

Heavy Metal Contamination of Tree Leaves

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Abstract

The study of heavy metal (HM_s) contamination of environment is of great interest due to their serious health hazard. In this work, the contamination of tree leaves with the HM_s in the most polluted industrial city, Korba, India is described. The leaves of common trees *i.e.* *Azadirachta indica*, *Butea monosperma*, *Eucalyptus*, *Ficus religiosa*, *Mangifera indica* and *Tectona grandis* were selected for assessment of the HM_s contamination as bioindicator. The elevated concentration of HM_s (*i.e.* As, Fe, Cr, Mn, Cu, Zn, Cd, Pb and Hg) in the tree leaves was observed, ranging from 2.8 - 43, 728 - 5182, 8.6 - 49, 48 - 1196, 43 - 406, 79 - 360, 1.12 - 1.65, 1.6 - 16.4 and 0.13 - 0.76 mg/kg, respectively. The concentration, enrichment and sources of the HM_s in the leaves are described. *Azadirachta indica* leaves, accumulating higher concentration of the HM_s, showed a higher efficiency as bioindicator for the urban pollution.

Keywords

Heavy Metal, Soil, Tree Leaf, Bioindicator, India

1. Introduction

The quality of environment (*i.e.* air, water and soil), microorganism activities, plant growth, etc. are affected by heavy metal (HM_s) contaminations [1]-[3]. The woody plants are being excellent tool for biomonitoring of the metals due to rapid growth, high biomass, profuse root apparatus and low impact on the food chain and human health [4]-[9]. The accumulation of HM_s in the tree leaves was reported to assess air quality and bioaccumula-

tion fluxes [10]-[18]. The coal is widely used as source of energy in India and its huge exploitation causes the contamination of the environment [19]-[23]. In the present work, concentration, enrichment, and sources of the HM_s (*i.e.* As, Fe, Cr, Mn, Cu, Zn, Cd, Pb and Hg) in the dried leaves of common woody trees (*i.e.* Eucalyptus, Butea monosperma, Ficus religiosa, Tectona grandis and Azadirachta indica) in the largest coal burning basin, Korba, India are described as a bioindicator to assess the HM_s contamination of the environment.

2. Methods and Materials

2.1. Study Area

The Korba coal basin, Chhattisgarh, India (22°21'N, 82°40'E, above >250 m from seas levels) was selected for the proposed investigation due to extreme environmental pollution. The area is covered by the dense tropical moist and deciduous forest dominated by trees *i.e.* Tectona grandis, Shorea Robusta, Pterocarpus marsupium, Anogeissus latifolia, Madhuca indica, Dendrocalamus strictus, Azadirachta indica, Butea monosperma, Eucalyptus, Ficus religiosa, Mangifera indica, etc. Several open and underground coal mines are in operation with production of >10,000 MT/Yr coal. The most of electricity (40,000 MW) of the state is produced by the thermal power plants emitting effluents in the city. The Asia biggest aluminium plant with captive power plant of 1200 MW is also in operation. The population of city is \approx 1 million, being exposed with severe particulate and fly ash pollution.

2.2. Collection of Soil and Plant Leaf Samples

The sampling networks of soil and plant samples are shown in **Figure 1**. Leaves of six trees (*i.e.* Azadirachta indica, Butea monosperma, Eucalyptus, Ficus religiosa, Mangifera indica and Tectona grandis) of great social economic values were selected for this work. Azadirachta indica is a fast-growing broad-leaved evergreen large tree of India. The leaves have antibacterial and antiviral properties, and are often used in cosmetic and skin treatment preparations. Butea monosperma is a medium sized dry season-deciduous \approx 15 m tall tree. The leaves are used as fodder for animals. Eucalyptus is quick growing tall tree with leaf of leathery in texture, hang obliquely and containing a fragrant volatile oil. Ficus religiosa is a large dry season—deciduous or semi-evergreen tree up to 30 m tall with a large trunk with long and broad leaves. The Mangifera indica is a fruity tree with leafy green foliage of height ranging from 0.5 - 15 m. Tectona grandis is a large deciduous tree having height up to 35 m with simple large leaves.

A 0.5 \times 5 kg of the surface soil samples (0 - 10 cm) from rhizospheric zone of five trees of each species was collected in January, 2013 from Manikpur, Korba as prescribed in the literature [24]. They were stored in polyethylene bottles and dried in an oven for overnight at 60°C.

The leaves from five trees of each species (\geq 10 Yrs old) were collected manually in January, 2013, washed thoroughly with deionized water and dried in a shed [25]. The samples were compressed into a powder with the help of a manual grinder and sieved out the particles of \leq 1 mm.

2.3. Analysis

The soil sample was mixed with deionised water into 1:2 (w/v) ratio in a 100-ml conical flask. The suspension was allowed to stand overnight, and pH value of the extract was measured by Hanna pH meter type-HI991300.

A 0.25 g each of soil sample was digested with 8 ml aqua regia in the closed microwave vessel for 15 min. Similarly, 0.25 g dried leaf sample was digested with 5 ml HNO₃ + 2 ml H₂O₂. An aliquot of the extract was diluted with deionized distilled water for further analysis. Similar procedure was applied for the digestion of the soil (NCS DC73382, Spex Certiprep, UK) and leaf (NIST-1515, USA) reference samples.

The Varian Liberty AX Sequential ICP-AES (plasma flow: 15 L/min, auxiliary flow: 1.5 L/min, power: 1 KW, PMT voltage: 650 V) was used for analysis of the metals *i.e.* Cr, Mn, Fe, Cu and Zn. A VARIAN "SpectraAA 220Z" model graphite furnace atomic absorption spectrometer (GF-AAS) equipped with a longitudinal Zeeman effect background corrector and THGA tube, auto sampler and automatic data processor was employed for analysis of metals *i.e.* Cd and Pb. The VARIAN "SpectraAA 55B" equipped with hydride/cold vapour regenerator accessories was selected for analysis of elements *i.e.* As and Hg. The accuracy of the method for analysis of the metals ($n = 3$) in the reference materials was found to be \leq 2%. The precision of the analysis for the metals in soil and leaf samples was \leq 5%.

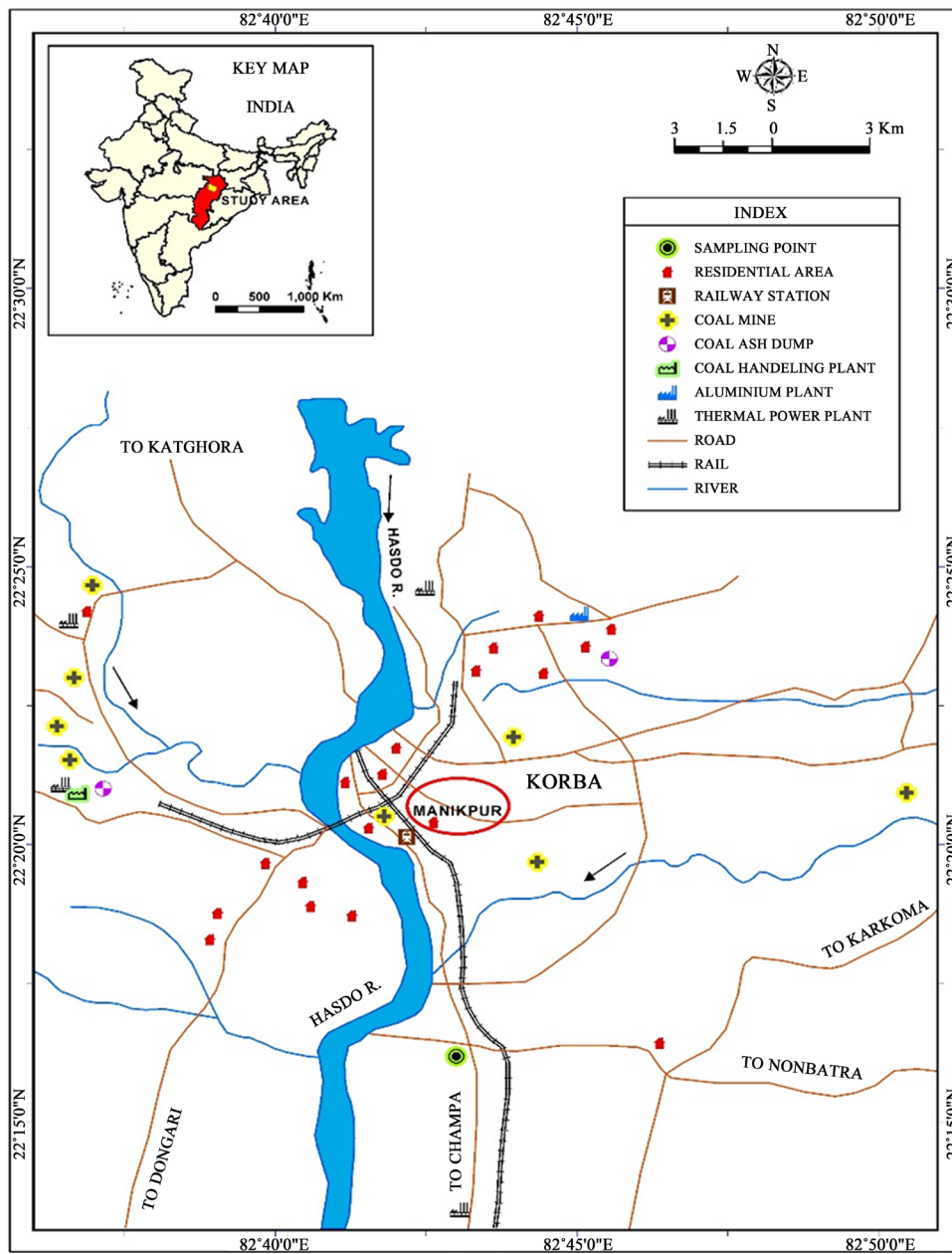


Figure 1. Representation of sampling location in Korba.

2.4. Pollution Indices

The enrichment factor (E_f) is used to assess pollution of heavy metals in soil with respect to crustal contributions [26].

$$E_f = \frac{([C_m]/[C_{Al}])_{soil}}{([C_m]/[C_{Al}])_{crust}}$$

where, symbols C_m and C_{Al} denote the concentration of the metal and aluminium in the soil and crust. The background concentration of Al, Fe, As, Cr, Mn, Cu, Zn, Cd, Pb and Hg in the earth crust reported was 81,500, 39,200, 4.8, 92, 775, 28, 67, 0.09, 17 and 0.05 mg/kg, respectively [27]. Five contamination categories are generally recognized on the basis of the enrichment factor: $E_f < 2$, depletion to mineral enrichment; $2 \geq E_f < 5$, moderate enrichment; $5 \geq E_f < 20$, significant enrichment; $20 \geq E_f < 40$, very high enrichment; and $E_f > 40$, extremely high enrichment [28].

3. Results and Discussion

3.1. Concentration of Metals in Soils

The physico-chemical characteristics of the rhizospheric soils are summarized in **Table 1**. The soils were colored, ranging from brown to blackish. The pH value of the soil extract ($n = 6$) was ranged from 6.2 - 7.2 with mean value of 6.6 ± 0.5 at 95% probability. The concentration of As, Cr, Mn, Fe, Cu, Zn, Cd, Pb and Hg in the soil ($n = 6$) was ranged from 10.8 - 20.0, 34 - 72, 314 - 1760, 17,718 - 45,426, 49 - 62, 26 - 62, 1.1 - 1.5, 19 - 48 and 1.2 - 2.0 mg/kg with mean value of 15.0 ± 2.5 , 57 ± 10 , 809 ± 395 , $34,730 \pm 7462$, 55 ± 4 , 43 ± 10 , 1.3 ± 0.1 , 33 ± 8 and 1.5 ± 0.3 mg/kg at 95% probability, respectively. The mean E_f value ($n = 6$) for Cr, Zn, Fe, Mn, Cu, Pb, As, Cd and Hg was found to be 7, 7, 10, 12, 22, 22, 35, 161 and 337, respectively. The metals *i.e.* Cr, Zn, Fe and Mn; Cu, Pb and As; and Cd and Hg were significantly, highly and extremely enriched in the soil, respectively. The concentration of the HM_s in the soil of Korba city was seen to be higher than reported in the soil of other region of the country, may be due to higher exploitation (*i.e.* mining and burning) of coal [21]-[23].

3.2. Concentration of Metals in Leaves

The concentration of HM_s in the dried leaves is summarized in **Table 2**. High concentration of As, Fe, Cr, Mn, Cu, Zn, Cd, Pb and Hg in the tree leaves was observed, ranging from 2.8 - 43, 728 - 5182, 8.6 - 49, 48 - 1196, 43 - 406, 79 - 360, 1.12 - 1.65, 1.6 - 16.4 and 0.13 - 0.76 mg/kg, respectively. The highest content of all metals (except Mn, Cd and Hg) was marked with the *Azadirachta indica* leaves, may be due to bio-adsorption of the metals with the inherent alkaloids [29]. Similarly, the highest accumulation of metals *i.e.* Mn, Cd and Hg was observed in the *Eucalyptus*, *Mangifera indica* and *Butea monosperma* leaves, respectively, **Table 2**. The recommended values of As, Fe, Cr, Mn, Cu, Zn, Cd, Pb and Hg in the vegetables were reported to be 0.1, 425, 2.3, 500, 40, 100, 0.1, 0.2 and 0.03 mg/kg, respectively [30]. Several folds higher concentration of metals *i.e.* As, Fe, Cr, Cu, Cd, Pb and Cd than the recommended values was marked in all tree leaves. Extremely high Mn content in the *Eucalyptus* leaves was observed, being higher than recommended value of 500 mg/kg.

The As content in the lichens of Mandav Monuments, India was reported maximum up to 51.95 mg/kg [10]. The content of Cu, Zn, Cd and Pb in leaves of natural and exotic plants of Samsun City, Turkey was ranged 40 - 60, 70 - 75, 0.1 - 0.3 and 12 - 35 mg/kg, respectively [12]. The Mn content in leaf of *holoptelia*, *cassia* and *neem* trees of Gumgaon, India was reported in the range of 168.59 - 437.56 mg/kg [17]. The content of Cu, Pb and Cd in the horse chestnut leaves at Studentski Park site was amounted to 110.2, 20.3 and 4.9 mg/kg, respectively [18]. The HM_s contents in the tree leaves of Korba city was found to be comparable with the values reported in other location of the country and World [10]-[12] [17] [18].

3.3. Bioaccumulation of Metals in Leaves

The bioaccumulation factor (B_f) of the metals (ratio of leaf to soil content) in the leaves is presented in **Table 3**. Significant B_f value (>1) of metals *i.e.* As, Fe, Cu, Zn and Cd in the *Azadirachta indica* leaves was observed. Similarly, high B_f value (>1) of Zn was marked in all tested leaves. The highest B_f value for metals *i.e.* As, Fe, Cr, Cu, Zn and Pb was observed with the *Azadirachta indica* leaves, may be due to interaction of bioactive compounds (*i.e.* *azadirachtin*, *nimbin*, *nimbidin* and *nimbolides*). Significant B_f value for Mn, Cd and Hg was seen with *Eucalyptus*, *M. Indica* and *B. Monosperma* leaves, respectively. The results showed that the *Azadirachta indica* leaves are seemed to be a hyperaccumulator for five heavy metals *i.e.* As, Fe, Cu, Zn and Cd in a huge coal burning area. Leaves of other trees *i.e.* *M. Indica*, *Eucalyptus*, *B. Monosperma*, *F. Religiosa* and *T. Grandis* were observed to be hyperaccumulator for heavy metals *i.e.* Cu, Zn and Cd, respectively. Among them, only *Eucalyptus* leaves was marked as good hyperaccumulator for Mn.

3.4. Factor Analysis

The result of factor analysis in tree leaves is given in **Table 4**. Three factors were extracted, and a 65.60% of the total variance was accounted by Factor-I. Six HM_s *i.e.* Cr, Cu, Fe, Pb, Zn and As were positively correlated ($r = 0.69 - 1.00$) to each other in the leaves, **Table 5**. A 13.90% of the total variance was included in the Factor-II, and positively and negatively correlated with Cd and Hg, suggesting aerial accumulation of Hg in the leaves rather than soil [31]. A 12.74% of the total variance was contributed by Factor-III, and is negatively correlated with Mn.

Table 1. Physico-chemical characteristics of rhizospheric soil.

Soil	Color	pH	Mean value (n = 5) mg/kg								
			As	Cr	Mn	Fe	Cu	Zn	Cd	Pb	Hg
S1	Br	6.96	15.5	59	749	33,818	50	36	1.31	36.2	1.37
S2	Bk	6.85	20.0	62	618	34,218	56	40	1.39	32.7	1.81
S3	Br	6.37	15.6	72	1760	38,499	56	44	1.38	47.7	1.71
S4	Bk	6.16	15.8	34	314	17,718	49	26	1.11	18.5	1.95
S5	Br	7.12	10.8	53	634	45,426	59	50	1.52	27.2	1.16
S6	Br	7.18	12.2	64	780	38,700	62	62	1.10	35.2	1.26

S = Soil, Br = Brown, Bk = Blackish.

Table 2. Mean concentration (n = 5) of heavy metals in tree dried leaves, mg/kg.

Plant	As	Fe	Cr	Mn	Cu	Zn	Cd	Pb	Hg
Mangifera indica	3.9	1570	9.5	302	77	86	1.65	3.3	0.17
Eucaliptus	2.8	728	8.6	1196	43	184	1.20	1.7	0.20
Butea monosperma	3.0	2400	14.6	343	55	86	1.15	1.6	0.76
Ficus religiosa	3.1	1700	21.3	58	48	83	1.12	1.8	0.17
Tectona grandis	6.4	2891	14.3	48	98	79	1.20	1.8	0.13
Azadirachta indica	43.1	5182	48.6	94	406	360	1.12	16.4	0.36

Table 3. Mean bioaccumulation factor of metals in leaves.

Plant	As	Fe	Cr	Mn	Cu	Zn	Cd	Pb	Hg
Mangifera indica	0.24	0.05	0.16	0.41	1.54	2.41	1.26	0.10	0.13
Eucaliptus	0.13	0.03	0.14	1.94	0.77	4.61	0.87	0.06	0.10
Butea monosperma	0.20	0.05	0.22	0.19	0.98	1.98	0.84	0.03	0.43
Ficus religiosa	0.20	0.10	0.62	0.19	0.98	3.17	1.01	0.10	0.10
Tectona grandis	0.59	0.05	0.27	0.08	1.66	1.58	0.78	0.06	0.10
Azadirachta indica	3.54	1.33	0.76	0.11	6.55	5.80	1.01	0.48	0.36

Table 4. Results of factor analysis of heavy metals in the tree leaves.

Variable	Factor-I	Factor-II	Factor-III
Cd	-0.35	0.79	0.03
Cr	0.93	-0.12	0.30
Cu	0.97	0.06	0.21
Fe	0.83	-0.15	0.50
Mn	-0.16	-0.02	-0.98
Pb	0.97	0.09	0.15
Zn	0.97	0.00	-0.23
Hg	-0.37	-0.75	0.03
As	0.98	0.02	0.17
Eigenvalue	5.90	1.25	1.15
% Variance	65.60	13.90	12.74
% Cumulative Variance	65.60	79.49	92.23

Loading value > 0.70, significant at $p < 0.05$.

Table 5. Correlation matrix of HM_s in the tree leaves.

	Cd	Cr	Cu	Fe	Mn	Pb	Zn	Hg	As
Cd	1.00								
Cr	-0.44	1.00							
Cu	-0.24	0.94	1.00						
Fe	-0.35	0.90	0.92	1.00					
Mn	0.06	-0.46	-0.35	-0.60	1.00				
Pb	-0.19	0.94	0.99	0.86	-0.29	1.00			
Zn	-0.32	0.84	0.90	0.69	0.07	0.92	1.00		
Hg	-0.19	-0.27	-0.34	-0.14	0.10	-0.33	-0.33	1.00	
As	-0.28	0.95	1.00	0.90	-0.32	0.99	0.92	-0.33	1.00

4. Conclusion

The soil of the Korba city, India is highly polluted with As, Cu, Pb and Hg due to coal burning and mining. The highest phytoextraction of the HM_s was observed with *Azadirachta indica* leaves; it may be due to interaction of the alkaloids with the metals. Significant B_f values (>1) for metals *i.e.* As, Cu and Zn with the *Azadirachta indica* leaves were marked. The *Azadirachta indica* leaves could be considered as bioindicator for soil pollution of the HM_s in the coal burning area of the country.

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