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Potentially toxic elements in soil and road dust around Sonbhadra industrial region, Uttar Pradesh, India: Source apportionment and health risk assessment

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ABSTRACT

Potentially toxic elements (PTEs) are directly linked with various kinds of adverse health issues. Available reports related to symptoms of mercury contamination in the local population of the study region motivated us to carry out this work in detail. To estimate potentially toxic elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn) contamination status, a total of 48 samples of soil & road dust from industrial clusters were collected and analyzed for source identification and human health risk assessment in the Sonbhadra region of Uttar Pradesh, India. As per upper continental crust (UCC) for soil and road dust, the highest increment of As value in Obra and Hg value in Anpara was observed. The value of Hg exceeded the background value by 6.5 and 12.25 times in soil and 5 and 11.5 times in road dust of Obra and Anpara clusters, respectively. Contamination factor (CF) and Enrichment factor (EF) value in soil and road dust showed very strong contamination and significant enrichment of Hg whereas moderate contamination and moderate enrichment of As were observed in both the clusters. The hazard quotient (HQ) value of potentially toxic elements in soil and road dust of Obra and Anpara were found <1 for three pathways in adults and children, except Fe for ingestion pathway for children in both clusters. The HQ value for adults was observed to be low compared to children. Cancer risk associated with potentially toxic elements in soil and road dust for both clusters were found safe (under the guideline 10^{-4} - 10^{-6}) in adult and children instances for three pathways. Principal component analysis (PCA) justified the metal content in soil and road dust controlled by the mixed type of both natural and anthropogenic sources.

1. Introduction

Potentially toxic elements are widely distributed on the earth's crust. It is a well-known fact that industrialization and urbanization lead to an increasing concentration of potentially toxic elements in different components of the environment. This results in many environmental hazards pertinent to the human population (Nagajyoti et al., 2010; Luo et al., 2011, 2012; Madhay et al., 2020).

In urban and industrial regions, soil and road dust are major indicators of degradation in the environment. The composite structures of urban soils are heterogeneous mixtures of various materials and associated pollutants that result from various processes. Road dust consists of both natural and anthropogenic particles. Natural particles mainly

constitute soil minerals whereas anthropogenic particles originate from road construction materials (concrete, asphalt, and road paint), automobiles (dust generated from tire & brake, tailpipe exhaust, and body rust), industrial inputs, or depositions of atmospheric emission. The key potentially toxic elements in road dust, therefore, are Pb from gasoline, and Zn, Cu, and Cd from tire abrasions, car components, lubricants, incinerator, and industrial emissions (Markus and McBratney, 1996; Wilcke et al., 1998). Several studies substantiate that potentially toxic elements pollution is principally derived from manmade sources like emission from the high load of traffic (particles generated from vehicular exhaust, brake lining wear, tire wear, weathered surface of street surface), emission from different types of industries (coal-fired power plant, chemical plant, Mining, metallurgical industry, auto repair shop,

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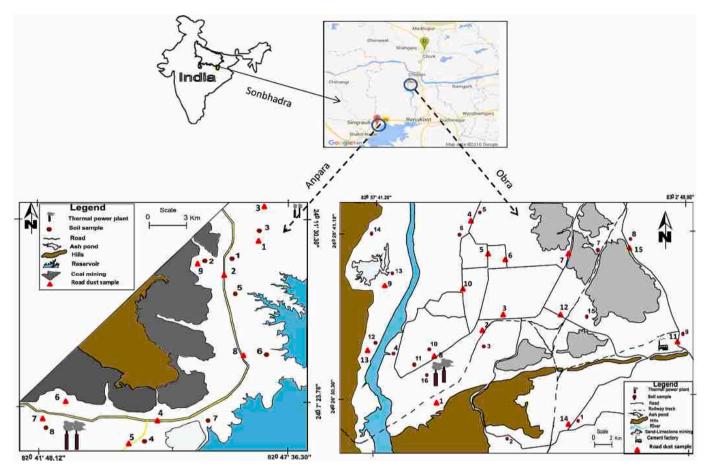


Fig. 1. Physiographic map showing the sampling locations of soil and road dust collected from Obra and Anpara industrial cluster.

etc.), emission from household activities, minute particles generated from weathering of building and pavement surface, atmospheric deposition, etc. (Sezgin et al., 2004; Ahmed and Ishiga, 2006; Banerjee, 2003; Faiz et al., 2009; Wei and Yang, 2010). Additionally, many studies have concluded that potentially toxic elements pollution not only degrades atmospheric quality, water bodies, soil, and food crops but also threaten the whole environment through their interaction with the food chain (Dong et al., 2011; Nabulo et al., 2010; Li et al., 2014). Humans are exposed to chemical mixtures than a single pollutant in soil and it is obvious that the interchanging of pollutants occurs between different environmental compartments (soil, dust, air, vegetation, water, and sediment).

During coal mining weathered and excavated materials are often deposited in nearby areas in the form of mine waste and mine dust (Bhuiyan et al., 2010). Annually, over 750 million tons (Mt) of ash is produced by coal-based power generation across the globe (Blissett and Rowson, 2012; Ram et al., 2015). Coal-burning exhaust is typically enriched with volatile inorganic species including cadmium, arsenic, mercury, boron, selenium, organometallic compounds, and other gaseous components (Hower et al., 2013). Furthermore, coal-dependent industries can singly emit fly ash along with fugitive dust originating from lignite transportation and ash disposal which results in the addition of toxic elements into a different component of the environment (Samara, 2005; Nanos and Rodriguez Martin, 2012; Usmani and Kumar, 2017; Sarode et al., 2010; Gao et al., 2013).

In recent years, there has been a growing concern for the probable contribution of potentially toxic elements toxicity in humans (Chirenje et al., 2006; Men et al., 2020). The direct accumulation of potentially toxic elements in the human body takes place through inhalation, ingestion, and dermal absorption present in soils and road dust (Poggio et al., 2008; Lim et al., 2008). A number of studies have reported that

these toxic metals could result in severe organ damage in bodies like liver damage, renal failure, muscle cramps, respiratory failures, birth defects, lung cancer, skin cancer, heart disorder, neurological problems among others (Ahamad et al., 2019, 2020; Khan et al., 2013; Alam et al., 2012).

In the Sonbhadra region, a hub of mining operations, there are a significant number of coal-dependent industrial establishments. Though, few studies have reported contamination of potentially toxic elements in soil (Agrawal et al., 2010, 2011; Sahu et al., 2014). As per the observation of available literature related to metal contamination of road dust in Sonbhadra district, this is the first attempt to assess the PTEs in road dust. No study has been done earlier on human health risk assessment due to exposure of PTEs in soil and road dust of the study area. A report published in 2012 by an environmental NGO, the Centre for Science and Environment (CSE) revealed the adverse effects of exposure to toxic metals especially mercury in the local population which motivated us to conduct this research work in detail. In that context, this study attempts to evaluate the contamination status of potentially toxic elements in soil and road dust along with their enrichment, source apportionment, and human health risk assessment (cancer risk and non-cancer risk) due to exposure of PTEs through different pathways in two industrial clusters of Sonbhadra region.

2. Study area and methodology

2.1. Location

Geographically, Sonbhadra district is located between $23^{\circ}52'$ to $24^{\circ}55'$ N latitude and $82^{\circ}30'$ to $83^{\circ}33'$ E longitude. For this study, two industrial clusters of Obra $(24^{\circ}26'30.3''-24^{\circ}28'41.10''N)$ and $82^{\circ}57'41.20''-83^{\circ}02'48.90''E)$ and Anpara $(24^{\circ}07'23.76''-104'')$

24°11′30.30″N and 82°41′48.12″-82°47′36.30″E) having 55.50 and 89.40 Km² area were selected. The study region is dominated by different industrial and commercial activities without taking proper pollution control measures, hence these two locations were considered to understand the industrial impact on soil and road dust of the surrounding environment. The Obra cluster mostly comprises of the thermal power plant, cement factory, sandstone-limestone mining. Anpara cluster comprises mostly major coal mining and thermal power plant. The general topography of this region is undulating, mixed with flats, hills, and valleys. The geology of the area comprises varied rock formations ranging from Archaean (Bundelkhand Granitic gneisses) to recent (Ganga) alluvium. In the southwestern Sonbhadra, while younger rocks are constituted of coal-bearing Gondwana, the lower Vindhyan sediments of Sonbhadra are composed of the deposits of cement grade limestone, flux grade dolomite, and building stone. This region has a huge reserve of coal near Uttar Pradesh and Madhya Pradesh border. Since the construction of the dam the coal mining has increased extensively. At present, around 83 million tons of coal is mined from fourteen mines annually. This region also contributes around 12,700 MW of electricity from several coal-fired thermal power plants. Because of these industrial activities and due to the release of industrial air-borne and water-borne contaminants, the surrounding areas have been polluted.

2.2. Soil and road dust sampling

A total of 48 samples from Obra (16 soil & 15 road dust) and Anpara (8 soil & 9 road dust) industrial clusters of Sonbhadra were collected and analyzed for various chemical characteristics (Fig. 1). The number of samples collected from the Anpara industrial cluster was less because of the difference in land-use pattern and less availability of habitable land. All sampling sites were chosen along the roads, proximity to industries and various emission sources and closer to the habitat to observe the health related effects on residents. Each soil sample represents a composite of three to five sub-samples collected from each location. Samples weighing approximately 1 kg were collected at a depth of 0-20 cm through the use of a stainless-steel shovel. After each sample collection, the shovel was properly cleaned with acetone to avoid crosscontamination. Road dust sampling was undertaken over three consecutive days after a dry weather condition. Approximately 400 g of road dust samples were collected using a new plastic broom and dustpan from the impervious surface (major and minor roads) within a 1 m² radius of circles around each sampling site. After each sample collection, plastic broom and the dustpan were properly cleaned with acetone to avoid cross contamination. Soil and road dust samples were stored in doublelayer zip-locked polyethylene bags for transportation to the laboratory and all samples were dried at room temperature for 5–7 days. Some parts of soil samples were disaggregated in the laboratory and non-mineral material and rock fragments higher than 2 mm were discarded. The impurities in road dust samples such as pebbles and visible plant and hair parts were removed before processing. Representative soil and road dust samples were isolated by coning and quartering method. Samples were grounded in agate mortar pestle for proper homogenization. For analysis, a 63 µm (230 mesh) size fraction was used. After processing, samples were kept in a small plastic air-tight zip bags and stored till further analysis.

2.3. Background data

The control site was selected based on their distance from two industrial clusters. The farthest site from the control soil sampling site is the Anpara cluster. The control site is located in the interfluves region of Son and Kanhar River. The control soil sample materials originated from weathered products and alluvium having similar rock and mineral characteristics to the investigated study region. Since Geochemical baseline maps are yet to be available in India (currently initiated under global geochemical baseline program), therefore, three soil samples

were collected from 0 to 30 cm depth and analyzed as background (control). These samples were collected far from anthropogenic emission sources like the thermal power plants, traffic emissions, mining operations, agricultural practices, and urbanization. All three samples were processed similarly like soil and road dust collected from the study area. The mean metal concentrations of these samples were taken as local natural background data which was used for normalization.

2.4. Soil and road dust analysis

Soil and road dust samples were processed using different analytical techniques. The pH and electrical conductivity (EC) were measured in a solution of soil/road dust and water with a ratio of 1:5. The content of organic matter (OM) was determined as the loss on ignition after heating 1 g soil and road dust samples at 550 °C for 2 h (Skrbic and Cupic, 2004). Potentially toxic elements in soil and road dust were extracted by Aqua Regia microwave digestion technique. For the digestion purpose 0.1 g sample of soil and road dust was taken in PTFE vessels by adding 2.4 ml HNO₃ (65% supra-pure), 7.2 ml HCl (35% supra-pure), and 1 ml miliQ water. The microwave temperature was raised to 160 °C in 6 min (power: 1000 W), then to 190 °C in 15 min (power: 1000 W) and then kept constant 190 °C in 30 min (power: 700 W). Samples were cooled down for 20 min with a mechanical fan and subsequently filtered for chemical analysis by discarding the residue. The extracted samples showed yellow solution with grey/brown suspended solids. The clear solution is diluted up to 50 ml with MiliQ water. The samples were then transferred to vials and stored in refrigerator for further analysis.

2.5. Quality control & quality assurance

In this study, inductive coupled plasma–optical emission spectrometry (ICP–OES; Ultima 2, Horiba Jobin-Yvon, Longjumeau, France) has been used for the quantification of various potentially toxic elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn). Certified stock solution of 1000 mg L⁻¹ (*E-Merck, Germany*) metal standards were used for the calibration by serial dilution. Analytical grade (AR) chemicals were used throughout the analysis. To prepare all other reagents and calibration standards, MiliQ water was used. All measurements were carried out in triplicate and an average value has been reported. Blank along with standards was run during all measurements. Standard reference material (SRM) NIST SRM 2711 was used for the validation of the analytical procedure. The analytical results showed 96–105% recovery for all the studied metals.

2.6. Statistical analysis

All statistical analysis and data interpretation were performed on Microsoft Office 2007 and SPSS Statistics V-21 (IBM, USA). As a multivariate analysis, principal component analysis (PCA) was done to identify the sources of different metals in soil and road dust. Before PCA analysis, initial data sets were standardized and transformed to z-score to eliminate the bias by individual elements as well as to get the normal distribution of individual variables. In this study, Varimax rotation with Kaiser Normalization was done. PCA method is widely used in various studies to identify sources of PTEs in soil and road dust (Gope et al., 2018; Tang et al., 2017; Sahariah et al., 2015).

2.7. Environmental risk assessment

2.7.1. Contamination factor (CF)

Contamination factor (CF) shows anthropogenic load in elemental pollution and it is the most common measurement used for the detection of overall soil contamination in Asian countries (Dantu, 2009; Bhuiyan et al., 2010; Pandey et al., 2016; Said et al., 2019; Gohain and Deka, 2020). CF is obtained by dividing the concentration of the element in soil by background concentration (Hakanson, 1980).

Table 1
Reference dose (RfD) and Slope factor (SF) value of different elements for different exposure pathways.

PTEs	RfD (mg/kg/d)			SF (kg·d/mg)		
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal
As ¹	0.0003	0.000123	0.000123	1.5	15.1	3.66
Cd^1	0.001	0.00001	0.00001	0.38	6.3	3
Cr^1	0.003	0.0000286	0.00006	0.5	42	20
Cu^1	0.04	0.0402	0.012	_	-	-
Hg^1	0.0003	0.0000857	0.000021	_	-	-
Mn^2	0.14	0.0000143	0.00184	_	_	-
Ni^1	0.02	0.0206	0.0054	0.84	1.7	42.5
Pb^1	0.0035	0.00352	0.000525	_	_	-
Zn^1	0.3	0.3	0.06	_	-	-
Fe ³	0.3	-	0.045	-	-	-

(¹Li et al., 2020; ²Verma et al., 2020; ³Alghamdi et al., 2019; ³Kumar et al., 2020).

$$CF = \frac{Ci}{Bi}$$
 (1)

Ci stands for concentration of the examined element i, and Bi denotes geochemical background value of that element. Based on CF values, the contamination grades are as follows: 0 = none; 1 = none to medium; 2 = moderate; 3 = moderate to strong; 4 = strongly polluted; 5 = strong to very strong; 6 = very strong (Varol, 2011).

2.7.2. Pollution load index (PLI)

For a set of polluting elements, the Pollution load index (PLI) can be described as the value calculated from the geometric mean of the contamination factors of those elements (Gope et al., 2018; Verma et al., 2020). The formula for calculation of PLI given by Tomlison et al. (1980) is as follows:

$$PLI = (CF1X CF2X CF3X....X CFn)^{1/n}$$
(2)

PLI value >1 indicates pollution existence whereas <1 shows no pollution load.

2.7.3. Enrichment factor (EF)

The enrichment factor (EF) of an element of interest can be defined as the concentration of the element against a reference value. Those geochemically distinct elements which have high values of concentration in the environment and do not show any characteristics such as antagonism and synergism towards the examined elements may be treated as reference elements (Gonzalez-Macias et al., 2006; Masih et al., 2019; Adimalla et al., 2020; Gohain and Deka, 2020). In this study, iron (Fe) is used as the reference element as it is extensively used for normalization (Bhuiyan et al., 2010; Gowd et al., 2010; Gohain and Deka, 2020; Zhao et al., 2021). Hence, EF is calculated by using the following relationship:

$$EF = \frac{\text{(Element concentration)/(Fe concentration)sample}}{\text{(Element concentration)/Fe concentration)background}}$$
(3)

The EF values near 1.0 indicate crustal origin; <1 depicts a probable mobilization or reduction of elements whereas EF values >1 indicate the element is of anthropogenic origin. In addition to these, the EF values > 10 belong to non-crustal origin (Buat-Menard and Chesselet, 1979). The standardization of a tested element against a reference one acts as a basis for the enrichment factor. Low occurrence variability is the main characteristic of a reference element and very frequent reference elements used for EF calculation include Sc, Mn, Ti, Al, and Fe (Sutherland, 2000). There are five contamination categories for the classification of the enrichment factor (Sutherland, 2000): 1. Deficiency to minimal enrichment (EF < 2); 2. Moderate enrichment (EF = 2–5); 3. Significant enrichment (EF = 5–20); 4. Very high enrichment (EF = 20–40); 5. Extremely high enrichment (EF > 40).

2.8. Human health risk assessment

Human health risks (Non-cancerous and Cancerous) associated with potentially toxic elements in soil and road dust of the study region were calculated by using equations from (4–9). Exposure to potentially toxic elements can be calculated for several pathways i.e. ingestion, dermal, and inhalation. Non-carcinogenic risks can be estimated through hazard quotient (HQ) and hazard index (HI). To calculate HQ through different pathways, the US Environmental Protection Agency equation was used (Chabukdhara and Nema, 2013; Adimalla et al., 2020). It is as follows:

$$Intake_{Ingestion} = (C xEFxED_{tot}xIngR) 10^{-6} / (BWaxATn)$$
 (4)

$$Intake_{Inhalation} = (C \times EF \times ED_{tot} \times InhR) / (PEF \times BWaxATn)$$
 (5)

Intake_{Dermal} = (C x EF xED_{tot}xSAx SAF xABS_{Dermal})
$$10^{-6}$$
/ (BWaxATn) (6)

$$HQ = Intake/RfD$$
 (7)

Here HQ_{Ingestion}, HQ_{Inhalation}, and HQ_{Dermal} represent the hazard quotient of three pathways. EF stands for exposure frequency (350 days year⁻¹); ED denotes exposure duration {24 years for adults and 6 years for children (Chabukdhara and Nema, 2013)}; IngR represents ingestion rate of soil/road dust (100 mg day⁻¹ for adults and 200 mg day⁻¹ for children); Characterizes metal concentration in soil/road dust (mg kg⁻¹); BW signifies body weight {which is 60 kg for adult and 15 kg for children (US EPA, 1989)); AT specifies the average time (EDtot X 365 days year⁻¹ for non-carcinogen) and 70 (lifetime year) X 365 days for carcinogen (USDoE, 2011); InhR denotes inhalation rate (20 m³ day⁻¹ for adults and 7.6 m³ day⁻¹ for children); PEF stands for Particle emission factor ($1.36 \times 10^9 \text{ m}^3\text{kg}^{-1}$); SA stands for skin surface area (5700 cm² for adult and 2800 cm² for children); SAF represents skin adherence factor (0.07 mg cm⁻²h⁻¹ for adult and 0.2 mg cm⁻²h⁻¹ for children) (US EPA, 2001); ABS_{dermal} stands for dermal absorption factor (0.001 for all metals) (Chabukdhara and Nema, 2013) and RfD represents the reference dose and their values are given in Table 1. The Hazard Index (HI) is used to describe the Cumulative non-carcinogenic effect for more than one element and is calculated as follows:

$$HI = \sum HQi \tag{8}$$

Here i denote the multiple exposure pathways. If the HQ and HI value is beyond unity (>1), then there is a possibility of noncancerous health risks. Cancer risk can be also calculated by using the following equation (Eq. (9)) of those metals for which slope factor is available.

Cancer risk
$$(CR)_i$$
 = Intake_i x Slope Factor (9)

Slope factor values are given in Table 1. The calculated value of cancer risk signifies the probability of an individual to develop cancer by exposure to carcinogens for their lifetime. The acceptable or tolerable CR is 1×10^{-6} - 1×10^{-4} (Ahamad et al., 2020).

Table 2
Statistical summary of potentially toxic elements and other parameters in soil and road dust of Obra and Anpara clusters and their comparison with background value Upper Continental Crust (UCC) and other countries guideline value.

	Metal	Cr mg	Mn mg	Ni mg	Cu mg	Zn mg	As mg	Pb mg	Fe mg	Cd mg	Hg mg	pH	EC	OM
	concentration	kg ⁻¹ <	kg ⁻¹	kg ⁻¹	kg ⁻¹	kg^{-1}	kg^{-1}	kg ⁻¹	kg^{-1}	kg ⁻¹	kg ⁻¹		μScm ^{−1}	%
Soil (N =	Min	17.23	210.62	11.93	16.59	37.4	4.94	6.85	15,004.1	0.08	0.03	6.28	114	1.40
16) Obra	Max	83.37	1180.51	53.35	74.15	164.1	16.07	59.24	82,022.98	0.27	0.58	7.50	405	8.80
cluster	Mean	42.59	460.59	29.23	40.02	83.04	8.6	26.04	35,457.56	0.14	0.26	7.13	226	4.65
Soil $(N = 8)$	Min	21.14	99.68	11.83	24.14	29.87	5.5	7.24	15,004.1	0.09	0.05	6.57	408	5.70
Anpara	Max	72.09	548.77	37.99	64.16	183.55	11.33	34.65	37,259.19	0.29	1.06	7.12	1475	9.80
cluster	Mean	43.52	306.78	26.6	39.96	96.26	7.67	22.09	29,119.01	0.2	0.49	6.85	899	7.45
Road dust	Min.	3.98	285.71	14.74	20.8	47.55	3.95	8.57	21,214.24	0.09	0.03	7.13	104	3.50
(N = 15)	Max	61.65	649.39	31.54	53.03	181.65	22.2	63.09	84,887.07	0.67	0.61	8.19	1191	6.20
Obra	Mean	39.64	417.03	22.21	34.01	98.2	6.89	23.6	33,887.26	0.18	0.2	7.55	401	4.83
cluster														
Road dust	Min	28.98	256.9	15.67	20.8	60.29	4.21	8.57	22,039.62	0.11	0.1	6.89	318	5.60
(N = 9)	Max	78.18	489.12	31.89	73.71	167.76	7.31	35.06	59,172.48	0.29	1.02	8.12	2140	11.50
Anpara cluster	Mean	51.01	394.28	24.69	39.49	109.72	6.21	22.24	35,681.78	0.15	0.46	7.28	958	8.32
	UCC ^a	83	600	44	25	71	1.5	17	35,000	0.098	0.056	_	_	_
	Background of study	16.89	125.47	10.48	17.68	40.67	5.31	7.53	19,939.33	0.07	0.04	-		
	Background of China ^b	61	0	27	23	74	11	26	0	0.1	0.065			
	Dutch Soil Guidelines Target value ^c	100	0	35	36	140	29	85	0	0.8	0.3			

^a Upper Continental Crust (Taylor and McLennan, 1985; McLennan, 2001).

3. Results and discussion

3.1. Chemical characteristics of soil and road dust samples

Statistical summary of different chemical parameters in the soil and road dust samples from Obra and Anpara clusters are shown in Table 2.

The pH value of soil samples of Obra and Anpara varied from 6.28 to 7.5 (mean 7.13), and 6.57-7.12 (mean 6.85), respectively. Overall pH of soil samples varied from slightly acidic to neutral for Obra and Anpara. The EC value of soil samples ranged between 114 and 405 µScm⁻¹ for Obra and 408–1475 µScm⁻¹ for Anpara. The highest mean value of EC is 899 μ Scm⁻¹ for Anpara. The organic matter (OM) value of soil samples ranged between 1.4 and 8.8 for Obra and 5.7-9.8 for Anpara. The mean values of potentially toxic elements for soil samples in Obra and Anpara industrial clusters were: Cr (42.59 and 43.52 mg kg^{-1}); Mn (460.59 and $306.78 \text{ mg kg}^{-1}$); Ni (29.23 and 26.60 mg kg $^{-1}$); Cu (40.02 and 39.96 ${\rm mg\,kg^{-1}}$); Zn (83.04 and 96.26 ${\rm mg\,kg^{-1}}$); As (8.60 and 7.67 ${\rm mg\,kg^{-1}}$); Pb $(26.04 \text{ and } 22.09 \text{ mg kg}^{-1})$; Fe $(35,457.56 \text{ and } 29,119.01 \text{ mg kg}^{-1})$; Cd $(0.14 \text{ and } 0.20 \text{ mg kg}^{-1})$; Hg $(0.26 \text{ and } 0.49 \text{ mg kg}^{-1})$, respectively. Earlier studies related to potentially toxic elements contamination in soil around the thermal plant of Anpara reported almost similar concentration except As which was three to four times lower than the current concentration (Agrawal et al., 2010). It may be due to increasing coal consumption activities to generate more electricity. Mercury concentration was found almost similar in comparison to the previous study (Sahu et al., 2014).

The pH value of road dust samples of Obra and Anpara varied from 7.13 to 8.19 (mean 7.55) and 6.89–8.12 (mean 7.28), respectively. Overall pH of road dust samples of Obra was found neutral to alkaline while Anpara pH varied from near neutral to alkaline category. The EC value of road dust samples ranged between 104 and 1191 μ Scm⁻¹ for Obra and 318–2140 μ Scm⁻¹ for Anpara. The highest mean value of EC was found for Anpara (958.22 μ Scm⁻¹). The organic matter (OM) content of road dust samples ranged between 3.50 and 6.20 for Obra and 5.60–11.50 for Anpara clusters. The mean values of Potentially toxic elements for the road dust samples in Obra and Anpara industrial clusters were: Cr (39.64 and 51.01 mg kg⁻¹); Mn (417.03 and 394.28 mg

 kg^{-1}); Ni (22.21 and 24.69 mg kg^{-1}); Cu (34.01 and 39.49 mg kg^{-1}); Zn (98.20 and 109.72 mg kg^{-1}); As (6.89 and 6.21 mg kg^{-1}); Pb (23.60 and 22.24 mg kg^{-1}); Fe (33,887.26 and 35,681.78 mg kg^{-1}); Cd (0.18, and 0.15 mg kg^{-1}); Hg (0.20 and 0.46 mg kg^{-1}), respectively.

3.2. Comparison of potentially toxic elements (PTEs) with upper continental crusts (UCC) and background value of the study area with other country's background value

3.2.1. Soil and road dust samples

The PTEs mean value in soil and road dust samples of Obra and Anpara clusters were compared with Upper Continental Crust and background value of study area with background value of other countries (Table 2).

Mean value of potentially toxic elements in soil samples of Obra and Anpara display enrichment of Cu, Zn, As, Pb, Cd, and Hg when compared to the value of UCC (Taylor and McLennan, 1985; McLennan, 2001) and depletion for the rest of the elements. Mean value of all potentially toxic elements analyzed in soil samples was found in order of Fe > Mn > Zn > Cu > Cr > Ni > Pb > As > Hg > Cd, and Fe > Mn > Zn > CdCu > Cr > Ni > Pb > As > Hg > Cd for Obra, and Anpara clusters, respectively. All metals in soil samples of Obra and Anpara clusters, except Cu, As, Pb, Cd and Hg, were found below UCC. The value of Cu, As, Pb, Cd, and Hg for the Obra and Anpara cluster exceeded UCC value by 1.6, 5.73, 1.53, 1.43, 4.64 times and 1.59, 5.11, 1.3, 2.04, 8.75 times, respectively. The higher value of these elements in comparison to UCC indicates the anthropogenic influence in the study region is very high and more specifically for the enrichment of Hg and As. All metals in soil samples of Obra and Anpara clusters were found above the background value of the study region. The value of Cr, Mn, Ni, Cu, Zn, As, Pb, Fe, Cd, and Hg for Obra and Anpara cluster exceeded background value by 2.52, 3.67, 2.79, 2.26, 2.04, 1.62, 3.46, 1.78, 2, 6.5 times and 2.57, 2.45, 2.54, $2.26,\, 2.37,\, 1.44,\, 2.93,\, 1.46,\, 2.86,\, 12.25$ times, respectively. All metals (except Cu, Zn, Cd, and Hg) in soil samples of Obra and Anpara clusters were found below the background value of China (CEMS, 1990). The value of Cu, Zn, Cd and Hg for Obra and Anpara clusters exceeded the background value of China by 1.74, 1.12, 1.4, 4 times, and 1.73, 1.3, 2,

^b CEMS1990.

^c VROM 2000.

Table 3
Comparative study of potentially toxic elements (PTEs) in soil of Obra and Anpara clusters within the country and elsewhere.

Study area	Cr	Mn	Ni	Cu	Zn	As	Pb	Fe	Cd	Hg	References
Obra, Sonbhadra	42.59	460.59	29.23	40.02	83.04	8.6	26.04	35,457.56	0.14	0.26	This study
Anpara, Sonbhadra	43.52	306.78	26.6	39.96	96.26	7.67	22.09	29,119.01	0.2	0.49	This study
Estarreja, central Portugal	25	_	16	122	302	120	115	_	0.7	4.4	Cabral-Pinto et al. (2019)
Rizhao city, China	61.12	_	27	16.25	64.12	6.6	31.71	_	0.092	0.033	Zhuo et al. (2020)
Jiedong District, China	31.02	_	9.95	20.89	79.87	15.24	53.44	_	0.238	0.126	Jiang et al. (2020)
Harran Plain, Turkey	85	679	89	27	68	6.36	10.6	37,505	-	-	Varol et al. (2020)
Beijing, China	58.5	593	26.5	29.6	81.7	10.49	29.1	_	0.153	0.275	Chen et al. (2016)
Puning, China	22.5	_	12	11.1	56.6	7.89	42.4	_	0.06	0.08	Wang et al. (2019)
Tianjin, China	45	_	33	33	136	11	48	-	0.18	0.4	Zhao et al. (2014)
Shenyang, China	68	_	-	92	235	23	117	-	1.1	1.3	Li et al. (2013b)
Changsha, China	121	_	-	51	276	33	89	-	6.9	0.41	Zhou et al. (2008)
Napoli, Italy	15	_	12	94	223	13	204	_	0.58	0.31	Cicchella et al. (2008)
Galway, Ireland	33		21	33	99	8.6	78		-	-	Zhang (2006)
Delhi-kolkata Highway, India	23.39	_	22.92	19.43	106	-	21.22	_	0.36	-	Ghosh et al. (2020)
Telangana, India	43.24	_	7.55	40.64	34.68	-	47.48	_	-	-	Adimalla et al. (2020)
Durgapur city, India	154.37	_	29.54	5008	-	-	116.03	321.2	32.96	2.97	Pobi et al. (2020)
Delhi, India	-	501.6	65.6	50.6	280.5	-	36.1	18,669.1	-	-	Siddiqui et al. (2020)
Jorhat, Assam, India	35.88	271.55	23.42	18.38	33.35	-	15.59	19,893.67	.096	-	Islam and Saikia (2020)

7.54 times, respectively. All metals (except Cu in Obra and Cu and Hg in Anpara) in soil samples were found below the background value of Dutch. The value of Cu for the Obra cluster exceeded the background value of Dutch (Netherland) by 1.78 times (VROM, 2000). The value of Cu and Hg for the Anpara cluster exceeded the background value of Dutch (Netherland) by 1.47 and 1.63 times, respectively.

Mean value of potentially toxic elements of road dust samples of Obra and Anpara clusters display enrichment for Cu, Zn, As, Pb, Cd, and Hg when compared to the value of UCC (Taylor and McLennan, 1985; McLennan, 2001) and depletion for rest of elements. Mean value of all analyzed potentially toxic elements in road dust samples of Obra and Anpara clusters were found in order Fe > Mn > Zn > Cr > Cu > Ni > Pb > As > Hg > Cd and Fe > Mn > Zn > Cr > Ni > Cu > Pb > As > Hg > Cd, respectively. All Metals (except Cu, As, Pb, Cd, and Hg) in road dust samples of Obra and Anpara clusters were found below UCC. The value of Cu, As, Pb, Cd and Hg for Obra and Anpara clusters exceeded UCC value by 1.36, 4.59, 1.39, 1.84, 3.57 times and 1.58, 4.14, 1.31, 1.53, 8.21 times, respectively. All metals in road dust samples of Obra and Anpara clusters were found above the background value of the study region. The value of Cr, Mn, Ni, Cu, Zn, As, Pb, Fe, Cd, and Hg for Obra and Anpara clusters exceeded the background value by 2.35, 3.32, 2.12, 1.92, 2.41, 1.30, 3.13, 1.70, 2.57, 5 times and 3.02, 3.14, 2.36, 2.23, 2.7, 1.17, 2.95, 1.79, 2.14, 11.5 times, respectively. All metals (except Cu, Zn, Cd, and Hg) in road dust samples of Obra and Anpara clusters were found below the background value of China (CEMS, 1990). The value of Cu, Zn, Cd, and Hg for Obra and Anpara clusters exceeded the background value of China by 1.48, 1.33, 1.8, 3.08 times and 1.71, 1.48, 1.5, 7.08 times, respectively. All metals (except Cu in Obra and Hg in Anpara) in road dust samples were found below the background value of Dutch (VROM, 2000). The value of Cu for the Obra cluster exceeded the background value of Dutch (Netherland) by 2.05 times. The value of Hg for the Anpara cluster exceeded the background value of Dutch (Netherland) by 1.53 times. Coal-burning in thermal power plants and various coal-dependent industries present in both the clusters are the major contributors for the enrichment of these elements in soil and road dust samples of the surrounding region. In addition to that, dust generated from coal mining and other mining practices and vehicular emissions is other sources for the higher value of these elements. All the sampling locations were chosen along the road and very close to the emission sources. Distance from the sources is the major cause of variations in the concentration of these elements. These soil and road dust particles are smaller in size (<63 µm), suspend in the air, and may enter the respiratory tract through the inhalation process in the population living around that area. The toxic elements attached to the surface of these particles may dissolve in the blood or absorb through the skin and cause several adverse health effects. It is already reported in the literature that

the Higher value of As may cause hyperpigmentation, keratosis and ultimately skin.

Cancer in humans (Kumar et al., 2010). The high value of Hg may cause negative effects on the nervous system, brain, liver, gingivitis tremors, and heart muscle (Nazarpour et al., 2018).

3.3. Comparative study of potentially toxic elements with other reported studies within country and all over the world

3.3.1. Soil and road dust

The mean values of potentially toxic elements in the soil of Obra and Anpara clusters were compared with other studies reported within the country and elsewhere (Table 3). The mean value of almost all studied potentially toxic elements in soil samples of Obra and Anpara cluster showed similarity with the soil of Beijing (Chen et al., 2016) and Tianjin city (Zhao et al., 2014) of China. Mean Cr value of Obra and Anpara cluster were found relatively low compared to Durgapur city, India (Pobi et al., 2020); Changsha, China (Zhou et al., 2008); Harran Plain, Turkey (Varol et al., 2020), and relatively higher than the value reported for Napoli, Italy (Cicchella et al., 2008); Puning, China (Wang et al., 2019); Ireland (Zhang, 2006); central Portugal (Cabral-Pinto et al., 2019); Delhi-Kolkata Highway India (Ghosh et al., 2020); Jorhat, Assam, India (Islam and Saikia, 2020). Mean Mn value was found lower than Turkey (Varol et al., 2020) and Beijing, China (Chen et al., 2016) and Delhi, India (Siddiqui et al., 2020). Mean Ni value was found lower than Harran Plain, Turkey (Varol et al., 2020), and Delhi, India (Siddiqui et al., 2020). Mean Cu value was found lower than central Portugal (Cabral-Pinto et al., 2019); Durgapur city, India (Pobi et al., 2020); Shenyang, China (Li et al., 2013b); Napoli, Italy (Cicchella et al., 2008) Telangana, India (Adimalla et al., 2020); Delhi, India (Siddiqui et al., 2020). Mean Zn value was found to be significantly lower than central Portugal (Cabral-Pinto et al., 2019); Changsha (Zhou et al., 2008); Shenyang (Li et al., 2013b) China; Napoli, Italy (Cicchella et al., 2008) Delhi-Kolkata Highway India (Ghosh et al., 2020) and Delhi, India (Siddiqui et al., 2020). Mean As value was found significantly lower than central Portugal (Cabral-Pinto et al., 2019). Mean Pb value was found to be relatively low compared with the value of Napoli, Italy (Cicchella et al., 2008); Durgapur city, India (Pobi et al., 2020); Shenyang, China (Li et al., 2013b); central Portugal (Cabral-Pinto et al., 2019); Telangana, India (Adimalla et al., 2020); Delhi, India (Siddiqui et al., 2020) and higher than Harran Plain, Turkey (Varol et al., 2020); Delhi-Kolkata Highway India (Ghosh et al., 2020) and Jorhat, Assam, India (Islam and Saikia, 2020). The mean value of Cd and Hg in soil samples of the study area was found to be lower in comparison with the reported concentration value for Durgapur city, India (Pobi et al., 2020); Changsha (Zhou et al., 2008); and Shenyang (Li et al., 2013b) China; Central

 Table 4

 Comparative study of potentially toxic elements (PTEs) in road dust of Obra and Anpara clusters within the country and elsewhere.

Study area	Cr	Mn	Ni	Cu	Zn	As	Pb	Fe	Cd	Hg	References
Obra, Sonbhadra	39.64	417.03	22.21	34.01	98.2	6.89	23.6	33,887.26	0.18	0.2	This study
Anpara, Sonbhadra	51.01	394.28	24.69	39.49	109.72	6.21	22.24	35,681.78	0.15	0.46	This study
Beijing, China	92.1	553.73	32.47	83.12	280.65	4.88	60.88	29,744.62	0.59	0.16	Men et al. (2018)
Nanjing, China	133	602	115	141	585	17	119	-	1.92	-	Li et al. (2013a)
Sanghai china	157	-	-	-	-	8.73	246	-	1.24	0.16	Wang et al. (2009)
Iran	67.16	438.5	77.52	136.34	403.46	6.58	115.71	20,254.6	0.5	1.05	Keshavarzi et al. (2015)
Egypt	85.7	503	38.5	102	1839	6.53	307	32,050	2.98	-	Khairy et al. (2011)
China, Nanjing	_	_	_	133.1	281.3	13.9	101.6	_	0.72	0.514	Wang et al. (2020)
Beijing china	99.5	536.29	40.76	97.37	255.9	4.08	62.29	28,697	0.51	0.26	Men et al. (2020)
Kolkata, India	54	619	42	44	159	23	1030	26,700	3.12	1.95	Chatterjee and Banerjee (1999)
Delhi, India	171	699	37	169	264	-	129	27,047	-	-	Rajaram et al. (2014)
Thessaloniki, Greece	105	336	89	662	453	-	209	21,300	-	-	Bourliva et al. (2017)
Dhanbad, India	45	1500	22	53	224	17.5	128	67,700	_	_	Masto et al. (2019)
Korba, Iindia	833	2740	571	152	231	_	98.6	7550	1.3	_	Das et al. (2020)
Vellore, India	50.44	281.03	11.68	77.87	633.27	_	80.57	22,059.74	_	_	Jose and Srimuruganandam (2020)
Delhi, India	-	596.9	74.7	91.9	436.5	-	42.1	16,397	-	-	Siddiqui et al. (2020)
Bhivadi, Rajasthan India	2584	698	79	217	523	-	254	360	-	-	Verma et al. (2020)

 Table 5

 Contamination factor (CF), Enrichment factor (EF) of each potentially toxic elements (PTEs) in soil and road dust samples of Obra and Anpara clusters.

			PTEs									
			Cr	Mn	Ni	Cu	Zn	As	Pb	Cd	Hg	Fe
Contamination Factor	soil	Obra	2.52	3.67	2.79	2.26	2.04	4.74	3.46	1.82	19.16	1.78
		Anpara	2.58	2.44	2.54	2.26	2.37	4.23	2.93	2.78	35.73	1.46
	road dust	Obra	2.35	3.32	2.12	1.92	2.41	3.8	3.13	2.52	14.84	1.7
		Anpara	3.02	3.14	2.36	2.23	2.7	3.42	2.95	2.14	33.93	1.79
Enrichment Factor	soil	Obra	1.42	2.06	1.57	1.27	1.15	2.67	1.94	1.02	10.77	_
		Anpara	1.77	1.67	1.74	1.55	1.62	2.89	2.01	1.9	24.46	_
	road dust	Obra	1.38	1.96	1.25	1.13	1.42	2.23	1.84	1.48	8.73	_
		Anpara	1.69	1.76	1.32	1.25	1.51	1.91	1.65	1.2	18.96	_

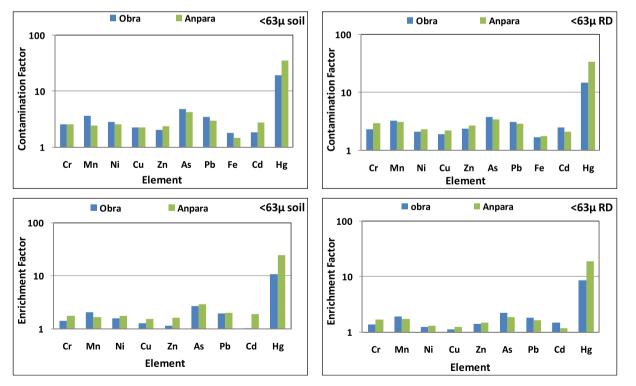


Fig. 2. Contamination factor (CF) and Enrichment factor (EF) of each metal in soil and road dust samples of Obra and Anpara clusters.

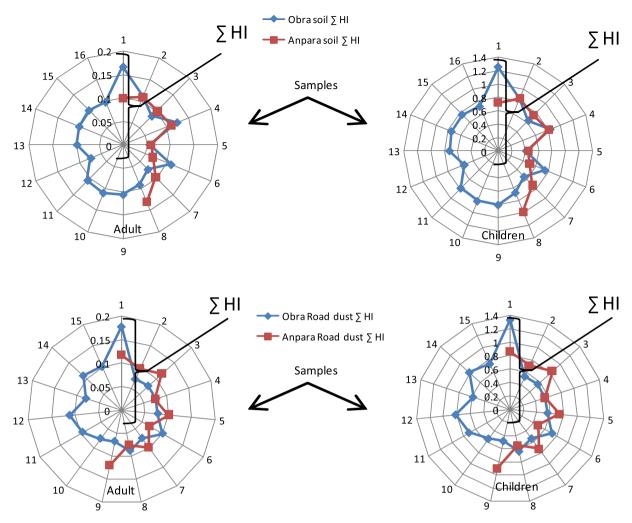


Fig. 3. Radar plot of Total exposure hazard index (HI) of each sampling location for adult and children in Obra and Anpara clusters of Sonbhadra region.

Portugal (Cabral-Pinto et al., 2019); Napoli, Italy (Cicchella et al., 2008) and Delhi-kolkata Highway India (Ghosh et al., 2020).

The mean values of potentially toxic elements in road dust of Obra and Anpara clusters were compared with other studies reported within and outside countries (Table 4). The Mean Cr value in road dust of Obra and Anpara cluster were found low compared with the value of Beijing (Men et al., 2018, 2020), Shanghai (Wang et al., 2009); & Nanjing city of China (Li et al., 2013a); Iran (Keshavarzi et al., 2015); Egypt (Khairy et al., 2011); Greece (Bourliva et al., 2017); Delhi (Rajaram et al., 2014) & Kolkata (Chatterjee and Banerjee, 1999) India, korba India (Das et al., 2020); Bhivadi Rajasthan India (Verma et al., 2020) (except Dhanbad, India {Masto et al., 2019}; Vellore India (Jose and srimurugunandam, 2020) for Obra cluster). Mean Mn values were found to be high compared to Thessaloniki, Greece (Bourliva et al., 2017); Vellore India (Jose and Srimurugunandam, 2020). Mean Ni values were found to be low compared to all the reported cities except Dhanbad India (Masih et al., 2019) and Vellore India (Jose and Srimurugunandam, 2020). Mean Cu, Zn, Pb, and Cd values were found to be low compared to all the reported cities all around the world and within India. Mean As value was found to be low compared to Shanghai (Wang et al., 2009) & Nanjing city (Li et al., 2013a; Wang et al., 2020) of China; Kolkata (Chatterjee and Banerjee, 1999) & Dhanbad, India (Masto et al., 2019). The mean Fe value was found to be relatively low compared to Dhanbad, India (Masto et al., 2019). The mean value of Hg in road dust samples of the study area was found lower than the concentration value reported for Iran (Keshavarzi et al., 2015); Nanjing China (Wang et al., 2020); Kolkata India (Chatterjee and Banerjee, 1999).

3.4. Different pollution indices for the study region

3.4.1. Soil and road dust samples

Various pollution indices were calculated for soil and road dust samples collected from Obra and Anpara clusters and results presented in Table 5. For the calculation of these pollution indices in soil and road dust samples, the mean value of each element of every sample in every industrial cluster was considered.

Contamination factor (CF) for soil samples showed following order: Hg > As > Mn > Pb > Ni > Cr > Cu > Zn > Cd > Fe; and Hg > As > Pb >Cd > Cr > Ni > Mn > Zn > Cu > Fe in Obra and Anpara clusters, respectively. CF value of Hg in the soil samples showed that both clusters come under the 'very strongly contaminated' category whereas for As it ranged from 'moderate to strong' to 'very strong polluted' category which indicates the highest anthropogenic input of mercury in comparison to the background value of the study region followed by arsenic (Fig. 2). CF value of Cr was found under the 'moderate' to 'strong to very strong' category for Obra and Anpara clusters. CF values for the rest of the elements in all the soil samples for both the clusters were under the 'none to medium' to 'moderate to strong' contaminated category. The pollution load index (PLI) value of both the clusters exceeds >1 indicating a high pollution load. When compared to both the clusters, the highest PLI value (3.30) was observed in the Anpara cluster. EF value of Hg in Obra and Anpara soil samples was found under the 'significant enrichment' and 'very high enrichment' category, respectively. EF value of As was found under the 'Moderate enrichment' category for the soil samples in both the clusters. EF value of Cr, Pb, Cd, Zn, Ni and Cu was

Table 6
Statistical summary of carcinogenic risk (CR) for adult and children via three exposure pathways in soil of Obra and Anpara clusters of Sonbhadra region.

			Adult				Children			
			Cr	Ni	As	Cd	Cr	Ni	As	Cd
CR Ingestion	Obra	Min	4.72E-06	5.49E-06	3.18E-06	1.51E-08	9.44E-06	1.10E-05	6.36E-06	3.01E-08
		Max	2.28E-05	2.46E-05	1.24E-05	5.50E-08	4.57E-05	4.91E-05	2.48E-05	1.10E-07
		Mean	1.17E-05	1.35E-05	6.23E-06	2.66E-08	2.33E-05	2.69E-05	1.25E-05	5.32E-08
	Anpara	Min	5.79E-06	5.45E-06	4.52E-06	1.80E-08	1.16E-05	1.09E-05	9.05E-06	3.59E-08
		Max	1.98E-05	1.75E-05	9.31E-06	6.13E-08	3.95E-05	3.50E-05	1.86E-05	1.23E-07
		Mean	1.19E-05	1.22E-05	6.30E-06	4.06E-08	2.38E-05	2.45E-05	1.26E-05	8.13E-08
CR Inhalation	Obra	Min	5.83E-08	1.63E-09	4.71E-09	3.67E-11	2.22E-08	6.21E-10	1.79E-09	1.40E-11
		Max	2.82E-07	7.31E-09	1.83E-08	1.34E-10	1.07E-07	2.78E-09	6.97E-09	5.10E-11
		Mean	1.44E-07	4.00E-09	9.22E-09	6.48E-11	5.48E-08	1.52E-09	3.50E-09	2.46E-11
	Anpara	Min	7.15E-08	1.62E-09	6.70E-09	4.38E-11	2.72E-08	6.16E-10	2.54E-09	1.66E-11
		Max	2.44E-07	5.20E-09	1.38E-08	1.49E-10	9.27E-08	1.98E-09	5.24E-09	5.68E-11
		Mean	1.47E-07	3.64E-09	9.33E-09	9.91E-11	5.60E-08	1.38E-09	3.55E-09	3.77E-11
CR Dermal	Obra	Min	7.53E-07	1.11E-06	3.10E-08	4.75E-10	1.06E-06	1.56E-06	4.34E-08	6.66E-10
		Max	3.65E-06	4.96E-06	1.21E-07	1.73E-09	5.12E-06	6.96E-06	1.69E-07	2.43E-09
		Mean	1.86E-06	2.72E-06	6.06E-08	8.37E-10	2.61E-06	3.81E-06	8.51E-08	1.17E-09
	Anpara	Min	9.24E-07	1.10E-06	4.40E-08	5.65E-10	1.30E-06	1.54E-06	6.18E-08	7.94E-10
		Max	3.15E-06	3.53E-06	9.06E-08	1.93E-09	4.42E-06	4.95E-06	1.27E-07	2.71E-09
		Mean	1.90E-06	2.47E-06	6.14E-08	1.28E-09	2.67E-06	3.47E-06	8.61E-08	1.80E-09
TCR	Obra	Min	5.53E-06	6.60E-06	3.22E-06	1.56E-08	1.05E-05	1.25E-05	6.40E-06	3.08E-08
		Max	2.68E-05	2.95E-05	1.25E-05	5.69E-08	5.09E-05	5.61E-05	2.50E-05	1.13E-07
		Mean	1.37E-05	1.62E-05	6.29E-06	2.75E-08	2.60E-05	3.07E-05	1.25E-05	5.43E-08
	Anpara	Min	6.79E-06	6.55E-06	4.57E-06	1.86E-08	1.29E-05	1.24E-05	9.11E-06	3.67E-08
	-	Max	2.31E-05	2.10E-05	9.41E-06	6.34E-08	4.40E-05	3.99E-05	1.88E-05	1.25E-07
		Mean	1.40E-05	1.47E-05	6.38E-06	4.20E-08	2.66E-05	2.80E-05	1.27E-05	8.31E-08

found under the 'deficient to minimal enrichment' category, whereas Mn show the 'moderate enrichment' category in the soil samples of the Obra cluster. EF value of Cr, Cd, Zn, Ni, Mn and Cu was found under the 'deficient to minimal enrichment' category in the soil samples of Anpara except for Pb which depicts the 'moderate enrichment' category.

Contamination factor (CF) value for the road dust samples revealed the following order: Hg > As > Mn > Pb > Cd > Zn > Cr > Ni > Cu > Fe and Hg > As > Mn > Cr > Pb > Zn > Ni > Cu > Cd > Fe in Obra and Anpara clusters, respectively. CF value of Hg in the road dust samples displayed 'very strongly contaminated', whereas 'moderately to strongly contaminated' with As and Mn in both the clusters. Road dust samples of Obra were found 'moderately to strongly contaminated' with Pb, 'moderately contaminated' with Cr, Ni, Zn and Cd and 'none to medium

contaminated' with Fe and Cu (Fig. 2). Road dust samples of Anpara were found 'moderately to strongly' contaminated with Cr, 'moderately contaminated' with Ni, Cu, Zn, Pb, and Cd and 'none to medium contaminated' with Fe (Fig. 2). The pollution load index (PLI) value of both the clusters exceeds >1 which depicts a high pollution load. The highest PLI value (3.35) was observed in road dust samples of the Anpara cluster. EF value of Hg in Obra and Anpara road dust samples was found under the 'significant enrichment' category. EF value of As for Obra road dust samples was found under 'Moderate enrichment' category and 'deficient to minimal enrichment' category with Cr, Mn, Pb, Cd, Zn, Ni and Cu. EF value of Cr, Mn, Pb, Cd, Zn, As, Ni and Cu was found under the 'deficient to minimal enrichment' category in the road dust samples of the Anpara cluster.

Table 7
Statistical summary of Carcinogenic risk (CR) for adult and children via three exposure pathways in road dust of Obra and Anpara clusters of Sonbhadra region.

			Adult				Children			
			Cr	Ni	As	Cd	Cr	Ni	As	Cd
CR Ingestion	Obra	Min	1.09E-06	6.78E-06	3.25E-06	1.84E-08	2.18E-06	1.36E-05	6.50E-06	3.67E-08
		Max	1.69E-05	1.45E-05	1.82E-05	1.40E-07	3.38E-05	2.90E-05	3.65E-05	2.81E-07
		Mean	1.09E-05	1.02E-05	5.66E-06	3.69E-08	2.17E-05	2.04E-05	1.13E-05	7.37E-08
	Anpara	Min	7.94E-06	7.21E-06	3.46E-06	2.33E-08	1.59E-05	1.44E-05	6.91E-06	4.66E-08
		Max	2.14E-05	1.47E-05	6.01E-06	5.96E-08	4.28E-05	2.94E-05	1.20E-05	1.19E-07
		Mean	1.40E-05	1.14E-05	5.11E-06	3.13E-08	2.80E-05	2.27E-05	1.02E-05	6.26E-08
CRInhalation	Obra	Min	1.35E-08	2.02E-09	4.81E-09	4.48E-11	5.12E-09	7.67E-10	1.83E-09	1.70E-11
		Max	2.09E-07	4.32E-09	2.70E-08	3.42E-10	7.93E-08	1.64E-09	1.03E-08	1.30E-10
		Mean	1.34E-07	3.04E-09	8.38E-09	8.99E-11	5.10E-08	1.16E-09	3.19E-09	3.42E-11
	Anpara	Min	9.81E-08	2.15E-09	5.12E-09	5.68E-11	3.73E-08	8.16E-10	1.94E-09	2.16E-11
		Max	2.65E-07	4.37E-09	8.90E-09	1.45E-10	1.01E-07	1.66E-09	3.38E-09	5.52E-11
		Mean	1.73E-07	3.38E-09	7.56E-09	7.64E-11	6.56E-08	1.29E-09	2.87E-09	2.90E-11
CR Dermal	Obra	Min	1.74E-07	1.37E-06	3.16E-08	5.79E-10	2.44E-07	1.92E-06	4.44E-08	8.12E-10
		Max	2.70E-06	2.93E-06	1.78E-07	4.42E-09	3.78E-06	4.11E-06	2.49E-07	6.20E-09
		Mean	1.73E-06	2.06E-06	5.51E-08	1.16E-09	2.43E-06	2.90E-06	7.74E-08	1.63E-09
	Anpara	Min	1.27E-06	1.46E-06	3.36E-08	7.34E-10	1.78E-06	2.04E-06	4.72E-08	1.03E-09
		Max	3.42E-06	2.96E-06	5.85E-08	1.88E-09	4.80E-06	4.16E-06	8.22E-08	2.63E-09
		Mean	2.23E-06	2.29E-06	4.97E-08	9.86E-10	3.13E-06	3.22E-06	6.98E-08	1.38E-09
TCR	Obra	Min	1.28E-06	8.16E-06	3.29E-06	1.90E-08	2.43E-06	1.55E-05	6.55E-06	3.76E-08
		Max	1.98E-05	1.75E-05	1.84E-05	1.45E-07	3.76E-05	3.32E-05	3.67E-05	2.87E-07
		Mean	1.27E-05	1.23E-05	5.73E-06	3.81E-08	2.42E-05	2.33E-05	1.14E-05	7.54E-08
	Anpara	Min	9.30E-06	8.67E-06	3.49E-06	2.41E-08	1.77E-05	1.65E-05	6.96E-06	4.77E-08
		Max	2.51E-05	1.76E-05	6.08E-06	6.16E-08	4.77E-05	3.35E-05	1.21E-05	1.22E-07
		Mean	1.64E-05	1.37E-05	5.16E-06	3.24E-08	3.11E-05	2.60E-05	1.03E-05	6.40E-08

PCA analysis for source identification of potentially toxic elements in soil and road dust of Obra and Anpara industrial clusters

	Soil								Road dust								
Parameters	Obra component	oonent				Anpa	npara component		Obra component	onent				Anpara component	nponent		
	1	2	3	4	2	1	2	3	1	2	3	4	2	1	2	3	4
Hd	0.103	-0.218	-0.879	0.169	-0.134	0.045	0.430	-0.588	-0.352	-0.044	-0.396	0.272	0.616	0.715	-0.091	0.351	0.208
EC	0.154	-0.886	0.044	-0.022	-0.023	0.045	-0.055	0.908	0.039	-0.095	0.927	0.164	0.122	0.908	0.235	-0.077	0.084
МО	0.942	-0.108	0.009	0.152	-0.139	-0.140	0.935	-0.126	0.385	0.767	0.047	0.336	0.095	0.208	0.942	-0.093	-0.017
Fe	0.104	0.533	0.405	0.170	0.643	0.769	0.517	0.285	0.803	0.494	-0.055	0.073	0.057	0.862	0.359	0.123	0.191
Mn	-0.111	-0.116	-0.134	-0.180	0.886	0.786	-0.461	-0.100	0.984	0.005	0.025	-0.019	-0.036	0.360	-0.058	0.185	0.816
Ç	0.940	0.098	0.093	0.000	0.140	0.062	0.921	-0.303	0.222	0.883	0.125	0.183	-0.116	0.207	0.956	-0.086	0.112
Ni	0.638	0.641	0.099	0.073	-0.229	0.804	0.541	0.244	-0.059	0.195	-0.252	-0.690	-0.478	-0.300	-0.238	0.521	-0.232
Cn	0.137	0.789	0.126	0.309	-0.061	0.919	-0.342	0.021	0.054	0.268	-0.030	0.840	-0.155	0.936	0.234	-0.210	-0.014
Zn	0.247	-0.042	0.843	0.131	-0.212	0.084	0.949	0.219	-0.168	960.0	0.914	-0.036	-0.158	-0.260	0.001	-0.903	0.047
As	0.628	092	-0.597	-0.294	-0.154	0.928	-0.109	0.138	0.938	0.037	-0.021	0.167	-0.108	0.741	0.540	0.164	-0.282
Pb	-0.006	0.617	0.333	0.332	0.397	0.567	0.308	-0.514	-0.060	0.082	0.040	-0.104	0.857	0.837	-0.175	-0.081	0.390
Cd	-0.083	0.267	-0.147	0.875	-0.034	0.221	0.269	0.927	0.948	0.093	-0.076	-0.013	-0.170	0.010	-0.183	0.322	-0.901
Hg	0.155	0.099	0.164	0.877	-0.078	0.805	0.433	-0.102	-0.219	0.775	-0.213	-0.377	0.121	-0.158	0.668	999.	0.141
Eigen Value	3.899	2.833	1.763	1.549	1.080	5.076	3.712	2.525	4.34	2.153	2.021	1.695	1.048	5.48	2.342	1.982	1.504
% Total variance	29.99	21.791	13.561	11.917	8.311	39.043	28.555	19.426	33.385	16.559	15.544	13.035	8.061	42.152	18.013	15.243	11.568
% Cumulative	29.99	51.781	65.342	77.259	85.57	39.043	67.598	87.024	33.385	49.943	65.487	78.522	86.583	42.152	60.165	75.408	86.976

3.5. Health risk assessment related to potentially toxic elements in soil and road dust

The potentially toxic elements accumulation in the soil and road dust in the industrial zone is likely to have a harmful effect on human health. Non-cancerous risk (NCR) and cancer risk (CR) were estimated to comprehend the overall health risks in the study region.

3.5.1. Non-carcinogenic risk (NCR)

Hazard quotient (HQ) and hazard index (HI) were used to calculate the NCR in soil and road dust of Obra and Anpara industrial clusters. For calculation of NCR three exposure pathways (ingestion, inhalation, and dermal) were chosen and the estimated result are presented in Tables S1 & S2. The estimated HQ value of all studied elements in soil and road dust samples of Obra and Anpara clusters were found <1 for all three pathways in adult and children both (except Fe for children in both the cluster). It means that the exposed adult and children population by all the toxic elements were found to be safely associated with noncarcinogenic risk, except Fe where exposed children population remain prone to non-carcinogenic risks mainly through ingestion pathway in both the clusters of study. The HO value for adults was observed to be low compared to children, which means that children will be more prone to non-carcinogenic health risks in the near future. The HQ value of almost all elements was found highest for the ingestion pathway followed by dermal and inhalation pathways in both clusters. The estimated Hazard Index (HI) value of all the studied elements in soil and road dust samples of Obra and Anpara clusters were found <1 for both adult and children. The total exposure hazard index value of all soil and road dust samples of Obra and Anpara clusters were found <1 in both adults and children with exception of one sample in children of the Obra cluster (Fig. 3).

3.5.2. Carcinogenic risk (CR)

Due to the availability of slope factors for Cr, Ni, As and Cd metals, cancer risk was estimated only for these elements in adult and children populations in Obra and Anpara clusters. The carcinogenic risk through different exposure pathways (*ingestion, inhalation, and dermal*) by each element in soil and road dust of Obra and Anpara clusters was calculated (Tables 6 and 7). Cancer risk associated with all the considered elements in soil and road dust of both the clusters were found safe (under the guideline $10^{-4} - 10^{-6}$) in both adults and children for all three pathways. The result of the calculated cancer risk indicated that a high value is found for children compared to adults for all three pathways which may be due to pica behavior and the habit of finger's sucking in both the clusters (Mohmand et al., 2015). The cancer risk value for ingestion pathways of almost all considered elements was found highest followed by dermal and inhalation pathways in both the clusters.

3.6. Source apportionment of the potentially toxic elements

3.6.1. Soil

In the present study, 13 variables from Obra (16 samples) and Anpara (8 samples) clusters were chosen for principal component analysis (PCA). Based on eigenvalues, these combined to produce 5 and 3 principal components in Obra and Anpara clusters, respectively. Results showed that Obra and Anpara clusters have a respective cumulative variance of 85.57% and 87.02% (Table 8). The 3D plots make it evident that the clusters of Obra and Anpara contain the higher value of % total variance (Fig. 4).

Obra cluster factors: Factor 1 displayed high loading for OM, Cr, Ni, As & Zn. It showed that the distribution of these metals in soil is affected by the presence of organic matter that reduces the bioavailability and mobility of potentially toxic elements, making the activity of potentially toxic elements in soil decreased, eventually leading to increased levels of toxic elements in the soil (Li et al., 2018). The combination of the variables may be due to the influence of mixed

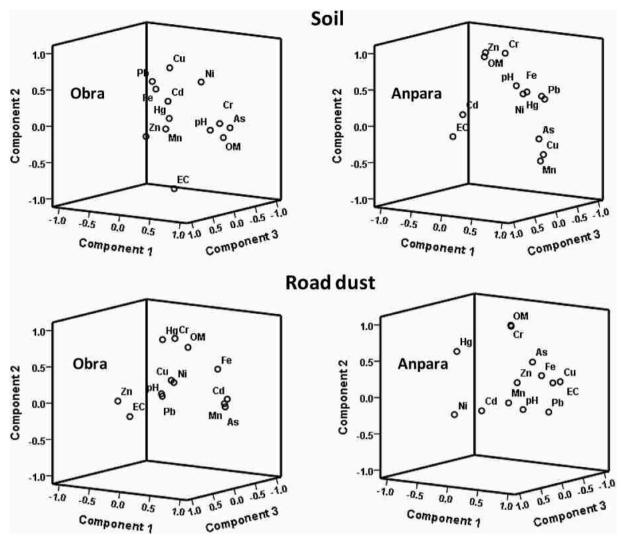


Fig. 4. 3D plots of PC1, PC2 and PC3 in Obra and Anpara clusters for soil and road dust.

sources as these metals are generated from coal-burning, cement factories, thermal power plants along vehicular emissions. Factor 2 displayed high loading for Fe, Ni, Cu, Pb, and Cd. Here the combination of loading reveals the sources are both natural and anthropogenic. Factor 3 displayed high positive loading for Fe and Zn and negative loading for pH and As. Fe and Zn element may be coming in the soil from natural sources or tire wear and fluid leakage while As is particularly from coal burning. Factor 4 displays high loading for Hg, Pb, Cd and Cu which indicate coal burning in thermal power plant & cement industry, improper disposal of fly ash are the major sources of these potentially toxic elements in the soil. Factor 5 displayed high positive loading for Fe, Mn and Pb which clues towards the mixed sources of both natural and anthropogenic origins.

Anpara cluster factors: Factor 1 displayed high loading for Fe, Mn, As, Cd, Ni, Cu, Pb, and Hg which indicates the influence of mixed sources i.e. coal mining activity, burning of coal in Thermal Power Plants and vehicular emissions. Factor 2 shows high loading for pH, OM, Fe, Cr, Ni, Zn, Pb, Cd, and Hg which suggested that both the pH and OM are controlling the accumulation and mobility of these metals. The sources of these metals may be natural and/or anthropogenic. Factor 3 showed high loading for EC & Cd which indicates that coal burning in several industries may influence the soil ionic constituents.

3.6.2. Road dust

In this study, 13 variables from Obra (15 samples) & Anpara (9

samples) were chosen to study the principal component analysis. Based on the eigenvalues, they combine to produce 5 and 4 principal components in Obra and Anpara clusters, respectively. Results showed that Obra and Anpara cluster have 86.58% and 86.98% cumulative variance, respectively (Table 8). It is clear from the 3D plots that Obra and Anpara clusters contain the higher value of % total variance (Fig. 4).

Obra cluster factors: Factor 1 displayed high loading for OM, Fe, Mn, As & Cd. It shows the distribution of these metals in road dust affected by the presence of organic matter. The combination of the variable may be due to the influence of mixed sources as these metals are generated from natural processes (soil particles) as well as anthropogenic activity i.e., coal burning, cement factory, thermal power plant, and vehicular emission. Factor 2 showed high loading for OM, Fe, Cr, and Hg. Here the combination of loading reveals the sources of Hg and Cr may be coal burning in various coal-dependent industries as well as vehicular emissions. Factor 3 displayed high positive loading for EC & Zn which validate that the Zn element in road dust may be from tire wear and fluid leakages. Factor 4 displayed high loading for OM and Cu which indicates the Cu value in road dust is affected due to organic matter content. Cu may be coming from vehicular components. Factor 5 showed high positive loading for pH & Pb which depicts coal burning and vehicular emission may be the main source occurrence.

Anpara cluster factors: Factor 1 displayed high loading for pH, EC, Fe, Mn, Cu, As & Pb which indicate the influence of mixed sources of natural and anthropogenic activities i.e. coal mining, burning of coal in

Thermal Power Plants and vehicular emissions. Factor 2 showed high loading of OM, Fe, Cr, As & Hg which explains that the OM is controlling the accumulation and mobility of these metals. The sources of these metals may be both natural (soil) and anthropogenic (dust from coal mining activities, fly ash from coal-burning and vehicular emissions). Factor 3 indicated high positive loading for pH, Ni, Cd & Hg while strong negative loading for Zn which justifies it may be coming from tire dust and others from coal mining and coal burning. Factor 4 showed high positive loading for Mn, & Pb whereas strong negative loading for Cd which depicts both are coming from different sources.

The study region is located in an industrial hub dominated by coalbased mining and thermal plants as well as the heavy movement of small and large vehicular traffic which contributes harmful substances and toxic elements to the environment. So there is a high possibility of metal content in the soil and road dust that may be contributed from these sources.

4. Conclusions

The present study was carried out to deduce the PTEs contamination status of soil and road dust along with source identification and its environmental and human health risk assessment. CF value of soil and road dust samples of both clusters showed Hg under the "very strongly" contaminated category. PLI value for soil and road dust of both the clusters exceeded unity. Hg enrichment factor (EF) in the soil of Obra and Anpara cluster was found under the "significant enrichment" and "very high enrichment" category, respectively. In the case of As it was found under the "moderate enrichment" category for both clusters. In road dust samples, Hg EF value was observed under the "significant enrichment" category for both clusters whereas the EF value of As was found under the "moderate enrichment" category for the Obra cluster. The estimated HQ values of all the studied PTEs were found to be less than one for all the three pathways in adults and children in both clusters. The HQ value for adults was observed to be low compared to children, which means that children will be more prone to noncarcinogenic health risks within the study area in near future. The HQ value of almost all PTEs for the ingestion pathway was found highest followed by dermal and inhalation pathways in both clusters. The total exposure hazard index (HI) value of almost all the soil and road dust samples were found to be less than one for both adult and children in both clusters. Cancer risk was found to be under the safe limit in both adults and children through all three pathways in both clusters. As per cancer risk assessment, ingestion pathway values were found to be highest followed by dermal and inhalation pathways in both clusters. Application of PCA indicated that PTEs in soil and road dust remained controlled by the mixed types of natural and anthropogenic sources for the metal enrichment in both clusters. There should be a proper regulatory system for these toxic metal emissions from the existing plant and any contravening of the provision of emission monitoring by these industries be penalised towards controlling metal pollution in the environment. There is a need for the continuous monitoring of PTEs in different environmental samples in and around these industrial clusters.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2021.111685.

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