

## Effect of Fly Ash Generated by Patratu Thermal Power Station on Properties of Cultivated Soils

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**Abstract** Soil and plants growing in the vicinity of thermal power plants display increased concentrations of heavy metals due to generation of huge amount of ashes. The purpose of this study is to quantify concentration of heavy metals in soil and plants in the vicinity of Patratu thermal power station (PTPS) located in Jharkhand State, India and discusses the results as against the standard prescribed limits. We quantified the concentration of heavy metals, viz. cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), manganese (Mn) and zinc (Zn) in soil and plant samples of the study area. The concentration of available micronutrients (Zn, Cu, Mn and Fe) in soil samples of the study area were above the

critical limit. Diethylene Triamine Penta Acetic Acid (DTPA) extractable Cd was detected in 50% of the samples and nearly all soil samples contained high DTPA extractable Pb, Ni and Co. The concentration of heavy metals in almost all the plants follows the order  $Fe > Mn > Zn > Ni > Co > Cu > Pb > Cd$ . Results indicated a significant degree of soil contamination for heavy metals and using these contaminated land for the production of food or feed crop constitute a greater risk of bioaccumulation of heavy metals in food chain. Therefore, it is suggested that policies and programs need to be adapted in such a way that local edaphic conditions and agricultural practices are taken into account to mitigate the accumulation of heavy metals in the topsoil and food chain over time.

**Keywords** Heavy metal, Monitoring soil quality, Plant samples, Thermal power plant.

### Introduction

Soil is essentially a non-renewable resource and not only a part of ecosystems, but also occupies a basic role for humans, because the survival of man is tied to the maintenance of its productivity. Soils normally contain low background levels of heavy metals and sources of heavy metals in soil are both natural, such as the weathering of primary minerals [1] and anthropogenic in origin, such as mining, industrial processes, energy production, agriculture, industry, vehicle ex-

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**Table 1.** The pH, EC (dS m<sup>-1</sup>), Org. C (g kg<sup>-1</sup>), available N, P and K (kg ha<sup>-1</sup>) content in soils.

Sample No.	pH	EC	Org. C	N	P	K
1	6.04	0.17	9.95	234	106	131
2	6.04	0.10	5.85	197	3	121
3	5.77	0.14	7.61	206	3	134
4	6.39	0.09	4.83	188	5	151
5	5.43	0.07	49.46	234	7	213
6	7.18	0.54	32.34	197	60	389
7	5.99	0.14	24.59	209	50	388
8	5.08	0.04	5.12	259	3	129
9	4.88	0.04	3.37	219	4	102
10	5.55	0.03	8.49	336	7	85
11	5.81	0.16	6.15	253	39	250
12	5.70	0.13	7.76	286	22	127
13	6.99	0.13	6.29	213	49	332
14	5.26	0.11	6.88	274	17	91
15	5.92	0.09	7.90	299	3	100
16	6.05	0.11	9.85	258	9	178
17	5.76	0.05	6.59	293	3	84
18	6.04	0.09	7.46	311	8	122
19	6.04	0.08	9.37	330	13	148
20	5.77	0.13	10.10	317	3	149
Range	4.88–7.18	0.03–0.54	3.37–49.46	188–330	3–106	84–389
Mean	5.90	0.12	11.00	256.5	21.5	180.6
SD ±	0.53	0.10	10.80	45.6	25.9	95.7

hausts, waste disposal and coal combustion [2]. The presence of heavy metals in agricultural soils continue to receive greater attention due to the greater understanding of their toxicological importance in ecosystems, agriculture and human health, while it is vital to consume small amounts of many metals to maintain good health, some metals cause particular concern if exposure is above the recommended limit [3].

The Patratu Thermal Power Station is located at 23°38'22"N and 85°17'12"E in the state of Jharkhand, India, was made by Russian collaboration in 1962 and has a power generation capacity of 800 MW thereby consuming several tons of coal annually. As a stationary source of pollution the thermal power plants directly and permanently pollute soil due to generation of huge amounts of ashes, which are a major source of heavy metal contamination in the adjacent areas. Using contaminated soils for the production of food or feed crop plants bears the risk that the con-

taminants are transferred into food and feed stuffs and ultimately create health risks for both humans and animals.

Keeping these facts in mind, this study was aimed to establish the pollution or contamination status of the agricultural soils as well as locally grown crops of the study area.

## Materials and Methods

Soil and plant samples were collected from agricultural fields around PTPS, Patratu, following standard sampling methods. Surface soil samples from a depth of 0–10 cm were collected from agricultural fields because the metal distribution in the top layer of soil down to 5 cm is important in relation with the bioavailability for plants and the risk to enter the food chain. Soil samples were air dried, ground and passed through sieve (2 mm). Locally grown plant parts were collected from the study area which included lady's finger (*Abelmoschus esculentus* L.), sponge gourd (*Luffa cylindrica* L.), bitter gourd (*Momordica charantia* L.), cucumber (*Cucumis sativus* L.), cow-pea (*Vigna unguiculata* L.), paddy (*Oryza sativa* L.) and maize (*Zea mays* L.). These are major plants grown in the study area for own consumption of the farmer and for supply to retail and wholesale markets of Patratu. After washing with clean tap water to remove the soil particles, plant samples were oven dried at 80°C to constant weight. The dried samples were ground, passed through a 2 mm sieve and stored at room temperature before analysis. Soil chemical properties were determined by standard procedures. The pH was determined with a 1:2.5 soil-to-solution ratio, electrical conductivity (EC) in a 1:5 extract by a conductivity bridge. The percentage of the organic carbon (OC) in the soil samples was measured by the titration method based on the oxidation of organic matter by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Available nitrogen was estimated by distilling soil with alkaline potassium permanganate and determining the liberated ammonia as per method. The soil was extracted with Bray P<sub>1</sub> extractant (0.03N NH<sub>4</sub>F in 0.025N HCl solution) and available P was determined on double beam spectrophotometer (Spectrascan UV2600). Available potassium was determined by flame photometer (Elico CL361)

**Table 2.** DTPA-extractable and total Zn, Cu, Mn, Fe, Cd, Pb, Ni and Co content (mg kg<sup>-1</sup>) in soils of study area. BDL=Below detection limit.

Sample No.	DTPA Zn	Total Zn	DTPA Cu	Total Cu	DTPA Mn	Total Mn	DTPA Fe	Total Fe	DTPA Cd	Total Cd	DTPA Pb	Total Pb	DTPA Ni	Total Ni	DTPA Co	Total Co
1	1.60	40	3.62	45	22.84	339	41.90	17660	BDL	1	2.10	57	1.38	201	2.06	79
2	0.43	126	1.63	74	24.94	698	19.94	19620	BDL	1	0.91	29	0.89	289	2.06	153
3	0.74	58	1.53	2	23.96	572	27.56	18220	0.02	1	1.02	29	0.48	260	2.15	190
4	1.16	24	3.20	59	24.88	931	11.50	18540	0.01	2	1.42	52	0.69	289	2.32	190
5	3.98	23	1.49	62	14.90	318	62.46	24640	0.02	1	0.68	45	0.41	407	1.21	153
6	4.51	31	1.34	74	11.78	536	14.52	12840	0.05	2	1.31	32	0.62	348	0.87	153
7	1.61	55	0.77	45	19.17	572	36.76	21820	0.04	3	1.99	29	0.41	465	0.79	190
8	0.31	28	0.79	45	18.31	482	27.10	16190	0.02	1	0.79	57	0.27	377	1.04	190
9	0.14	37	0.44	45	10.78	231	30.88	9939	BDL	4	0.63	84	0.28	174	0.87	153
10	0.90	43	1.78	117	18.60	231	36.10	14940	BDL	1	1.14	29	0.48	201	1.47	153
11	1.53	70	1.29	31	24.00	159	46.22	16890	0.03	2	0.45	24	0.04	231	1.29	5
12	1.36	39	2.30	59	19.95	716	52.92	15880	BDL	23	0.85	31	0.07	148	1.64	5
13	1.85	21	1.15	31	21.78	698	20.58	17490	BDL	16	0.80	33	0.41	55	1.55	5
14	1.06	46	2.34	31	24.62	752	51.90	19970	BDL	8	1.40	36	0.89	348	2.23	153
15	1.11	73	2.47	45	23.80	877	41.26	20880	BDL	12	0.97	57	0.96	84	2.23	5
16	0.99	83	1.40	88	24.66	1075	35.00	22520	0.01	12	0.57	57	1.10	172	1.72	42
17	0.26	24	1.50	16	24.32	1541	35.00	21610	0.01	4	0.28	29	1.38	231	2.40	116
18	0.61	39	2.34	74	23.94	1164	37.48	22660	BDL	19	1.20	29	0.90	172	1.98	42
19	1.16	21	1.98	88	18.78	1290	46.86	21790	0.01	12	2.52	32	1.17	84	1.64	79
20	0.83	3	2.74	88	21.48	1129	40.14	21510	BDL	1	1.58	32	1.03	201	1.89	42
Range	0.14-4.51	3-126	0.44-3.62	2-117	10.78-24.94	159-1541	11.50-62.46	9939-24640	BDL-0.05	1-23	0.28-2.52	24-84	0.04-1.38	55-465	0.79-2.40	5-190
Mean	1.47	43.6	1.77	52.4	21.12	689.4	36.33	183	0.01	6.3	1.13	40.2	0.69	236.9	1.67	104.9
SD±	1.18	26.7	0.80	28.9	4.20	374.7	12.61	3740.3	0.01	6.9	0.58	15.3	0.41	111.3	0.52	71.1

after extraction of soil with neutral normal ammonium acetate. DTPA extractable heavy metals (Zn, Cu, Mn, Cd, Pb, Ni and Co) were determined by extracting soil with diethylene triamine penta acetic acid (DDTP) solution (0.005 M DTPA + 0.01 M CaCl<sub>2</sub> + 0.1 M TEA at pH=7.3). For total heavy metal extraction, 1 g dried sample of plant or soil sample was accurately weigh and transferred into a beaker. Concentrated nitric acid (10.0 mL) was added, the beaker was covered with a watch glass and material was boiled gently on a hot plate provided with a tunable thermostat until digestion was complete. The complete digestion took about 3 h. 5.0 mL portion of 70% perchloric acid was then added and gentle heating was continued for another 1 h. Small aliquots of ultrapure water were added to prevent dryness due to evaporation and about 3 to 5 drops of hydrogen peroxide were added to discharge any coloration in the digest. After the digest was cooled, it was filtered using a Whatman No. 42 filter paper and transferred to a 50 mL volumetric flask that

has been rinsed with ultrapure water. Three replicate digestions were made for each sample. All necessary precautions were adopted to avoid any possible contamination of the sample [4]. The content of trace metal was determined on Atomic Absorption Spectrophotometer (EICL-AAS-4139) by employing the appropriate hollow cathode lamp.

## Results and Discussion

Soil reaction, electrical conductivity and organic carbon

Analytical results on pH, EC and OC content in soil samples ranged from 4.88 to 7.18, 0.03 to 0.54 dS m<sup>-1</sup> and 3.37 to 49.46 g kg<sup>-1</sup> respectively (Table 1). 65% soil samples collected from study area showed moderately acidic pH value. It may be ascribed to be due to leaching of bases in these high rain fall areas. The electrical conductivity of soil samples were within the

**Table 3.** Correlation coefficient (*r*) between soil properties and heavy metal content in soil. \*Significant at 5% level of significance, \*\*Significant at 1% level of significance.

	pH	EC	Org. C
DTPA extractable heavy metal content			
Zn	0.490*	0.699**	0.856**
Cu	0.176	0.002	-0.170
Mn	0.118	-0.305	-0.514*
Fe	0.509*	-0.312	0.279
Cd	0.299	0.630**	0.569*
Pb	0.220	0.175	0.075
Ni	0.183	-0.035	-0.035
Co	0.066	-0.279	-0.455
Total heavy metal content			
Zn	-0.010	-0.030	-0.184
Cu	0.106	0.028	0.152
Mn	0.227	-0.137	-0.243
Fe	0.045	-0.295	0.266
Cd	0.186	-0.094	-0.237
Pb	-0.366	-0.234	-0.103
Ni	-0.189	-0.201	0.543*
Co	-0.247	0.001	-0.001

safe limit. High OC content was observed in about 55% of the soil samples collected from the study area.

#### Available N, P and K in Soil

Status of available nitrogen, phosphorus and potassium in soils of study area are presented in Table 1. The available N content in soil ranged between 188–330 kg ha<sup>-1</sup> and around 90% of soil samples collected from study area showed low N rating (>280 kg ha<sup>-1</sup>) whereas, 60% soil samples were low in available P content and 25% samples exhibited high P availability (>28 kg ha<sup>-1</sup>). Low availability of P in soil may be due to the acidic nature of lateritic soil, where precipitation of soil phosphate with iron and aluminium reduced the P availability. Available K content ranged from 84 to 389 kg ha<sup>-1</sup> and 60% soil samples low available K status.

#### DTPA-extractable and total heavy metal content in soil samples

The DTPA extractable Zn, Cu, Mn, Fe, Cd, Pb, Ni and

Co content in soil samples of the study area ranged from 0.14–4.51, 0.44–3.62, 10.78–24.94, 11.50–62.46, Below Detection Level (BDL)–0.10, 0.28–4.24, 0.04–1.38 and 0.41, 2.32 mg kg<sup>-1</sup> (Table 2). As compared with critical limit for heavy metals, it may be concluded that DTPA-Zn was above the critical value (0.6 mg kg<sup>-1</sup>) in 75% soil samples, however, all soils collected from the study area contained Cu (0.2 mg kg<sup>-1</sup>), Mn (2.0 mg kg<sup>-1</sup>) and Fe (4.5 mg kg<sup>-1</sup>) above their respective critical limit values. Thus, the soils may be regarded as sufficient in available micronutrient content. Alarming presence of some toxic heavy metals were noticed. Cd was detected in 50% samples, however, these were below the maximum allowable limit (0.5 mg kg<sup>-1</sup>). DTPA-Pb was detected in all the samples, but these were below the maximum allowable limit (3.0 mg kg<sup>-1</sup>). DTPA extractable Ni and Co were found in all soil samples, but it was observed that none of the samples crossed the maximum allowable limit for Ni (2.0 mg kg<sup>-1</sup>), however all the samples crossed the maximum allowable limit for Co (0.5 mg kg<sup>-1</sup>). The normal range of heavy metals in soils are reported to vary widely. Detection of heavy metals in many soils in considerable amount is a matter of concern as acidic condition favors their accumulation and availability in soils, leading to enhanced uptake and accumulation in the plant parts and ultimately entering in the food chain. The danger lies in the fact that once heavy metal enters into the soil-plant-animal continuum, their removal is extremely difficult and expensive. Build up of micronutrient cations in sewage irrigated soils, effluent irrigated soils [5] and soils nearer to industrial activity have been reported earlier.

Table 2 depicts the total content of Zn, Cu, Mn and Fe (3–126, 2–117, 159–1541 and 9939–24640 mg kg<sup>-1</sup> respectively) in agricultural soils collected from study area. Mean total Zn concentration in lithosphere is reported to be 80 mg kg<sup>-1</sup> and total Zn content in world soil ranges between 10 to 300 mg kg<sup>-1</sup>. In present study none of the sample collected from all three locations crossed the upper limit (300 mg kg<sup>-1</sup>) of total Zn content in soils.

The total Cu content in different soils of world ranges from 4.4 to 63.5 mg kg<sup>-1</sup>. Higher value of total Cu in about 35% soil samples collected from study area was observed during investigation.

**Table 4.** Concentration of heavy metals (mg kg<sup>-1</sup>) of selected plant species\* (26).

Botanical name	Common name	Zn	Cd	Pb	Ni	Co	Fe	Cu	Mn
<i>Abelmoschus esculentus</i> L.	Lady's finger	34.42	1.27	10.82	17.35	11.95	826.50	8.25	96.20
<i>Vigna unguiculata</i> L.	Cowpea	47.40	0.65	1.90	13.55	17.95	1082	8.60	39.20
<i>Cucumis sativus</i> L.	Cucumber	29.30	5.00	11.90	6.90	11.95	1130	6.50	87.00
<i>Luffa cylindrica</i> L.	Sponge gourd	42.95	2.50	10.55	19.15	15.95	889	8.60	45.85
<i>Momordica charantia</i> L.	Bitter gourd	91.70	0.65	11.45	17.30	9.95	916	3.05	73.05
<i>Zea mays</i> L.	Maize	49.82	BDL	3.92	12.62	4.5	1165	12.05	105.00
<i>Oryza sativa</i> L.	Paddy	44.32	3.26	BDL	5.57	20.17	1600	11.71	356.12
	Range	29.30–	BDL–	BDL–	5.57–	4.5–	826.50–	3.05–	39.20–
		91.70	5.00	11.90	19.15	20.17	1600	12.05	356.12
Safe limit (PFA) (mg kg <sup>-1</sup> )		50	1.5	2.5	3.0	3.0*	–	–	–

Average Mn concentration in earth's crust is reported to be 900 mg kg<sup>-1</sup>, while worldwide average total Mn content in soil is 600 mg kg<sup>-1</sup>. About 55% of the soils collected from study area exceeded the world average.

Iron is one of the principle elements in the Earth's crust and is mainly associated with coarse atmospheric particles. If associated with other sources, it is generally deposited in the neighbourhood of the emission sources. Lithosphere contains 5.1% Fe (51000 mg kg<sup>-1</sup>), however, total Fe content in world soil ranges from 0.02 to 10% (200 to 100000 mg kg<sup>-1</sup>). In present study total Fe content in soils collected from all locations were within the reported range.

Total Cd, Pb, Ni and Co content in soil samples collected from study area are presented in Table 2. It was noticed that samples collected from study area had total Cd from 1 to 23, total Pb from 24 to 84, total Ni from 55 to 465, while total Co from 5 to 190 mg kg<sup>-1</sup> with respective mean values of 6.30, 40.20, 236.90 and 104.90 mg kg<sup>-1</sup>.

Heavy metal is emitted into the atmosphere from both natural sources (weathering of basaltic rocks) and anthropogenic sources like metallurgical operations (2). About 65% of the soils of study area crossed the worldwide range for total Cd reported to be 0.06 to 1.1 mg kg<sup>-1</sup>. He also reported the range of Pb, Ni

and Co in world soil as 10–84, 4–55 and 1.6–21.5 mg kg<sup>-1</sup> respectively. In the soils of the study area except Pb both Ni and Co was above the highest range as compared with the world soil range.

#### Relationship amongst Soil pH, EC and Org C and trace metal availability in soil

Correlation study between DTPA-extractable and total trace metal content of soil with pH, EC and OC are presented in Table 3. A positive significant relationship among pH and DTPA-Zn ( $r=0.49^*$ ) and DTPA-Fe ( $r=0.509^*$ ) was observed. DTPA-Zn and DTPA-Cd showed positive and significant correlation with EC ( $r=0.69^{**}$  and  $0.63^{**}$ ). However, organic carbon showed positive and significant relationship with DTPA-Zn ( $r=0.856^{**}$ ), DTPA-Mn ( $0.514^*$ ), DTPA-Cd ( $0.569^*$ ) and total Ni ( $r=0.543^*$ ). The studies thus suggest that soil reaction and soil organic carbon content influence total as well as DTPA extractable trace metals in soil, which is in conformity [6].

#### Heavy metal content in plant samples

Plants are known to be source of vitamins, minerals, proteins and carbohydrate essential for growth of living beings. Heavy metals, like other mineral is present in different proportion in the plant parts and become

an issue of growing concern.

The concentration of various heavy metals such as Pb, Cd, Ni, Zn, Mn, Fe, Cu and Co in locally available plant species (Lady finger, cow pea, cucumber, sponge gourd, bitter gourd, maize, paddy) collected from study area are summarized in Table 4.

In the present investigation, the value of Cd ranges from BDL to 3.26 mg kg<sup>-1</sup> (paddy). Cd is one of the most toxic heavy metal and its presence is a dangerous proposition and a wakeup call for our ecosystem and human beings in general. Even low-level chronic exposure to Cd may cause health disorders.

The cobalt (Co) content varies from 4.5 (maize) to 20.17 mg kg<sup>-1</sup> (paddy). Deficiency of Co in diet results into pernicious anemia, severe fatigue, shortness of breath and hypothyroidism, while overdose may lead to angina, asthma, cardiomyopathy, polycythemia and dermatitis. The safety limit for human consumption of Co is 0.05 to 1 mg/day in humans. The safe limit of Co for vegetables as per PFA is 3.0 mg kg<sup>-1</sup> and thus the recorded range of Co concentration in vegetables has crossed the prescribed limit.

Due to richness of chlorophyll, Cu concentration (22.19–76.50 mg kg<sup>-1</sup>) was found higher in leafy vegetables when compared to non-leafy vegetables in Turkey [7]. Present study revealed that, vegetables like lady's finger (8.25), cow pea (8.60), cucumber (6.50), sponge gourd (8.60), bitter gourd (3.05) showed less concentration of Cu when compared to maize (12.05) and paddy (11.71).

Fe is an essential element in production of Red Blood Cells. The concentration of Fe content varies from 826.50 (lady's finger) to 1600.00 mg kg<sup>-1</sup> (paddy). The lowest concentration (826.50 mg kg<sup>-1</sup>) was observed in lady's finger and the highest concentration (1600.00 mg kg<sup>-1</sup>) was observed in paddy. However among all the metals under investigation, Fe shows the maximum concentration which may be due to the iron rich soil in which the plants are grown.

Average concentration of Ni was highest in lady's finger (17.35) and lowest in paddy (5.57 mg kg<sup>-1</sup>) in the samples collected from study area. Major sources

of Ni in the soil are poorly treated wastewater that is discharged from ceramics, steel and alloys and other metal processing industries. Long term exposure of Ni through the food chain may contribute to health problems like skin allergies, dermatitis, rhinitis, nasal sinusitis, lung injury and nasal mucosal injury [8].

During the present study, Pb content varies from BDL (paddy) to 11.90 mg kg<sup>-1</sup> (cucumber). Present results are in conformity with [9] who found the presence of Pb in vegetables. Small scale industries, vehicular emissions, re-suspended road dust and diesel generator sets are main source of Pb production and accumulation in environment. Uptake of Pb in plants is regulated by pH, particle size and cation exchange capacity of soil as well as by root exudation and other physico-chemical parameters [10]. The introduction of Pb into the food chain may affect human health and thus, studies concerning lead accumulation in vegetables have increasing importance.

Among all metals, Zn is the least toxic and an essential element as it is involved in numerous aspects of cellular metabolism. It is required for the catalytic activity of enzymes and plays a role in immune function, protein synthesis and wound healing. Zn deficiency in the diet may be more detrimental to human health than too much zinc in the diet. A varied Zn concentration in leafy vegetables in peri urban areas of Bangalore was observed [11]. During present study, the concentration of Zn was found high in bitter gourd (91.70 mg kg<sup>-1</sup>), while low concentration of Zn was observed in cucumber (29.30 mg kg<sup>-1</sup>).

Among the samples collected from the study area the Mn concentration was recorded maximum in paddy (356.12 mg kg<sup>-1</sup>) and minimum concentration was recorded in cow pea (39.20 mg kg<sup>-1</sup>). Mn occurs naturally in many food sources, such as leafy vegetables, nuts, grains and animal products and it is the most important source of manganese exposure in the general population.

## Conclusion

Soil is the most important component of the human biosphere, as it is a great geochemical reservoir for

contaminant as well as a natural buffer for transportation of chemical materials and elements in the atmosphere. Therefore, any harmful change to this segment of the environment seriously affects the overall quality of human life. In the present work, heavy metal concentration study in soil and agricultural plants grown around the PTPRS, Patratu, Jharkhand was estimated and it was observed that all the plants show significant heavy metal content. The concentration of metals in almost all the plants follows the order  $Fe > Mn > Zn > Ni > Co > Cu > Pb > Cd$ . An important issue is that the contamination levels were frequently higher than permissible limits in the plant tissue, whereas at the same site the soil samples complied with established safe standards. Therefore it is suggested that policies and programs need to be adapted so that local edaphic conditions and agricultural practices are taken into account to mitigate the accumulation of heavy metals in the topsoil and food chain over time, as the toxic effects of these heavy metal fallouts are of grave consequence to human existence.

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