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SPECIATION OF SOME SELECTED ELEMENTS IN FLY ASH OF PARICHHA THERMAL POWER PLANT JHANSI FOR POTENTIAL, ECOLOGICAL, RADIOLOGICAL AND HEALTH EFFECTS.

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Abstract: Imprudent disposal of industrial by-products leads to many geo-environmental impacts. Fly ash, a by-product from thermal power plants has an adverse effect on the environment but it has also been reported as a source of diverse rare-earth elements. The quantification of various rare-earth elements in the fly ash sample collected from the Parichha thermal power plant (PTPP) at Jhansi, Uttar Pradesh, India, is being reported using inductively coupled plasma mass spectrometry (ICPMS). Results show that fly ash from PTPP contains micro nutrients such as Mn, Cu, Zn, Ni and Co in normal sub-range and diminutive range of rare earth elements. The toxic elements such as Hg, Pd, Pt, Rh and Zr, and radioactive elements such as ^{238}U and ^{232}Th were below detection limit. These results indicate that the PTPP's fly ash imparts no ecological or health damage. The presence of elemental concentration in optimal quantities may be useful in the agricultural field for better crop production. The only threat was the incidence of soluble Ba, although its concentration was found very low.

Key word: Fly ash; ICP-MS; Rare-earth elements; radioactive elements; Agricultural Field.

1. INTRODUCTION

The need of energy in the overall development of any country is of paramount importance. India being a developing country is no exception. India is primarily dependent on thermal power plants for its electricity requirements. Coal of different varieties and obtained from various mines is being used in these thermal power plants. Elements present in varying concentrations in fly ash, a coal by-product from thermal power plants, lead to geochemical, physical, biological and radiological effects. The presence of elements such as B, Ba, Mg, Na, Fe, Zn, U, Rn and Th in fly ash has been reported (Sharma & Kalra 2000). The toxic and radioactive elements present in fly ash may cause harmful effects on soil, surrounding water and human beings. A small amount of Ba in water can cause breathing difficulties, change in heart rhythm and nerve reflexes, increased blood pressure, muscle weakness, and stomach irritation and low Mg levels in the body may result in diseases like osteoporosis, high blood pressure, clogged arteries, heredity, heart disease, dialysis and stroke (Baaji et al., 2015). A high concentration of radioactive minerals in soil because of fly ash disposal has been reported in Slovenia, Bangladesh, Brazil and China. Radiation from the coal-fired thermal plant may show a pernicious effect in the area within 0.8-1.6 km radius of the thermal power plant (Habib et al., 2019). Gabbard has reported that Americans who live near the coal-fired thermal power plants are exposed to higher radiation than those who live near the nuclear power plant (Gabbard, 1993). In India limited research on radiation from fly ash has been reported. Singh et al., (2015) and Kant et al., (2010) have reported radiation of Radon (Rn) from coal and fly ash collected from different thermal power plant in northern India. However, the distribution and enrichment of other naturally occurring radioactive metals like U and Th in fly ash have not been characterized in India.

In contrast, many researchers have reported fly ash as a possible source of various useful micro and macro elements (Chem et al., 2001). Sharma & Kalra have suggested the usefulness of trace elements from fly ash to improve crop growth and its addition generally decreased the bulk density of soil (Sharma & Kalra 2000). A study on the coal fly ash of mine reveals it to be a propitious resource of Rare Earth Elements (REE), a composite group of 17 metallic elements of lanthanide series from $^{139}La_{57}$ to $^{175}Lu_{71}$ and $^{45}Sc_{21}$ and $^{89}Y_{39}$ (Rim, 2016, Rim et al., 2013) and have been reported to have major effects on soil and environment (Wang & Liang, 2015). Hu et al. have reported the use of REEs in pedogenic processes, geochemical study and agronomic fertilizers (Hu et al. 2002). REEs also act synergistically with the plant's hormones to stimulate seed germination (Shtangeeva & Ayrault, 2007). The average global value of REE is 445 mg/kg in fly ash, in which Ce is only soluble REE, which causes soil pollution (Franus & Malgorzata, 2015). There is a need to quantify the various constituents present in fly ash as their occurrence may cause health issues for living beings or can serve as a potential source of many elements.

2. MATERIAL AND METHODS

2.1 Study area

Parichha Thermal Power Plant (PTPP) is a coal-based thermal power plant located near NH 25 on the northern bank of Betwa River in Jhansi, U.P., India. Jhansi district is situated at 24’ 11” N to 25’ 57” N latitude and 78’ 10” E to 79’ 23” E longitude in the country's semi-arid region at the height of about 250 meters above mean sea level.

2.2 Sampling, sample preparation and methodology

The PTPP is used bituminous coal [taken from Bharat coalfield company ltd (BCCL) and Northern coalfield (NCL)], burning at 1100-1300°C for electricity generation. It is having SiO_2, Al_2O_3, and Fe_2O_3. The reported loss of ignition value of this coal is 0-15%. Fly ash sample has been collected in July 2018 from ESP and ash slurry at 27 °C environmental temperature. The S-W sample was directly collected from ash-slurry and filtered twice to get the clear solution. S-A and S-B samples were digested by taking 1g fly ash (collected from ESP) in 25 ml of N/10 HCl acid and N/10 NaOH base solvent separately at ±60°C for 30 minutes. The samples were analysed by using Inductively Coupled Plasma Orthogonal Acceleration Time-of-Flight Mass Spectrometer (ICP-oa-TOFMS), Model no Optimass 8000R from GBC Australia. The operating instrumental conditions can be found in Saha et al., 2016. In ICP-MS analysis, the nuclides of every element have been chosen based on maximum abundance and minimum polyatomic interference. Multi-element standard solutions containing 5-500 ng mL^{-1} of individual analytes were analyzed to construct the calibration curve for each element. The detection limit values were determined using the formula $3\sigma/s$ (where “σ” is the standard deviation of the blank sample and “s” is the slope of the calibration curve). Pure water, N/10 solution of HCl and N/10 solution of NaOH were analyzed to get the respective detection limit values.

2.3 Sampling and methodology for radiation measurement

A thermo-scientific radiation meter, model-RADEYEB20 α, β, γ survey meter, was used for radiation measurement. The following solid samples were analyzed by radiation meter. For radiation measurement samples placed directly in contact with the instrument.

1. F_{Esp} (Fresh fly ash collected from Electrostatic precipitator (ESP).
2. F_{Bottom} (Bottom fly ash collected from ash-slurry).
3. $F_{Dumping}$ (Fly ash collected from dumping site).
4. F_{Brick} (Fly ash made brick).

range of water through leaching during acid rain on the surrounding of PTPP. A lower Mg concentration

3. RESULTS

Results of the samples obtained from ICPMS analysis are presented in Table 1.

4. DISCUSSION

Total 37 elements are estimated in fly ash of Parichha thermal power-plants (Table 1). Among them, 23 elements belong to s, p and d block, 14 elements belong to f block in which 12 elements are rare-earth elements, and 2 are naturally abundant radioactive elements. It is analysed that Li's concentration is low than its average concentration of 15.6 mg/kg in coal, as reported by U.S. National Committee for Geochemistry (USNCG, 1980).

Table 1. Indicating the concentration of various elements.

Elements	Isotopes monitored in ICP-MS	Water digested (S-W)(mg/L)	Acid digested sample (S-A)(mg/kg)	Base digested sample (S-B)(mg/kg)
Li	^{3}Li	0.060	0.875	0.625
Mg	^{24}Mg	9.100	275.000	325.000
V	^{51}V	0.435	1.250	0.750
Ti	^{48}Ti	0.048	12.750	8.750
Mn	^{55}Mn	ND	62.500	57.500
Co	^{59}Co	ND	1.525	1.250
Ni	^{60}Ni	0.012	0.125	0.125
Cu	^{65}Cu	ND	1.350	1.100
Zn	^{66}Zn	ND	7.650	5.700
Ga	^{69}Ga	0.035	ND	ND
Ge	^{74}Ge	ND	ND	ND
Sr	^{88}Sr	0.300	5.625	4.375
Y	^{89}Y	ND	2.125	1.875
Zr	^{90}Zr	ND	ND	ND
Ru	^{102}Ru	ND	ND	ND
Rh	^{103}Rh	ND	ND	ND
Pd	^{106}Pd	ND	ND	ND
Cs	^{133}Cs	ND	ND	ND
Ba	^{138}Ba	0.480	3.250	1.850
La	^{139}La	ND	1.000	0.700
Ce	^{140}Ce	0.005	2.375	1.900
Pr	^{141}Pr	ND	0.300	0.250
Nd	^{142}Nd	ND	1.800	1.500
Sm	^{152}Sm	ND	0.375	0.300
Eu	^{153}Eu	ND	0.100	0.075
Gd	^{158}Gd	ND	0.400	0.350
Dy	^{164}Dy	ND	0.300	0.250
Tm	^{169}Tm	ND	ND	ND
Yb	^{174}Yb	ND	ND	ND
Hf	^{180}Hf	ND	ND	ND
Lu	^{175}Lu	ND	ND	ND
Pt	^{195}Pt	ND	ND	ND
Au	^{197}Au	ND	ND	ND
Hg	^{202}Hg	ND	ND	ND
Th	^{232}Th	ND	ND	ND
Pb	^{208}Pb	ND	0.250	0.100
U	^{238}U	ND	ND	ND

*ND-not detected. *The detection limit of these elements can be seen in supplementary table. 1.

Supplementary table 1.

Elements	Isotopes monitored in ICP-MS	Water digested (S-W) (ng/L)	Acid digested sample (S-A) (ng/L)	Base digested sample (S-B) (ng/L)
Li	^{3}Li	1200	1350	1500
Mg	^{24}Mg	20	22	30
V	^{51}V	25	28	36
Ti	^{48}Ti	28	30	40
Mn	^{55}Mn	22	25	28
Co	^{59}Co	35	40	52
Ni	^{60}Ni	200	280	400
Cu	^{65}Cu	45	52	65
Zn	^{66}Zn	20	21	28
Ga	^{69}Ga	22	25	32
Ge	^{74}Ge	55	70	92
Sr	^{88}Sr	12	15	22

Y	^{89}Y	15	17	20
Zr	^{90}Zr	22	26	33
Ru	^{102}Ru	22	24	30
Rh	^{103}Rh	12	15	21
Pd	^{106}Pd	20	25	35
Cs	^{133}Cs	11	12	15
Ba	^{138}Ba	15	16	28
La	^{139}La	10	12	18
Ce	^{140}Ce	15	20	26
Pr	^{141}Pr	8	10	15
Nd	^{142}Nd	24	30	40
Sm	^{152}Sm	22	25	32
Eu	^{153}Eu	15	18	25
Gd	^{158}Gd	25	30	40
Dy	^{164}Dy	21	25	36
Tm	^{169}Tm	8	12	18
Yb	^{174}Yb	15	18	24
Hf	^{180}Hf	18	22	30
Lu	^{175}Lu	6	10	16
Pt	^{195}Pt	12	15	18
Au	^{197}Au	8	10	12
Hg	^{202}Hg	50	90	150
Th	^{232}Th	5	5	6
Pb	^{208}Pb	8	10	10
U	^{238}U	6	8	6

The detection limit values were determined using the formula 3σ/s (where "σ" is the standard deviation of the blank sample and "s" is the slope of the calibration curve). Pure water, N/10 solution of HCl and N/10 solution of NaOH were analyzed to get the respective detection limit values.

Table 2. Radiation ranges of fly ash samples**.**

Sample	Background radiation value	Sample radiation value
F_{Esp}	747 cps	805 cps
F_{Bottom}	747 cps	791 cps
$F_{Dumping}$	747 cps	796 cps
F_{Bricks}	747 cps	801 cps

Magnesium (Mg) is found in much higher concentrations in acid and base digested samples than S-W, which indicates that insoluble Mg in fly ash may be responsible for increasing the hardness in soil (below 4 mg/kg) is supposed to be responsible for falling of leaves (GOI, 2015). Similarly, Sr is present in higher concentrations in S-A and S-B compared to S-W. Its intake helps teeth and bone health but may disrupt bone if taken in thousands of ppm (Specht et al., 2014). Sr level in the fly ash of PTPP is not higher to cause harmful effects. Ba is found in all the digested samples, but the water-soluble Ba concentration is only 0.48 mg/L, which is less than the USEPA range of 2.0 mg/L (WQ). Water-soluble Ba causes adverse health effects and even fatality due to the absorption of its compounds like hydroxide, nitrate and chloride. But fortunately, it forms an insoluble salt with other standard components present in the environment, such as carbonates and sulphate and hence poses little risk. Cs and Ge are found below detectable limit in all samples. Pb has been found in low concentrations in S-A and S-B. Oxides of lead such as PbO, PbO_2 and Pb_3O_4 are toxic and can accumulate in the human body by long term exposure (Wani et al., 2015). In the present study, the soluble Pb is not detected in fly ash samples which suggest it doesn't pose any severe effect on soil health and the environment. Water-soluble Ga is present only in S-W. Ti is showing higher solubility in acidic medium (S-A) than aqueous medium S-W. It is not poisonous, and the human body can tolerate Ti in a large dose (Barksdale, 1968). Humans can ingest 0.8 mg of titanium daily, but most of its passes through without being absorbed by tissue (Emsley, 2011). V is found to be in higher concentration in acidic medium (S-A) than in basic (S-B) and water medium (S-W). More than 1.8 mg per day of V is harmful to humans, animals, and plants (Rodriguez et al., 2016). The average concentration of V in soil has been reported to be 90 mg/kg. It plays an essential role in plant growth and takes part in nitrogen fixation and accumulation (Teng et al., 2011). Mn is found in S-A and S-B. Its recommended daily intake concentration is 5.0 mg, and its higher dose may hinder the absorption of iron (Joode et al., 2016). Co is showing solubility S-A and S-B. Co is a vital component of various enzymes and co-enzymes involved in plants and animals' growth and metabolism (Elbagir et al., 2018). Significantly less concentration of Ni has been found in all the samples. Its oral intake of 1 mg/day is safe for human beings, whereas a higher dose may cause toxicity and carcinogenicity (Ahamad & Ashraf, 2011). The concentrations of Cu and Zn are found in S-A and S-B. According to GOI 2015, a minimum of 0.2 mg/kg of Cu and 0.6 mg/kg of Zn is essential for plant nutrition in the soil. Y has been found in S-A and S-B. Although officially there is no information on Y's acceptable intake value, its exposure has been reported to result in lung disease (Xi et al., 2015). The platinum group of elements viz., Pd, Ru, Rh and Pt, Zr, Hf, Au and Hg are below detection limit in the fly ash samples. Naturally, light REEs are found in an elevated amount in this type of sample, and concentrations vary from 0.30 to 2.375 mg/kg. Commonly in the light REEs, Ce's concentration remains high and the same is found in our case (Table 1). Ce is the only soluble REE, and the S-W sample also confirms it. Here the value of Ce is trivial than the naturally occurring value of 60 mg/kg in soil (Sneller et al., 2000). La is present in an appreciable amount in S-A and S-B. La is being used in agriculture to enhance yield for improving the quality of crops (He & Lo, 2000). The proportion of the two elements viz., La and Ce show a similar trend as their natural abundance, i.e., Ce concentration is twice of La concentration. Nd concentrations have been found in S-A and S-B. Zhan et al., 2013, have suggested that low concentrations of Nd^{3+} (1, 3 and 5 mg per liter) significantly promote seed germination. Eu is present in low concentrations in S-A and S-B. According to the previous literature, Eu concentrations above 10 mg/l can promote callus growth, while lower concentrations can adversely affect callus subculture (Shtangeeva & Ayrault, 2007). The present investigation suggests that the total REE concentration in fly ash is much less than the average global value. The results are not consistent with Franus (Franus & Malgorzata, 2015). In this analysis, U and Th are absent in all three samples. The absences of these naturally occurring radionuclides are further verified by a radiation meter. The results have been shown background radiation 747 cps, and all four samples represented a radiation range between 791-805 cps. The results exhibit an insignificant difference between background value and radiation value from fly ash. This study concludes that the fly ash of PTPP may not exert any harmful radiological effect on the environment.

In conclusion, the huge amount of generated fly ash can disturb and alter the chemistry of surrounding soil, water, and air. This study reflects that among 37 analysed elements, 8 water-soluble elements may spread from fly ash to soil, groundwater and surface water. In contrast, acid rain would increase the solubility of 13 other elements in the surrounding industrial area. However, any element's bio availability and toxicity depend on its characteristics like oxidation state, metal phase, soil nature, and pH. The non-existence of naturally occurring radionuclides viz., U and Th show no radiological effect of PTPP's fly ash. The absence of the platinum group of elements and other toxic elements viz., Hg, Hf and Zr suggest no exposure of these elements upon using the fly ash. The optimum concentrations of well-established micro nutrients viz., Mn, Cu, Zn, Ti, Ni and Co suggest that PTPP's fly ash can be incorporated in soil without any adverse effect. The level of REE in PTPP's fly ash is in the sub-normal range and no adverse effect on the environment is expected.

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