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Soil contamination status due to large scale discharge of Fly Ash Slurry during Ash Pond Breach of OPGC-ITPS at Banaharpali, Western Odisha

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Abstract
This study was part of a comprehensive research project undertaken during 2024-25 to assess the environmental damage caused by the spillage of fly ash slurry due to ash pond breach during December 2023 in Banaharpali, Odisha. To assess the impact of such large scale spillage on sub-surface soil, samples were collected from ,10 cm depth and analysed for nutrients, pH, electrical conductivity (EC), and heavy metal concentrations. Pollution indices—Contamination Factor (CF), Geo-accumulation Index (Igeo), and Pollution Load Index (PLI)—were computed to quantify contamination levels. The Geoaccumulation Index (Igeo) confirmed uncontaminated conditions for most metals, with Hg showing minor contamination in pre-monsoon. The Pollution Load Index (PLI) remained ≤1 across all locations, suggesting no significant cumulative pollution. The study concludes that while the overall pollution load is low, localized hotspots of Cd, Hg, and Cl require attention. Natural dilution reduced Hg levels post-monsoon

Key words: *Cations ,Anions ,Heavy metals ,Spillage ,fly ash Slurry ,Ash pond breach*

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I. Introduction

A large majority of the thermal power plants (about 84%) operating globally are coal-based, while the remaining 13% run on gas and 3% on oil (Sarode et al., 2010). About 197 coal/lignite based thermal power plants operating in India produce around 133 million tons of coal fly ash annually (Yadav et al., 2022). Therefore, there is significant environmental challenges (Palma-Lara et.al., 2020, Genchi et al. ,2020, Kumar e. al., 2020). Fly ash contains several of the elements found in coal, including silica, alumina, and iron, which are significant oxides, as well as minor oxides of sodium, magnesium, calcium, phosphorus, potassium and titanium (Wu et al., 2022). Coal might also incorporate one or more hazardous elements, such as arsenic, beryllium, boron, cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium, in either significant or minute quantity, based on the source /origin of coal. (O'Neal and Zheng, 2015, Yuan et al., 2021; Park et al., 2021; Chen et. al., 2022; Schoofs et. al., 2024, Yadav et al., 2021; Yadav et al., 2021; Yadav et al., 2022). Disposal of ash is done either by dry or wet disposal methods. In the dry disposal method, the ash is dumped into open surface scientifically, whereas in the wet disposal method, the ash is mixed with water and transported through pipes to the ash pond. The leaching potential of heavy metals from ash ponds, which depends on the acidic or alkaline conditions of aqueous environment (Singh et al., 2016) is expected to be greater due to diurnal and seasonal variation in temperature, moisture and other parameters (Verma et al., 2016, Mandel et al.,2006,2022).

On December 9, 2023, there was unfortunate incident of breach of one ash pond of the IB Thermal Power Station (ITPS) located in Banaharpali of Jharsuguda district, Odisha leading to a sudden and large scale spillage of fly ash and slurry into nearby surrounding agricultural fields, grazing lands, and water bodies. The breach necessitated an assessment of contamination of surface water in nearby small and large waterbodies as well as soil of grazing land and agriculture fields. A portion of the observation and assessment has already been published by the authors involving surface water and surface soil (Chander et al.2026). The present paper reports a

comparative assessment between surface and sub-surface soil using data published by authors on surface soil (Chander et al.2026).

II. Study Site

The power station, located on the bank of the Hirakud reservoir in Banaharpalli village of Jharsuguda district, is equipped with electrostatic precipitators and a flue-gas desulfurization system to control emissions. The water required for the operation of the power plant is sourced from the Hirakud reservoir through 5.45 km long intake canal. Coal is supplied from the Lakhanpur open-cast mines in the Ib valley area, and from Odisha Power Generation Corporation's own captive mines in the vicinity. There are two ash pond complexes (Ash Pond A, B,C & Tilia Ash Pond) for discharge of ash slurry.

III. Methodology

The study area was divided into several grids of 500m each as given below (Fig 1). A total of 42 centroids were marked for each of the grid for sampling and depending on the season and accessibility the number of samples were restricted to maximum possible that could be collected, the details of which are given in respective sections.

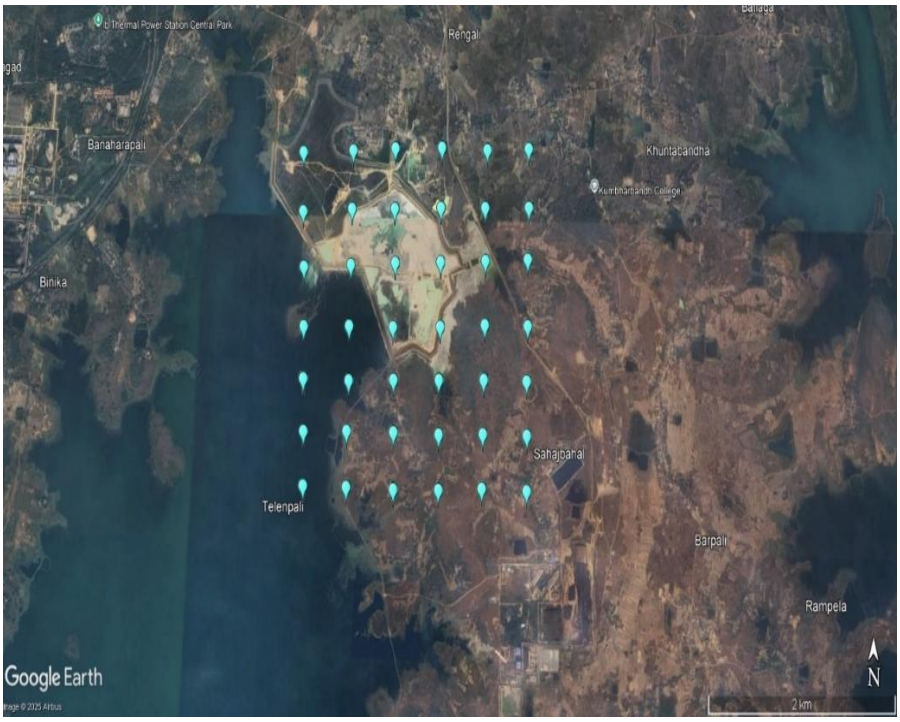


Fig 1. Sampling grids for sample collection in the study area.

3.1 Sub-surface Soil Sampling

Standard Methods for analysis of soil was followed as per Misra (1968) and Jackson (1973). A total of 62 sub-surface soil samples were collected from 10 cm depth using augur in polyethylene bags from the grids during pre-monsoon (27), monsoon (12), and post-monsoon (23). The locations of the samples were marked using the global position system (GPS).

3.2 Soil Sample Preparation and Analysis

The samples were air dried in natural condition then sieved to remove the pebbles, small stones and gravels if any. Soil samples were homogenised, sieved and 1-2 gram of soil sample were taken for analysis. The samples were digested using EPA 3050B method. 10 mL of 1:1 HNO_3 (nitric acid) was added and slurry prepared was heated at 95°C +/- 5°C for 10-15 minutes. After the samples were cooled, concentrated HNO_3 was added and then heated for 30 minutes. Formation of brown fumes indicate digestion of the soil samples with HNO_3. Addition of more HNO_3 and repeated heating continued until the brown fumes stopped appearing, indicating completion of digestion reaction. After cooling, 2 ml water and 30% H_2O_2 (hydrogen peroxide) was added and heated again. The slurry was heated with addition of H_2O_2 in intervals till the effervescence get minimised. The slurry was cooled down and then diluted to 100ml with double-distilled water. The slurry was filtered through Whatman No. 41 filter paper followed by centrifugation at 3000 rpm for 15 minutes and filtrate was used for analysis.

3.3 pH Measurement

Air dried and sieved samples were homogenised. A 50g soil sample was taken and sufficient water was added to moisten the soil, stirred with a glass rod and added water till the soil became saturated. The sample was left overnight to get the soil fully saturated at 25°C. Next day it again stirred with a glass rod, and more water added if required. The calibration of the pH meter was done using a standard buffer solution of pH 4.01, 7.0, 10.02. After calibration, samples were tested for their pH using water saturated samples in a beaker. After every measurement the electrode was washed with distilled water and cleaned with tissue paper.

3.4 Electrical Conductivity and Total Dissolved Solids measurement

Electrical conductivity (EC) was measured using Oakton multi-parameter electrodes. Before testing, the probe was calibrated with 84 µS/cm, 1413 µS/cm and 12.8 mS/cm standard solutions. Once the instrument was calibrated, 50mL extracted samples were taken in a beaker and then a probe was dipped into it. EC and TDS values were recorded.

3.5 Chloride, Fluoride, Sulphate, Nitrate and Phosphate analysis

The chloride analysis was done using the silver nitrate titration method using a chromate indicator after extraction from soil samples. The chloride content was calculated from the amount of silver nitrate used in the titration. The SPANDS method was used for the determination of fluoride from digested soil samples. The turbidimetric method was used to perform sulphate analysis. Extracted soil sample diluted to100mL and taken in a beaker, then conditional reagent added to it. The $BaCl_2$ crystals were added with stirring and stirred for 60 seconds in a magnetic stirrer. Turbid solution was then poured into a photometric cell to determine absorbance at 420nm. Extracted sample was taken in a beaker and Hanna HI98191 electrode was used for the determination of nitrate. For phosphate analysis, sodium bicarbonate extracted sample aliquot was taken into the volumetric flask and 1.5% ammonium molybdate, and distilled water added to it. After that, a working stannous chloride solution was added to it, followed by addition of distilled water to make up the volume. A blue colour solution was obtained, whose absorbance was determined by a spectrophotometer at 660nm.

3.6 Major Cation Analysis

The standard solutions were prepared for Na^+, K^+, Ca^{2+} using sodium chloride, potassium chloride and calcium carbonate to calibrate the flame photometer. The major cations Na^+, K^+ and Ca^{2+} were analysed using flame-photometer Systronics 128 from a digested liquid sample of soil.

3.7 Heavy metals analysis

Aliquot of digested liquid samples were taken and analysed with ICP-MS for heavy metals As, Pb, Cd and Zn. The iron was analysed using phenanthroline spectroscopic method and mercury was analysed using dithizone method. The ICP-MS was calibrated using a standard reference solution (Agilent) for heavy metals before analysis. For iron and mercury analysis calibration was done using different concentration standard solutions. (Kharazi et al 2021 , Kumar et al 2019).

3.8 Pollution assessment

Comprehensive assessment of the degree of soil pollution is estimated through various pollution indices. The contamination factor (CF), geo-accumulation index (I_{geo}) pollution load index (PLI) was used to assess the status of contamination of soil and water.

3.8.1 Contamination factor (CF)

Contamination factor (CF) is an effective method for monitoring sediment pollution over time. It is the ratio of individual metal in the sample to the metal's background values

$CF = (C_{metal}$ in sample/C_{metal} in background)

Geo-accumulation Index

The Geo-accumulation index showing the degree of contamination is estimated using the following formula:

$I_{geo} = \log_2[C_{metal}$ in sample/$1.5 \times C_{metal}$ in background]

3.8.2 Pollution load index (PLI)

The pollution load index (PLI) measures the quantity of harmful heavy metals in the area. The PLI was calculated as a ratio of each heavy metal's concentration to the soil's background value.

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

3.9. Student t test

Student t test was performed following Arora and Malhan (2014) to find out the existence of significant difference in soil quality between control and experimental sites.

3.10 Sampling Locations

Sub-surface soil samples were collected around the ash ponds. The description of sampling sites and distance from breaching point are presented in figure 2 and tables 1-3.

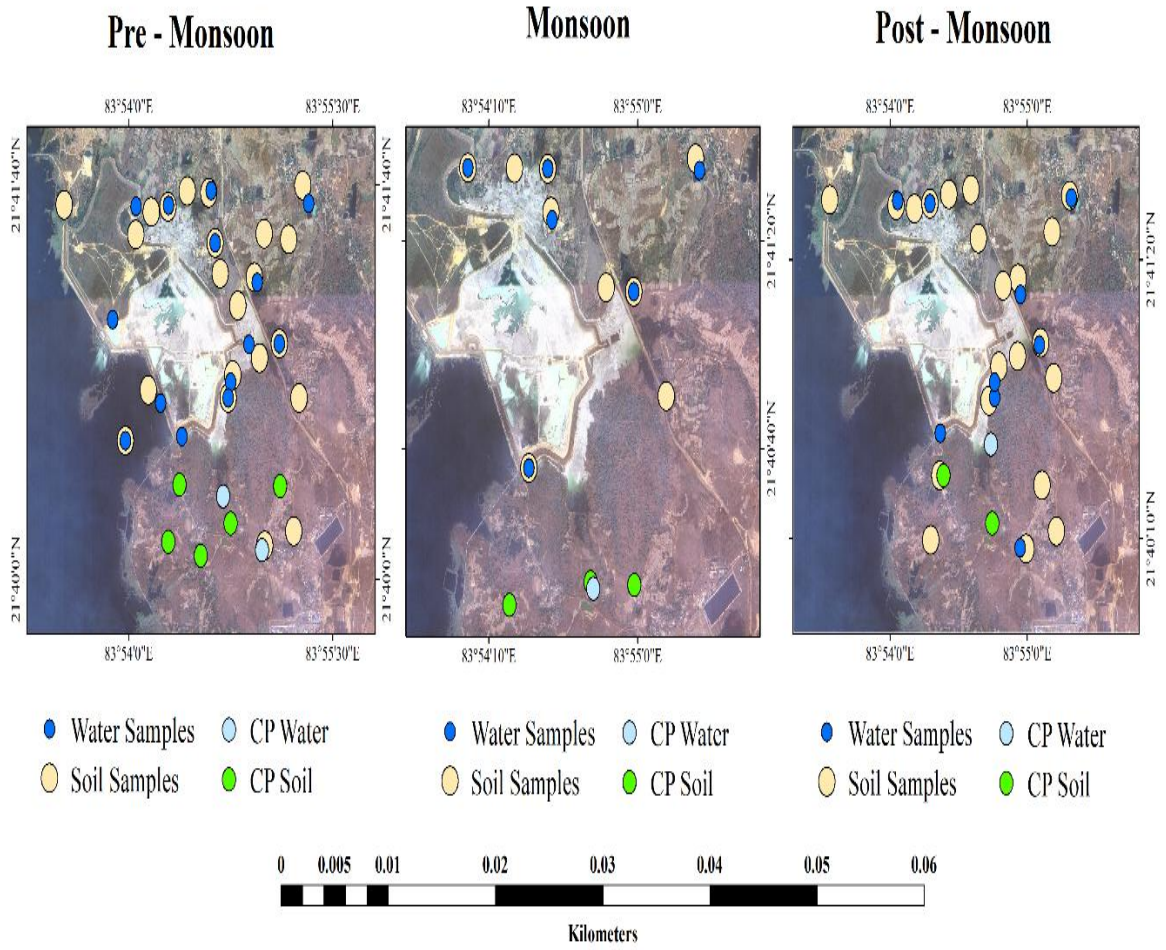


Fig 2. Map showing locations of soil samples in pre-monsoon, monsoon and post-monsoon seasons.

Table 1. Location of soil samples collected during pre-monsoon (*prefix with C is control sample*)

S. No.	Latitude	Longitude	Distance from breach point (m)
JHS1	21.67999	83.90239	1253.5
JHS 2	21.67643	83.89959	1737.02
C JHS 3	21.67335	83.9062	1466.69
JHS 4	21.68103	83.91272	423.08
JHS 5	21.67943	83.91218	595.77
JHS 6	21.69095	83.90084	1496.92
JHS 7	21.6929	83.90481	1343.83
JHS 8	21.69387	83.90981	1096.75
JHS 9	21.69304	83.89206	2423.83
JHS 10	21.691	83.9166	835
JHS 11	21.68793	83.91538	440.6
JHS 12	21.68327	83.91844	537.26

JHS 13	21.67943	83.92086	713.6
JHS 14	21.69441	83.92133	1390.69
JHS 15	21.67018	83.91267	946.47
JHS 16	21.69254	83.90275	1436.03
JHS 17	21.694	83.90715	1262.7
JHS 18	21.69035	83.91059	716.09
JHS 19	21.68819	83.9112	481.4
JHS 20	21.68594	83.91335	309.69
JHS 21	21.68226	83.91603	382.78
JHS 22	21.67008	83.92021	1735.26
JHS 23	21.66906	83.91665	1771.91
C JHS 24	21.67325	83.91856	1346.62
C JHS 25	21.67064	83.91246	1568.86
C JHS 26	21.668.357	83.9088	1917.34
C JHS 27	21.66932	83.90484	1888.65

Table 2. Location of soil samples collected during monsoon (*prefix with C is control sample*)

S. No.	Latitude	Longitude	Distance from breach point (m)
JHS1	21.676732	83.906498	1131.54
C JHS2	21.669392	83.904691	1888.81
C JHS3	21.670605	83.912284	1487.12
C JHS4	21.670466	83.916359	1502.83
JHS5	21.693311	83.922065	1317
JHS6	21.686176	83.9163	328.13
JHS7	21.69279	83.900828	1706.86
JHS8	21.686385	83.913716	280.86
JHS9	21.680589	83.919324	635.55
JHS10	21.692781	83.90517	1172.53
JHS11	21.692754	83.908279	1183.82
JHS12	21.690446	83.908583	933.51

Table 3. Location of soil samples collected during post-monsoon (*prefix with C is control sample*)

S. No.	Latitude	Longitude	Distance from breach point (m)
JHS 1	21.676752	83.906180	1167.54
C JHS 2	21.673867	83.906484	1410.08
JHS 3	21.669365	83.904938	1923.88
C JHS 4	21.670553	83.912397	1581.77
JHS 5	21.668773	83.916515	1802.73
JHS 6	21.673196	83.918451	1384.85

JHS 7	21.669997	83.920182	1780.58
JHS 8	21.693361	83.921819	1282.72
JHS 9	21.690863	83.919687	929.95
JHS 10	21.687595	83.915529	375.66
JHS 11	21.683121	83.91829	532.72
JHS 12	21.680674	83.91987	805.06
JHS 13	21.687085	83.913728	254.76
JHS 14	21.679093	83.912003	650.12
JHS 15	21.681459	83.91321	372.53
JHS 16	21.682189	83.915475	357.74
JHS 17	21.693071	83.892678	2338.3
JHS 18	21.69271	83.900738	1581.96
JHS 19	21.69247	83.902948	1380.54
JHS 20	21.69283	83.904824	1259.65
JHS 21	21.693481	83.907132	1164.73
JHS 22	21.690402	83.910712	682.48
JHS 23	21.693802	83.909828	1065.27

IV. Results and Discussion

Table 4 presents a comparative view on soil quality parameters ,cations and anions as well as heavy metals in mg / kg of soil with mean and standard deviation during pre-monsoon, monsoon and post-monsoon in control and experimental sites.The Electrical conductivity has been expressed in mS/cm.

4.1 Pre-Monsoon analysis report

4.1.1 Cation and Anion Analysis and heavy metal Content of Pre-Monsoon sub-surface Soil Samples in control sites

Table 4 presents a comparative view on soil quality parameters with mean and standard deviation during pre-monsoon, monsoon and post-monsoon in control and experimental sites.

Table.4. Physico-chemical analysis and heavy metals content in sub-surface soil (expressed in mean)

Sl.N	Parameters	Units	Control Sites					Experimental Sites					Students t test	
			PrM	M	PoM	Mean	Sd	PrM	M	PoM	Mean	Sd	t value	Significance at 0.05 level
Cations and Anions														
1	pH													
2	EC	mS cm^{-1}	5.71	6.38	5.49	5.86	0.464	6.10	6.21	5.71	6.007	0.263	0.477	NS
3	Na	mg Kg^{-1}	214.98	180.07	70.10	155.05	75.61	240.07	201.04	177.98	206.363	31.38	1.086	NS
4	K	mg Kg^{-1}	23.54	10.10	15.28	16.303	6.77	22.67	6.85	13.69	14.403	7.93	0.316	NS
5	Ca	mg Kg^{-1}	53.18	41.35	98.89	64.473	30.39	65.07	31.92	148.95	81.98	60.32	0.449	NS
6	F	mg Kg^{-1}	227.54	360.53	401.79	329.953	91.06	224.25	245.73	218.45	229.477	14.37	1.888	NS
7	Cl	mg Kg^{-1}	0.02	0.02	0.01	0.01667	0.00577	0.02	0.02	0.02	0.02	0.0	1.0	NS
8	SO_4	mg Kg^{-1}	93.06	82.72	53.18	77.987	21.65	96.68	79.76	65.84	80.76	15.44	0.298	NS
9	PO_4	mg Kg^{-1}	45.35	52.52	1.67	33.18	27.52	74.33	22.09	5.50	33.973	35.92	0.030	NS
10	NO_3	mg Kg^{-1}	0.02	0.04	0.02	0.02667	0.01155	0.02	0.05	0.03	0.03333	0.01528	0.603	NS
Heavy Metals														
1	Mn	mg Kg^{-1}	43.77	8.64	8.64	20.35	20.28	24.43	0.34	6.55	10.44	12.51	0.728	NS
2	Co	mg Kg^{-1}	1.77	0.32	0.32	0.8033	0.837	0.72	0.05	0.30	0.3567	0.339	0.857	NS
3	Ni	mg Kg^{-1}	2.05	0.43	0.43	0.97	0.935	1.03	0.00	0.81	0.6133	0.5884	0.571	NS
4	Cu	mg Kg^{-1}	1.53	0.27	0.27	0.69	0.727	0.67	0.00	0.39	0.3533	0.337	0.727	NS
5	Zn	mg Kg^{-1}	2.15	0.69	0.69	1.1767	0.843	1.20	0.43	1.26	0.9633	0.463	0.359	NS
6	As	mg Kg^{-1}	0.56	0.08	0.08	0.24	0.277	0.27	7.49	0.67	2.81	4.058	1.049	NS
7	Mo	mg Kg^{-1}	0.03	0.00	0.00	0.01	0.01732	0.08	0.34	0.20	0.2067	0.130	2.575	NS
8	Cd	mg Kg^{-1}	0.01	0.00	0.00	0.00333	0.00577	0.00	0.05	0.21	0.0867	0.1097	1.360	NS

9	Pb	mg Kg $^{-1}$	2.66	0.84	0.84	1.4467	1.051	0.74	0.00	0.40	0.38	0.370	1.658	NS
10	Fe	mg Kg $^{-1}$	10.16	11.86	11.86	11.2933	0.981	8.07	0.00	5.90	4.6567	4.176	2.679	NS
11	Hg	mg Kg $^{-1}$	0.07	0.05	0.05	0.05667	0.01155	0.09	0.43	0.00	1.733	0.227	0.890	NS
PrM – Pre-Monsoon M-Monsoon PoM-Post-Monsoon ,NS-Not significant														

During pre-monsoon the pH of soil samples was acidic, having a minimum value of 5.14 to a maximum value of 6.53 with a mean value of 5.71. The EC of samples was found to be in the range of minimum 81.70 mS/cm and maximum 450 mS/cm, with a mean of 214.98. The sodium concentration was found to be having a minimum concentration of 18.98 to maximum concentration of 27.53, with the mean concentration of 23.54. The potassium concentration was found to be in the range of 45.08 minimum and 68.78 maximum, with the mean value of 53.18. While the mean concentration of calcium was found to be 227.54 with the range of 29.93 minimum and 570.86 maximum. It was found that fluoride has a minimum concentration of 0.01 and maximum concentration of 0.02, with a mean concentration of 0.02 in the analysed samples. The chloride was having 53.18 minimum concentration, 132.94 maximum concentration, and 93.06 mean concentration in the analysed samples. The sulphate in analysed samples was found to be in the range of 7.27 minimum, 135.17 maximum, while mean was found to be 45.35. The phosphate concentration in the analysed soil samples ranged from a minimum of 0.01 to a maximum of 0.04, with a mean concentration of 0.02 mg kg^{-1}. Nitrate levels were found to be having a minimum concentration of 4.75, a maximum of 29.14, and an average of 13.54.

Out of the heavy metals analysed, manganese concentrations ranged from 14.89 to 95.94, (mean- 43.77). Cobalt levels were detected between 0.63 and 2.69, (mean- 1.77). [1] across samples. Nickel concentrations spanned from 0.78 to 2.98 (mean- 2.05), 0.69 to 2.42 Copper mean 1.53), Zinc with a relatively narrow distribution range of 1.42 to 2.82(mean 1.53), Arsenic 0.10 - 1.38 (mean 0.56), Molybdenum from below detection limit to 0.07 a mean value of 0.03, Cadmium ranged from non-detectable to 0.01 (mean 0.01) , Lead contamination varied from 1.37 to 4.18 (mean 2.66). Iron exhibited substantial variability across samples, ranging from 6.61 to 18.76 with a mean of 10.16. Mercury concentrations were consistently low throughout the study area, ranging from 0.06 to 0.08 with a mean value of 0.07.

4.1.2 Pre-monsoon Cation and Anion Analysis and heavy metals content in sub-surface soil Samples in Experimental sites

The pH of soil samples was predominantly acidic, having a minimum value of 4.81 to a maximum value of 7.39 with a mean value of 5.93. About 91.00 % of samples were found to be acidic, whereas 9.09% were found to be alkaline in nature. The EC of samples was found to be in the range of minimum 69.2 and maximum 2041, with a mean of 604.59. The sodium concentration was found to be having a minimum concentration of 9.34 mg/kg to maximum concentration of 36.9, with the mean concentration of 22.65. The potassium concentration was found to be in the range of 7.24 minimum and 118.13 maximum, with the mean value of 63.38. While the mean concentration of calcium was found to be 185.49 with the range of 26.66 minimum and 523.01 maximum. It was found that fluoride has a minimum concentration of 0.011 and maximum concentration of 0.022, with a mean concentration of 0.018 in the analysed samples. The chloride was having 53.18 minimum concentration, 212.7 maximum concentration, and 102.72 mean concentration in the analysed samples. The sulphate in analysed samples was found to be in the range of 14.53 minimum, 505.81 maximum, while mean was found to be 78.88. The phosphate concentration in the analysed soil samples ranged from a minimum of 0.02 to a maximum of 0.16, with a mean concentration of 0.04. Nitrate levels were found to be having a minimum concentration of 4.95, a maximum of 25.4 and an average concentration of 14.65.

Analytical results of heavy metals content showed copper concentrations ranging from 0.08 to 2.45 with a mean of 0.67, while zinc exhibited a concentration between 0.14 and 2.61(mean: 1.20). Arsenic levels varied from 0.02 to 1.29 (mean: 0.27), with molybdenum ranging from below detection limit to 0.83 (mean: 0.08). Cadmium concentrations were minimal, ranging from non-detectable to 0.01 (mean below detection level), whereas lead showed a wider distribution from 0.07 to 2.6 (mean: 0.74). Iron demonstrated the greatest variability, with concentrations spanning 1.51 to 20.83 kg (mean: 8.07 mg/kg), while mercury maintained relatively consistent levels between 0.06 and 0.13 (mean: 0.09). Manganese concentrations averaged 24.43, with cobalt and nickel showing mean values of 0.72 and 1.03 respectively.

4.2. Monsoon Results

4.2.1 Cations and Anions Analysis and heavy metals content in sub-surface soil Samples of control sites during Monsoon

The sub-surface soil exhibited acidic characteristics with pH values ranging from 5.93 to 6.94 and averaging 6.38 across all samples. Electrical conductivity measurements showed moderate salinity levels varying between 155.20 and 228 mS/cm, with a mean value of 180.07 mS/cm. Sodium concentrations ranged from 6.90 to 12.75, with a mean of 10.10 throughout the sampled locations. Potassium levels displayed greater variability, spanning from 18.60 to 59.85 with a mean content of 41.35. Calcium emerged as the dominant cation, showing

concentrations between 249.08 and 539.03 and averaging at 360.53 in the soil. Fluoride contents remained consistently low at 0.02 across all sampling locations. Chloride levels varied from 70.90 to 106.35, with an average of 82.72 observed in the samples. Sulphate contents showed moderate variation, ranging from 42.44 to 59.30 with mean of 52.52 throughout the study area. Phosphate levels were relatively low, measuring between 0.02 and 0.07 with a mean value of 0.04. Nitrate exhibited the widest variation among anions, ranging from 5.96 to 22.13 and mean 14.38 across the sampling locations. The comprehensive analysis revealed calcium as the most abundant cation, followed by potassium and sodium in the soil matrix. Anion distribution patterns showed sulphate as the predominant anion, followed by chloride and nitrate, while phosphate and fluoride were present in minimal quantities.

The heavy metal analysis of soil samples showed manganese concentrations averaging 8.64 (range: 4.28-12.67), while cobalt levels averaged 0.32 (0.18-0.48). Nickel concentrations averaged 0.43 (0.41-0.45), and copper showed a mean of 0.27 (0.22-0.35). Zinc levels averaged 0.69 (0.25-1.56), with arsenic demonstrating a mean concentration of 0.08 mg/kg (0.05-0.13 mg/kg). Molybdenum was either undetectable or present in trace amounts (0-0.01), while cadmium was completely absent from all samples. Lead contamination averaged 0.84 (0.52-1.27), and iron showed the highest mean concentration at 11.86 (8.10-15.55). Mercury levels averaged 0.05 (0.01-0.08), completing the heavy metal profile. The results indicate iron and manganese as the predominant metals, with other elements present at significantly lower concentrations. Most measured heavy metals fell within typical background ranges, suggesting minimal anthropogenic influence. The consistent absence of cadmium and negligible molybdenum levels further confirm the relatively uncontaminated nature of the sampled soils.

4.2.2 Cations and Anions Analysis and heavy metals content in sub-surface soil samples in experimental sites during Monsoon

The pH values ranged from 5.35 to 7.12 with an average of 6.21, where 88.89 percent of samples were acidic and 11.11 percent exhibited alkaline conditions. Electrical conductivity measurements indicated moderate salinity levels varying between 104.4 and 287 mS/cm with a mean value of 201.04 across all samples. Sodium concentrations ranged from 2.74 to 12.75 with an average of 6.85, while potassium levels showed greater variability from 10.31 to 59.85 with an average of 31.92. Calcium emerged as the dominant cation with concentrations spanning 77.55 to 547.69 and a mean of 245.73, demonstrating significant spatial variability in the soil profile. Fluoride content remained consistently low at 0.02 in most samples, with a minimum detection of 0.01. Chloride levels varied from 35.45 to 141.8 with an average of 79.76, whereas sulphate exhibited more pronounced variation ranging from 2.03 to 59.3 averaging at 22.09. Phosphate was relatively low throughout the study area, measuring between 0.02 and 0.08 with a mean value of 0.05. Nitrate levels displayed moderate variability from 5.96 to 29.06 and average of 15.36, potentially reflecting differential organic matter decomposition or fertilizer inputs across sampling locations.

The soil analysis revealed distinct concentration patterns for eleven heavy metals, with iron showing the highest accumulation ranging from 2.16 to 15.55 and average value of 7.49. Manganese varied from 0.28 to 12.67 with a mean value of 3.99, while lead levels ranged between 0.09 and 1.27 and mean of 0.43. Zinc was detected at a range of 0.11 to 1.56 with a mean of 0.34, and copper showed lower levels ranging from 0.02 to 0.35 with an average of 0.14. Cobalt and nickel exhibited similar ranges, with cobalt measuring 0.01 to 0.48 (mean 0.15), while nickel ranged from 0.01 to 0.45 (mean 0.19. Arsenic contents were relatively low, varying between 0.01 and 0.13 and averaging 0.05. Mercury showed minimal presence with levels from undetectable to 0.08 and a mean of 0.03. Notably, molybdenum was either absent or present only in trace amounts up to 0.01, while cadmium was completely undetectable in all analysed samples. The results demonstrate iron and manganese as the predominant heavy metals, with other elements present at significantly lower concentrations. Most measured heavy metals fell within typical background ranges, suggesting minimal anthropogenic influence in the sampled soils. The consistent absence of cadmium and negligible molybdenum levels further indicate an uncontaminated soil environment.

4.3 Post-Monsoon Results

4.3.1 Cations and Anions Analysis and heavy metals content in sub-surface Control Soil Samples during Post-Monsoon

The soil exhibited acidic characteristics with pH values ranging from 5.93 to 6.94 and averaging 6.38 across all samples. Electrical conductivity measurements showed moderate salinity levels varying between 155.20 and 228 mS/cm, with a mean value of 180.07 mS/cm. Sodium ranged from 6.90 to 12.75, averaging 10.10. Potassium levels displayed greater variability, spanning from 18.60 to 59.85 with a mean concentration of 41.35. Calcium emerged as the dominant cation, showing concentrations between 249.08 and 539.03 and averaging 360.53 in the soil profile. Fluoride concentrations remained consistently low at 0.02 across all sampling locations. Chloride levels varied from 70.90 to 106.35, with an average concentration of 82.72 observed in the samples. Sulphate concentrations showed moderate variation, ranging from 42.44 to 59.30 and averaging 52.52 throughout

the study area. Phosphate levels were relatively low, measuring between 0.02 and 0.07 with a mean value of 0.04. Nitrate concentrations exhibited the widest variation among anions, ranging from 5.96 to 22.13 and averaging 14.38. The comprehensive analysis revealed calcium as the most abundant cation, followed by potassium and sodium in the soil matrix. Anion distribution patterns showed sulphate as the predominant anion, followed by chloride and nitrate, while phosphate and fluoride were present in minimal quantities.

The samples showed manganese contents averaging 8.64 (range: 4.28-12.67), while cobalt levels averaged 0.32 (0.18-0.48). Nickel concentrations averaged 0.43 (0.41-0.45), and copper showed a mean of 0.27 (0.22-0.35). Zinc levels averaged 0.69 (0.25-1.56) and arsenic demonstrated a mean value of 0.08 (0.05-0.13). Molybdenum was either undetectable or present in trace amounts (0-0.01), while cadmium was completely absent from all samples. Lead content averaged 0.84 (0.52-1.27), and iron showed the highest mean value of 11.86 (8.10-15.55). Mercury levels averaged 0.05 (0.01-0.08), completing the heavy metal profile. The results indicate iron and manganese as the predominant metals, with other elements present at significantly lower concentrations. Most measured heavy metals fell within typical background ranges, suggesting minimal anthropogenic influence. The consistent absence of cadmium and negligible molybdenum levels further confirm the relatively uncontaminated nature of the sampled soils.

4.3.2 Cations and Anions Analysis and heavy metals content in sub-surface soil samples in Experimental sites during Post-Monsoon

Analysis of soil samples revealed predominantly acidic conditions, with pH values ranging from 4.97 to 7.26 and averaging 5.71, where 95.24% of samples were acidic and 4.76% exhibited alkaline properties. Electrical conductivity measurements indicated variable salinity levels spanning 43.9 to 362 mS/cm with a mean value of 177.98. Sodium ranged from 7.58 to 25.13 with an average of 13.6, while potassium levels demonstrated greater variability from 37.76 to 340.01 and averaged 148.95. Calcium concentrations varied substantially from 49.61 to 371.06 with a mean of 218.45, establishing it as the dominant cation despite measurement units differing from other parameters. Fluoride levels remained consistently low across all samples, ranging from 0.01 to 0.02 and averaging 0.02. Chloride showed moderate variation between 35.45 and 141.8 with a mean of 65.84, while sulphate levels ranged from 2.48 to 11.01 with an average of 5.5. Phosphate varied from 0.01 to 0.24 with a mean of 0.03, whereas nitrate demonstrated the widest variation among anions, ranging from 3.32 to 26.79 and averaging 16.79.

Out of the eleven heavy metals, manganese varied from 0.01 to 31.01 (mean 6.55), while iron levels varied between 0.4 and 16.36 (mean 5.99), Zinc level varied from 0.1 to 4.89 (mean 1.26) and lead was detected from 0.01 to 1.43 (mean0.4). Nickel levels ranged from 0.01 to 2.06 (mean 0.81) and cobalt showed a range of 0 to 1.2 (mean 0.3). Copper was present at 0.01 to 1.06 (mean 0.39) , while arsenic varied more substantially from 0 to 5.77(mean 0.67). Molybdenum was detected between 0 and 1.34 (mean 0.2) and cadmium showed trace levels from 0 to 2.31 (mean 0.21). Mercury was not detected in any samples. The results indicate iron and manganese as the most abundant metals, with zinc and arsenic showing occasional elevated concentrations, while other elements generally occurred at lower levels. The consistent absence of mercury and generally low cadmium levels suggest minimal contamination from these particularly toxic elements.

4.4. Percent of heavy metals in soil samples exceeding average crustal values

Table 5 represents the global natural background concentration of heavy metals in water and soil of the earth (Kabata-Pendias **2010,** Alloway 2013 **)** . Table 6 reveals percent of soil samples exceeding average crustal values**.** In comparison to the global natural concentration, variation in the values at the study site is insignificant. Above tables 5 and 6 reveals percent of soil samples exceeding average crustal values**.** Control soil sample analysis revealed nearly all elements undetectable in subsurface samples across pre-monsoon, monsoon, and post-monsoon periods, with concentrations below detection limits for manganese, cobalt, nickel, copper, zinc, arsenic, molybdenum, cadmium, lead and iron. Mercury exhibited seasonal and depth-specific patterns, detected in 60% of subsurface samples during pre-monsoon but completely absent during monsoon and post-monsoon periods. The data suggest most elements remain tightly bound in soil matrices or exist at concentrations too low for detection under current analytical methods. Mercury's higher detection frequency in subsurface samples may reflect downward leaching or accumulation patterns. These findings demonstrate the control site's overall geochemical stability but highlight mercury as requiring special attention due to its sporadic presence. Seasonal variations appear limited to mercury, with other metals remaining non-detectable year-round. In comparison to the global natural concentration, variation in the values at the study site is insignificant.

Table 5. Global Natural Background Concentrations of heavy metals in soil

Heavy Metal / Metalloid	Typical Soil Background Range (mg/kg or ppm)
Lead (Pb)	10 – 40 mg/kg *(Global mean ~15 mg/kg)*
Cadmium (Cd)	0.01 – 1.0 mg/kg *(Global mean ~0.36 mg/kg)*
Arsenic (As)	1 – 40 mg/kg *(Global mean ~5 mg/kg)*
Mercury (Hg)	0.01 – 0.3 mg/kg *(Global mean ~0.07 mg/kg)*
Chromium (Cr)	10 – 100 mg/kg *(Global mean ~50 mg/kg)*
Copper (Cu)	5 – 50 mg/kg *(Global mean ~25 mg/kg)*
Zinc (Zn)	10 – 100 mg/kg *(Global mean ~70 mg/kg)*
Nickel (Ni)	5 – 50 mg/kg *(Global mean ~20 mg/kg)*

Table 6. Percentage of control and experimental sub-surface soil samples exceeding average concentration in upper continental crust/ crustal values

		Sub- surface Soil Sample in Control Sites			**Sub- surface Soil Sample in Experimental Sample**		
Elements	UCC/Crustal Avg.(mg/Kg)	PrM (%)	Mon (%)	PoM (%)	PrM (%)	Mon (%)	PoM (%)
Na	23600	0	0	0	0	0	0
K	20900	0	0	0	0	0	0
Ca	41500	0	0	0	0	0	0
Cl	130	40	0	0	13.63	11.11	4.76
Mn	950	0	0	0	0	0	0
Co	25	0	0	0	0	0	0
Ni	75	0	0	0	0	0	0
Cu	55	0	0	0	0	0	0
Zn	70	0	0	0	0	0	0
As	1.8	0	0	0	0	0	0
Mo	1.5	0	0	0	0	0	0
Cd	0.2	0	0	0	0	0	9.52
Pb	12.5	0	0	0	0	0	0
Fe	56300	0	0	0	0	0	0
Hg	0.08	60	0	0	50	0	0
F	625	0	0	0	0	0	0
PrM-Pre-Monsoon ,Mon-Monsoon,PoM-Post-Monsoon							

The assessment of experimental soil samples revealed that while most elements remained within natural crustal background levels, chloride, cadmium, and mercury exhibited significant seasonal mobility patterns. Subsurface samples demonstrated more persistent chloride mobility, with exceedances observed in 13.63 % of pre-monsoon, 11.11% of monsoon, and 4.76% of post-monsoon samples. Cadmium mobilization became particularly evident during post-monsoon conditions, with 14.28% of surface and 9.52% of subsurface samples surpassing the 0.2 mg/kg limit, suggesting wetting-front induced displacement of this metal. Mercury displayed the most pronounced transport behaviour, with 22.72% of pre-monsoon surface samples and 50% of subsurface samples exceeding the 0.08 mg/ kg.

4.5 Contamination/Pollution Indices

Three indices were used to assess the extent of soil contamination/pollution: contamination factor, geo - accumulation index and pollution load index which were calculated using concentration of heavy metals in sub-surface samples.

4.5.1 Contamination Factor (CF)

The contamination factor shows the extent of pollution of sub-surface soil samples. It is the ratio of concentration of metal in the samples to the average background value. The CF value of < 1 means low, > 1 to < 3 indicates moderate, > 3 to < 6 considerable, and > 6 is considered very high concentration. The Cf value for Zn, As, Cd, Pb and Fe is less than 1 in pre-monsoon samples at all the locations, which suggests low contamination of these heavy metals at all the locations. The CF value for Hg is greater than 1 and less than 3 in 9 locations of pre-monsoon, suggesting moderate pollution due to Hg at these locations. The Cf value for Zn, As, Cd, Pb and Fe is less than 1 in monsoon at all the locations, which suggests low contamination of these heavy metals at all the locations. The CF value for Hg is > 1 to < 3 in 2 locations in monsoon suggesting moderate contamination at these two locations. The Cf value for Zn, Pb, Fe and Hg is < 1 in post-monsoon at all the locations suggesting low contamination. 3 locations have CF value > 1 to < 3 for As and Cd in the post-monsoon season suggesting moderate contamination at these locations due to As and Cd.

4.5.2 Geo-accumulation Index (I_{geo})

The geo-accumulation index was calculated for the heavy metals in sub-surface soil samples taken from the study site. The geo-accumulation index is divided into seven categories (i) practically un-contaminated ≤ 0, (ii) uncontaminated to moderately contaminated =0-1, (iii) moderately contaminated = 1-2, (iv) moderately to heavily contaminated = 2-3 (v) heavily contaminated = 3-4, (vi) heavily to extremely contaminated = 4-5, (vii) extremely contaminate ≥ 5. The I_{geo} index value is ≤0 for Zn, As, Cd, Pb and Fe in all the three seasons suggesting all the locations are un-contaminated from these heavy metals. The I_{geo} index value of Hg is between 0 to 1 in 11 locations of pre-monsoon, suggesting these locations are uncontaminated to moderately contaminated. While the I_{geo} index value of Hg is ≤0 in monsoon and post-monsoon in all locations suggesting these locations are un-contaminated.

4.5.3 Pollution Load Index (PLI)

The pollution load index was computed for the heavy metals in sub-surface soil samples taken from the study site. The PLI value ≤ 1 shows that background levels of pollution are present, whereas PLI>1 indicates a significant pollution load, in which the soil has degraded due to metal concentrations. The PLI value of all the locations in the three seasons pre-monsoon, monsoon and post-monsoon is ≤ 1 suggesting there is no significant pollution load at these locations.

V. Conclusion

Status of sub-surface soil contamination was assessed following the ash pond dike breach at IB Thermal Power Station in Banaharpali, Jharsuguda. Soil samples were tested for cations, anions and heavy metal content. Pollution indices including contamination factor (CF), geo-accumulation index (Igeo), and pollution load index (PLI) were employed to assess soil contamination levels. Soil analysis revealed most heavy metals like Mn, Co, Ni, Cu, Zn, As, Mo, Pb, Fe, Hg maintained concentrations below upper continental crustal (UCC) across all seasons. Cadmium exceeded UCC values in only 9.52% of samples in post-monsoon, while mercury surpassed thresholds in 50% of subsurface pre-monsoon samples. Control samples showed elevated mercury in 60% of subsurface pre-monsoon collections. Contamination factor analysis indicated low pollution for Zn, As, Cd, Pb and Fe during pre-monsoon and monsoon periods at all locations. Mercury displayed moderate contamination at 9 pre-monsoon and 2 monsoon locations but showed natural dilution by post-monsoon. Post-monsoon samples revealed low contamination for Zn, Pb and Fe, but moderate contamination for As and Cd at 3 locations. Geo-accumulation index values confirmed uncontaminated conditions for Zn, As, Cd, Pb and Fe across all seasons and locations. Mercury showed variable Igeo values ranging from uncontaminated to moderately contaminated at 11 pre-monsoon locations but remained uncontaminated during monsoon and post-monsoon periods. Pollution load index calculations suggested no significant cumulative contamination at any location throughout the study period. The findings demonstrate seasonal variations in metal mobility, with mercury showing the most pronounced contamination that naturally attenuates by post-monsoon. The study thus concludes that while localized heavy metal contamination exists, particularly for mercury and cadmium, overall pollution levels remain within acceptable limits across most monitored parameters and locations.

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