The Ecoscan 10(1&2): 13-17, 2016
AN INTERNATIONAL QUARTERLY JOURNAL OF ENVIRONMENTAL SCIENCES
www.theecoscan.com

STUDY ON HEAVY METAL STATUS IN SOILS UNDER THE IMPACT ZONE OF RAICHUR THERMAL POWER STATION (RTPS)

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ABSTRACT

The soil samples were collected within the impact zone of RTPS at two depths (0-15 and 15-30 cm) consisting of red and black soils. On the other hand soils were compared with cultivated soils of college of Agriculture, UAS Raichur. The results revealed that the heavy metal concentration of soils within the impact zone of RTPS were comparatively higher over the control soils irrespective to the type of soils and direction. Among the soil types within the impact zone, black soils had higher content of Cd (57.1 and 53.6 mg kg^{-1}), Mn (30.1 and 26.2 mg kg^{-1}), Ni (, Pb, Si and Zn than the red soils and the red soils were higher in Cu (7.32 and 7.04mg kg^{-1}) and Fe (142 and 134 mg kg^{-1}) than the black soils. The comparison of heavy metal contents in soils with reference to distance and direction from the RTPS indicated no clear trend in the distribution of heavy metals in the soils studied. The marginal higher concentration of heavy metals observed in the soils under the impact zone might also be due to pollutants that are released from the other industries which are located near to the RTPS.

KEY WORDS
Black soil
Coal
Fly ash
Heavy metals

Received : 24.06.2015
Revised : 07.01.2016
Accepted : 11.02.2016

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INTRODUCTION

Fly ash is an amorphous mixture of ferro-alumino-silicate minerals generated from the combustion of ground or powdered coal at 400-1500ºC and belongs to the coal combustion by-products in power plants produced from bituminous, subbituminus, and lignite combustion. Flyash production depends on the quality of the coal,which contains a relatively high proportion of ash that leads to 10-30% fly ash formation (Jabeen *et al.,* 2010).Thermal power generation contributes to more than 70% of the power generation in the country (Mishra., 2004). Indian coal is of bituminous type, with 55-60% ash (Mishra., 2004). Combustion of coal thus generates huge amount of ash which are disposed-off eitherin dry or slurry form. Fly ash generated from coal combustion has a greater tendency to absorb trace elements that are transferred from coal to waste productsduring combustion due to its small size and hence, large surface area (Gulec *et al.*, 2001). Fly ash can promote soil microbial activity and mixing with an organic substrate enhances its benefits, which assumes importance owing to eco-friendly disposal of fly ash. The application of wastes to soil as a recycling option can only be sustained if there are demonstrable 'ecological benefits' which is usually justified in terms of elevated organic carbon and its effect on soil conditions and stimulation of microbial activity and nutrient supply and this is sustainable only if threshold levels of pollutants does not exceed (Jabeen and Sinha, 2012). Trace elements from coal-burning power plants are released to the environment via atmospheric emissions of volatile phases and also through the leaching of solid combustion by-products, during their disposal or after deposition on the soil of the surrounding area. The emission levels of trace elements dependon the original concentration of each element in the coal, on the specific chemistry of the coal ash, relative fractions of removed ash and combustion conditions. Khan and Wajidkhan (1996) evaluated the higher level of Mn, Cu, Zn, B in field soil exposed to the fly-ash emission from thermal power plant.

The Raichur thermal power station, situated in Raichur District, Karnataka,India. Ituses nearly 80 lakh tonnes of coal every year for power generation and produces about 15 lakh tonnes of fly ash per year. The drifting of fly ash and suspended particulates matter in and around the thermal plant may cause environmental pollution and contribute to the heavy metal concentration in surface soil, ground water sources etc. However, this paper evaluates the heavy metal concentration in soils around the impact zone of RTPS.

MATERIALS AND METHODS

The present study (2013-14) was conducted in areas affected mainly by the Shaktinagar power plant emissions. The study arealies between the latitude 16º 21' 18" N and longitude 77º20' 30.84" E in the Raichur district of Karnataka, India. The elevation ranges from 450 m above mean sea level.

Study sites

Ten study sites were selected within the impact zone of RTPS (10 kms) in all the directions (Table 1). The 100 soil samples were collected at two depths 0-15 cm and 15-30 cm with different distances and directions within the impact zone of RTPS. Two representative soil samples comprising black and red soil collected from agricultural farm, College of Agriculture, UAS, Raichur were used for comparative study which is 22 kms apart from RTPS towards Northwest direction.

Soil processing

The collected soil samples were air dried,processed using wooden pestle and mortar, passed through 2 mm sieve. The two mm sieved samples were preserved in polythene bags for further analysis. For organic carbon analysis, the 2 mm sieved samples were subjected for further grinding and passed through 0.2 mm sieve.

Chemical analysis

The chemical composition of soil and fly ash was analysed by following methods. The pH was measured in 1:2.5 soil-water suspension using pH meter (Jackson, 1973). The clear supernatant solution of the above suspension was used for EC measurement using Conductivity Bridge (Jackson, 1973). Easily oxidizable organic carbon of soil samples was determined by Walkley and Black's wet oxidation method (Walkey-Black, 1934). $CaCO_3$ was estimated by rapid titration method (Piper, 1966).The CEC of soil was determined by sodium saturation method using flame photometer (Black, 1965).

Heavy metal analysis

The heavy metal concentration in soil and fly ash was determined by using aquaregia digestion method (Forster. 1995).The extract was prepared by digesting the soil samples using aquaregia (3:1 HCL:HNO_3) solution. The concentration of heavy metals was analysed by using the instrument (ICP-OES). The chemical composition of fly ash was pH-8.36, EC-1.9 dS m^{-1}, OM-Nil, CEC-7.49 cmol (p^+) kg^{-1} and $CaCO_3$-6.27 % and composition of heavy metal concentration was Cd-1.89 ppm, Cu-100 ppm, Fe-50.5 ppm, Mn-198 ppm, Zn-170 ppm, Pb-11.8 ppm, Ni-18.1 ppm and Si- 55.6 %.

Pearson correlation coefficients and curve estimation procedures were used to determine relationships between different heavy metals and soils properties by standard procedure of SPSS statistical software (Snedectorand and Cochran, 1968).

RESULTS AND DISCUSSION

The drifting of fly ash in around the impact zone of RTPS has influenced on the heavy metal concentration of surface and subsurface soil. The chemical composition and heavy metal concentration in and around the RTPS (Table 1, 2, 3 & 4) were found to be higher when compared with the control soils.

The pH value of surface and subsurface soil ranged from 6.96 to 8.08 and 7.10 to 7.26 respectively. The highest pH of surface and subsurface soil in Kukanoor and lowest was recorded in Korvihall for surface and Gudeballuru for subsurface soil. Black soil recorded high pH compared to red soil due to high calcium carbonate content and exchangeable basic cations on exchange complex. The results revealed that fly ash falling from the chimneys through the power plant doesn't have impact on pH of the soil, when compared to the control. The result are in accordance with the findings of Singh *et al.* (1995) reported that soil pH was mostly alkaline at polluted sites.

The EC value of surface and subsurface soil ranged from 0.15 to 0.49 dS $m^{-1}$and 0.22 to 0.68 dS m^{-1} respectively. Whereas, the highest EC of surface and subsurface soil recorded in Kudluru and Kukanoor respectively and in surface and subsurface soil lowest was recorded in Jagarkall and Rangapura respectively.Chemical analysis of all the soil samples revealed that they are non saline (<1 dS m^{-1}) in nature.Red soil recorded less EC when compared to black soil. It was also found that the EC increased with depth. It might be due to leaching of salts and its accumulation in lower layers.The results are in contradictory to the finding of Singh *et al.* (1995), trend of decreasing EC across the distance around Shaktinagar and Renusagar thermal power plant of Uttar Pradesh, India.

The organic matter content of the surface and subsurface soil varied from 7.20 to 11.2 g kg^{-1}and6.27 to 9.54 g kg^{-1} respectively. The village Kudluru recorded highest organic matter content for surface and subsurface soil and lowest was Korvihall for surface and Kadluru for subsurface soil.Compared to red soil, organic matter content in black soil was high due to less oxidation of organic matter, on other handhighly oxidised state of red soil readily oxidise OC from soil to give

Table 1: Average values of physico-chemical parameters of surface (0-15 cm) soil samples collected from different locations around the RTPS

Location	Aerial distance from RTPS (km)	Direction from RTPS	No. of Samples	Soil type	pH	EC(dS m^{-1})	OM (g kg^{-1})	CEC(cmol (p^+) kg^{-1})	$CaCO_3$ (%)
Ganjalli	6	East	5	Red soil	7.09	0.18	9.76	19.6	2.74
Gudeballuru	6	North	5	Red soil	7.02	0.16	8.58	20.6	2.14
Hindhupur	6	North west	5	Black soil	7.42	0.39	9.54	48.2	6.66
Jagarkall	8	South west	5	Black soil	7.92	0.15	7.82	47.9	7.28
Rangapura	8	North west	5	Black soil	7.83	0.20	8.65	55.7	7.28
Korvihall	9	North east	5	Red soil	6.96	0.16	7.20	22.1	3.88
Kadluru	10	West	5	Red soil	7.04	0.17	9.13	19.3	4.68
Kudluru	10	South east	5	Black soil	7.94	0.49	11.2	49.4	7.02
Kukanoor	10	South	5	Black soil	8.08	0.38	9.54	46.9	10.3
Marched	10	South west	5	Black soil	7.74	0.19	10.7	48.2	3.78
Control 1	22	North	1	Black soil	7.40	0.24	16.5	52.0	3.01
Control 2	22	North	1	Red soil	6.90	0.14	14.6	19.0	2.10

Table 2: Average values of physico-chemical parameters of subsurface (15-30 cm) soil samples collected from different locations around the RTPS

Location	Aerial distance from RTPS (km)	Direction from RTPS	No. of Samples	Soil type	pH	EC (dS m^{-1})	OM (g kg^{-1})	CEC(cmol (p^+) kg^{-1})	$CaCO_3$(%)
Ganjalli	6	East	5	Red soil	7.15	0.25	7.67	25.5	3.14
Gudeballuru	6	North	5	Red soil	7.10	0.24	6.66	24.6	2.64
Hindhupur	6	North west	5	Black soil	7.54	0.46	7.96	50.6	10.4
Jagarkall	8	South west	5	Black soil	7.98	0.25	6.45	54.2	9.82
Rangapura	8	North west	5	Black soil	8.09	0.22	7.27	62.0	9.48
Korvihall	9	North east	5	Red soil	7.12	0.23	6.65	24.9	4.64
Kadluru	10	West	5	Red soil	7.26	0.24	6.27	25.0	5.56
Kudluru	10	South east	5	Black soil	8.17	0.59	9.54	53.5	7.58
Kukanoor	10	South	5	Black soil	8.22	0.68	7.55	52.3	11.5
Marched	10	South west	5	Black soil	7.92	0.39	9.13	53.2	5.18
Control 1	22	North	1	Black soil	7.50	0.30	15.0	60.5	6.50
Control 2	22	North	1	Red soil	7.10	0.20	11.8	22.7	2.50

Table 3: Average heavy metals status (mg kg^{-1}) of surface (0-15 cm) soil samples collected from different locations around the RTPS

Location	Aerial distance from RTPS (km)	Direction from RTPS	No. of Samples	Soil type	Cd	Cu	Fe	Mn	Ni	Pb	Si	Zn
Ganjalli	6	East	5	Red soil	54.2	4.91	126	21.8	176	69.2	40.3	52.9
Gudeballuru	6	North	5	Red soil	31.7	2.98	91.1	17.9	102	68.9	376	40.2
Hindhupur	6	North west	5	Black soil	43.2	3.30	29.7	18.3	150	67.5	87.2	49.3
Jagarkall	8	South west	5	Black soil	38.7	2.88	30.3	19.4	106	67.8	133	55.3
Rangapura	8	North west	5	Black soil	39.9	3.98	28.0	18.9	109	71.2	193	63.4
Korvihall	9	North east	5	Red soil	29.9	7.32	133	10.5	101	69.1	41.6	38.3
Kadluru	10	West	5	Red soil	50.8	4.91	142	19.1	161	69.6	185	49.4
Kudluru	10	South east	5	Black soil	50.2	4.30	27.1	30.1	157	70.3	338	53.7
Kukanoor	10	South	5	Black soil	57.1	2.91	26.4	21.0	303	75.3	326	62.8
Marched	10	South west	5	Black soil	46.6	2.71	24.5	17.8	130	69.5	17.4	51.4
Control 1	22	North	1	Black soil	35.4	2.38	23.8	17.3	199	69.0	338	49.4
Control 2	22	North	1	Red soil	22.8	4.74	119	6.20	89.3	68.7	38.3	33.3

rise to CO_2 which eventually escaped into the atmosphere.this could be linked to the oxidation of OC present in coal as oxides of carbon during the combustion of coal (Bern, 1976).

The CEC of surface and subsurface soil ranged from 19.3 to 55.7 cmol (p^+) $kg^{-1}$and 24.6 to 62.0 cmol (p^+) kg^{-1} respectively. The village Rangapura recorded highest CEC and lowest was Kadluru. In subsurface soil the highest CEC was recorded in Rangapura and lowest was Gudeballuru.Red soil recorded low CEC compared to black soil. It might be due to low clay content. Compared to control plot the soil around the impact zone does not have any influence of fly ash on the CEC of soil with distance and direction. The results are in disagreement with the finding of Singh *et al.* (1995), trend of decreasing cations content across the distance around Shaktinagar and Renusagar thermal power plant of Uttar Pradesh, India.

The data pertaining to calcium carbonate in surface and subsurface soil ranged from 2.14 to 10.3 per cent and 2.64 to 11.5 per cent respectively. The soils were slightly calcareous in nature. The highest and lowest $CaCO_3$ content was recorded in Kukanoor and Gudeballuru for both surface and subsurface soil. in black soil. $CaCO_3$ content increased with depth. It may due to the basic parent material of lime stone existing in the area. The results showed that there was no impact of fly ash on $CaCO_3$ content in and around soils of impact zone of RTPS. These results are similar with the findings of by Singh *et al.* (1995) there was no effect of fly ash on calcium carbonate content in soil.

The cadmium content of surface and subsurface soil in impact zone of RTPS were ranged from 29.9 to 57.1 mg kg^{-1} to 26.6 to 53.6 mg kg^{-1} respectively. Among the soils in the impact zone of RTPS the highest cadmium content in surface and subsurface soil was found in Kukanoor (Black soil) and lowest was observed in Korvihall (Red soil). When compared with the control.It might be due to dispersion of cadmium ions with the fallout of fly ash from the thermal power plant. The emission of Cd extends it residual time in the atmosphere thus facilitates long range transport of element from the point of release. The results were in accordance with Keegan *et al.* (2006) the higher concentrations of heavy metals in the soils around the coal fired power plant in Slovakia.

The copper content in soils was widely distributed with the distance and direction. The copper content in surface and subsurface soil were varied from 2.71 to 7.32 mg kg^{-1} and 2.04 to 7.04 mg kg^{-1} respectively. Whereas, the highest copper content in surface and subsurface soil was found in Korvihall (Red soil) and lowest was found in surface soil of Marched (Black soil) and subsurface in Hindupur (Black soil). It might be due to the presence of high Cu oxides in both red and black soils, which are toxic in nature and the results were in accordance with those found in soils around coal fired power plant in Slovakia (Keegan *et al.*, 2006).

The iron (Fe) content in surface and subsurface soil were ranged

Table 4: Average heavy metals status (mg kg^{-1}) of subsurface (15-30 cm) soil samples collected from different locations around the RTPS.

Location	Aerial distance from RTPS (km)	Direction from RTPS	No. of Samples	Soil type	Cd	Cu	Fe	Mn	Ni	Pb	Si	Zn
Ganjalli	6	East	5	Red soil	53.2	2.75	119	21.1	174	53.7	28.2	50.3
Gudeballuru	6	North	5	Red soil	29.3	2.60	77.4	10.5	85.9	68.2	139	30.2
Hindhupur	6	North west	5	Black soil	41.2	2.04	26.1	11.9	140	48.5	85.2	44.7
Jagarkall	8	South west	5	Black soil	37.9	2.41	23.0	9.74	101	42.0	58.4	53.5
Rangapura	8	North west	5	Black soil	37.2	2.41	22.7	15.3	94.7	32.8	182	57.2
Korvihall	9	North east	5	Red soil	26.6	7.04	134	7.96	97.7	27.3	28.4	30.5
Kadluru	10	West	5	Red soil	50.4	3.03	134	18.0	150	48.9	143	43.1
Kudluru	10	South east	5	Black soil	48.7	4.21	26.0	26.2	152	48.0	325	51.4
Kukanoor	10	South	5	Black soil	53.6	2.64	24.1	17.8	179	35.4	319	61.5
Marched	10	South west	5	Black soil	45.0	2.37	24.3	11.6	122	43.9	8.46	50.0
Control 1	22	North	1	Black soil	32.7	2.03	21.6	8.25	104	21.7	305	49.0
Control 2	22	North	1	Red soil	16.2	2.63	98.0	3.10	82.9	19.16	11.7	29.2

Table 5: Correlation analysis of soil parameters (Pooled) in surface soil (0-15 cm) samples with the heavy metals

	Cd	Cu	Fe	Mn	Ni	Pb	Si	Zn
Clay	.022	-.200	-.604**	.134	.037	-.010	.058	.317*
pH	.234	-.213	-.630**	.237*	.321*	.120	.074	.574**
EC	.250*	-.002	-.268*	.313*	.212	-.138	.212	.185
OM	.508**	-.137	-.253*	.140	.228	.040	.136	.083
CEC	.146	-.146	-.842**	.130	.103	.108	.104	.482**
$CaCO_3$	.249*	-.077	-.478**	.052	.399**	.298*	.249*	.366**

**. Correlation is significant at the 0.01 level.*. Correlation is significant at the 0.05 level.

from 24.5 to142 mg kg^{-1} and 22.7 to 134 mg kg^{-1}. The Fe content in surface soil were found to higher in Kadluru and lowest was observed in Marched. In subsurface soil highest was observed in Korvihal and lowest in Rangapur. The Fe concentrations in soils around the RTPS were widely distributed with the distance and direction of RTPS and found to be higher compared with the control. It might be due to the presence of high Fe oxides released during the weathering of minerals under reduced conditions in the both soils.

The manganese (Mn) content in surface and subsurface soil were ranged from 10.5 to 30.1 mg kg^{-1} and 7.96 to 26.2 mg kg^{-1}. The Mn content in surface and subsurface soil within the impact of Zone of RTPS were found to higher in Kudluru and lowest was observed in Korvihall. The Mn concentrations in soils around the RTPS were widely distributed with the distance and direction of RTPS and found to be higher compared with the control. It might be due to the presence of high Mn oxides released during the weathering of minerals under reduced conditions in the both soils.

The black soils of Kukanoor recorded highest Ni content in surface and subsurface soil and lowest in Korvihall and Gudeballuru (Red soil) for surface and subsurface respectively. The gradual increase of trace elements concentration with an increase in distance was observed in the nickel compared to control. This might be attributed to the drifting of fly ash with wind direction. The gradual increase of trace element (Cd, Cr, Cu, Fe, Mn and Ni) concentrations around coal power plant in Turkey were noticed by Cicek and Koparal (2004) and Stalikas *et al.* (1997).

The lead content in surface and subsurface soil was in the range of 67.5 to 75.3 mg kg^{-1} and 27.3 to 68.2 mg kg^{-1} respectively. Among the surface soil the highest lead content was recorded in Kukanoor (Black soil) and lowest was found in Hindupur (Black soil). The highest lead content in subsurface soil was noticed in Gudeballuru (Red soil) and lowest was recorded in Korvihall (Red soil). The concentration of lead in soils were slightly higher than the control and widely distributed in the soil.

The silicon content in surface and subsurface soil samples ranged from 17.4 to 376 mg kg^{-1} and 8.46 to 325 mg kg^{-1} respectively. Among the surface soil the highest was found in Gudeballuru (Red soil) and lowest was found in Marched (Black soil). The highest silicon content in subsurface soil recorded in Kudluru (Black soil) and lowest was found in Marched (Black soil). As Fly ash is rich in silicon, drifting of fly ash from the thermal power plant with wind direction had slight impact on the silica content. The results are in accordance with the results of Cicek and Koparkal (2004).

The zinc content in surface and subsurface soil ranged from 38.3 to 63.4 mg kg^{-1} and 30.2 to 61.5 mg kg^{-1} respectively. Whereas, the highest zinc content in surface soil in Rangapura (Black soil) and lowest was found in Korvihal (Red soil). The highest zinc content in subsurface soil in Kukanoor (Black soil) and lowest was recorded in Gudeballuru (Red soil). Concentrations of Zn in soils around the RTPS were widely distributed with the distance and direction.It might be due to the soils are rich in oxides of Zn under reduced condition which are released during the weathering of minerals. Swaine (1984) found that concentrations of Zn deposited from an Australian power station, burning pulverized bituminous coal, decreased with distance from the power station.

The data on correlation studies showed that CEC was significantly negatively correlated with Fe (r= -0.842** in surface) at 0.01 level of significance (Table 5). Study conducted by Dragovic *et al.* (2013) also showed significant correlation in both positive and negative way in comparing with soil properties.

The concentrations of heavy metal were comparatively higher in soils within the impact zone over the control soils, irrespective of the type of soils and direction of the wind. Among the soil types within the impact zone, black soils had higher contents of Cd, Mn, Ni, Pb, Si and Zn than the red soils. On the other hand, the concentration of Cu and Fe were little higher in red soils than the black soils under study. The comparison of heavy metal content in soils of study area indicated no clear trend in the distribution of heavy metals with reference to distance and direction from the RTPS. In general, the concentration of heavy metals studied were within the permissible limit.However,the slight increase in concentration of heavy metals over the control was observed in the soils under the impact zone might also be attributed to pollutants that are released from the other industries which are located near to the RTPS. A study need to be taken up to know the impact of other industries near the RTPS for heavy metal accumulation.

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INSTRUCTION TO AUTHORS

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The figures should be drawn on a good quality tracing/ white paper with black ink with the legends provided on a separate sheet. Photographs should be black and white on a glossy sheet with sufficient contrast.

References should be kept to a minimum and listed in alphabetical order. Personal communication and unpublished data should not be included in the reference list. Unpublished papers accepted for publication may be included in the list by designating the journal followed by "in press" in parentheses in the reference list. The list of reference at the end of the text should be in the following format.

1. **Witkamp, M. and Olson, J. S. 1963.** Breakdown of confined and non-confined Oak Litter.*Oikos*. **14**:138-147.
2. **Odum, E.P. 1971.** *Fundamentals of Ecology*. W. B. Sauder Co. Publ. Philadelphia.p.28.
3. **Macfadyen, A.1963.** The contribution of microfauna to total soil metabolism. In:*Soil organism*, J. Doeksen and J. Van Der Drift (Eds). North Holland Publ. Comp., pp 3-16.

References in the text should be quoted by the **author's name and year** in parenthesis and presented in year order. When there are more than two authors the reference should be quoted as: first author followed by *et al.,* throughout the text. Where more than one paper with the same senior author has appeared in on year the references should

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