted ($0 < I_{geo} \leq 1$); 3) moderately polluted ($1 < I_{geo} \leq 2$); 4) moderately to heavily polluted ($2 < I_{geo} \leq 3$); 5) heavily polluted ($3 < I_{geo} \leq 4$); 6) heavily to extremely polluted ($4 < I_{geo} \leq 5$), and 7) extremely polluted ($I_{geo} \geq 5$).

3.2.4. Principal component analysis (PCA)

Principal component analysis (PCA) is the most common multivariate statistical method used in environmental studies and is employed to extract a small number of latent factors for analyzing relationships among the observed variables (Caeiro et al., 2005). Pearson correlation analysis and PCA were used to find association among metals and the sources of metals, respectively, in the surface and sub-surface soil of the study area. The PCA was carried out on the metal data of all surface soil samples of two seasons for source identification using statistical package for social science (SPSS) version 16. Varimax rotation was used to maximize the variance explained by each factor. The components with eigenvalue greater than unity were only considered following the Kaiser criteria.

4. Results and discussion

The analytical details for major metals Al, Fe and Mn, trace metals Cd, Cr, Co, Cu, Ni, Pb, V and Zn, and alkaline earth metal Ba on surface and sub-surface soils collected during pre and post monsoon season from Faridabad industrial area are provided in the Supplementary Table S1. Since the data set is large and to make discussion part simple and communicable, the average concentrations of metals in soil samples are given in Table 2.

4.1. Surface soils

The average concentrations of Fe and Mn in surface soils are comparable with the LSS and those of Al are lower than LSS (Table 2, Panel A). In general, the local sediments as well as soils in the study area are quartz rich and the high weight percentage of silica (70–90%) caused the dilution effects on bulk distribution of major elements (Al, Fe, MN, Ca, Mg, Na, K and Ti) resulting in their lower concentrations compared to the average composition of the upper continental crust (UCC) (Tripathi and Rajamani, 1999). The slight increase in Fe and Mn content compared to LSS is associated with their common usage in industrial processes and their subsequent presence in the emissions. Iron and Mn in surface soils are higher in post monsoon samples compared to pre-monsoon. Among the trace metals, the concentrations of Ba, V, Co and Cd show very limited changes whereas concentrations of Pb, Ni and Cu are slightly, and that of Zn and Cr are significantly higher in surface soils compared to LSS (Table 2). Barium concentrations in surface soils ranged between 273 to 2088 mg kg^{-1} with an average of 588 mg kg^{-1} as compared to the average of 550 mg kg^{-1} in LSS and are indication of vehicular emission source of Ba to surface soils (Yadav and Rajamani, 2004). The observed metal enrichment in surface soils during post monsoon compared to pre-monsoon period indicates that the precipitation and or adsorption processes are more effective than the wash out process by rainwater. The hydrated insoluble complexes of Al, Fe and Mn have attracted other metals ions through adsorption (Bhuiyan et al., 2010) and stayed in soil matrix after rainy periods.

Surface soils with average concentration (mg kg^{-1}) of 1827 ± 7195 for Zn, 1085 ± 3357 for Cr, 178 ± 168 for Pb, 2.5 ± 1.9 for Cd and 14.7 ± 6.5 for Co can adversely affect the plant metal uptake balance and human health in the region (Bhuiyan et al., 2010; Nagajyoti et al., 2010). Occupational exposure could result in serious health hazards in children, old age persons and those who are already suffering from some disease (Chen et al., 2005; Dao et al., 2010; Madrid et al., 2002; Simon et al., 2013; Wei and Yang, 2010). The re-suspension of these contaminated surface soils will lead to atmospheric pollution on a regional scale in the study area (Cyrys et al., 2003; Gray et al., 2003). Tandon et al. (2008) have observed that nearly 27% of atmospheric aerosols in Delhi region arise from re-suspension of local surface earth materials. The total organic carbon content varies in the range of 5–25 mg kg^{-1} in the surface soil samples except two samples with 50 and 70 mg kg^{-1}.

4.1.1. Levels of metal contamination

The average contamination factors (CFs) of metals in surface soils of two seasons are given in Table 2. All the sampling sites show contamination irrespective of sampling seasons for all metals, except for Al which is attributed to silica dilution effect as discussed before. The CFs values in the range of one to 1.5 for Fe, Mn and V show lower levels of contamination on these elements in the soils. The CFs of Al, Fe, Mn, V and Ba show lower seasonal dependency. Zinc, Cr and Cd (average CFs vary between 25 and 31), and Cu and Pb (average CFs vary between 7 and 11) show very high contamination (CFs of these metals is greater than six) in surface soils with respect to LSS in both seasons; more contamination of these metals is observed in soils in post monsoon season compared to pre-monsoon (Table 2). Soils show considerable contamination by Ni, with the average CF of 4.1 ± 4.5 and 4.2 ± 3.5 for pre and post monsoon samples, respectively. Such high CFs of metals in the surface soils of industrial or urban cities in the world have rarely been observed by others (Bhuiyan et al., 2010; Nriagu and Pacyna, 1988; Rasmussen, 1998; Tume et al., 2011; Wei and Yang, 2010). Manta et al. (2002) have reported similar or even higher enrichment factors for metals in urban soils of Palmero, Italy affected by both industrial and vehicular emissions.

Table 2

Metals concentrations (mg kg^{-1}), total organic carbon (TOC) and contamination factor (CF) in (A) surface (0–10 cm depth) and (B) sub-surface (10–20 cm) soil samples collected in pre and post monsoon seasons in the Faridabad industrial area.

(A)

Metals in mg kg^{-1}	Pre-monsoon season surface soil samples				Post monsoon season surface soil samples				
	Minim- maxim concentration	Average	Std. Dev.	Average Contamination Factor (CF)	Minim- maxim concentration	Average	Std. Dev.	Average Contamination Factor (CF)	Average concentrations in LSS*
Al	19999-163988	36538	14103	0.5	11646-110293	43300	20848	0.5	80408
Fe	19161-55157	33420	11053	1.1	21858-53912	36325	10641	1.2	31430
Mn	294-2900	904	745	1.5	110-2476	687	588	1.1	619.6
Ba	273-2088	588	439	1.1	211-1178	500	193	0.9	550
Zn	89-10202	1048	2359	14.8	82-34034	1827	7195	25.7	71
V	45-150	71	24	1.2	54-192	88	29	1.5	60
Cr	30-5406	675	1209	19.3	23-2865	1085	3357	31.0	35
Cu	19-927	208	284	8.3	25-2574	274	547	11.0	25
Ni	16-299	82	91	4.1	24-245	85	70	4.2	20
Pb	62-778	178	168	8.9	59-675	148	142	7.4	20
Co	6.4-48	15.1	12.6	1.5	8-33	14.7	6.5	1.5	10
Cd	0.7-.78	2.3	2.2	23.6	1-7	2.5	1.9	25.6	0.098
TOC (g kg^{-1})	2-75	21	20	-	3-50	18	14	-	-

(B)

Metals in mg kg^{-1} units	Pre-monsoon season sub-surface soil samples				Post monsoon season sub-surface soil samples			
	Minim- maxim concentration	Average	Std. Dev.	Contamination Factor (CF)	Minim- maxim concentration	Average	Std. Dev.	Contamination Factor (CF)
Al	17251-136538	35910	15734	0.5	28827-153800	60094	33032	0.7
Fe	15097-58900	35885	11871	1.1	22235-58529	37917	10746	1.2
Mn	254-2517	903	673	1.4	263-2188	863	609	1.4
Ba	332-1131	495	201	0.9	319-1087	569	212	1.0
Zn	102-5225	564	1144	7.9	125-842	358	212	5.0
V	37-195	74	33	1.2	55-444	117	97	2.0
Cr	137-2862	577	679	16.5	24-1103	274	335	7.8
Cu	38-3686	224	245	9.0	33-941	190	237	7.6
Ni	26-228	75	66	3.7	28-613	110	149	5.5
Pb	79-944	166	92	8.3	68-226	134	49	6.7
Co	0.8-30	12.6	8.0	1.2	5.5-26	14.4	5.6	1.4
Cd	0.8-6.8	2.3	1.8	23.3	0.9-15	3.0	3.6	30.7
TOC (g kg^{-1})	3-24	11	7	-	5-67	24	18	

*LSS: Local Surface Sediments (data taken from Tripathi and Rajamani, 1999, Yadav and Rajamani, 2004).

Thus, it appears that the industrial activities/emissions are major cause of such high metal contamination in the surface soils of Faridabad region. The atmospheric depositions could also contribute to surface soil pollution as aerosols in north India contain high metal contents (Yadav and Rajamani, 2003, 2006). Further, the average PLI value of 2.77 indicates high pollution load in the city irrespective of sampling season. Sampling sites P8, P9, P11 P20, and P21, around small scale industries, are more polluted (PLI = 3.28–8.77) compared to the sampling sites around large scale industries (Supplementary Table S2).

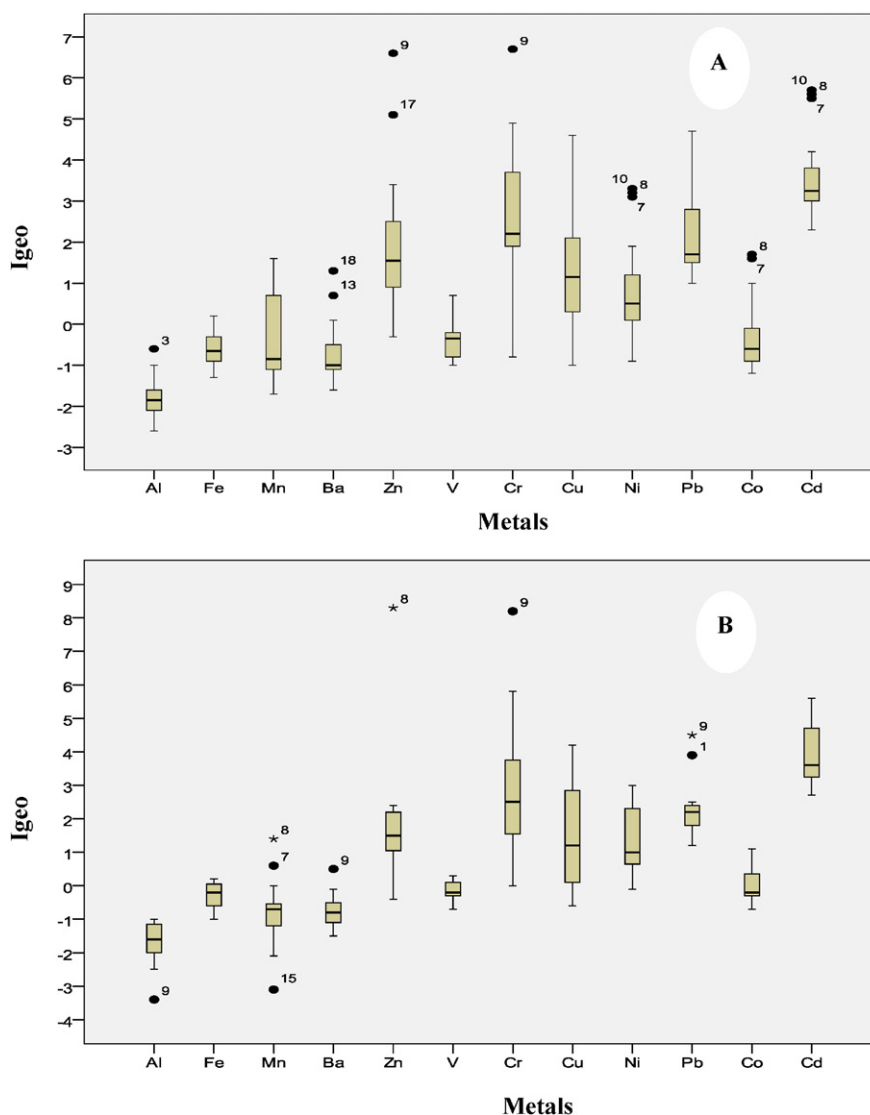### 4.1.2. Geo-accumulation index (I_{geo})

The I_{geo} values of metals in surface soils are plotted in box and whisker diagram in Fig. 2A and B for pre and post monsoon seasons, respectively. All the sampling sites are less polluted for Al, Fe, V, Mn, Ba and Co, except that sampling sites P7, P8 and P10 are moderately polluted for Ba, Co and Mn. The study area is moderately to heavily polluted for Zn, Cr, Cu, Pb, Ni and Cd with limited deviations. The I_{geo} values for Zn, Cr and Cd are recorded as high as 6.6, 6.7 and 5.6, respectively, for some sampling sites. In post monsoon season, Igeo values for Al, Fe, Mn, Ba and Co always fall in class 1 except Ba and Mn that are class 2 at two sampling sites. Similar to pre-monsoon season, I_{geo} values for Zn, Cr, Cu, Pb, Ni and Cd in post monsoon season fall in moderately to heavily polluted category. The geo-accumulation indices of metals vary depending on the sampling site and metal (Fig. 2A and B). In pre-monsoon season, sampling sites P13 and P18 are moderately polluted for Ba, site P9 for Zn and Cr, site P17 for Zn and sampling sites P7, P8, P10 for Ni, Co and Cd. Whereas the sampling site P8 have I_{geo} value of 8.3 for Zn, 5.8 for Cr and 5.1 for Cd and sampling site 9 is severely

polluted for Cr (I_{geo} = 8.2) in post monsoon season. All the sampling sites with high I_{geo} values for metals are situated around small scale industries related with metal work (Table 1). Similar to our observations about high metal pollution around small scale electro plating industries in Faridabad area, Liu et al. (2011) have also reported hazardous levels of Cr, Ni, Cu in water and paddy soils affected by electroplating industry in China.

4.1.3. Identification of sources

The results of principal component analysis (PCA) are provided in Table 3, Panel A. In pre-monsoon season, four principal components namely PC1 (with loading of Fe, Mn, Cu, Ni, Co and Cd), PC2 (Zn and Cr), PC3 (Al and V) and PC4 (Ba and Pb) are identified which explained nearly 88% of the variance in the dataset. The PC1 is marked as industrial source, however, it is difficult to decipher that this is a single or a mix of different individual industrial sources. The PC1 is the dominant source of metals as it explains 46% variance of the data. The PC2 explains 17% of the data variance and has loading of Zn and Cr. The PC2 is linked to electro plating industries that are operational in large numbers in the study area and use Zn and Cr in their processes. The PC3 explaining 16% of variance is associated with Al and V and is marked as geogenic source. The PC4 explains only 9% variance with loading of Ba and Pb and is attributed to vehicular and fossil fuel burnings (Moller et al., 2005).

In post monsoon samples, only three principal components were recorded compared to four in pre-monsoon season. The PC1 has loadings of Mn, Cu, Ni, Co and Cd and explains 41.53% of the data variance. The negative correlation of Al, which is primarily derived in soils from

Fig. 2. Geo-accumulation (I_{geo}) of metals in surface soil samples collcetd in (A) pre and (B) Post monsoon season from the Faridabad industrial area [Lower line of box indicate 1st quartile i.e. 25% of the data is less than this value; middle line in box represent median or second quartile i.e. 50% data is higher than this value; upper line of box indicate 3rd or 75% quartile i.e. 25% of data is greater than this value; upper and lower whiskers indicate maximum and minimum values excluding outliers; outliers indicate more than 3/2 times higher and lower value than the upper and lower quartile respectively].

geogenic sources, with other metals indicates that the anthropogenically added metals might not have mixed with geogenic component in surface soils. The PC2 shows loadings of Ba, Zn and Pb and explained 32% of the data variance. This component is marked as contributions from fossil fuel and used battery burnings, and vehicular emissions (Li et al., 2001; Pathak et al., 2013; Wilcke et al., 1998; Yadav and Rajamani, 2006). These sources are responsible for the accumulation of metals in the urban surface soils (Manta et al., 2002). Aluminium and V association in PC3 is indicative of geogenic source.

The correlation matrix provided additional information about metal associations in surface soils during post monsoon season (Supplementary Table S3). Correlations of Cr with Pb ($r^2 = 0.8$) and Zn ($r^2 = 0.98$) suggest that Cr in surface soils could also have been contributed by vehicular emissions and fossil fuel burning in addition to electroplating industry. Chromium in the environment has both geogenic and anthropogenic sources (Moller et al., 2005; Yadav and Rajamani, 2004). Further, metals show negative correlation with total organic carbon content in surface soils. It reflects that addition of metallic pollutant to urban surface soils is a recent phenomenon in the area, and the mixing of metals with the soil organic material and the formation of organo-metal complex has not taken place.

4.2. Sub-surface soils

Aluminium, Fe and Mn abundances and variations in sub-surface soils are similar to that observed in surface soils except Al, which is slightly enriched in sub-surface soils during post monsoon season (Table 2). Barium, V, Co and Cd concentrations in sub-surface soils are close to the LSS values whereas Zn, Cu, Ni, Pb and Cr are enriched in sub-surface soils compared to LSS in both seasons (Table 2, Panel B). Zinc and Cr show significant enrichment compared to both LSS and surface soils; Copper shows similar behavior only in post monsoon samples. Similar to our results, Velea et al. (2009) have also reported high metal content in sub-surface soils (10–20 cm depth) in an industrial area in Bucharest.

The average CFs of metals in sub-surface soil samples of two seasons are given in Table 2. The average CFs for the metals Al, Fe, Mn, Ba, V and Co are less than two, however, these metals also show higher CFs (>2) around some selected sampling sites suggesting that anthropogenic addition of metals in soils is sampling site specific. The CF of other metals in sub-surface soils are 8–5 (pre-post monsoon season) for Zn, 16–8 for Cr, 23–30 for Cd, 9–8 for Cu, 4–5 for Ni and 8–7 for Pb. Soils show more contamination in pre-monsoon samples compared to post monsoon for

Table 3
Results of principal component analysis (PCA) for the identification of metal sources in surface and sub-surface soils of the Faridabad industrial area.

	Surface soils (0–10 cm depth)						
	Pre-monsoon				Post-monsoon		
	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3
Al	−0.25	−0.18	**0.93**	−0.03	**−0.65**	−0.28	**0.56**
Fe	**0.95**	0.16	0.03	0.04	**0.9**	0.09	0.01
Mn	**0.89**	0.06	−0.1	−0.13	0.39	−0.22	−0.34
Ba	−0.09	0.45	0.1	**−0.58**	0.02	**0.92**	0.22
Zn	0.04	**0.94**	−0.16	0.1	0.26	**0.94**	−0.17
V	0.2	−0.11	**0.95**	−0.02	0.18	−0.03	**0.97**
Cr	0.22	**0.93**	−0.16	0	0.37	−0.65	−0.21
Cu	**0.96**	0.11	−0.09	0.12	**0.85**	0.44	−0.16
Ni	**0.98**	0.1	−0.05	0.07	**0.98**	0.12	−0.03
Pb	0.07	0.22	0.01	**0.83**	0.15	**0.9**	0.05
Co	**0.92**	−0.07	0.21	0.13	**0.9**	0.19	0.29
Cd	**0.98**	0.04	−0.06	0.11	**0.93**	0.34	−0.04
Eigen Values	5.54	2.09	1.9	1.1	4.98	3.8	1.61
Variance (%)	46.13	17.39	15.79	9.14	41.53	31.69	13.38

	Sub-surface soil samples (10–20 cm depth)						
	Pre-monsoon			Post-monsoon			
	PC1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 4
Al	−0.13	**0.97**	0.04	**0.96**	−0.06	−0.09	0.1
Fe	0.38	−0.04	−0.49	0.49	**0.82**	0.15	−0.06
Mn	**0.91**	−0.11	−0.1	0.29	**0.9**	−0.19	0.06
Ba	0.3	−0.13	**0.71**	0.18	−0.18	**0.72**	**−0.51**
Zn	**0.78**	−0.23	0.45	−0.14	0.01	**0.9**	0.35
V	0.06	**0.97**	−0.07	**0.98**	0.14	−0.03	−0.01
Cr	**0.8**	−0.16	0.39	−0.06	**0.96**	−0.03	0.15
Cu	**0.84**	−0.07	0.18	0.13	0.04	0.06	**0.94**
Ni	**0.97**	0	0.08	**0.89**	0.39	−0.07	0.02
Pb	0.19	0.06	**0.69**	−0.15	−0.01	**0.93**	−0.05
Co	**0.87**	0.06	0.09	**0.57**	**0.66**	−0.05	−0.37
Cd	**0.98**	0.11	0.09	**0.88**	0.41	−0.08	0.01
Eigenvalues	5.71	2.01	1.65	4.2	3.21	2.29	1.45
Variance (%)	47.62	16.73	13.74	34.99	26.71	19.07	12.07

all metal except Ni and Cd. The contaminations factors of metals in sub-surface samples are comparable to those observed in the surface samples during pre-monsoon season but the same is not true for post monsoon season (Table 2). The surface samples show high contamination compared to sub-surface samples in post monsoon season.

The average PLI in sub-surface soils of all sampling sites is 2.77 ± 1.36 and 2.78 ± 1.15 for pre and post monsoon seasons, an observation similar to surface soil samples (supplementary Table S2). This indicates high metal pollution load in both types of samples irrespective of sampling season in the study area. The PLI in surface and sub-surface soils vary as function of sampling site, a statement true for both seasons. However, the sampling sites P8, P9, P12, P14, and P15 situated around small scale industries are significantly polluted for their sub-surface soils irrespective of the sampling season, an observation similar to surface soils.

Geo-accumulation index (I_{geo}) values calculated for sub-surface soil samples of both seasons are presented in box and whisker diagram in Fig. 3A and B. Similar to the surface soil samples, Al, Fe, Ba, V and Co follow class 1 behavior; Cr, Zn, Pb, Cd Cu and Ni show moderate to extreme level of pollution in sub-surface soils of both seasons. The geo-accumulation indices of metals vary depending on the sampling site, metal (s) and sampling season. All metals show more accumulation in post monsoon season. In pre-monsoon season, similarly to the surface soil samples, the sampling sites P7, P8 and P11 are extremely polluted for Ni, Co, Cd. Sampling site P13 shows Pb pollution. In post monsoon season, sampling sites P15 and P4 are extremely polluted for V, Ni and Cd, and Ba respectively. The variations in values of CFs, I_{geo} and PLI for different metals in the study area indicate that anthropogenic contributions and distribution of metals in surface and sub-surface soils are heterogeneous in nature and sampling site specific in urban soils (Dao et al., 2013; Moller et al., 2005).

The results of PCA on metals data on sub-surface soils are provided in Table 3, Panel B. In pre-monsoon season, three principal components namely PC1 (with loading of Mn, Zn, Cr, Cu, Ni, Co and Cd), PC2 (Al and V), PC3 (Ba and Pb) were identified which explained nearly 78% of the total variance in the dataset. The PC1, similar to that observed in surface soils, is marked as industrial sources and is the dominant source that explained 47.6% of the total variance. The PC2 explained 17% of the data variance and is marked as geogenic source with loadings of Al and V. The PC3, explaining 14% of variance, is associated with Ba and Pb and is attributed to vehicular emissions and fossil fuel burnings (Moller et al., 2005; Morawska & Zhang, 2002; Yadav and Rajamani, 2006).

In post monsoon samples, PCA could identify four sources as compared to three in pre-monsoon season. The PC1 has loadings of Al, V, Ni, Co and Cd and explained 35% of the data variance. This association of metals indicates mixing of geogenic and anthropogenic sources as opposed to surface soils with negatively associations of Al with other elements. The PC2, with loading of Fe, Mn, Cr and Co, explained 27% of the data variance and is marked as mixed metal industry source. The PC3, similar to PC2 in surface soils, shows loadings of Ba, Zn and Pb and explained 19% of the data variance. This component is marked as contributions from fossil fuel, and battery burning and vehicular emissions (Li et al., 2001; Pathak et al., 2013; Wilcke et al., 1998). The fourth source (PC4) explains 12% of the data variance with loadings of only Cu.

Based on the source identification of metals in surface and sub-surface soils in pre and post monsoon seasons, it is suggested that there are at least three to four sources of metals, of which the industrial sources are dominant. The mixing of sources was also observed. Rainwater leaching could also affect distribution of metals in surface and sub-surface layers on long term basis. More detailed studies are required on the urban geochemistry, which should take into account a large suite of samples in such industrial area.

5. Conclusions

The metal analysis of surface and sub-surface soils collected during pre and post monsoon season from twenty sampling sites in Faridabad industrial area adjoining Delhi indicated spatial and temporal dependence of metal pollution in the area. The concentrations of metals in surface and sub-surface soils are higher than the selected background. The contamination factors of ≥ 5 for Zn, Cu, Cd, Cr, Pb and Ni in surface soils with respect to background and the average metal pollution load index (PLI) of 2.77 in both surface and sub-surface soils indicated the sever levels of metal pollution in this industrial township. Sampling sites P8, P9, P11, P20, and P21, situated around small scale industries are more polluted (PLI = 3.28–8.77) compared to the sampling sites around large scale industries. Soils of these sampling sites show metal contamination factor value of greater than 5 and high geo-accumulation indices of Zn, Cr, Pb, Mn, Ni, Co, Cd and Ba. Overall there are four and three dominant sources of metals in surface soils during pre and post monsoon seasons, respectively. Industrial sources (PC1) dominate with large contributions of Fe, Mn, Cu, Ni, Co and Cd, electroplating industry (PC2) make addition of Zn and Cr, geogenic source (PC3) contributes with Al and V, and vehicular emission (PC4) contributes with Ba and Pb to the soils. In post monsoon season, PC2 and PC4 merge together and result in one source PC2, which contributes with Ba, Pb and Zn; the other two sources remain the same.

Sub-surface soils are moderately to extremely polluted for Cr, Cd, Cu, Ni, Pb and Zn in both seasons. The CFs of metals in sub-surface soils are comparable to that observed in surface soils. In surface and sub-surface soils of both seasons, metal are not associated with total organic carbon content of soils indicating that inorganic processes are responsible for metal accumulation and distribution in the soils of the region. The observed pollution loads and higher geo-accumulation indices of metals in surface and sub-surface soils are expected to have long term impact on human health, plants and crop productivity. The policy makers and the urban administrators should take efforts to regularize the small scale industry, equip them with pollution control measures as well as
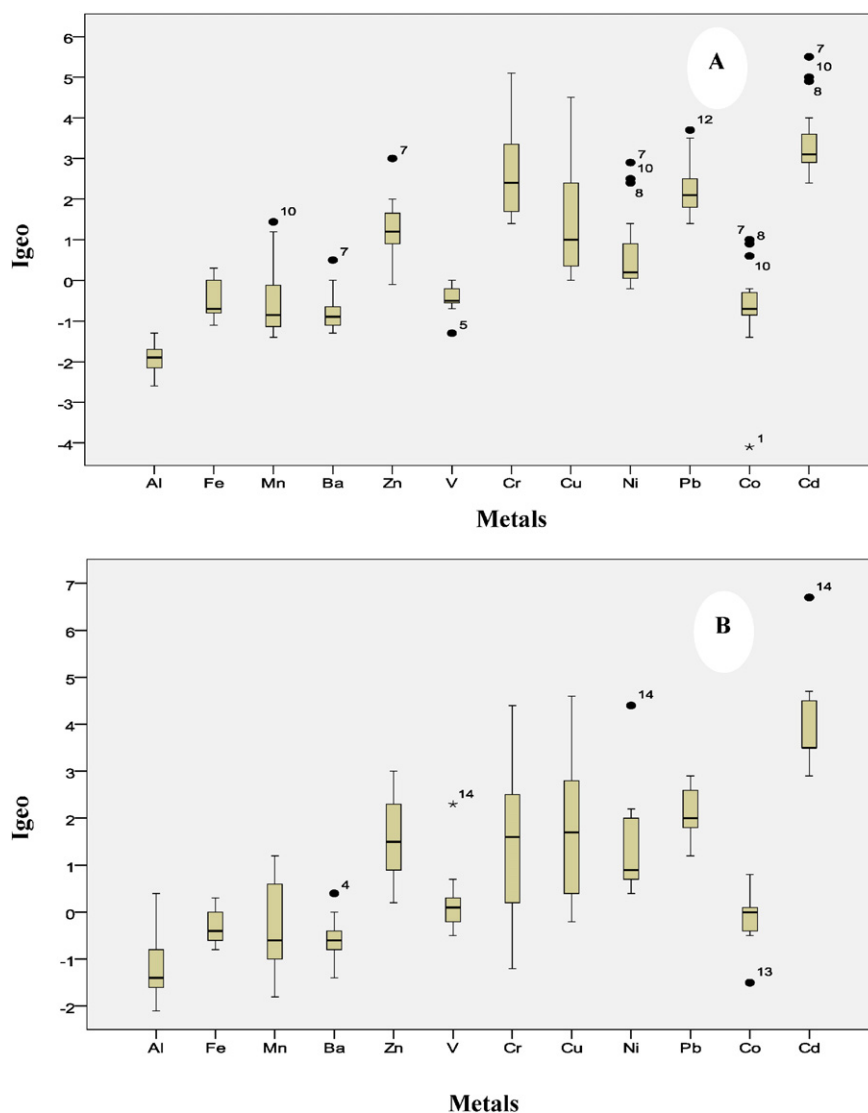
Fig.3. Geo-accumulation (I_{geo})of metals in sub-surface soil collected in (A) pre and (B) post monsoon season from the Faridabad industrial area [Lower line of box indicate 1st quartile i.e. 25% of the data is less than this value; middle line in box represent median or second quartile i.e. 50% data is higher than this value; upper line of box indicate 3rd or 75% quartile i.e. 25% of data is greater than this value; upper and lower whiskers indicate maximum and minimum values excluding outliers; outliers indicate more than 3/2 times higher and lower value than the upper and lower quartile respectively].

relocate them from the residential areas to dedicated separate industrial zones. Pollution activities must be restricted in order to safe guard public health and environment in the region.

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