



Sources evaluation, ecological and health risk assessment of potential toxic metals (PTMs) in surface soils of an industrial area, India

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Received: 29 May 2019 / Accepted: 14 January 2020 / Published online: 13 February 2020
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Abstract The present study aims to appraise the spatial distribution of potential toxic metals by using geostatistical technique and find their associated ecological and human health risks from surface soils of Durgapur industrial area, India. The results show that the mean metal concentrations are 116.03, 32.96, 154.37, 321.20, 50.08, 29.54 and 2.97 mg/kg for Pb, Cd, Cr, Fe, Cu, Ni and Hg, respectively, and majority of them is found higher than their background and world natural soil concentrations. The GIS contour map of pollution load index values clearly distinguished the studied sampling area is highly to very

highly polluted by the toxic metals. Contamination factor (C_f) and geo-accumulation index (I_{geo}) values of studied metals show a similar sequence of $Hg > Cd > Pb > Fe > Cr > Ni > Cu$. Calculated enrichment factor (EF) value for Hg (13.29), Cd (5.26) and Pb (1.11) in studied soils was found significantly higher, which suggests that their primary sources are higher industrial activities in the studied area. Computation of potential ecological risk index reveals that the entire study area is under high risk level (1941.60–3367.23), in which Cd (588.52) and Hg (1979.26) possess the maximum ecological risk factor in all the sampling sites. The results of correlation analysis, principle component analysis and cluster analysis explore that industrial discharges, atmospheric disposition and waste disposal are the major sources of soil metal pollution in the studied region. Human health hazard indices are lower than 1 for all metals, indicating low non-carcinogenic risks to children and adults. Carcinogenic risk assessment reveals the existence of cancer risk of Cd ($5.5E-03$), Cr ($8.6E-04$) and Ni ($3.0E-04$) to child and Cd ($8.2E-04$) and Cr ($1.3E-04$) to adults in Durgapur.

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Keywords Risk assessment · Potential toxic metals · Industrial soil · Multivariate analysis · Pollution indices

Introduction

Contamination of industrial soils by potential toxic metals (PTMs) has become a serious environmental concern in many developing countries across the world including India (Pathak et al. 2015). Soils are being considered as life-supporting environmental resources and also serve as recipients of potential toxic metals and other pollutants. The occurrence of PTMs in industrial top soils is mainly derived from different anthropogenic sources such as industrial activities, coal and fuel combustion, agricultural input, surface runoff and leachate from industrial and municipal solid waste disposal (Gupta et al. 2010; Hossain et al. 2014) and natural weathering of soil parent materials (Ghrefat et al. 2012; Wang et al. 2017). Generally, the phenomenon of metal enrichment in surface soils is very much prominent near intense industrial site/area. Long-term exposures of PTMs in soils lower their buffering capacity and also alter the physical, chemical and biological parameters of soils that could result in groundwater contamination (Severini et al. 2018). In many industrial cities, extensive industrial and vehicular emissions are considered to be potential sources of soil metal pollutions (Khillare et al. 2004; Bhuiyan et al. 2010; Hu et al. 2013). Further, industrial effluents are being widely used for irrigation for the cultivation of various vegetables and crops in the urban soils and also considered to be the potential sources of soil PTMs (Nayek et al. 2010). Since the previous few decades, rapid industrialization and urbanization along with the changes in land-use patterns have been accelerated the deterioration of soil quality in various industrial cities in India (Khillare et al. 2012; Chabukdhara and Nema 2013; Pathak et al. 2015; Krishna and Mohan 2016). Hence, the persistence, contamination and accumulation of such PTMs in surface soils have provoked potential risk on existing ecosystem and on biota (Machender et al. 2011; Liu et al. 2015).

Various pollution indices such as contamination factor (C_f), enrichment factor (EF), pollution load index (PLI), geo-accumulation index (I_{geo}) and ecological risk index (RI) are extensively used for evaluating the degree of metal pollution in industrial soils (Bhuiyan et al. 2010; Liu et al. 2015; Krishna and Mohan 2016). Multivariate statistical analysis, viz. correlation analysis, principal component analysis (PCA) and cluster analysis (CA), might provide

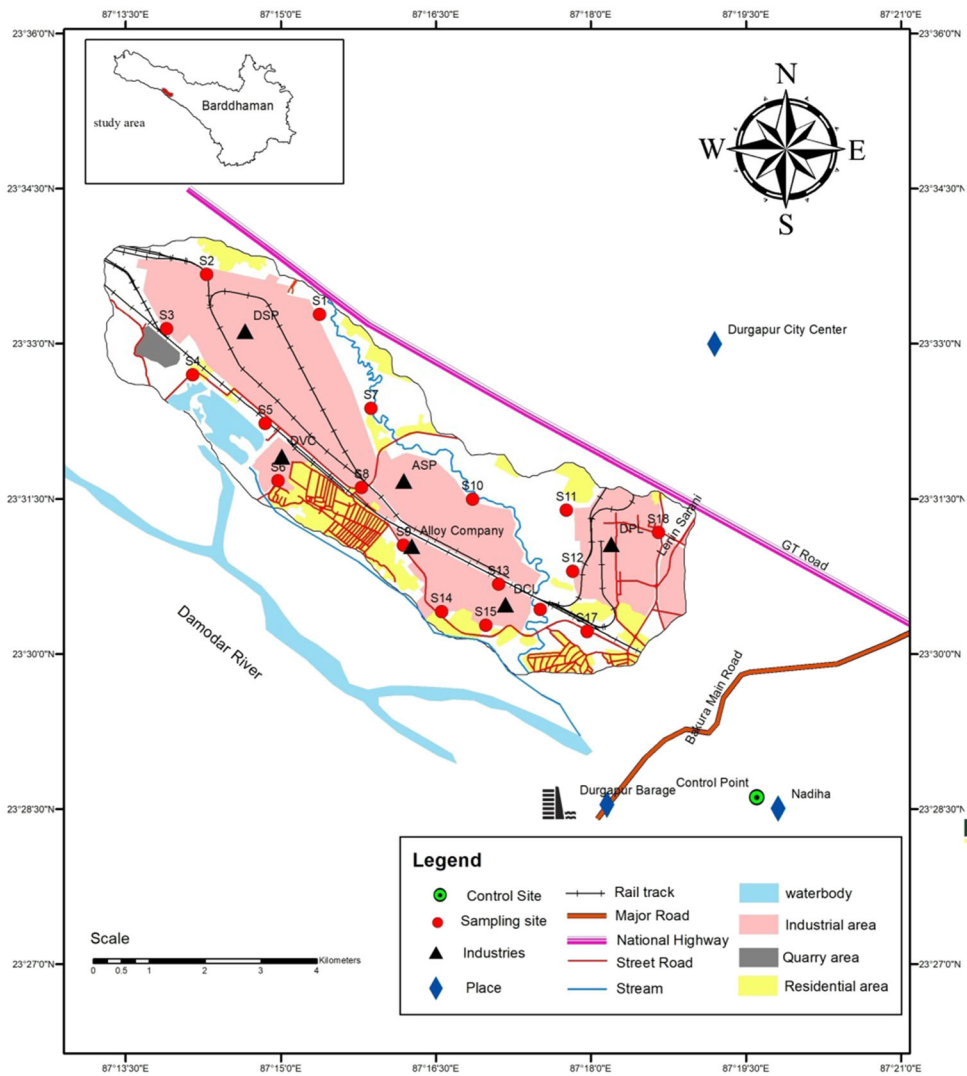
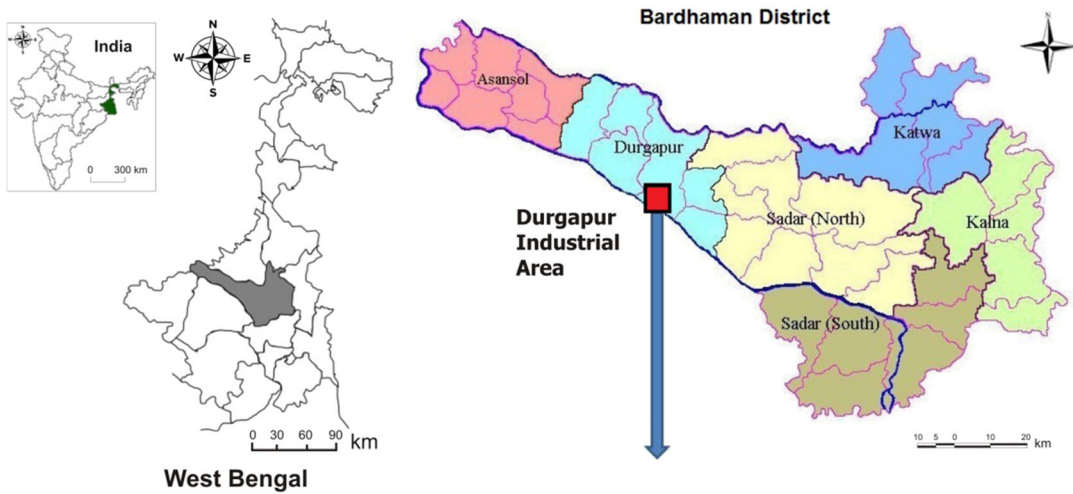
Fig. 1 Location map of the study area showing sampling sites and major industries such as Durgapur Steel Plant (DSP), Damodar Valley Corporation (DVC), Alloy Steel Plant (ASP), Durgapur Chemicals Ltd. (DCL), Durgapur Projects Ltd. (DPL)

comprehensive knowledge to discriminate the potential sources of toxic metals in surface soils from the surroundings (Liu et al. 2015; Krishna and Mohan 2016; Wang et al. 2017). The origin of PTMs in soils is partially sourced from various natural processes, but the anthropogenic activities are considered to be the major contributor of PTM contamination in different environmental samples such as water, soil, sediments, road dusts and plant parts in urbanized area in both developed and developing countries (Alsoub and Al-Khashman 2018). Several investigations were performed to examine the level of PTMs contamination and evaluated their possible sources in surface soils in India (Khillare et al. 2012; Chabukdhara and Nema 2013; Pathak et al. 2015; Krishna and Mohan 2016) and Worldwide (Bhuiyan et al. 2010; Ghrefat et al. 2012; Guo et al. 2012; Hossain et al. 2014; Liu et al. 2015; Wang et al. 2017; Barkett and Akün 2018).

Visual representation always provides better understanding of distinguishing between the polluted and unpolluted zone in the monitored area. To obtain the clear view of risk zone in the monitored area, geographical information system (GIS) mapping technique is very significant tool which can be applied with the resulted data of PTMs concentrations and different pollution indices values (Barkett and Akün 2018; Severini et al. 2018).

Potential toxic metals cause carcinogenic and non-carcinogenic health effects to humans by their exposure through ingestion, inhalation and dermal absorption of soil particles (Gope et al. 2018). Thus, health risk assessment is emerging as an important tool to assess the probable health risk with respect to total metal concentrations in soil (Acosta et al. 2009; Guney et al. 2010; Hamad et al. 2014).

Field study of present investigation was conducted at Durgapur industrial area (Fig. 1), one of the oldest steel cities in eastern India, established in 1950s. The city is surrounded by the Damodar River (on south) and Ajay River (on north). With a population density of 3800/km² (Indian Census 2011), this small city is listed among the 20 most polluted cities in India (Gupta et al. 2013). Rapid urbanization and lack of



proper solid waste disposal facility coupled with industrial emissions result in PTMs contamination of soil in vicinity to industrial areas. PTMs contamination in agricultural soils due to wastewater irrigation and their subsequent accumulation in cultivated vegetation are reported by earlier researchers (Barman et al. 2000; Gupta et al. 2010; Kisku et al. 2011). But limited work was conducted to evaluate PTMs contamination in surface soils of Durgapur and surrounding industrial areas (Nayek et al. 2011; Pobi et al. 2017, 2019). Therefore, to reduce the gap, the present investigation focuses on: (1) evaluating the spatial variation of seven PTMs (Pb, Cd, Cr, Fe, Cu, Ni and Hg) in surface soil of Durgapur industrial area; (2) identifying the potential sources and dominant affecting factors of PTMs using multivariate statistical analysis; (3) analyzing the health risk of specific PTMs and potential ecological risk connected with the accumulation and exposure to studied PTMs; and (4) applying GIS mapping to get a clear visual picture of PTMs distribution and potential ecological risk-prone area in the examined region.

Materials and methods

Geology of the study area

The study area is situated on the southeastern part of Durgapur City and lies at 23.48° N, 87.32° E, with an average elevation of 213 ft. The average rainfall in the Durgapur industrial area is 1320 mm and followed tropical climatic conditions. The geology of the Durgapur area is overlain by hard crust laterites (origin belongs to Cenozoic age), which was extension of Panchet and Gondwana super-group formation and the southeastern part of the study area having moderately hard to very hard rock types comprises red shale, sandstone and very coarse sandstone, respectively. Extreme southern part of the study area, i.e., adjacent to the Damodar River, is predominantly dominated by clay alternating with silt and sand of Panskura formation (Quaternary) having the characteristics of soft, unconsolidated sediments (oxidized).

Sampling and analysis of industrial soils

A total of 54 soil grab samples were taken from 18 different sampling sites (S1 to S18) in Durgapur

industrial area, which are shown in Fig. 1. Surface soil samples were taken from 0 to 15 cm depth by using a stainless steel hand digger and quickly transferred into zipped polythene bags. Soil samples were dried normally, finely crushed and then sieved by mesh (2 mm) to remove the large debris or particles. The soil pH was measured with 1:5 ratio of soil and water suspension, (w/v) by using Orion star pH meter (A214, Thermo Scientific); electrical conductivity (EC) of the suspension was determined by using EC-meter (Multi-Parameter PCS Testr™ 35, Oakton) (Rhoades 1982). Cation exchange capacity (CEC) was determined using standard method taken from Reeuwijk (1995). Organic matter (OM in %) was determined by using Walkley and Black (1934) method, and soil particle size (sand, silt and clay) was determined by hydrometer method (Bouyoucos 1951). For estimation of PTMs concentrations, 0.5 g of composite soil sample was digested with a mixture of concentrated HNO₃ and HClO₄ (3:1, v/v) (USEPA 2007). The solution was filtered using Whatman filter paper (Grade 42), and the filtrates were diluted to 50 mL by using deionized water. Pb, Cd, Cr, Fe, Cu and Ni were examined by an atomic absorption spectrophotometer (AAS, model: GBC Avanta), and Hg was assessed by cold vapor atomic absorption. As there were no pre-industrial recorded values for background metal concentrations, the mean metal concentration of the three surface soil samples collected from non-urban area, i.e., Nadiha, Durgapur, which is approximately 5 km away from the study area and considered to be devoid of any industrial or anthropogenic contamination (Gupta et al. 2010), was considered as background reference values for this study.

Quality control and assurance

During sample collection, preservation and performing analytical procedure, special care has been taken. All the glassware was soaked in diluted (10%, v/v) HNO₃ acid over night for cleanup and further rinsed with deionized water before use. The chemicals used for analysis were of AR grade from Merck, India. Deionized water (18.2 MΩcm⁻¹, Arrium®61316, Sartorius Stedim Biotech) was used for solution preparation. To ensure the accuracy, soil samples were analyzed in triplicates, in good agreement with the results of within ± 5%. The experimental results of PTMs concentrations in soil samples were compared

with the standard reference materials (SW 8022) from National Material Testing Laboratory, India. The accuracy and reproducibility of analyzed PTMs concentrations were within 5% standard error (SE) level of certified values for individual metal.

Statistical analysis

The descriptive statistics such as minimum, maximum and standard deviations (SD) of soil parameters and PTMs in the industrial were calculated. In this study, multivariate statistical analysis, i.e., Pearson’s correlation, principal component analysis (PCA) and cluster analysis (CA), was executed (SPSS statistical software, version 20.0) to understand the possible sources, relative behavior and the interdependency among the metals in the studied soils. The spatial distribution of PTMs pollution map was obtained using ArcGIS 10.5. Hierarchical cluster analysis (CA) (dendrogram) was performed on the normalized data set of soil properties and PTMs in the present study to identify relatively homogenous groups or clusters of objects based on their similarities (Gope et al. 2018).

Pollution indices

The quantification of metal pollution in studied soils is generally evaluated by comparing PTMs concentrations with the measured geochemical background values or connected environmental guidelines (Barkett and Akün 2018). In this study, several pollution indices such as contamination factor (C_f), pollution load index (PLI), enrichment factor (EF) and geo-accumulation index (I_{geo}) are used for evaluating the degree of PTMs contamination in the Durgapur industrial soils.

Contamination factor (C_f)

The single-element index, contamination factor (C_f), is applied to measure the degree of metal contamination in soil. The contamination factor (C_f) was firstly established by Muller (1969), and the modified form of the method for calculating the C_f value is assessed by the ratio of analyzed metal concentration value to the geochemical background reference value (Hakanson 1980; Bhuiyan et al. 2010; Machender et al. 2011). The contamination factor is based on Eq. 1.

$$C_f^i = (C_n^i/B_n^i) \tag{1}$$

where C_f^i represents the contamination factor and C_n^i and B_n^i represent the measured concentration (mg/kg) of metal i in soil sample and the geochemical background reference value of the same metal, respectively. The categorization of contamination factor (C_f) value is suggested by Hakanson (1980) and summarized in Table 1a.

Pollution load index (PLI)

The PLI is a simple realistic index and widely used in a comparative way to measure the cumulative metal pollution load in the study area (Tomlinson et al. 1980; Bhuiyan et al. 2010; Hossain et al. 2014). The C_f value has been used for the PLI value calculation and is estimated by Eq. 2.

$$PLI = (C_{f_1} \times C_{f_2} \times C_{f_3}, \dots, C_{f_n})^{1/n} \tag{2}$$

where C_{f_i} and n represent the contamination factor (C_f) of metal i and the number of metals (i.e., seven metals in this study), respectively. The categorization of PLI value and the corresponding grades of soil quality (Zhang et al. 2011) are represented in Table 1a.

Enrichment factor (EF)

The magnitude of PTMs contamination in the study area is generally assessed by using EF and may assist to quantify between anthropogenic and geogenic metal sources (Krishna and Mohan 2016). Generally, the EF value < 1 suggests that the metal is originated from crustal contribution, and the EF value > 1 specifies that the metal is sourced from non-crustal materials (anthropogenic sources) (Hu et al. 2013). The normalized EF is computed by using Eq. 3.

$$EF = \frac{(C_n/C_{ref})_{sample}}{(B_n/B_{ref})_{background}} \tag{3}$$

where C_n and B_n are the analyzed metal concentrations (mg/kg) and C_{ref} and B_{ref} are the background reference metal concentrations (mg/kg). The classifications of EF are governed by Sutherland (2000) in five categories and are shown in Table 1a.

Table 1 Grades of different pollution indices in relation to soil quality

I_{geo}	Contamination level	EF	Enrichment level	C_f	Degree of contamination	PLI	Soil quality
(a) Geo-accumulation index (I_{geo}), enrichment factor (E_F), contamination factor (C_f) and pollution load index (PLI)							
$I_{geo} \leq 0$	Practically uncontaminated	$EF < 2$	Deficiency to minimal	$C_f < 1$	Low contamination	$PLI \leq 0$	Background concentration
$0 < I_{geo} \leq 1$	Uncontaminated to moderately contaminated	$2 < EF \leq 5$	Moderate	$1 \leq C_f < 3$	Moderate contamination	$0 < PLI \leq 1$	Unpolluted
$1 < I_{geo} \leq 2$	Moderately contaminated	$5 < EF \leq 20$	Significant	$3 \leq C_f < 6$	Considerable contamination	$1 < PLI \leq 2$	Unpolluted to moderately polluted
$2 < I_{geo} \leq 3$	Moderately to heavily contaminated	$20 < EF \leq 40$	Very high	$C_f \geq 6$	Very high contamination	$2 < PLI \leq 3$	Moderately polluted
$3 < I_{geo} \leq 4$	Heavily contaminated	$EF > 40$	Extremely high			$3 < PLI \leq 4$	Moderately to highly polluted
$4 < I_{geo} \leq 5$	Heavily to extremely contaminated					$4 < PLI \leq 5$	Highly polluted
$I_{geo} > 5$	Extremely contaminated					$PLI > 5$	Very highly polluted
RI	Degree of ecological risk			E_r^i	Pollution degree		
(b) Potential ecological risk index (RI) and potential ecological risk factor (E_r^i)							
$RI < 150$	Low			$E_r^i < 40$	Low		
$150 \leq RI < 300$	Moderate			$40 \leq E_r^i < 80$	Moderate		
$300 \leq RI < 600$	Considerable			$80 \leq E_r^i < 160$	Considerable		
$RI \geq 600$	Very high			$160 \leq E_r^i < 320$	High		
				$E_r^i \geq 320$	Very high		

Geo-accumulation index (I_{geo})

The index of geo-accumulation (I_{geo}) is usually used for evaluating the metal contamination by comparing the recent metal concentrations with their pre-industrial metal concentrations (Muller 1969). Wide application of proposed method for the evaluation of soil pollution (Machender et al. 2011; Wang et al. 2017; Barkett and Akün 2018) is formulated using Eq. 4.

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right) \quad (4)$$

where C_n and B_n represent the analyzed soil metal concentration (mg/kg) and the geochemical background (control site) metal concentration (mg/kg), respectively; and the correction factor 1.5 is used to

minimize the effect of variations of the regional metal concentration due to geochemical inconsistency (Barkett and Akün 2018). The classifications of I_{geo} values are recommended by Muller (1969) and presented in Table 1a.

Ecological risk assessment

The ecological risk index (RI) is widely used for assessing the ecological toxicity due to the contamination of PTMs in the specific soil environment (Hakanson 1980). This method reflects the combined ecological and environmental effects with toxicology of all examined metals in the study area (Hakanson 1980; Hu et al. 2013; Shen et al. 2017). RI is the

cumulative of ecological risk factors (E_r^i) of PTMs and determined by Eq. 5.

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n C_f^i \times T_r^i \tag{5}$$

where E_r^i , T_r^i and C_f^i represent the ecological risk factor, toxic-response factor and contamination factor of metal i , respectively. The toxic-response factors are assigned as Pb = 5, Cd = 30, Cr = 2, Cu = 5, Ni = 5 and Hg = 40 (Hakanson 1980). The toxic-response factor for Fe is unavailable and not included for E_r^i and RI calculations. The classification and toxicity level of E_r and RI are shown in Table 1b.

Health risk assessment

Human health risk assessment to quantify non-carcinogenic risk as well as carcinogenic risk of PTMs in Durgapur industrial soil in the present study is based upon considering three different pathways, i.e., ingestion, inhalation and through dermal/skin contact. The daily intake doses via each of the three exposure pathways for child and adult can be estimated by the following equations (Ferreira-Baptista and De-Miguel 2005; USEPA 1989):

$$ADI_{ing} = C \times \frac{R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avrg}} \times 10^{-6} \tag{6}$$

$$ADI_{inh} = C \times \frac{R_{inh} \times F_{exp} \times T_{exp}}{PEF \times ABW \times T_{avrg}} \tag{7}$$

$$ADI_{dermal} = C \times \frac{SAF \times A_{skin} \times DAF \times F_{exp} \times T_{exp}}{ABW \times T_{avrg}} \times 10^{-6} \tag{8}$$

where ADI = average daily intake (mg/kg/day); C = metal concentration; ingestion rate (R_{ing}) [child (1–6 year) 200 mg soil/day and adults 100 mg soil/day], inhalation rate (R_{inh}) [child 7.6 m³/day and adults 20 m³/day], exposure frequency (F_{exp}) [365 day/year, exposure duration (T_{exp}) [child (6 years) and adults (24 years)], skin area (A_{skin}) [child (2800 cm²) and adults (5700 cm²)], SAF = skin adherence factor [child (0.2 mg/cm²/h) and adults (0.07 mg/cm²/h)], DAF = dermal absorption factor (unit less) [for both child and adults 0.001], particle emission factor (PEF) [1.36 × 10⁹ m³/kg for

both cases], average body weight (ABW) [child (18 kg) and adults (60 kg)], T_{avrg} = averaging time; for non-carcinogens, $T_{avrg} = T_{exp} \times 365$ (Gope et al. 2018).

The probable non-carcinogenic risk of specific metal in Durgapur industrial soils is calculated by the following equations (Gope et al. 2017):

$$\text{Hazard quotient (HQ)} = ADI / R_f D, \tag{9}$$

$$\text{Hazard index (HI)} = \sum HQ_{(ingestion/inhalation/dermal)} \tag{10}$$

$R_f D$ is the reference dose and $ADI_{ing/inh/dermal}$ is the average daily intake rate via ingestion, inhalation or dermal pathways. $R_f D$ values have been taken from Ferreira-Baptista and De-Miguel (2005) and Gope et al. (2018). Hazard index (HI) is computed as the sum of HQs of three different pathways for individual metal. The value of HI > 1 signifies non-carcinogenic effects and that of HI < 1 suggests no significant risk (USEPA 2001).

The carcinogenic risk (CR) is estimated by the following equation (Chen et al. 2015):

$$CR = \sum ADI_i \times CSF_i \tag{11}$$

where i is the exposure pathway, i.e., ingestion, inhalation or dermal contact; CSF is the carcinogenic slope factor. Out of seven studied PTMs, CSF is available for Cd, Cr and Ni and that is only for inhalation exposure route. CR values > 1 × 10⁻⁴ are considered as intolerable, while CR < 1 × 10⁻⁶ signified no substantial health effect. CR value ranged 10⁻⁶–10⁻⁴, which indicated probable occurrence of carcinogenic health effect (Chen et al. 2015).

Results and discussion

Physicochemical properties and PTMs contents in soil samples

The analytical results of soil physicochemical properties and PTMs concentrations of surface soils from Durgapur industrial area are shown in Table 2. The overall pH of experimental soil samples ranges from 7.05 to 8.68 with an average value of 7.70, indicating neutral to sub-alkaline nature of the studied soil. This variation of pH in soil samples is mainly due to the

Table 2 Spatial distribution of physicochemical properties, total heavy metal concentrations and descriptive statistics of surface soils of Durgapur industrial area

Sampling sites	pH	EC	CEC	OM	Clay	Silt	Sand	Pb	Cd	Cr	Fe	Cu	Ni	Hg
S1	8.14	748	16.5	1.28	2.34	49.25	48.41	110.82	22.24	172.15	360.14	51.85	34.25	2.65
S2	7.15	765	15.4	2.45	23.42	41.65	34.93	108.56	18.25	165.62	350.24	47.26	31.36	2.36
S3	8.02	785	17.42	3.32	26.85	43.78	29.37	109.45	20.84	170.66	354.55	50.54	32.85	2.48
S4	8.12	872	20.8	4.38	32.48	32.15	35.37	129.25	32.86	182.55	338.12	57.15	38.85	3.14
S5	7.32	832	17.4	3.05	7.45	46.28	46.27	127.24	24.98	179.55	335.25	55.65	37.15	2.85
S6	7.92	746	15.6	1.32	2.62	48.55	48.83	128.6	28.28	180.54	337.48	55.82	38.62	3.06
S7	8.68	844	22.62	2.92	32.65	31.65	35.7	132.45	49.56	168.95	344.16	58.86	32.45	3.65
S8	8.08	838	12.2	2.55	4.26	46.56	49.18	130.54	46.65	165.55	341.75	57.25	30.95	3.25
S9	8.42	857	17.8	1.98	9.65	44.65	45.7	129.36	48.32	168.5	342.85	58.58	31.86	3.58
S10	7.88	852	24.6	2.15	4.16	36.45	59.39	117.45	41.12	154.25	325.55	53.24	28.74	3.24
S11	7.22	838	21.4	2.15	5.65	34.35	60	115.34	39.55	150.28	320.68	50.34	26.58	3.16
S12	7.86	925	24.5	4.54	34.24	28.56	37.2	116.8	40.56	152.64	322.24	52.85	28.46	3.18
S13	7.65	768	20.86	3.22	33.54	28.86	37.6	107.15	34.54	139.25	296.5	45.86	24.48	2.98
S14	7.12	912	23.4	4.89	32.95	26.42	40.63	105.62	32.52	134.5	292.55	43.65	23.95	2.82
S15	7.64	765	18.24	3.04	8.86	45.52	45.62	106.5	34.12	138.2	294.48	45.15	24.15	2.86
S16	7.26	791	18.5	3.84	28.26	45.25	26.49	105.35	27.88	120.5	281.35	40.45	22.78	2.78
S17	7.05	895	22.8	3.95	32.95	24.74	42.31	103.58	24.32	116.65	265.55	37.15	21.95	2.68
S18	7.14	868	19.28	4.92	2.48	35.85	61.67	104.42	26.64	118.24	278.18	39.78	22.36	2.72
Min	7.05	746	12.2	1.28	2.34	24.74	26.49	103.58	18.25	116.65	265.55	37.15	21.95	2.36
Max	8.68	925	24.6	4.92	34.24	49.25	61.67	132.45	49.56	182.55	360.14	58.86	38.85	3.65
Mean	7.70	827.83	19.41	3.11	18.05	38.36	43.59	116.03	32.96	154.37	321.20	50.08	29.54	2.97
SD	0.49	56.49	3.45	1.13	13.52	8.24	10.09	10.65	9.63	21.88	29.04	6.83	5.59	0.35
Control soil	7.17	167.67	168.67	5.01	6.01	7.01	8.01	28.11	1.68	64.80	85.78	32.30	14.74	0.06
Unpolluted soil ^a	–	–	–	–	–	–	–	15	0.1	100	5(%)	55	20	0.07
Unpolluted soil ^b	–	–	–	–	–	–	–	27	0.41	54	3.5(%)	20	29	1.1

Except pH, EC (uS/Cm) and CEC (Cmol/kg), clay, silt, sand and OM contents in % and all heavy metals in mg/kg

^aAverage crustal abundance of elements from Wedepohl (1986), Bowen (1979) and Kabata-Pendias (2011)

^bAverage content in world natural soils, from Bowen (1979) and Kabata-Pendias (2011)

influence of industrial discharges and waste dumping in the studied region and consistent with earlier studies (Al-Khashman and Shawabkeh 2006; Banerjee and Gupta 2013). The electrical conductivity (EC) and cation exchange capacity (CEC) in the soil samples are widely varied from 746 to 925 $\mu\text{S}/\text{Cm}$ and 12.2 to 24.6 Cmol/kg, respectively. The mean values of EC and CEC are recorded as 925 $\mu\text{S}/\text{Cm}$ and 24.6 Cmol/kg, respectively, which signify the higher presence of ionic constituents and are influenced by soil pH, OM contents and clay minerals in the soil samples (Sofianska and Michailidis 2015). The high fluctuation of EC and CEC values in the examined soil samples

may be due to the industrial waste discharges, agricultural runoff and the wastewater coming from urban areas and highly influenced by the variation of other soil properties in the studied region (Adriano 1986; Banerjee and Gupta 2013). In this study area, organic matter (OM) value ranges from 1.28 to 4.92% (Table 2) and higher value is observed at S4, S12, S14 and S18 only. Generally, the organic matter contents in industrial soils are comparatively lower than in the uncontaminated soils (OM, 5.01%) because of soil disruptions caused by industrial wastes dumping in the studied area (Barkett and Akün 2018). The study of soil OM contents is the particular interest to get

information of the bioavailability, mobility and/or retention of PTMs as their organometallic complexes in the soil environment (Adriano 2001; Sofianska and Michailidis 2015). The spatial distribution of OM in studied soil is found low in majority sites that determined the lower presence of vegetation and animals in the study area (Al-Khashman 2012; Ghrefat et al. 2012). The value of clay, silt and sand contents of the samples is varied between the range of 2.34–34.24, 24.74–49.25 and 26.49–61.67%, respectively. The mean percentage of clay, silt and sand contents is found as 18.05, 38.36 and 43.59, respectively, which suggests that the studied soils are sandy loam to clayey loam.

The spatial distribution of PTMs (Pb, Cd, Cr, Fe, Cu, Ni and Hg) from industrial area is compared with regional background value, average metal concentrations in the earth's crust (Wedepohl 1986; Bowen 1979; Kabata-Pendias 2011) and world natural soils (WNS) (Bowen 1979; Kabata-Pendias 2011). The level of metal concentrations (mg/kg) is in the range of 103.58–132.45 for Pb, 18.25–49.56 for Cd, 116.65–182.55 for Cr, 265.55–360.14 for Fe, 37.15–58.86 for Cu, 21.95–38.85 for Ni and 2.36–3.65 for Hg. The mean concentration of Pb, Cd, Cr, Fe, Cu, Ni and Hg in the surface soil of studied area is 116.03, 32.96, 154.37, 321.2, 50.08, 29.54 and 2.97 mg/kg, respectively, following the sequence of Fe > Cr > Pb > Cu > Cd > Ni > Hg (Table 2). In this study, the concentrations of all examined metals are well above than their background reference value. The majority of the PTMs concentrations in all sampling sites exceed the average earth's crust metal contents and WNS reference value [except Cu (sites S1–S3 and S10–S18) for average earth's crust metal contents; Cu (in all sampling sites) and Ni (sites S10–S18) contents are exceeded WNS reference value; Fe contents (in all sites) for both]. Naturally, the abundance of Fe is high on earth crust. In the present study, the higher values of Fe in all sampling site are primarily corresponded to the lateritic soil type in the studied region (Banerjee and Gupta 2013; Pobi et al. 2019) and also due to industrial discharge, atmospheric deposition with industrially emitted dust particles (Al-Khashman and Shawabkeh 2006). The concentration of Cr, Pb, Cu, Ni and Hg in surface soils of Durgapur industrial area is notably much comparable or even higher than the other industrial areas (Al-Khashman and Shawabkeh 2006; Sofianska and

Michailidis 2015; Pastrana-Corral et al. 2017). Elevated Cr and Pb concentrations imply their higher accumulation in soils due to industrial activities, agricultural input and leachate from dumped waste materials (urban as well as industrial) along with chemical weathering of soil parent materials. The concentrations of Hg and Cd in surface soil are generally least abundant. Though, previous many researchers explored that the main input of toxic Hg and Cd in urban and industrial surface soil is due to fossil fuel combustion (Pastrana-Corral et al. 2017; Wang et al. 2017). Additionally, the presence of Hg, Cd, Cu, Pb and Ni in the surface soil of studied region could also be due to atmospheric transport by the wind as solid particles emitted from various industries such as coal-based thermal power plant, steel and alloy, chlor-alkali and sponge iron industries in the Durgapur industrial belt (Nayek et al. 2013).

Pollution indices

The C_f and PLI are commonly used to assess the level of toxic metal contamination in the soils (Bhuiyan et al. 2010). The C_f values in various sampling sites are represented in Table 3. The average value of C_f for the PTMs in the studied soils follows the decreasing order of Hg > Cd > Pb > Fe > Cr > Ni > Cu. As shown in Table 3, the soils in the study region are classified as moderately contaminated with Cr (1.80–2.82), Cu (1.15–1.82) and Ni (1.49–2.64); considerably contaminated with Pb (3.68–4.71) and Fe (3.10–4.20); and highly contaminated with Cd (10.86–29.50) and Hg (39.33–60.83). The average C_f value is high for Pb (4.13), Cd (19.62) and Hg (49.48) in the studied soils due to industrial emission, higher traffic density and unplanned disposal of industrial wastes (Barman et al. 2000; Al-Khashman and Shawabkeh 2006; Gupta et al. 2010; Pobi et al. 2017). The surface soil of the Durgapur industrial area is moderately to highly contaminated by the aforementioned metals in different degrees in the all sampling sites and shows a certain pollution trend. Therefore, the analyzed C_f values suggest that the Durgapur industrial soil is heavily affected by large-scale industrial and urban activities, consistent with earlier researchers (Bhuiyan et al. 2010; Banerjee and Gupta 2013). The overall metal pollution load index (i.e., PLI) is calculated for every sampling site using background reference value and shown in Fig. 2. The resulted PLI values (Fig. 2)

Table 3 Contamination factor (C_f) of heavy metals in soil samples of Durgapur industrial area

Sampling sites	Pb	Cd	Cr	Fe	Cu	Ni	Hg
S1	3.94	13.24	2.66	4.20	1.61	2.32	44.17
S2	3.86	10.86	2.56	4.08	1.46	2.13	39.33
S3	3.89	12.40	2.63	4.13	1.56	2.23	41.33
S4	4.60	19.56	2.82	3.94	1.77	2.64	52.33
S5	4.53	14.87	2.77	3.91	1.72	2.52	47.50
S6	4.57	16.83	2.79	3.93	1.73	2.62	51.00
S7	4.71	29.50	2.61	4.01	1.82	2.20	60.83
S8	4.64	27.77	2.55	3.98	1.77	2.10	54.17
S9	4.60	28.76	2.60	4.00	1.81	2.16	59.67
S10	4.18	24.48	2.38	3.80	1.65	1.95	54.00
S11	4.10	23.54	2.32	3.74	1.56	1.80	52.67
S12	4.16	24.14	2.36	3.76	1.64	1.93	53.00
S13	3.81	20.56	2.15	3.46	1.42	1.66	49.67
S14	3.76	19.36	2.08	3.41	1.35	1.62	47.00
S15	3.79	20.31	2.13	3.43	1.40	1.64	47.67
S16	3.75	16.60	1.86	3.28	1.25	1.55	46.33
S17	3.68	14.48	1.80	3.10	1.15	1.49	44.67
S18	3.71	15.86	1.82	3.24	1.23	1.52	45.33
Min	3.68	10.86	1.80	3.10	1.15	1.49	39.33
Max	4.71	29.50	2.82	4.20	1.82	2.64	60.83
Mean	4.13	19.62	2.38	3.74	1.55	2.00	49.48
SD	0.38	5.73	0.34	0.34	0.21	0.38	5.79

range from 4.19 to 6.21 (mean 5.22, > 5), confirming high to very high metal pollution in the study soil. The map of PLI value for PTMs displays that 44% of sampling sites (at S2, S3 and S13–S18) are highly polluted, whereas 56% sampling sites (S1 and S4–S10) are at very highly polluted level. Obtained PLI values from studied sampling sites do not show any specific trend, which can be linked to the diverse characteristics of each sites, such as various pollution sources, amount of waste disposal from the industrial as well as urban sectors (Ahmad et al. 2010; Islam et al. 2018).

The enrichment factor (EF) is widely used to find their occurrences and also to evaluate the magnification of metal contamination by comparing soil metal concentrations with the relevant geochemical background values (Barkett and Akün 2018). The results of EF of surface soils are represented in Fig. 3, where Fe has been chosen as a reference element for calculation. The calculated enrichment factor value for the examined PTMs in surface soils is as follows: Pb (0.94–1.19); Cd (2.66–7.35); Cr (0.56–0.71); Cu (0.36–0.45); Ni (0.47–0.67); and Hg (9.63–15.16).

As shown in Fig. 3, significant metal enrichment is observed for Hg (at all sampling sites) and Cd (at S7–S16) and moderate enrichment for Cd (at S1–S6, S17 and S18) of studied soils. However, the obtained results of EF for remaining toxic metals show minimal enrichment in all industrial soils. Based on EF values, PTMs in studied soils follow the order of $Hg \gg Cd \gg b > Cr > Ni > Cu$. The abundance of Hg and Cd is generally low in surface soils in comparison with other PTMs, and their high enrichment is mainly derived from various anthropogenic sources such as metallic industries, fossil fuel combustion and high traffic density and slightly influenced by lithogenic contributions (Al-Khashman and Shawabkeh 2006; Wang et al. 2017). The EF value of Pb is found > 1 in most of the sampling sites (except S1, S2 & S3), suggesting the higher Pb enrichment in surface soils may be due to the burning of fossil fuel and radial transportation in the studied region (Al-Khashman 2012; Krishna and Mohan 2016). Such high EF value of PTMs in the surface soils of many industrial or urban areas in the world has been examined by earlier studies (Bhuiyan et al. 2010). Most of the studies have

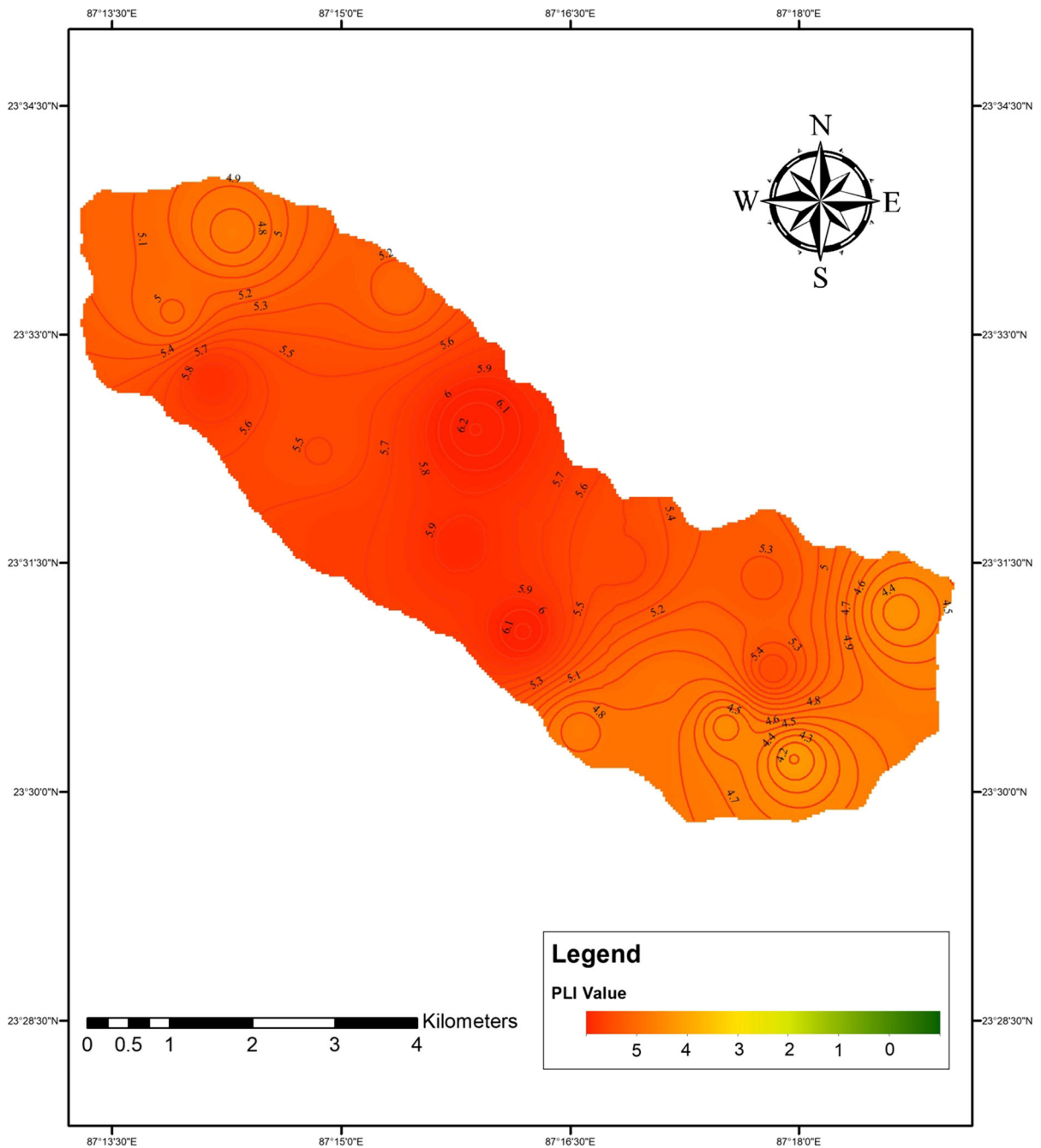


Fig. 2 Spatial distribution of pollution load index (PLI) in Durgapur industrial soils

reported similar or even higher enrichment factors for PTMs in urban and industrial soils caused by industrial and vehicular emissions. In this study, the observed values for PTMs enrichment in surface soils of Durgapur industrial area are consistent with the earlier investigations (Barman et al. 2000; Gupta et al. 2010;

Kisku et al. 2011) and very much comparable with other industrial areas in India and worldwide (Al-Khashman and Shawabkeh 2006; Chabukdhara and Nema 2013; Pathak et al. 2015; Krishna and Mohan 2016; Alsbou and Al-Khashman 2018). Therefore, the above results infer that the examined metals in surface

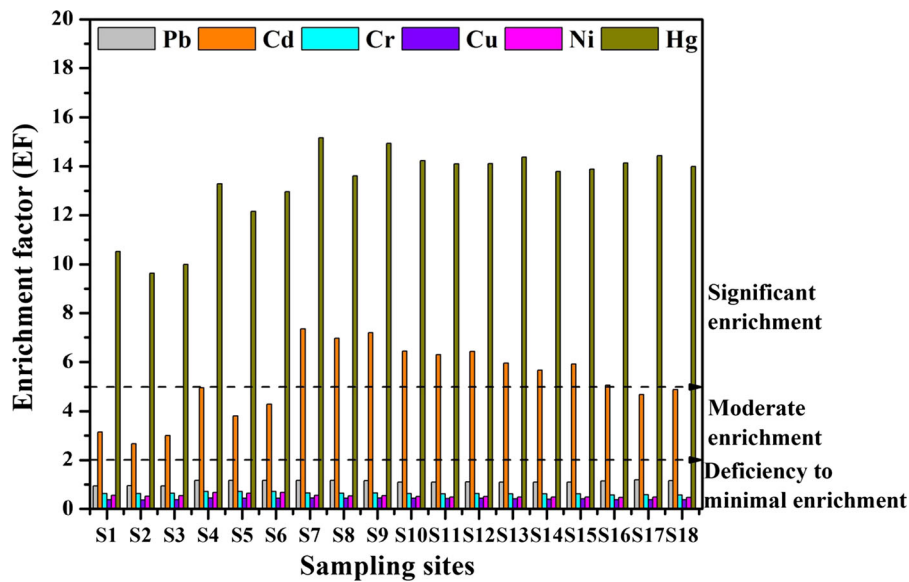


Fig. 3 Spatial variations of enrichment factor (EF) for heavy metals in the study area

soils of Durgapur industrial area may be originated from various anthropogenic activities such as industrialization, urbanization, vehicular emission, leachate from industrial/urban wastes and atmospheric depositions (Gope et al. 2018).

The geo-accumulation index (I_{geo}) is the quantitative indicator to evaluate the magnitude of PTMs accumulation in the soils (Muller's 1969). The map of I_{geo} value for each metal is shown in Fig. 4. The range of I_{geo} values for the studied metals is 1.31–1.63, 3.02–4.26, 0.29–0.90, 1.10–1.46, –0.31 to 0.27, 0.02–0.79 and 4.73–5.22 for Pb, Cd, Cr, Fe, Cu, Ni and Hg, respectively. Based on I_{geo} value, the sequence of PTMs in studied soils (Fig. 4) is as follows: Hg > Cd > Pb > Fe > Cr > Ni > Cu and consistent with the contamination factors (C_f). According to Muller's (1969) classification, I_{geo} values for Cu (in S2 and S13–S18) and Ni (in S17) are ≤ 0 and correspond to class 1, indicating that there is no pollution by these metals. While the I_{geo} values for Cr (in all sampling site) and Cu and Ni (in rest sites) fall in class 2, reflecting that the investigated soils are uncontaminated to moderately contaminated by these metals. However, the contamination of Cu and Ni at these sites is may be due to excessive industrial emissions and solid waste disposal (Krishna and Mohan 2016). The values of I_{geo} for Pb and Fe in all sampling site correspond to class 3, suggesting that the investigated soils are moderately contaminated by

these metals. However, the determined I_{geo} values demonstrate that studied soils are moderately to heavily contaminated (Class 4) for Cd (at S2); heavily contaminated (class 5) for Cd (at S1, S3–S6, S11 and S14–S18); heavily to extremely contaminated (class 6) for Cd (at S7–S10 and S12) and Hg (at S1–S3, S5 and S14–S18); and extremely contaminated (class 7) for Hg (at S6–S13). Therefore, it can be assumed that the higher metal accumulation in the study soils is mainly due to industrial activities, including industrial emissions, sewage sludge, municipal/industrial solid wastes and slightly influenced by agricultural input and/or geological factors (Charlesworth et al. 2003; Krishna and Mohan 2016). The higher accumulation of PTMs in surface soils of Durgapur may cause alteration in physicochemical properties of soils and thus influence the distribution of vegetative species in the study area (Al-Khashman 2012; Sofianska and Michailidis 2015).

The results of potential risk factor (E_r^i) and ecological risk index (RI) for selected PTMs (viz., Pb, Cd, Cr, Cu, Ni and Hg) are shown in Table 4 and Fig. 5. The calculated potential ecological risk factor (E_r^i) of PTMs in soil samples is as follows: 18.42–23.56 for Pb, 325.89–885 for Cd, 3.6–5.63 for Cr, 5.75–9.11 for Cu, 7.45–13.18 for Ni and 1573.33–2433.33 for Hg (Table 4). The mean value of E_r^i of the studied metals in soil samples is in the order of Hg (1979.26) >> Cd (588.52) >> Pb (20.64) > Ni (10.02) > Cu

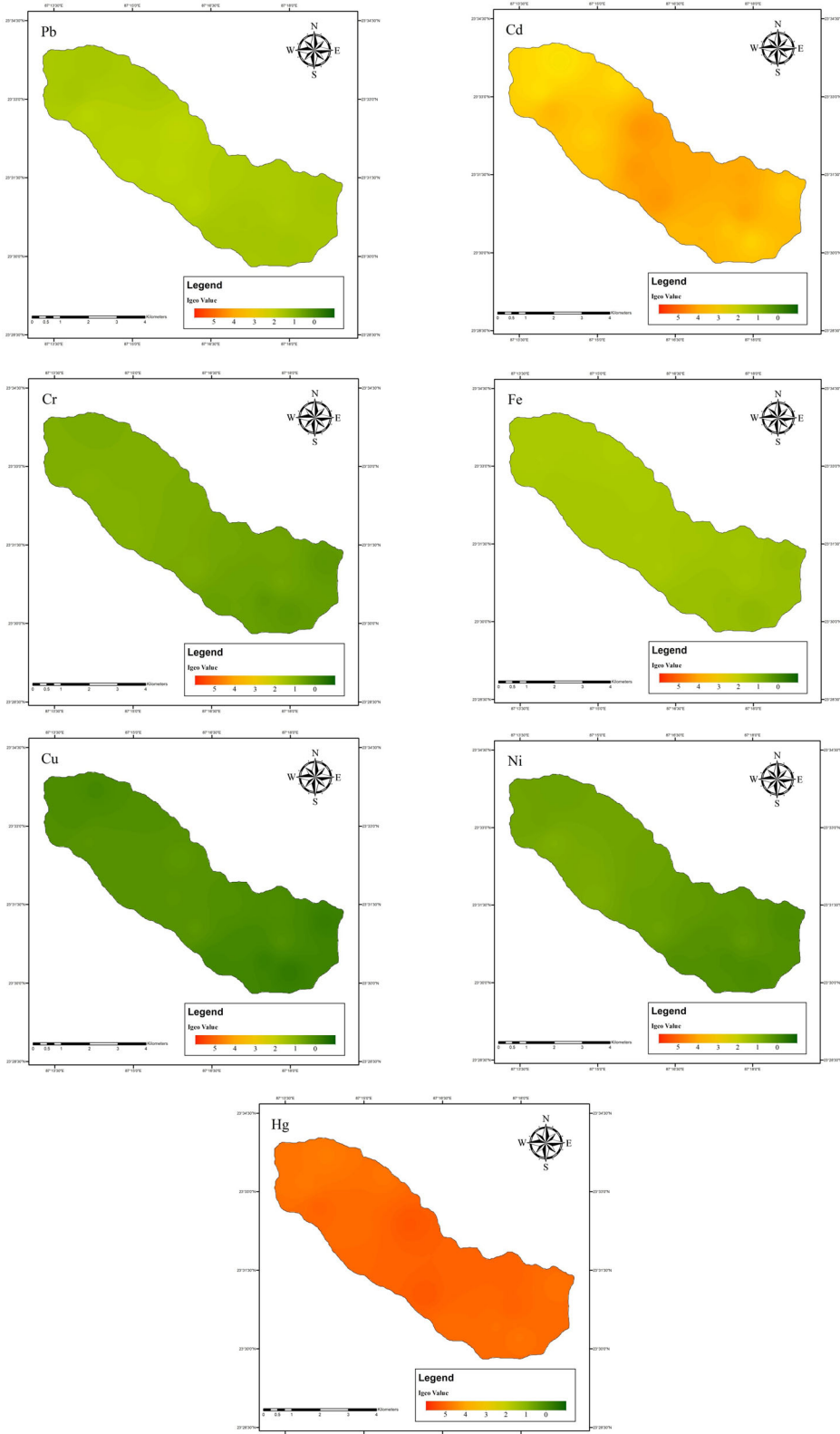


Fig. 4 Spatial distribution of geo-accumulation index (I_{geo}) values for each metal in Durgapur industrial soils

(7.75) > Cr (4.76). The calculated E_r^i values (Table 4) for Pb, Cr, Cu and Ni are much lower than 40 in all sampling sites, which indicates low potential ecological risk criteria (Hakanson 1980). Among the selected PTMs, only Cd and Hg show higher E_r^i values and possess very high ecological potential risk in all sampling sites, suggesting that Cd and Hg are the main causes of potential ecological risk in surface soils in Durgapur industrial area which is consistent with earlier findings on various urban and industrial cities worldwide (Krishna and Mohan 2016; Wang et al. 2017).

A comprehensive potential ecological risk index (RI) is used to quantify the degree of ecological risk in surface soils and is calculated by using the sum of potential ecological risk factor (E_r^i) of selected PTMs (Hakanson 1980). As shown in Fig. 5, the calculated

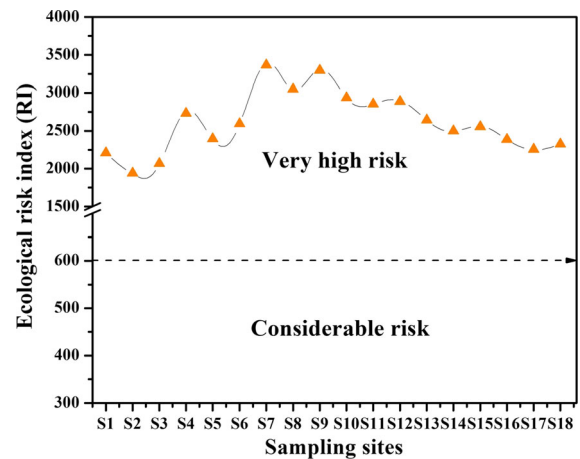


Fig. 5 Potential risk index (RI) of the heavy metals at the different sampling sites in the Durgapur industrial soils

RI value varies from 1941.60 to 3367.23 (mean 2610.96) which is much higher than 600 (Hakanson 1980). The above results demonstrate high ecological

Table 4 Potential ecological risk factor (E_r^i) for the heavy metals in Durgapur industrial soils

Sampling sites	Pb	Cd	Cr	Cu	Ni	Hg
S1	19.71	397.14	5.31	8.03	11.62	1766.67
S2	19.31	325.89	5.11	7.32	10.64	1573.33
S3	19.47	372.14	5.27	7.82	11.14	1653.33
S4	22.99	586.79	5.63	8.85	13.18	2093.33
S5	22.63	446.07	5.54	8.61	12.60	1900.00
S6	22.87	505.00	5.57	8.64	13.10	2040.00
S7	23.56	885.00	5.21	9.11	11.01	2433.33
S8	23.22	833.04	5.11	8.86	10.50	2166.67
S9	23.01	862.86	5.20	9.07	10.81	2386.67
S10	20.89	734.29	4.76	8.24	9.75	2160.00
S11	20.52	706.25	4.64	7.79	9.02	2106.67
S12	20.78	724.29	4.71	8.18	9.65	2120.00
S13	19.06	616.79	4.30	7.10	8.30	1986.67
S14	18.79	580.71	4.15	6.76	8.12	1880.00
S15	18.94	609.29	4.27	6.99	8.19	1906.67
S16	18.74	497.86	3.72	6.26	7.73	1853.33
S17	18.42	434.29	3.60	5.75	7.45	1786.67
S18	18.57	475.71	3.65	6.16	7.58	1813.33
min–max	18.42–23.56	325.89–885.00	3.60–5.63	5.75–9.11	7.45–13.18	1573.33–2433.33
Mean	20.64	588.52	4.76	7.75	10.02	1979.26
Overall risk status	Low	Very high	Low	Low	Low	Very high

risk of the selected PTMs, and the entire study area is classified under the category of very high risk level.

Health risk assessment in the study area

Ingestion of soil particles is considered to be the main exposure route for metal and metalloids to the human body (Ferreira-Baptista and De-Miguel 2005). The present investigation (Table 5) reveals that children are in higher risk from ingestion of soil compared to adults in Durgapur industrial area, which can be explained that children have a tendency to ingest substantial quantities of the soil due to their hand-to-mouth activity while playing on the ground (Cao et al. 2018). This observation is very much consistent with earlier reports on PTMs contents in street dust of Durgapur industrial belt (Gope et al. 2018). The sequence of occurrence of non-carcinogenic effects of studied PTMs to the children among the different exposure route is: ingestion > dermal > inhalation except for Fe, where the sequence is: dermal > ingestion > inhalation (Table 5). For adults, the prime exposure to Cu, Ni, Pb and Hg is through the ingestion route, while Cd, Cr and Fe follow dermal route as the major exposure pathway (Gope et al. 2018).

HI values are < 1 for all the metals studied in the present work, indicating the absence of non-carcinogenic risks to children and adults. The HI values of Cr

and Cd for children are 0.637 and 0.471, respectively, which indicated an alarming condition for near future in Durgapur industrial area. HI values in the industrial soil of Durgapur for studied PTMs decrease in the order: Cr > Cd > Pb > Hg > Ni > Cu > Fe for child, whereas for adult the sequence is: Cd > Cr > Pb > Hg > Fe > Ni > Cu (Table 5).

Carcinogenic risks of Cd, Cr and Ni to children and Cd and Cr to adults are higher than the unacceptable level (1×10^{-4}) of health risk in the present study (Table 5). Children are much more susceptible to cancer health effects of soil PTMs as carcinogenic risk to children is higher compared to that to adults (Gope et al. 2018). Cd is the foremost contributor for the carcinogenic risk compared to Cr, Ni and Pb. Cd ($5.5E-03$), Cr ($8.6E-04$) and Ni ($3.0E-04$) have displayed the presence of carcinogenic risk to children, while Cd ($8.2E-04$) and Cr ($1.3E-04$) have indicated the presence of cancer risk to adults in Durgapur (Table 5). Pb ($4.5E-05$) and Ni ($1.6E-06$) for adults and only Pb ($1.1E-05$) for children have revealed a chance of occurrence of cancer risk to adults in near future as health risk values are between 1×10^{-6} and 1×10^{-4} . It is an alarming condition in Durgapur as the carcinogenic risk assessment revealed existence of cancer risk mainly to children followed by adults.

Table 5 Calculated hazard quotient (HQ) and hazard index (HI) values for heavy metals in Durgapur industrial soils

Target	Type of risk	Exposure route		Cd	Cr	Cu	Fe	Ni	Pb	Hg		
Child	Non-carcinogenic risk	Ingestion	HQ	3.7E-01	5.7E-01	1.4E-02	4.2E-04	1.6E-02	3.7E-01	1.1E-01		
		Inhalation		1.8E-03	1.7E-03	3.9E-07	1.4E-06	4.5E-07	1.0E-05	1.1E-05		
		Dermal		1.0E-01	6.4E-02	1.3E-04	4.5E-03	1.7E-04	6.9E-03	4.4E-03		
		HI		0.471	0.637	0.014	0.005	0.017	0.375	0.114		
	Carcinogenic risk	Ingestion		5.5E-03	8.6E-04	–	–	3.0E-04	1.1E-05	–		
		Inhalation		6.4E-08	2.0E-06	–	–	7.7E-09	1.5E-09	–		
		Total		5.5E-03	8.6E-04	–	–	3.0E-04	1.1E-05	–		
		Adult	Non-carcinogenic risk	Ingestion	HQ	5.5E-02	8.6E-02	2.1E-03	6.4E-05	2.5E-03	5.5E-02	1.6E-02
				Inhalation		1.4E-03	1.4E-03	3.1E-07	1.1E-06	3.5E-07	8.1E-06	8.5E-06
Dermal				2.2E-01	1.4E-01	2.8E-04	9.7E-03	3.6E-04	1.5E-02	9.4E-03		
HI		0.276		0.224	0.002	0.010	0.003	0.070	0.026			
Carcinogenic risk	Ingestion		8.2E-04	1.3E-04	–	–	4.5E-05	1.6E-06	–			
	Inhalation		5.1E-08	1.6E-06	–	–	6.1E-09	1.2E-09	–			
	Total		8.2E-04	1.3E-04	–	–	4.5E-05	1.6E-06	–			

The hazard index (HI) values and total values of carcinogenic risk for potential toxic metals are highlighted in bold

Statistical summary

Pearson's correlation analysis

The statistical correlation analysis has been performed between soil properties and PTMs concentrations in the studied soils to assess the dynamics of measured variables and identify possible similar sources. The Pearson's correlation matrix of analyzed variables is represented in Table 6a. Very strong significant positive correlation is observed between Pb–Cu (0.929), Cd–Hg (0.957), Fe–Cr (0.934), Cr–Cu (0.9) and Ni–Cr (0.967) and significant positive correlation is also observed between Fe–Cu (0.834), Fe–Ni (0.849) and Cu–Ni (0.825), which clearly suggest that these metals in the studied soil have a common source/origin, i.e., anthropogenic inputs, such as large scale of industrial activities, leachate from industrial/urban waste and agricultural activities (Banerjee and Gupta 2013; Krishna and Mohan 2016; Wang et al. 2017). The presence of Hg, Cd and Pb in studied soils could be due to the atmospheric deposition resulted from various industrial (i.e., coal-based thermal power plant, pharmaceutical and many other chemical industries) emissions as solid particulate form (Zhao et al. 2014). The abundance of PTMs in soil environment is influenced by various soil physicochemical properties, such as pH, EC, CEC, OM and soil texture (Laing et al. 2008). Soil pH shows significant positive correlation with Pb (0.833) and Cu (0.902) and moderate positive correlation with other PTMs (Table 6a), suggesting that higher pH values favor the accumulation of PTMs in the studied soils (Gao et al. 2013). Further, significant strong relationships among Cr, Ni, Fe and Cu, and their abundance and distribution in industrial soils are primarily contributed by the discharges from different metallurgical industries (such as iron and steel, sponge iron and ferro-alloy industries) in the study area (Zhao et al. 2014; Pobi et al. 2017). Soil clay content is strongly correlated with Cr (0.869) and moderately correlated with Fe (0.8) and Cu (0.777) and suggests that these PTMs are secondarily associated with a different source, most likely related to natural processes (surface influx) and geogenic sources (Banerjee and Gupta 2013; Wang et al. 2017). Overall, the results show that the PTMs in studied soils are predominately originated from large-scale industrial discharges, leachate from urban and industrial wastes and radial

vehicular transportation. The natural process and geogenic input could be additional sources of metal pollution in the study area. A portion of toxic metals in studied soil may also be attributed due to industrial emissions containing appreciable amounts of particular heavy metals with fume and dusts (Guo et al. 2012; Čujić et al. 2016) and can be a possible source of metal pollution.

Principal component analysis (PCA)

Principal component analysis (PCA) is used to evaluate the grouping behavior of PTMs in soils in order to identify the potential sources (Yu et al. 2011; Krishna and Mohan 2016). The PCA results were obtained by employing varimax rotation with Kaiser normalization, and the factor loading matrix, eigenvalues and cumulative variance are presented in Table 6b. Three principal components (PC1, PC2 and PC3) were extracted with eigenvalues > 1, accounting for cumulative variance of 83.74% for the soil samples. The first component (PC1) describes 40.71% of the total variance and shows strong positive loadings for Pb (0.915), Cr (0.882), Fe (0.822), Cu (0.979), Ni (0.822) and Hg (0.657) along with pH (0.859), indicating that these metals might be derived from mixed pollution sources, showing primarily higher anthropogenic control (such as large industrial activities and leachate from urban and industrial overburden waste materials) and slightly geogenic inputs and weathering of soils, which is consistent with the above results of correlation analysis (Zhao et al. 2014). The second component (PC2) explains 27% of the total variance and exhibits strong positive loadings for EC (0.836), CEC (0.807), Cd (0.643) and silt (− 0.817) and moderate loading for Hg (0.588) and OM (0.553), suggesting their strong connection with agricultural runoff containing organic components and metals from residues of pesticides and insecticides. Cd and Hg show notable loading in both PC1 and PC2, suggesting Cd and Hg may be attributed to different pollution sources in the Durgapur industrial areas such as industrial emissions and atmospheric deposition in the study area. Herein, EC, CEC and OM in PC2 show their individual soil characteristics. The third component PC3, explaining 16.03% of the total variance, is strongly associated with clay (− 0.857) and sand (0.911) with less association of some PTMs, and they

Table 6 (a) Pearson's correlation matrix for soil physicochemical properties and total metal concentration in studied soils. (b) Rotated component matrix from PCA analysis

Variables	pH	EC	CEC	OM	Clay	Silt	Sand	Pb	Cd	Cr	Fe	Cu	Ni	Hg
(a)	1													
pH	1													
EC	-0.109	1												
CEC	0.629**	0.629**	1											
OM	0.401	0.638**	0.469*	1										
Clay	0.049	0.328	0.489*	0.603**	1									
Silt	0.240	-0.685**	-0.826**	-0.630**	-0.669**	1								
Sand	-0.130	0.120	0.019	-0.293	-0.794**	0.079	1							
Pb	0.693**	0.100	-0.211	-0.377	-0.216	0.247	0.087	1						
Cd	0.557*	0.395	0.261	-0.103	-0.038	-0.195	0.210	0.574*	1					
Cr	0.643**	-0.264	-0.381	-0.546*	-0.219	0.444	-0.069	0.767**	0.107	1				
Fe	0.662**	-0.313	-0.417	-0.607**	-0.242	0.487*	-0.074	0.629**	0.104	0.932**	1			
Cu	0.794**	-0.033	-0.209	-0.498*	-0.239	0.321	0.058	0.922**	0.523*	0.896**	0.833**	1		
Ni	0.576*	-0.249	-0.386	-0.467	-0.210	0.449	-0.085	0.758**	-0.021	0.964**	0.845**	0.825**	1	
Hg	0.646**	0.348	0.259	-0.189	-0.068	-0.140	0.206	0.737**	0.940**	0.272	0.195	0.651**	0.203	1
Variables	Components													
	PC1													
	PC2													
	PC3													
(b)														
pH	0.859								0.059					0.015
EC	-0.038								0.836					-0.022
CEC	-0.184								0.807					-0.138
OM	-0.458								0.553					-0.453
Clay	-0.093								0.461					-0.857
Silt	0.270								-0.817					0.291
Sand	-0.095								0.049					0.911
Pb	0.915								0.090					0.187
Cd	0.517								0.643					0.397
Cr	0.882								-0.367					-0.073
Fe	0.822								-0.422					-0.054
Cu	0.979								-0.032					0.137
Ni	0.822								-0.396					-0.118
Hg	0.657								0.588					0.370

Table 6 continued

Variables	Components		
	PC1	PC2	PC3
Eigenvalue	5.699	3.780	2.245
Variability (%)	40.707	27.002	16.033
Cumulative (%)	40.707	67.710	83.742

The significant correlation values are highlighted in bold, and the significance level mentioned at the bottom of the table

*Correlation is significant at the 0.05 level (two-tailed)

**Correlation is significant at the 0.01 level (two-tailed)

might be attributed due to the geogenic factors or soil properties (Banerjee and Gupta 2013).

Cluster analysis (CA)

Hierarchical cluster analysis (CA) is usually performed for grouping of soil variables by looking at their strong interrelationship and to identify the possible sources (Krishna and Mohan 2016; Wang et al. 2017; Barkett and Akün 2018). In the present study, cluster analysis is performed using Ward's Euclidean distance method and results shown in dendrogram (Fig. 6). The results of CA are in good agreement with those of correlation matrix and principal component analysis (PCA). Three distinct clusters are observed from Fig. 6, as in dendrogram. The first cluster C1 comprises two sub-clusters. The first sub-cluster includes Cr, Fe and Ni, and it clearly represents that these elements in studied soil are predominantly controlled by parent materials as well as other anthropogenic activities in the studied region (Yu et al. 2011; Wang et al. 2017) and consistent well enough with PC1. Second sub-cluster associates with Pb, Cu and pH and confirms that these metals have a similar pollution source. It also shows that Pb and Cu are principally originated by various anthropogenic activities such as large industrial activities, agricultural input and solid waste disposal (Hu et al. 2013). Another source of Pb in the surface soils is probably attributed from intensive vehicular emissions in the studied region (Hu et al. 2013; Gope et al. 2018). The second cluster C2 is associated with Cd, Hg, silt and sand. Soil Cd and Hg in this cluster are mainly attributed from higher industrial activities and atmospheric deposition in the study area and correlated fairly well with PC2. However, third cluster C3 comprises soil basic properties, i.e., OM, EC, CEC and clay, which is consistent with PC3.

This study provides the baseline information about the distribution of potentially toxic metal and suggests their significant origin in surface soils of the studied area. The application of GIS mapping tool on pollution indices clearly distinguishes the overall pollution status due to the toxic metal enrichments and ecotoxicity. Human health risk assessment study reveals that the carcinogenic risk on exposure of total metals concentrations is in an alarming condition. Further investigation is needed on chemical speciation of studied metals in relation to soil properties to explore

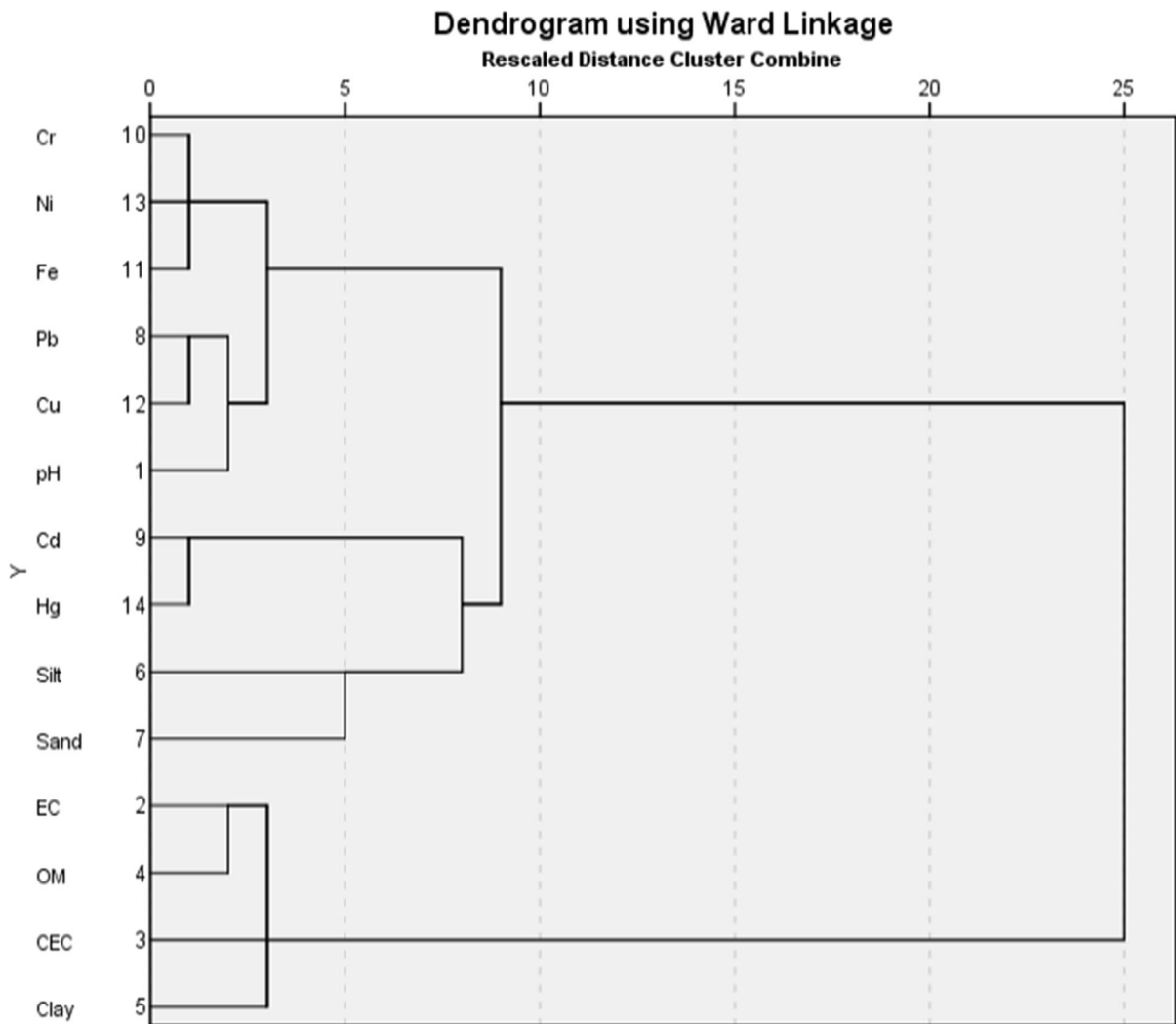


Fig. 6 Hierarchical cluster analysis of analyzed variables in soil samples

the bioavailability and mobility of toxic metals which are sufficient threats for biota and groundwater contamination. In addition, future study on other alternative human exposure pathways can be very much crucial and preventive measures should be taken before discharging/releasing the industrial hazards to the surface soils and aquatic environment in the examined area.

Conclusions

The investigation shows that the surface soils of Durgapur industrial area are moderately to highly

contaminated by the PTMs. The results of enrichment factor values exhibit that the studied soils are moderately enriched by Cd and highly enriched by Hg. Based on PLI values, the plotted GIS map indicates that 56% of sampling sites (S1 and S4–S10 sites) are classified as ‘very highly polluted,’ while remaining 44% of sampling sites (S2, S3 and S13–S18) are at ‘highly polluted’ level. However, the result for geo-accumulation index reveals that the examined soils are practically uncontaminated to moderately contaminated with Cr, Cu and Ni, moderately contaminated with Pb and Fe and heavily to extremely contaminated with Cd and Hg. The calculated value of contamination factor and geo-accumulation index exhibits the

similar sequence of metal contamination: Hg > Cd > Pb > Fe > Cr > Ni > Cu. Soil physicochemical properties, i.e., pH, EC, CEC, OM and clay contents, play an important role in distribution and retention of PTMs in studied soils. The potential ecological risk index illustrates that Cd and Hg possess very high potential ecological risk of all soil samples and sampling sites, while the risk of other toxic metals is in moderate to lower range. Multivariate statistical analysis demonstrates that PTMs enrichment in soils is mainly associated with industrial discharges, anthropogenic sources and atmospheric deposition, with limited contribution from geological weathering. The present study provides baseline information on exposure of PTMs and can assist governmental or non-governmental authorities to take necessary steps. Results of non-carcinogenic health risk assessment show no risk of PTMs in the studied region. Carcinogenic risk assessment of PTMs displays the presence of cancer risk in the studied soils, which leads to frightening situation in Durgapur. Detailed in-depth investigation regarding bioavailable metal fractions in industrial soil and associated health risk is still required considering other exposure routes (water, food) to analyze the total hazard caused by individual metal.

Acknowledgements Authors sincerely acknowledge DST-FIST (SR/FST/CSI-267/2015 (C)) and National Institute of Technology (NIT), Durgapur, for creating and providing infrastructural facilities throughout the research work. Authors also greatly acknowledge DST, GOI, for partial financial support (Project No. SB/EMEQ-115/2013 dated 08.07.2013).

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