Contamination of arsenic and heavy metals in coal exploitation area

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ABSTRACT: The coal is a dirty fuel, containing As and other heavy metals (HMs) at the trace levels. Several millions tons of coals are exploited in the Korba basin, CG, India to generate electricity. In this work, distribution of As and other HMs i.e. Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb and Hg in the surface soil and sediment are described. Three metals i.e. Mn, Fe and Ni occurred at higher concentrations, ranging ($n = 30$) from 2.3–6.4, 0.08–0.22 and 0.04–0.16% with mean value ($p = 0.05$) of 4.3 ± 0.4 , 0.14 ± 0.02 and $0.08 \pm 0.01\%$, respectively. The concentration of elements i.e. As, Cr, Cu, Zn, Cd, Pb and Hg in the soil was ranged ($n = 30$) from 49–164, 30–78, 44–131, 87–220, 0.11–0.56, 72–194 and 0.11–0.39 mg kg⁻¹ with mean value ($p = 0.05$) of ($p = 0.05$) 106 ± 11 , 51 ± 5 , 86 ± 8 , 156 ± 10 , 0.33 ± 0.04 , 130 ± 10 and 0.22 ± 0.03 mg kg⁻¹, respectively. The concentration of the As in the sediments ($n = 26$) was ranged from 36–154 mg kg⁻¹ with mean value of 93 ± 12 mg kg⁻¹. The toxic inorganic As(III) and As(V) species are found to exist in the soil and sediment. The concentration variations, pollution indices and sources of the contaminants in the geomeadia are discussed.

1 INTRODUCTION

Pollution of urban geomeadia is of a great public health interest due to receiving of large amounts of pollutants from multiple sources including industrial wastes, vehicle emissions, coal and biomass burnings, etc. (Li *et al.*, 2012; Obaidy *et al.*, 2013; Plyaskina & Ladonin, 2009). India is the third-largest producer of coal in the world. Coal is a naturally occurring combustible material contains elemental carbon, sulfur, hydrocarbons, trace metals, etc. (Chou, 2012). Several environmental issues i.e. acid mine drainage, deposition of toxic compounds, environmental pollution, halting of acid rain, health hazards, storage of solid waste, etc. were observed due to coal burnings (Agrawal *et al.*, 2010; Bhuiyan *et al.*, 2010; Guttikunda *et al.*, 2014; Pandey *et al.*, 2011; Sengupta *et al.*, 2010; Sheoran *et al.*, 2011; Singh *et al.*, 2010).

Several millions tons of coal is mined out and burnt in the Korba basin for generation of electricity by pouring the effluents into the environment. The whole environment is covered by the fly ash and black carbon (BC). The rain and groundwater are acidic with high content of metals and fluoride Patel *et al.*, 2001; 2016). The HMs contamination of the Korba basin has not been carried out so far. Hence, in this work, the contamination of surface soil and sediment of the Korba basin with elements i.e. BC, As, Fe, Cr, Mn, Ni, Cu,

Zn, Cd, Pb and Hg is described. The concentration variations, enrichments and sources of the metals in the soil and sediment are discussed.

2 METHODS AND EXPERIMENTAL

2.1 Study area and sampling

Korba coalfield (22.35°N and 82.68°E) is located in the Chhattisgarh state, India in the basin of the Hasdeo river, extending over ≈ 530 km². The population of Korba area is ≈ 1.0 million. Several coal mines are in operation with annual production of ≈ 3 BT coal annually since year 1960. A huge amount of coal (≈ 20 MT yr⁻¹) is consumed by various units of thermal power plants to produce 6000 MW electricity with emission of ≈ 6 MT ash into the environment. The Asia biggest aluminum plant (3.2×10^5 TPY Aluminum smelter) is also in the operation in the Korba area.

The soil and sediment samples were collected from 30 and 26 locations of Korba area lie over ≈ 500 km² areas (Fig. 1). One kilogram of sample from each site (0–10 cm) was collected in a clean polyethylene container during January, 2011–2017 as prescribed in the literature (Tan, 2005). For depth profile studies, the soil samples were collected at depth of 0–10, 11–20 and 21–30 cm.

Figure 1. Representation of sampling locations in Korba basin.

2.2 Analysis

The soil samples were dried, milled and particles of ≤ 1 mm were sieved out. A 10 g sample with 20 mL deionized water in a 100-mL conical flask was agitated in an ultrasonic bath for 6 h. The pH values of the extract were measured by the Hanna pH meter type-HI991300.

The weighed amount of soil sample (0.25 g) was digested with acids (3 mL HCl and 1 mL HNO_3) in closed system with P/T MARS CEM (Varian Company) microwave oven. The acid extract was used for monitoring of the elements.

The CHNSO-IRMS Analyzer, SV Instruments Analytica Pvt. Ltd. was used for analysis of the black or elemental carbon (BC or EC). The total carbon (TC) in the soil sample was oxidized at 1020°C with O_2 into CO_2 with constant helium flow.

The analytical techniques i.e. Varian ICP-OES-700-ES, GF-AAS SpectrAA 220 and CV-AAS SpectrAA 55B were used for monitoring of metals i.e. Cr, Mn,

Fe, Ni, Cu, Zn and Pb; As and Cd; and Hg in the soil extract, respectively. The standard soil sample (NCS DC 73382 CRM) was used for the quality control.

A 0.2 g of sediment sample was taken into a 10-mL Teflon centrifuge tube by subsequent addition of 5 mL of 0.5 M H_3PO_4 and kept overnight. A 2 mL of filtered solution was diluted to 10 mL with sodium phosphate to use as HPLC mobile phase. The As-species (i.e. As(III), As(V), MMA and DMA) were quantified by using the technique i.e. HPLC-AFS

The pollution indices i.e. enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) are used to determine element contents in the soil samples with respect to the base line concentration. These relate the concentration of an element, X, to a crustal element (e.g. Al) in the soil sample, and this ratio is then normalized to the ratio of those elements in the earth's crust. The following equations were used for the calculation of the pollution indices (Sinex & Helz, 1981; Tomlinson *et al.*, 1980):

$$EF = \{[X_s]/[Al_s]\} / \{[X_e]/[Al_e]\}$$

$$CF = \{[X_s]/[X_e]\}$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \dots CF_n)^{1/n}$$

where, symbols: X_s , X_e , Al_s and Al_e denote concentration of metal and Al in the soil and earth crust, respectively.

The IBM SPSS Statistics 23 software was used for the preparation of the dendrogram.

3 RESULTS AND DISCUSSION

3.1 pH of extract

The soil and sediment were colored, ranging from brown to blackish. The pH values of the soil and sediment extracts ($n = 30$) ranged from 5.4–7.5 and from 5.4–8.1 with mean value ($p = 0.05$) of 6.6 ± 0.2 and 6.6 ± 0.3 , respectively. The extracts were observed to be slightly acidic, may be due to high chloride and sulfate contents. The lowest pH value was seen in the Korba city, may be due to the high anthropogenic activities.

3.2 Distribution of black carbon

The BC concentration in the soil and sediment was ranged from 3.4–7.9 and 3.6–14.0% with mean value ($p = 0.05$) of 5.6 ± 0.4 and $9.2 \pm 1.0\%$, respectively. The higher loading of the BC in the sediment samples was observed, may be due to its transport by the runoff water. The BC content in the geomeidia of the studied area was found to be higher than reported in other regions, probably due to huge coal burning (Han *et al.*, 2009; He & Zhang, 2009; Muri *et al.*, 2002).

3.3 Distribution of elements

The metals i.e. Mn, Fe and Ni occurred in the soil of Korba basin at high levels, ranging ($n = 30$) from 2.3–6.4, 0.08–0.22 and 0.04–0.16 % with mean value ($p = 0.05$) of 4.3 ± 0.4 , 0.14 ± 0.02 and $0.08 \pm 0.01\%$, respectively. The concentration

Table 1. Distribution of major metals in soil, mg kg⁻¹.

S. No.	Location	As	Cd	Pb	Hg
1	Niharica	146	0.47	163	0.21
2	Kuan Bhatta	80	0.26	119	0.18
3	Railway Station	78	0.11	95	0.11
4	Sitamani	140	0.43	126	0.23
5	Rajgamar	164	0.56	189	0.39
6	Rumgara	60	0.21	126	0.24
7	Darri dam	96	0.27	116	0.19
8	Children Garden	61	0.35	116	0.20
9	Dipka-I	61	0.27	117	0.14
10	Dipika-II	49	0.21	137	0.23
11	Gevera Chowk	102	0.31	114	0.22
12	Kusmunda-I	96	0.17	127	0.21
13	Kusmunda-II	106	0.29	126	0.25
14	Kusmunada-III	130	0.41	154	0.25
15	Korba	145	0.54	190	0.37
16	Banki mongra	120	0.21	110	0.26
17	Balgi	111	0.38	88	0.25
18	Kuchaina	97	0.25	72	0.13
19	Balco	134	0.44	168	0.22
20	bhadrapara	86	0.33	106	0.11
21	Risdi Chowk	83	0.34	102	0.13
22	Manikpur	79	0.30	96	0.15
23	Dadar	94	0.39	138	0.24
24	SECL	98	0.41	140	0.21
25	Mudapar	105	0.38	119	0.24
26	Rampur, PWD	101	0.32	125	0.22
27	SECL Hospital	149	0.49	160	0.31
28	Belakachar	131	0.29	149	0.30
29	Urga	134	0.21	129	0.26
30	Patadi	163	0.48	194	0.38

Figure 2. Distribution of As in surface soil.

of elements i.e. As, Cr, Cu, Zn, Cd, Pb and Hg ranged ($n = 30$) from 49–164, 30–78, 44–131, 87–220, 0.11–0.56, 72–194 and 0.11–0.39 mg kg⁻¹ with mean value ($p = 0.05$) of 106 ± 11 , 51 ± 5 , 86 ± 8 , 156 ± 10 , 0.33 ± 0.04 , 130 ± 10 and 0.22 ± 0.03 mg kg⁻¹, respectively (Table 1).

The concentration of elements i.e. As, Cr, Cu, Zn, Cd, Pb and Hg in the sediments ranged from 36–154, 29–7, 18–92, 42–294, 0.14–1.19, 26–127 and 0.12–0.82 mg kg⁻¹ with mean value of 93 ± 12 , 49 ± 5 , 49 ± 8 , 142 ± 28 , 0.59 ± 0.11 , 72 ± 13 and 0.44 ± 0.08 mg kg⁻¹, respectively (Table 2). The lower concentration of the elements (except Cd and Hg) in the sediment than the soil was observed.

Table 2. Distribution of heavy metals in sediments.

S. No.	Location	As	Cd	Pb	Hg
1	Shakti Nagar	63	0.14	33	0.16
2	Gevra, Dipka	96	0.24	37	0.17
3	PN, Dipka	98	0.27	49	0.23
4	Banki, Dipka	36	0.52	47	0.25
5	Delwadih	100	0.63	81	0.31
6	Shingali	82	0.36	78	0.28
7	Kusmunda	92	0.50	92	0.36
8	Rajgamar-3	65	0.45	74	0.26
9	Mudapur	114	0.65	35	0.21
10	PN, Darri	138	0.82	106	0.61
11	Darri west	127	0.95	127	0.77
12	Jamnipali	154	1.19	82	0.63
13	Gopalpur	149	1.18	120	0.82
14	HTPP, Darri	111	0.84	112	0.74
15	Manuikpur-1	127	0.77	107	0.63
16	Manikpur-2	51	0.39	31	0.30
17	Dader-1	79	0.66	54	0.54
18	Dader-2	99	0.72	87	0.65
19	Kudarikhar	43	0.42	37	0.33
20	Naktikhar	93	0.64	75	0.53
21	Danras-1	98	0.62	53	0.46
22	Danras-2	41	0.20	26	0.12
23	SN-Balco	47	0.22	48	0.32
24	Pathadi	79	0.96	125	0.71
25	Dhendheni	69	0.62	108	0.61
26	Sukhri	30	0.35	35	0.31

They occurred in the following increasing order: Hg < Cd < Cr < Cu < As < Pb < Zn < Ni < Mn < Fe in the soil. The highest concentration of As was seen near the point sources i.e. thermal power plant, coal mine, urban area, etc. as shown in Figure 2. The concentration of As in the geomeidia of studied area was several folds (>10) higher than permissible limit of 5 mg kg⁻¹. The concentration of the As and heavy metals in the soil and sediment of the Korba basin was higher than values reported in other region of the country and world, probably due to huge coal mining and burning (Dahal *et al.*, 2008; Ilwon *et al.*, 2003; Kwon *et al.*, 2017; Muller, 1969; Sheela *et al.*, 2012; Rudnick & Gao, 2003; Shrivastava *et al.*, 2014; Whitmore *et al.*, 2008).

3.4 Vertical distribution of elements

The concentration of elements (i.e. As, Cr, Ni, Cu, Zn, Cd and Hg) was increased as the depth profile was increased up to 30 cm unlikely to Mn, Fe and Pb, may be due to their less binding with the organic compounds (Fig. 3).

3.5 Temporal variation of elements

The increased temporal variation of As over periods: 2011–2015 was observed due to continuous mining and burning of the coals (Fig. 4). The rate of temporal increase in the As concentration was $\approx 6\%$ in the geomeidia due to continuous coal burning. At least 15% higher concentration of the As in the soil with respect

Figure 3. Vertical distribution of As and other metals in soil, x = 0–10, 2x = 10–20, 3x = 20–30 cm.

Figure 4. Temporal variation of As in soil and sediment.

Table 3. Speciation of arsenic in sediments, mg kg⁻¹.

S. No.	As(III)	DMA	MMA	As(V)	AsT	EE, %
S1	1.08	—	—	14.0	15.08	27.1
S2	—	—	—	9.08	9.08	110.7
SE1	0.1	—	—	2.10	2.20	73.3
SE2	0.15	—	—	6.0	6.15	130.8
SD3	—	—	—	2.40	2.4	75

EE = Extraction efficiency (100%).

the sediment was observed due to its washout by the aqueous media.

3.6 Speciation of arsenic

The As(III), As(V), MMA and DMA were quantified in the soil and sediment extracts by using technique i.e. HPLC-AFS (Table 3). The organic species i.e. MMA and DMA were not detected in the soil and sediment extracts. The whole As in soil and sediment samples of studied area was found in the toxic inorganic forms.

3.7 Sources

The correlation coefficient matrix for BC and nine metals in the soil is presented in Table 4. A fair correlation ($r=0.58$ – 0.82) of the metals with BC was observed, may be due to deposition by multiple sources

Table 4. Correlation coefficient matrix of elements.

	BC	Fe	Ni	Cr	Cu	Zn	Pb	Hg	Cd	As
BC	1.00									
Fe	0.58	1.00								
Ni	0.59	0.41	1.00							
Cr	0.70	0.55	0.39	1.00						
Cu	0.74	0.60	0.56	0.73	1.00					
Zn	0.74	0.64	0.45	0.56	0.75	1.00				
Pb	0.81	0.77	0.59	0.59	0.72	0.72	1.00			
Hg	0.76	0.55	0.52	0.52	0.65	0.67	0.80	1.00		
Cd	0.82	0.68	0.57	0.57	0.58	0.67	0.69	0.59	1.00	
As	0.78	0.42	0.49	0.49	0.61	0.64	0.67	0.72	0.68	1.00

Figure 5. Dendrogram for group linkage of chemical characteristics of locations.

i.e. coal burning, fly ash, alumina roasting, etc. Similarly, fair correlation coefficient (0.39–0.80) among the metals was marked, showing deposition by the multiple sources.

A dendrogram to know linkage between similar groups is plotted, using sum of total concentration of three metals i.e. As, Zn and Pb as discriminating factor. The dendrogram was categorized into two groups: group-I and -II with inclusion of 20 and 10 locations as shown in Figure 5. The higher concentration of the As+Zn+Pb (>400 mg kg⁻¹) was seen in group-II, may be due to loading of point sources (i.e. coal mines, aluminum plant and thermal power plant) effluents.

3.8 Enrichment

The background concentration of Al, Fe, Mn, Cr, Zn, Ni, Cu, Pb, As, Cd and Hg reported was 8.2%, 3.9%, 775 mg kg⁻¹, 92 mg kg⁻¹, 67 mg kg⁻¹, 47 mg kg⁻¹, 28 mg kg⁻¹, 17 mg kg⁻¹, 4.8 mg kg⁻¹, 0.09 mg kg⁻¹ and 0.05 mg kg⁻¹, respectively. The elements i.e. Ni and As; P, Cd, Pb and Hg; and S, Cl, Mn, Cu and Zn were highly ($20 \geq EF < 40$), significantly ($5 \geq EF < 20$) and moderately ($2 \geq EF < 5$) were enriched in the soil, respectively. Similarly, the soil was highly ($CF \geq 6$), considerably ($3 \geq CF < 6$) and moderately ($1 \geq CF < 3$) contaminated with As, Ni and Pb; S, Cl, P, Cu, Cd and Hg and Mn, Fe and Zn, respectively. The PLI value for heavy metals i.e. As, Ni, Pb, Cd and Hg was found to be 8.6 indicating their high contamination in the soil.

4 CONCLUSIONS

The enormous coal burning tends to increase the concentration of elements i.e. As, Zn, Cd, Pb and Hg in the geomedial of the Korba basin. The highest pollution indices for elements i.e. As, Ni and Pb were recorded. The vertical transport of elements i.e. As, Cr, Cu, Ni, Zn, Cd and Hg via the soil media was enhanced with increasing soil depth profile, may be due to less binding with the organic compounds. The whole As exists in the toxic inorganic forms i.e. As(III) and As(V) in the geomedial.

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