

Black Carbon and Heavy Metal Contamination of Soil

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Abstract

Black carbon (BC) and heavy metals (HM_s) are of great interest to researchers due to their hazardous impact on the environment. Coal is a dirty fuel and its huge exploitation (mining and combustion) causes serious pollution of the environment. In this work, the contamination by BC and HM_s of the soil of the coal basin in Korba, India, was evaluated. Higher concentrations of BC and Fe were detected in the soil samples, ranging (n = 9) from 4.5-7.3 and 4.1-9.3% with mean value of 5.5 and 6.6%, respectively. Concentrations of As, Cr, Mn, Cu, Zn, Cd, Pb, and Hg in the surface soil (n = 9) ranged from 91-116, 88-109, 2,423-5,063, 140-479, 128-377, 1.25-2.73, 858-4,973, and 0.88-2.37 mg kg⁻¹ with values of 101±5, 98±5, 3409±721, 229±72, 227±48, 1.84±0.35, 2068±882, and 1.45±0.33 mg kg⁻¹, respectively. Among HM_s, Pb is extremely enriched in the soil. The main sources of HMs in the soil apportioned are coal burning and mining.

Keywords: black carbons, heavy metals, soil, India

Introduction

Coal is a natural combustible material that contains elemental carbon, sulfur, trace metals, hydrocarbons, etc. [1-3]. Complex environmental issues, i.e., acid drainage, storage of solid waste, air pollution, deposition of toxic compounds, halting of acid rain, health hazards, etc., have appeared due to huge exploitation (mining and burning) of coal [4-14]. The ash contributes ≥ 30% of the lignite coal and its main constituents are carbon, alumina, iron, silica, heavy metals, etc. [15-17]. The coal ash exits in the form of fine particles and is linked to various health problems,

i.e., organ disease, cancer, respiratory illness, neurological damage, and developmental problems, and it even kills plants and animals [18].

Black carbon (BC), a major constituent of air and fly ash particulates, contributes to global warming through absorption of solar irradiance [19-20]. BC is a good adsorbent for toxic chemicals, i.e., heavy metals, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans (PCDD/Fs), PCBs, and PBDEs due to its high surface-to-volume ratio and a strong affinity [21-24]. The BC in soil changes the cyclic process of organic matter and increases cation exchange capacity of soil [25]. The HM_s in soil affects the quality of food, groundwater, micro-organism activity, and plant growth [26-27]. The rain, runoff, and groundwater were suspected to be contaminated with HM_s

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in the Korba Basin due to the burning of several million tons of coal [28-29]. Keeping all the above facts in mind, the present work was undertaken to evaluate the status of soil in terms of the contamination and sources of BC and HM_s in the surface soil of the Korba Basin.

Material and Methods

Study Area

The richest coal deposits in India are found in the Korba Basin (22°35'N; 82°68'E). Several open and underground coal mines are in operation with annual production of ≈ 3 BT coal annually since year 1960. A huge amount of lignite coal (>10000 MT annually) is consumed by various thermal power plants that emit several million tons of fly ash in the environment. The population of the Korba area inclusive of suburbs is ≈ 0.5 million. The environment of Korba city is polluted due to the huge exploitation of coal [28-29].

Sample Collection

The soil samples were collected from nine locations of the Korba Basin situated over a $\approx 1,000$ km² area

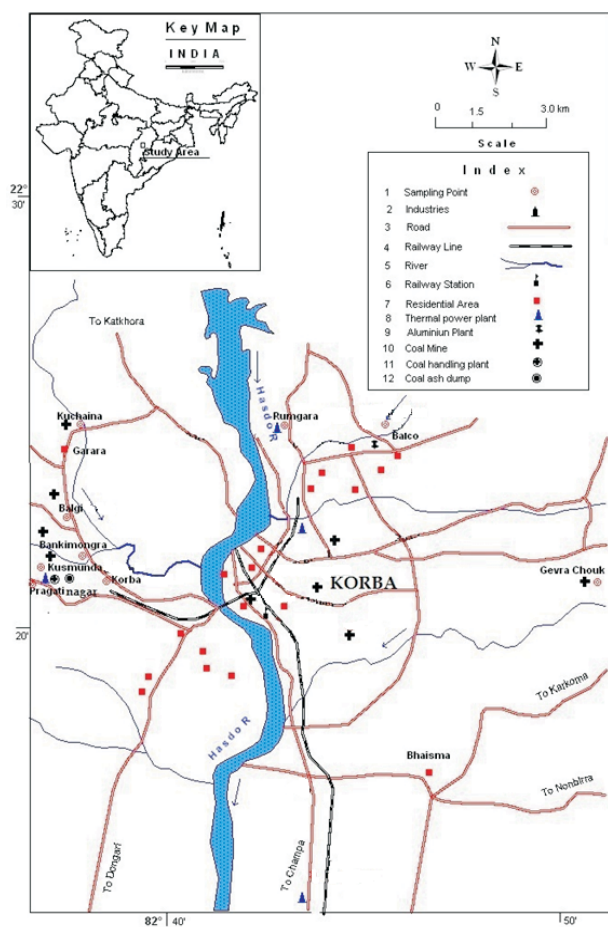


Fig. 1. Representation of sampling locations in the Korba area, India.

(Fig. 1). A 5-cm surface layer of the core was stripped off and the rest of the sample was taken. Approximately 1 kg of surface soil samples (0-15 cm) were collected at a radius of ≈ 5 cm in a clean polyethylene container during January, 2011, as prescribed in the literature [30]. For depth profile studies, the samples were collected in an airtight container at depths of 0-15, 15-30, and 30-45 cm as per the standard procedure. The samples were transported to a laboratory for analysis.

Sample Preparation

Soil samples were air dried, ground with a mortar and pestle, and then sieved through a 1-mm sieve to achieve a homogenous sample.

The P/T MARS CEM (Varian Company) microwave digester was used for the digestion of soil samples at 200°C with a hold time of 15 min. The soil sample (0.25 g) was digested with aqua regia (2 mL of HNO_3 , 65%, v/v + 6 mL of HCl , 37%, v/v) using the EN 13346-2001 method [31].

pH Determination

Soil particles of ≤ 1 mm were used to determine pH values using a suspension of 1:2 (m/v) soil-to-deionized water in a 100-mL conical flask. The suspension was allowed to stand overnight (12 hr) and measured by a Hanna pH meter type-HI991300.

Metal Analysis

The ICP OES (Varian Liberty-II Radial) was used for analysis of metals, i.e., Fe, Cr, Mn, Cu, and Zn due to good detection limits (≈ 2.5 mg kg⁻¹). A SpectrAA 220 Zeeman GFAAS (detection limits of <0.3 μ g kg⁻¹) was employed for analysis of As, Cd, and Pb. The CVAAS SpectrAA 55B (detection <0.02 μ g kg⁻¹) was used for the monitoring of Hg. The standard NCS DC 73382 CRM soil sample was employed quality control of the analysis. All measurements were carried out in triplicate and their mean values were reported.

Carbon Analysis

A CHNSO-IRMS Analyzer by SV Instruments Analytica Pvt. Ltd was used for analysis of total carbon (TC). TC, i.e., black carbon or elemental carbon (BC or EC), organic carbon (OC), and carbonate carbon or inorganic carbon (CC or IC) were analyzed in the soil samples. The soil sample (15 mg) was oxidized with O_2 at 1,020°C with constant flow of helium. The resulting CO_2 gas was detected by a thermal conductivity detector. The H_3PO_4 -treated soil sample (10 drops) was oxidized with O_2 at 1,020°C in a similar way to determine BC and OC contents. The OC content was analyzed by titration method using $K_2Cr_2O_7$ as oxidant, and the excess of $K_2Cr_2O_7$ was determined by back titration with the $FeSO_4 \cdot 7H_2O$ solution [32]. The CC content in the soil was evaluated by

Table 1. Physico-chemical characteristics of surface soil.

S. No.	Location	Color	pH	BC (%)	OC (%)	CC (%)
1	Rumgara	Br	6.94	6.3	0.65	0.33
2	Pragati Nagar	Gr	6.94	4.5	0.34	0.19
3	Gevera Chowk	Bk	6.65	4.8	0.35	0.22
4	Kusmunada colony	Br	6.68	4.6	0.34	0.20
5	Korba	Gr	5.37	5.4	0.44	0.22
6	Banki mongra	Br	6.47	5.6	0.54	0.23
7	Balgi	Bk	7.03	5.5	0.44	0.24
8	Kuchaina	Br	6.75	7.3	0.75	0.36
9	Balco	Bk	5.70	5.7	0.64	0.32

Br = Brown, Bk = Blackish, Gr = Gray, SECL = South eastern coal Ltd.

subtracting the BC and OC content to the TC by using the following equation:

$$CC = TC - (BC + OC)$$

Pollution Indices

The pollution indices, i.e., enrichment factor (EF), contamination factor (CF), geo-accumulation index (GAI), pollution load index (PLI), and ecological risk index (ERI), were used for geochemistry assessment of the HM_s [33]. Among them, the EF value was used to assess pollution of HM_s in soil with respect to crustal contributions [34]:

$$EF = ([C_m]/[C_{Al}]_{soil}) / ([C_m]/[C_{Al}]_{crust})$$

...where, C_m and C_{Al} denote the concentrations of the metal and aluminum in the soil and crust. Five contamination categories were recognized on the basis of the enrichment factor: $EF < 2$, depletion to mineral enrichment; $2 \leq EF < 5$, moderate enrichment; $5 \leq EF < 20$, significant enrichment; $20 \leq EF < 40$, very high enrichment; and $EF > 40$, extremely

high enrichment [35].

A contamination factor (CF) was used to describe the contamination of a given toxic substance in the geomeia [36]:

$$CF = ([C_m]_{soil} / [C_m]_{crust})$$

The following terminologies were used to mention the contamination factor: $CF < 1$, low contamination factor; $1 \leq CF < 3$, moderate contamination factors; $3 \leq CF < 6$, considerable contamination factors; and $CF \geq 6$, very high contamination factor. A root of the product of CF can be defined as pollution load index (PLI):

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

The pollution load index (PLI) provides a simple and comparative means for assessing the level of heavy metal pollution. An index of the geo-accumulation index (GI) is used to determine metal contamination in the geomeia by comparing current concentrations with pre-industrial levels [37-38]:

Table 2. Heavy metals contents in surface soil (mg kg⁻¹).

S. No.	Fe (%)	As	Cr	Mn	Cu	Zn	Cd	Pb	Hg
1	7.6	110	107	4969	336	249	2.41	1670	2.05
2	4.1	102	91	2656	140	128	1.25	858	0.88
3	4.9	96	96	2934	189	183	1.32	1250	1.12
4	6.6	95	97	2466	147	177	1.3	1132	1.02
5	5.6	96	88	2423	169	207	1.56	1410	1.31
6	6.8	91	94	2854	197	286	2.08	1798	1.4
7	7.4	97	98	2801	172	254	1.77	1892	1.19
8	9.3	116	109	5063	479	377	2.73	4973	2.37
9	7.4	104	105	4518	230	183	2.11	3628	1.74

Table 3. Statistics of metal concentrations in surface soil (mg kg⁻¹).

Parameter	Fe (%)	As	Cr	Mn	Cu	Zn	Cd	Pb	Hg
Min	1.8	91	34	314	140	126	1.1	858	0.10
Max	9.3	116	109	5063	479	510	2.73	4973	2.37
AM	5.3	100	81	2365	200	219	1.62	1776	0.92
GM	4.8	99	77	1762	187	201	1.56	564	0.53
MV	4.9	98	91	2466	165	183	1.39	858	1.02
STD, ±	2.2	7	24	1593	92	107	0.5	1350	0.80
CL, ±	1.1	3	12	779	61	61	0.3	882	0.40
Skew	0.16	0.93	-0.63	0.40	2.52	1.74	1.10	1.62	0.39
Ku	-0.91	0.62	-0.95	-0.85	6.37	3.14	0.28	1.9	-0.99

AM = Arithmetic mean, GM = Geometric mean, MV = Median value, CL = Confidence limit, Skew = Skewness, Ku = Kurtosis

$$GI = \log_2 \left(\frac{[C_{m,soil}]}{[1.5 C_{m,crust}]} \right)$$

The geo-accumulation index (GAI) was distinguished into seven classes by Müller: $GI \leq 0$, class 0, unpolluted; $0 > GI \leq 1$, class 1, from unpolluted to moderately polluted; $1 > GI \leq 2$, class 2, moderately polluted; $2 > GI \leq 3$, class 3, from moderately to strongly polluted; $3 > GI \leq 4$, class 4, strongly polluted; $4 > GI \leq 5$, class 5, from strongly to extremely polluted; and $GI > 5$, class 6, extremely polluted.

Ecological risk index (ERI) was used to measure both risk factor and metal concentrations in soil. The ERI value was determined through the following equation:

$$ERI = Tr \times CF$$

...where, Tr is the potential ecological risk factor/index. The toxic response value for metals reported are As = 10, Cr = 2, Cd = 30, Cu = 5, Pb = 5, Hg = 40, and Zn = 1 [39].

Statistical Analysis

The confidence limit of the data was reported at 95% probability. Factor analysis was used to assess BC and HM_s contamination in the soil [40-41].

Results and Discussion

pH of Soil Extract

The physico-chemical characteristics of the soils are summarized in Table 1. The soil was colored, ranging from brown (Br) to blackish (Bk). The pH value of the soil extracts was ranged from 5.4-7.0 with mean value of 6.4 ± 0.4 . The soil of the studied area was found to be slightly acidic due to deposition of acids by the burning coal [42].

Carbon Concentration

Three types of carbons: BC, OC, and CC were analyzed in the soil. Their concentrations ranged ($n = 9$) from 4.5-7.3, 0.34-0.75, and 0.19-0.36%, with mean values of 5.5 ± 0.6 , 0.50 ± 0.13 , and $0.26 \pm 0.04\%$, respectively. Good correlations ($r = 0.91-0.95$) of the BC with the OC and CC were observed, may be due to their similarity in origin. The carbon concentration in the soil of the study area was found to be higher than the soils of other regions of the world [43-49].

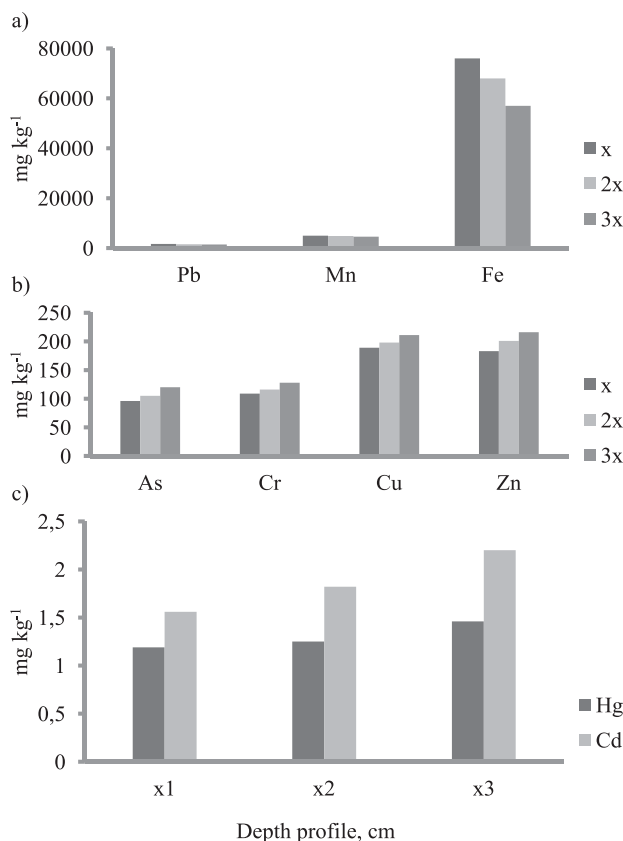


Fig. 2. Vertical distribution of metals, a) x1 (0-15 cm), b) x2 (15-30 cm), and c) x3 (30-45 cm).

Table 4. Results of Factor analysis of heavy metals in the soil.

Variable	Factor 1
BC	-0.98
Fe	-0.98
As	-0.93
Hg	-0.89
Pb	-0.76
Zn	-0.95
Cd	-0.75
Cu	-0.85
Mn	-0.84
Cr	-0.90
Eigen value	7.85
% Variance	78.50
% Cumulative Variance	78.50

Loading value > 0.70 (in absolute value), significant at $p < 0.05$.

Heavy Metal Concentrations

The concentrations of nine metals in the surface soil of Korba Basin is presented in Table 2. Among them, the highest concentration of Fe was observed, ranging from 4.1-9.3% with mean value of 6.6%. The concentration of other HM_s , i.e., As, Cr, Mn, Cu, Zn, Cd, Pb, and Hg in the surface soil ($n = 9$) ranged from 91-116, 88-109, 2,423-5,063, 140-479, 128-377, 1.25-2.73, 858-4,973, and 0.88-2.73 $mg\ kg^{-1}$ with mean value of 101 ± 5 , 98 ± 5 , $3,409 \pm 721$, 229 ± 72 , 227 ± 78 , 1.84 ± 0.36 , $2,068 \pm 882$, and $1.45 \pm 0.33\ mg\ kg^{-1}$, respectively. The geometric mean (GM) values for As, Cr, Mn, Cu, Zn, Cd, Pb, and Hg were 101, 98, 3,266, 211, 217, 1.77, 1,776, and 1.38, and were

found to be comparable with the arithmetic mean value. The skewness and kurtosis values ranged from -0.1-1.8 and -0.02-2.9, respectively (Table 3). The highest concentration of the HM_s (i.e., Fe, Mn, Zn, Cd, Pb, and As) was seen at the location of Kuchaina and may be due to running the thermal power plant at a distance of ≈ 5 km away in the wind direction (Table 2). The HM_s content in the soil of the basin was seem to be higher than the contents reported in the soil of other regions of the country and the world [50-55].

Depth Profile Studies

The vertical distribution of the metals in the soil is presented in Fig. 2. The distribution ratio of metals, i.e., Fe, Mn, and Pb, was decreased vertically when the depth profile was increased from 0-45 cm due to chemical reactions with organic matters. These metals remained deposited in the topsoil layers. Among them, the highest concentration of Fe was observed in the topsoils due to the lowest distribution ratio ($d = 0.8$). The vertical transport of other HM_s , i.e., As, Cr, Cu, Ni, Zn, Cd, and Hg, was increased when the depth profile was increased 0-45 cm, perhaps due to their decreased binding with organic matter. Among them, the highest distribution ratio ($d = 1.4$) was observed for Cd, possibly due to the higher solubility of its compounds.

Pollution Indices

The background concentrations of Al, Fe, As, Cr, Mn, Cu, Zn, Cd, Pb, and Hg in the earth's crust were recorded as 81,500, 39,200, 4.8, 92, 774, 28, 67, 0.09, 17, and 0.05 $mg\ kg^{-1}$, respectively [56]. The HM_s incursion in soil of the study area was described by four factors: EF, PLI, GAI, and ERI.

The mean EF values for Pb, Hg, As, Cd, Cu, Mn, Zn, Fe, and Cr were found to be 137, 31, 22, 22, 8.5, 4.7, 3.6, 2.0, and 1.2, respectively. The metals: Pb; Hg, As, and Cd; Cu; and Mn, Zn, and Fe were extremely, highly, significantly, and moderately enriched in the soil me-

Table 5. Correlation matrix of the variables for soils.

	BC	Fe	As	Hg	Pb	Zn	Cd	Cu	Mn	Cr
BC	1.00									
Fe	0.87	1.00								
As	0.74	0.57	1.00							
Hg	0.75	0.82	0.79	1.00						
Pb	0.82	0.72	0.88	0.93	1.00					
Zn	0.93	0.78	0.87	0.82	0.88	1.00				
Cd	0.88	0.83	0.45	0.54	0.53	0.80	1.00			
Cu	0.96	0.88	0.70	0.79	0.87	0.88	0.83	1.00		
Mn	0.83	0.80	0.69	0.74	0.76	0.80	0.69	0.80	1.00	
Cr	0.96	0.83	0.81	0.84	0.93	0.95	0.76	0.96	0.82	1.00

dia, respectively. The EF values for metals in the studied area were observed in the following decreasing trend: $Pb > Hg > As \approx Cd > Cu > Mn > Zn > Fe > Cr$.

The mean CF values for Pb, Hg, As, Cd, Cu, Mn, Zn, Fe, and Cr were 122, 29, 21, 20, 8.2, 4.4, 3.4, 1.7, and 1.1, respectively. The similar decreasing trend of the HM_s contamination of the soil was marked. The PLI value for Pb, Hg, As, Cd, Cu, Mn, Zn, Fe, and Cr was 104, 28, 21, 20, 7.5, 4.2, 3.2, 1.6, and 1.1, respectively. The PLI values confirmed that soil was polluted strongly with metals, i.e., Pb, Hg, As, and Cd.

Similarly, the mean GAI values for Pb, Hg, As, Cd, Cu, Mn, Zn, Fe, and Cr were 6.4, 4.3, 3.8, 3.8, 2.5, 1.6, 1.2, 0.2, and -0.49, respectively, and their pollutions are categorised into the following classes. The soils are severely to extremely, strongly, moderately, and unpolluted with Pb; As and Cd; Cu, Mn, and Zn; and Fe and Cr, respectively. The ERI values for Hg, Pb, Cd, As, Cu, Zn, and Cr for the soil of the studied area were found to be 1,160, 610, 600, 210, 41, 3.4, and 2.0, respectively. Very high risk exposures ($ERI \geq 320$) of the three metals Hg, Pb, and Cd in the environment were expected, whereas, high ($ERI < 320$) and moderate ($ERI > 40$) risk exposures for As and Cu were assumed.

Sources

The results of the factor analysis (FA) are shown in Table 4. In this work, only one factor of the FA, including 78.5% of the total variance, was extracted. All the loadings were significant in the absolute value and well associated with Factor 1. This factor was negatively correlated with all the metals. The higher association of the HM_s with the BC was marked (Table 5). This identified the activities related to the coal burning and mining as the source of the HM_s in the soil. The HM_s in the soil were also strongly correlated with the Fe content, but to a smaller extent than with the Mn.

Conclusions

The high BC content in Korba Basin surface soil tends to accumulate the HM_s at dangerous levels. The soil is highly polluted with very toxic metals, i.e., Pb, Hg, As, and Cd due to continuous coal exploitation (i.e., burning and mining) at huge levels. Among toxic metals, the highest mobility for Cd through soil media was observed. The multi-pollution index analysis approaches showed that toxic metals, i.e., Pb, Hg, As, and Cd can cause serious environmental problems in the Korba Basin ecosystem. The alarming situation of these toxic metals in the studied area should be regularly monitored for health-related problems in the inhabitants.

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