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Original Research

Chemical Characteristics and Trace Element Concentration of Non Coking Coals from Talcher Coal Fields, Orissa, India

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Abstract

The present study investigates the details on the aspects of Coal quality such as proximate, ultimate, calorific value and trace element concentration and its impact on human health. Trace elements are present in very low percentage in coal but their concentration increases manifold after coal combustion and utilization. Throughout the process of coal production as well as consumption, trace elements are released from coal. Their release into the surrounding atmosphere largely depends on the nature of their association with coal, also known as, their modes of occurrence. A number of samples have been collected by using Channel Sampling method from different locations of Talcher coalfield. The statistical analysis of trace elements has also been computed. The coal of the study region has moderate moisture content (2.9% to 7.6%, average 5.04%), volatile matter (19% to 24%, average 21.57%), fixed carbon content (16.6% to 27.5%, average 21.3%) and ash content (42.7% to 61.5%, average 51.86%). It has been observed that most of the trace elements in coal have higher concentration as compared with the World and USA values. The matrix correlation coefficient of ash indicates that iron and sodium show positive correlation, hence it can be regarded to have inorganic association. It gives a better knowledge of coal quality characteristics which may help to reduce some of the health problems caused by the trace elements.

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INTRODUCTION

Coal seams usually originate from peat deposited in swamps, especially a stable, continually subsiding swamp in a warm and humid climate. Besides the major elements C, H, O, N, S, trace elements (<1 wt %) may also reflect the depositional environment of peat. Furthermore, a better knowledge of coal quality parameters may help to minimize some of the health problems caused by coal use. The information about the concentration and distribution of potentially toxic elements in coal may assist people to avoid those areas of coal deposit having high concentration of these elements. In the process of combustion, organic and inorganic materials undergo a complex variation. A part of them will become volatiles together with coal smoke which enter into atmosphere in the form of solid particles and the rest will be retained in ash and slag. Coal ashes are the residues of organic and inorganic substances in coal left after coal combustion (Abernethy *et al*., 1969). The concentrations of trace elements are much higher than those of bottom ash (Swaine, 1975). The coal combustion not only produce heat and energy but significantly harm the environment and human health (Hepplaston *et al*., 1984; Borm, 1994; Vanhee *et al*., 1995; Borm and Driscoll, 1996; Driscoll *et al*., 1996, 1997; Paul, 1997; Frinkelman *et al*., 1999). Under leaching action the ashes find their way into underground water, causing underground water pollution (Mareal Pires *et al*., 2000; Liu guijian, 2000a). Therefore, coal combustion and ash slag formation lead to obvious redistribution of elements on the earth surface.

The main constituents of coal are carbon, hydrogen, nitrogen and sulphur. Apart from these constituents, any other element may be present in coal in traces which range up to 1000 ppm. Goldschmidt (1935) was the first to study the abundances of trace elements in coal ash. Swaine (1975) discussed the concentration, origin and enrichment of trace elements in coal. Gluskoter *et al*. (1981) described the affinity of trace elements according to their association with organic or inorganic materials in coal. Finkelman (1981) pointed out that in a low rank coal such as lignite and sub-bituminous coal, trace elements such as Na, Mg, Ca, Sr, and Ba usually associated with organic constituents in coal. Finkelman (1982) studied the modes of occurrence of trace elements in detail. Pareek and Bardhan (1985) studied the association of trace elements with macerals and found that Cu, Ni, Co, V, Ga, and B usually associated with vitrinite, although, Cu and Ni can originate from both organic and inorganic sources. Trace elements in coal may have organic or inorganic association and most of these elements are found simultaneously in both forms (Gurdal, 2011; Radenovic, 2006; Singh,1991; Swaine, 1990). The concentration, distribution and modes of occurrence of trace elements in coal depends mainly upon the geological factors like depositional environments, the interaction between the organic matter and basinal fluids, sediment diagenesis and synsedimentary volcanic inputs (Dai *et al*., 2011; Singh, 1991). Thus, the study of trace elements in coals provides geologic information about depositional conditions, coal-bearing sequence formation, and regional tectonic history as well as identification and correlation of coal in different basined areas. Moreover, Trace elements in coal can provide useful information relating to environment for possible contamination of toxic trace elements to air, soil and to the surface as well as the groundwater regime during coal combustion and utilization (Senapaty *et al*., 2012; Tang *et al*., 2009; Finkelman *et al*., 2002; Gupta,1998; Tripathy and Patra,1998;). There are also occurrences of valuable trace elements (e.g., Au, Ge, Ga, Nb, Zr, U, Re, rare earth elements, and platinum group elements) in some coals or coal-bearing strata which can be potentially recovered from coal ashes (Dai *et al*., 2011; Seredin and Finkelman, 2008). In view of these aspects, the study of trace elements of coal has received considerable attention in recent years, coincident with increasing coal consumption. Coal quality is now generally recognized as being an impact, often significant, on coal combustion sulfur and moisture contents are regarded as determining factors in combustibility as it relates to both heating value and ease of reaction. The coals are mostly bituminous to sub-bituminous grade and have maximum use in the power sector. The production of the coalfield was 0.91 MT in 1972-73 and now it has reached the target of 53.54MT in the year 2011-12 per annum. Coals are the store house for many trace elements which are released to the atmosphere by thermal power plants and also contaminate the ground water through leaching process. It pollutes the atmosphere, biosphere and affects human health. The study related to Coal ashes analysis will provide a scientific basis for their comprehensive utilization and for reducing environmental pollution. Therefore, this study is made to know the chemical characterization and element composition of non-coking coals of Talcher coalfield. Coal samples have been collected from Talcher coalfield to study the aspects of quality such as proximate, ultimate, calorific value and trace element concentration and its impact on human health.

Location of the Area and Accessibility

Talcher coalfield, bounded by latitudes $23^0 53'$N and $21^0 12'$N and longitudes $84^0 20'$E and $85^0 23'$E, covers an area of about 1800 sq km. It constitutes south-eastern part of the Lower Gondwana basins within Mahanadi Valley Graben. Major part of the coalfield including the present coal mining area falls in Angul district. Location map of the Talcher coal field is shown in figure 1.

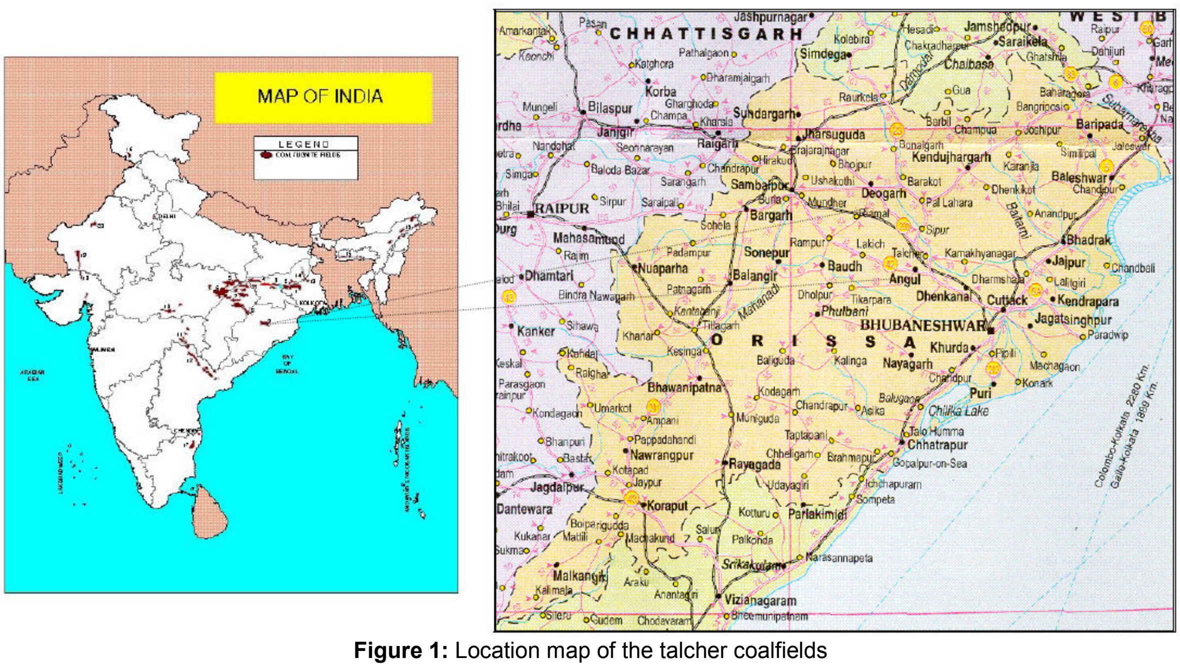

Figure 1: Location map of the talcher coalfields

Geology and Stratigraphy

The Talcher coalfield is located in the north of the Mahanadi River and occupies the valley of the Brahmani River which drains directly into the Bay of Bengal, north of the Mahanadi delta. It occurs as a detached elliptical basin surrounded by metamorphics of Precambrian age and represents the southeastern most member of the Lower Gondwana basins within the Mahanadi valley graben. It is located at the tectonic junction of granite-greenstone rocks to the north belonging to Singhbhum craton and high grade granulite facies of rocks in the south belonging to the Eastern Ghat. The Gondwana sediments belong to Talchir, Karharbari, Barakar, Barren measures and Kamthi Formations. The geological map of the study area is given in figure 2. The generalized stratigraphic sequence of the formations present over the study area is given in table 1.

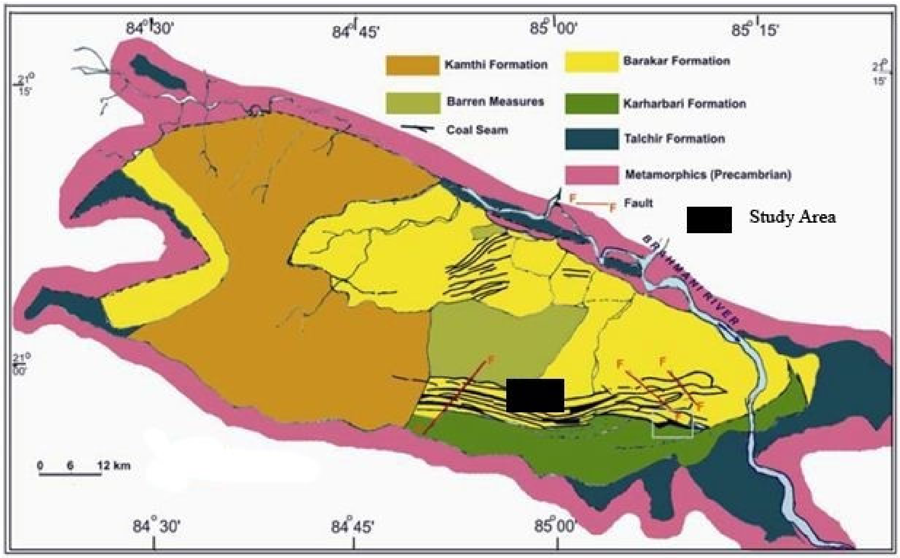

Figure 2: Geological map of talcher coal field (after Manrekar *et al*., 2012 and Senapaty *et al*., 2012)

Table 1: Geological succession of talcher coalfield (after Manrekar *el al*. and Raja Rao, 1982)

Age	Formation	Lithology
Recent Alluvium		Alluvium and Laterite
Sub-Recent		Laterites/ Recent gravel and conglomerate eds.
Up. Permian To Lower Triassic	Kamthi	Fine to medium grained Sandstone, Shale, Coal bands, with greenish sandstone, pink clays and pebbly sandstones at top (250m+)
Upper permian	Barren measures	Greenish gray to buff colored pebby, course to medium grained highly ferruginous sandstone
Lower Permian	Barakar	Medium to coarse grained sandstones, shales, coal seams with oligomictic conglomerate at base (500m+)
Lower Permian	Karharbari	Medium to coarse grained sandstones, shales and coal seams (270m)
Lower Permian	Talchir	Dimictite, fine to medium grained greenish sandstones, shales, rhythmite, turbidite etc. (170 m +)
-----------------------------**UNCONFORMITY**------------------------------		
Precambrian		Granites, Gneisses, amphibolites, migmatites, Khondalites etc

The Karaharbari and the Barakar formations are the major coal bearing formations in the Talcher coalfield. Thin coal bands have also been encountered in the lower part of the Kamthi Formation within the strata previously referred to as Raniganj Formation. Out of the 13 coal seams exposed so far, only Seam-I (the bottom most seam) belongs to the Karharbari Formation whereas the overlying 12 seams i.e. from Seam II to Seam XIII belong to the Barakar Formation. The different seams are separated from one another by different litho types like sandstone, shale, carbonaceous shale, boulders, fireclay etc. The largest outcrops of coal are in the eastern part of the coal field and are seen near Gopal Prasad in the Singhada Jha for a distance of 4.8 km (Behera and Mohanty, 2009). The individual coal bands in the outcrops vary in thickness from 15 cm to 90 cm with intercalations of shales and sandstones. The total thickness of the beds in Gopal Prasad area has been calculated to be about 107 meters of which 75% are carbonaceous shales. The coal seams of Talcher coal field are usually of high moisture, medium to high volatiles, high ash non-coking type and they are dull in appearance.

MATERIALS AND METHODS

The channel sampling method has been used for collection of coal samples from different locations of the Talcher coalfield, Orissa. A freshly exposed coal surface was chosen for sampling. A face was selected normal to bedding plane. Coal was cut back with a hand pick at the top and bottom to produce a proper surface. Two parallel, vertical lines using (crayon) about 10 cm apart were marked on the coal surface. The digging was started at the bottom of the coal bed and the coal between the lines to a depth of approximately 8 cm was chipped out. The steps were repeated from bottom to the top of the channel. The entire sample was transferred into bags and labeled properly. Representative splitting was done later in the laboratory. To remove the surplus moisture, the large samples were kept on a table for 24 hours in the laboratory.

A numbers of samples have been prepared for the present study. The coal has been characterized with respect to proximate, ultimate and trace element analysis. A weight of 500 grams of coal sample was taken for trace element study. The coal samples are finely powdered up to -200 mesh by steel and then with agate mortar. One gram of fine powdered coal is taken in a silica crucible. The sample is taken for spectrometric analysis by AAS. The AAS used is USA make Perkin Elmer Model no-AA-200. The detailed procedure for the trace element analysis has been used as described by (Nadkami, 1980 and Senapaty *et al*., 2012). Elements like Hg and As analysis in coal has been estimated by acid digestion method. Proximate analysis of the coal sample has been made by standard methods (IS: 1350, Part I-1984). Perkin Elmer elemental analyzer (model 2400) has been used to analyze carbon, hydrogen and nitrogen. The standard method is explained in (IS: 1350, Part II-2000). Total sulphur has been determined by using sulphur determinator (Leco, SC132) and oxygen percentage calculated by difference. The forms of sulphur has been determined by standard methods (ASTM D 2492).

RESULTS AND DISCUSSION

The coal quality has been determined through proximate analysis (table 2), ultimate analysis and calorific value (table 3), trace element concentration (table 4). The statistical analysis of the trace elements has also been made.

It has been observed from table 2 that there are major variations in the moisture, ash, volatile matter and fixed carbon contents in the coals of different samples of the study area. The moisture content in the coals of the study area ranges from 2.9% to 7.6% (average 5.04%), volatile matter ranges from 19% to 24% (average 21.57%), fixed carbon content varies from 16.6% to 27.5% (average 21.3%) and ash content from 42.7% to 61.5% (average 51.86%). High ash contents in these coals indicate relatively slow burial and transportation of long distance of vegetative matter. The variation in the volatile matter contents may be due to the compounds released from organic and mineral matter in coals.

Table 2: Proximate analysis of coal samples

Sample No	Moisture %	Ash %	Volatile Matter %	Fixed Carbon %
Sample 1	4.4	57.5	19.3	18.8
Sample 2	4.5	55.3	20.5	19.7
Sample 3	4.0	52.2	20.3	23.5
Sample 4	2.9	61.5	19.0	16.6
Sample 5	3.7	51.2	21.2	23.9
Sample 6	5.7	42.7	24.1	27.5
Sample 7	5.3	55.8	21.1	17.8
Sample 8	7.2	44.2	24.0	24.6
Sample 9	5.1	47.7	24.3	22.9
Sample10	7.6	50.5	21.9	20
Average	**5.04**	**51.86**	**21.57**	**21.53**

It has been observed from table 3 that the coal contains less C (23.9% to 38.44%, average 30.49%), relatively low H (1.98% to 3.60%, average. 2.81%), low nitrogen (0.70% to 1.14%, average 0.927%), sulphur (0.31 to 0.54%, average 0.438%), oxygen (11% to 15.20%, average 13.469%) and O+N combined comprise 14.39%. The atomic H/C and O/C ratios have also been determined which is indicative of humic nature of coal. Thermal value is amount of heat produced by burning one kilogram of coal. It has been measured by calorimeter. The minimum Calorific value is 2110 Kcal/Kg and maximum calorific value is 3600 Kcal/Kg (average 2823 Kcal/Kg).

Table 3: Ultimate analysis of coal samples

Sample No	C (%)	H (%)	N (%)	S (%)	O (%)	O/C	H/C	GCV Kcal/Kg
Sample 1	25.45	1.98	0.70	0.46	13.90	0.55	0.08	2370
Sample 2	28.79	2.30	0.84	0.43	12.30	0.43	0.08	2540
Sample 3	29.9	2.57	0.86	0.54	13.90	0.46	0.09	2710
Sample 4	23.9	2.34	0.78	0.52	11.00	0.46	0.10	2100
Sample 5	31.13	2.82	1.09	0.47	13.29	0.43	0.09	2930
Sample 6	38.44	3.50	0.94	0.46	14.00	0.36	0.09	3600
Sample 7	27.63	2.25	0.89	0.41	13.00	0.47	0.08	2520
Sample 8	35.48	3.60	1.14	0.40	15.20	0.43	0.10	3390
Sample 9	34.33	3.26	1.04	0.31	13.40	0.39	0.09	3190
Sample10	29.91	3.48	0.99	0.38	14.70	0.49	0.12	2880
Average	**30.496**	**2.81**	**0.927**	**0.438**	**13.469**	**0.44**	**0.09**	**2823**

Concentration of Trace Elements

Depending on the chemical characteristics and the rank of the coal, the individual trace elements associate with the various constituents of the coal (Raask, 1985). As a general rule, every element is both inorganically and organically associated to some degree in coal (Raask, 1985). Elements associated with the inorganic fraction in coal may be present either within the structures or adsorbed onto the surface of the mineral (Rimmer, 1991). Organically associated trace elements are present as chelated ions or in ion exchange positions (Rimmer, 1991). Here, thirteen trace elements are studied and the concentrations are presented in the table 4.

The concentration of cadmium ranges from 0.56 -3.2 ppm. but most coals have in the range of 0.1-3 ppm (Swaine, 1990). Cadmium is predominantly associated with the mineral matter in coal, and particularly sphalerite (Swaine, 1990). There may also be minor amounts of cadmium associated with other sulfide minerals

(Finkelman, 1994). Gluskoter, *et al* (1977) supports cadmium is inorganically associated in coal. Most of the data collected to date suggest that cobalt is associated with the sulfide minerals present in coal. The cobalt concentration for most coal is in the range of 0.5 - 30 ppm (Swaine, 1990) but in this study, it ranges from 1.98 - 13.5 ppm. However, cobalt also shows some degree of association with the organic matter and the clays present in coal (Finkelman, 1994). Chromium ranges from 7.2-143.2 ppm. The mode of occurrence of chromium in coal is not clear (Swaine, 1990). Finkelman (1994) assumes chromium to either be associated with the organic matter in coal or with the clays in coal. When studying the Lower Kittanning seam, (Rimmer, 1991) found strong indications that chromium was associated with the clays. The concentration of lead ranges from 23.6-40.5 ppm. Finkelman (1994) states that lead occurs mainly as sulfides or associated with sulfide minerals mainly with galena which is the most common form of lead in coal. The probable range of concentrations of manganese in coal is 5-300 ppm (Swaine, 1990). Here, manganese ranges from 54.5-254.2 ppm. Swaine (1990) lists the major modes of occurrence for manganese as associations with carbonate minerals and in clays (1990).

Table 4 : Average concentration (in ppm) of trace elements in coal of the study area

Sample ID	Ash	Mn	Cr	Zn	Fe	Cd	Cu	Ni	Co	Na	Ca	K	Mg	Pb	Hg*	As*
Sample 1	57.5	66.6	102	78.6	2432	0.56	63.3	45.6	3.54	643.5	55.6	334.7	89.5	25.4	0.1979	1.1
Sample 2	55.3	69	89	85.9	2275	0.98	72.7	69.8	2.13	653.1	102.8	340.6	93.2	27.9	0.2021	1.01
Sample 3	52.2	98.4	92.1	99.4	2201	3.2	68.5	84.4	4.2	639.6	95.5	386.1	19.1	29.9	0.1744	1.3
Sample 4	61.5	54.5	72	94.6	2456	1.94	59.4	43.2	1.98	660.2	58.9	325.6	73.7	23.6	0.2226	0.98
Sample 5	51.2	144.5	95.6	91	2174	3.1	66.8	70.5	4.7	626.5	89.4	503.7	134.4	30.2	0.6431	1.3
Sample 6	42.7	254.2	143.3	174	2422	2.5	98.0	201.5	13.5	430.5	292.6	558.3	179.5	40.5	0.0923	2.21
Sample 7	55.8	112	85.7	87	2311	1.29	79.0	89.1	2.9	604.1	103.5	340.6	112.1	28.1	0.9834	1.14
Sample 8	44.2	239.1	112.2	107.3	1924	2.3	87.3	178.4	7.8	455.2	253.9	443.9	173.7	38.9	0.1123	1.9
Sample 9	47.7	189.7	98.4	110	2059	2.02	80.5	154.7	9.1	389.5	228.1	468.2	170.1	35.2	0.1353	1.64
Sample10	50.5	85.5	141	131	2217	1.43	72.6	85.9	5.53	472.5	198.4	494.6	145.9	32.5	0.1643	1.53

*estimated by acid digestion method

The concentration of Ni varies from 43.2 to 201.5 ppm with an average of 102.31 ppm. Some of the earliest work on trace elements in coal indicates that nickel is contained in coal as organic complexes (Goldschmidt, 1935). The mode of occurrence for nickel in coal is not precisely known. In fact, the indirect evidence presented to date is contradictory (Finkelman, 1994). Finkelman (1994) has found that a large portion of the nickel present in coal is organically bound. Mukherjee *et al*. (1988) found nickel at least in part as an organic chelate. However, Swaine (1990) also suggests that nickel may be inorganically bound with sulfide minerals. The concentration of zinc ranges from 78.6-174 with an average of 105.8. Zinc is predominantly associated with the mineral matter in coal, and particularly sphalerite (Swaine, 1990). Iron concentartion ranges from 1924-2456 ppm with an average of 2247.1 ppm. Concentrations of Cu, Na, Ca, K and Mg ranges from 59.4-98.0 ppm, 389.5-660.2 ppm, 55.6-292.6 ppm, 325.6-558.3 ppm and 19.1-179.5 ppm respectively. The concentration of Hg varies from 0.0923 -0.9834 ppm and As concentration varies from 0.98-2.21 ppm.

The concentration of trace elements as determined in different coal samples collected form Talcher coalfield have been compared with the average concentration of Karharbari and Barakar Coals (Senapaty *et al*., 2012), USA coal (Finkelman, 1993), and the world coal (Senapaty *et al*., 2012) in table 5.

Table 5: Comparison of Average Concentration (in ppm) of Trace Elements in the present Study Area with Karharbari and Barakar Coal, USA coal and World coal

Elements	Study Area	Karharbari (Talcher)[b]	Barakar (Talcher)[b]	USA[a]	World[c]
Mn	155.82	325.8	70.33	43	50
Cr	115.24	208.5	92.43	15	10
Zn	105.88	94.6	104.5	53	50
Fe	2247.1	2456.3	2125.48	1300	1000
Cd	3.25	1.64	3.46	0.47	0.03
Cu	85.15	149.6	55.93	16	15
Ni	131.05	254.7	75.28	14	15
Co	5.538	13.5	4.43	6.1	5
Na	626.14	590.6	638.3	80	20
Ca	147.87	274.4	173.5	460	1000
K	523.84	521.3	524.18	180	100
Mg	119.12	179.5	117.01	110	200
Pb	32.54	32.5	38.18	11	25
Hg	0.2928	-	-	-	-
As	**1.4110**	**-**	**-**	**-**	**-**

[a]USA coal (Finkelman, 1993); [b]Talcher coal (Senapaty *et al*., 2012) and [c]World coal average (Senapaty *et al*., 2012)

It has been observed from the table 5 that most of the trace elements in the study area show higher concentrations as compared with the USA coals and the world average value. The concentration of Zn in the coal samples is higher than the Karharbari, Barakar and USA as well as World coal value, but the concentration of Fe is higher except Karharbari. However, the concentrations of Ca are lower than Karharbari, Barakar, USA and World coal values. The average concentration of Co in these coalfields is observed lower than USA but its shows higher than the world average. For Mg the scenario is reverse, the average concentration of Mg in these coalfields is observed lower than world but its shows higher than the USA average.

Statistical Analysis

The statistical analysis of ash and trace elements has been carried out. The elements have been subjected to univariate (minimum, maximum, mean, standard deviation and skewness) and the comparative statistical parameters of trace elements have been presented in table 6. Since most of the measured parameters are not normally distributed, thus, the Spearman's rank correlation has been used to examine the correlation between elements. The correlation coefficient matrix measures the variance of each constituent which can be explained by relationship with each other.

Table 6: Statistical analysis of ash (%) and trace elements (in ppm)

Parameter	Mean	Min	Max	STDEV	SKW
Ash	51.86	42.7	61.5	5.910	-0.078
Mn	131.35	54.5	254.2	72.899	0.788
Cr	103.13	72	143.3	23.105	0.898
Zn	105.88	78.6	174	28.247	1.800
Fe	2247.1	1924	2456	170.434	-0.556
Cd	1.932	0.56	3.2	0.875	0.006
Cu	74.81	59.4	98	11.676	0.760
Ni	102.31	43.2	201.5	55.694	0.878
Co	5.538	1.98	13.5	3.635	1.294
Na	557.47	389.5	660.2	106.874	-0.556
Ca	147.87	55.6	292.6	86.776	0.607
K	419.63	325.6	558.3	84.680	0.307
Mg	119.12	19.1	179.5	51.467	-0.611
Pb	31.22	23.6	40.5	5.558	0.491
Hg	0.2928	0.0923	0.9834	0.2887	2.0144
As	1.4110	0.9800	2.2100	0.4063	0.9185

From basic statistical data, all elements show good skewness. The standard skewness should be in the range ±2, otherwise it is considered as extreme (Reimann *et al*., 2008). It has been observed from the table 6 that the skewness values are positive i.e. right-skewed value for Mn, Cr, Zn, Cu, Ni, Co, Ca, K, Pb, Hg and As which have been considered to be extreme. The relationships between trace element concentration and ash yield have been widely reported (Dai *et al*., 2011; Spears and Zheng, 1999; Spears *et al*., 1999; Finkelman, 1988; Goodarzi, 1987). The ash content of coal and its geochemical character depends on the environment of deposition and subsequent geological history. It is generally considered that most trace elements in coal are associated with the mineral matter (Goodarzi, 2002). Elements exhibiting positive correlation with ash yield indicate inorganic affinity (Nicholls, 1968). The inorganic affinity may be explained as a result of the causes such as : (1) presence of the element in the inorganic detritus accumulating together with the peat from which the coal is formed, (2) sorption from circulating waters by this inorganic detritus during original peat accumulation, (3) sorption from groundwater by the inorganic fraction during diagenesis, (4) precipitation from circulating waters of compounds stable under physicochemical environment of peat formation, (5) precipitation from groundwater by reaction with compounds already present in the formation during diagenesis and (6) introduction of mineral matter into coals at a late stage in their formation or even after their formation operating in isolation or in union.

The matrix correlation coefficients have also been calculated which is given in table 7. A correlation matrix has been prepared taking into account the percentage of ash with other elements.

It has been observed from the table 7 that the matrix correlation coefficient with percentage of ash indicates that Fe (r=0.5662) and Na (r= 0.8323) has a high positive correlation with ash. Whereas, Hg (r= 0.3240) shows low positive correlation with ash. These elements have high inorganic affinity. The other elements like Mn (r= -0.9149), Cr (r= -0.7256), Zn (r= -0.7216), Cd (r= -0.4621), Cu (r= -0.8531), Ni (r= -0. 9201) , Co (r= -0.8929), Ca (r= -0.9159), K (r= -0.8429), Mg (r= -0.7252), Pb (r = -0.9873) and As (-0.9486) show varying negative correlation with ash. These elements may have an organic affinity. They may be present as primary biological concentrations either with tissues in living condition and/or through sorption and formation of organo-metallic compounds. Thus, it can be inferred that the contribution of the inorganic sources towards the enrichment of trace elements in the coal samples is lower as compared with the organic sources.

The concentration of trace elements like Mn, Cr, Zn, Cd, Co, Ni, Cu and Pb are higher in the study area (as evident from table 5). The concentrations of toxic trace elements in most of the samples analyzed have been found to be higher than the levels in most USA and world coals (Finkelman *et al*., 1999 and 1993; Senapaty *et al*., 2012). It may give a danger to human health. Thus, proper use of the coal with best processing technology may minimize the significant health concerns regarding exposure to potentially toxic trace elements. Most of the trace element content in coal is associated with three major minerals: pyrite, kaolinite, and illite (Robert M. Davidson, 1996). However, the minerals in coal are not uniform, either in chemical composition or physical properties (such as particle size and density). Many minerals in coal show different generations of formation, with distinct morphologies and trace element contents. These mineral phases will behave differently in physical separation and in combustion, especially in their ash forming behavior. If the minerals can be removed from the coal, their associated trace elements should follow. However, the use of conventional cleaning as the primary means of controlling trace element emissions is probably not economical. The economics of advanced cleaning processes, even if they are successful in removing a higher proportion of trace elements, may not be particularly attractive.

Table 7 : Matrix correlation coefficient of ash and trace elements of coals of study area

	Ash	Mn	Cr	Zn	Fe	Cd	Cu	Ni	Co	Na	Ca	K	Mg	Pb	Hg	As
Ash	1	-0.9149	-0.7256	-0.7216	0.5662	-0.4621	-0.8531	-0.9201	-0.8929	0.8323	-0.9159	-0.8427	-0.7252	-0.9873	0.3240	-0.9486
Mn	-0.9149	1	0.5177	0.6406	-0.4773	0.4723	0.8760	0.9541	0.8929	-0.7794	0.8608	0.7279	0.7612	0.9326	-0.1850	0.9171
Cr	-0.7256	0.5177	1	0.8271	-0.0936	0.0544	0.6234	0.5903	0.7295	-0.6901	0.7543	0.7754	0.6183	0.7262	-0.3933	0.7833
Zn	-0.7216	0.6406	0.8271	1	0.0495	0.3140	0.7332	0.7325	0.8590	-0.7169	0.8195	0.7887	0.5705	0.7681	-0.4099	0.8511
Fe	0.5662	-0.4773	-0.0936	0.0495	1	-0.3609	-0.2929	-0.4452	-0.2262	0.4829	-0.4403	-0.3247	-0.3814	-0.5243	0.1039	-0.3654
Cd	-0.4621	0.4723	0.0544	0.3140	-0.3609	1	0.1850	0.3513	0.3720	-0.1608	0.2422	0.5275	0.0146	0.4118	-0.0431	0.4072
Cu	-0.8531	0.8760	0.6234	0.7332	-0.2929	0.1850	1	0.9448	0.8438	-0.7694	0.8956	0.6102	0.7188	0.9002	-0.1423	0.8713
Ni	-0.9201	0.9541	0.5903	0.7325	-0.4452	0.3513	0.9448	1	0.9157	-0.8610	0.9458	0.6792	0.7357	0.9612	-0.3140	0.9416
Co	-0.8929	0.8929	0.7295	0.8590	-0.2262	0.3720	0.8438	0.9157	1	-0.8563	0.9047	0.8259	0.7330	0.9147	-0.3996	0.9601
Na	0.8323	-0.7794	-0.6901	-0.7169	0.4829	-0.1608	-0.7694	-0.8610	-0.8563	1	-0.9439	-0.7339	-0.8336	-0.8728	0.3742	-0.8671
Ca	-0.9159	0.8608	0.7543	0.8195	-0.4403	0.2422	0.8956	0.9458	0.9047	-0.9439	1	0.7627	0.8102	0.9614	-0.4131	0.9497
K	-0.8427	0.7279	0.7754	0.7887	-0.3247	0.5275	0.6102	0.6792	0.8259	-0.7339	0.7627	1	0.7192	0.8122	-0.2218	0.8305
Mg	-0.7252	0.7612	0.6183	0.5705	-0.3814	0.0146	0.7188	0.7357	0.7330	-0.8336	0.8102	0.7192	1	0.7611	-0.0952	0.7455
Pb	-0.9873	0.9326	0.7262	0.7681	-0.5243	0.4118	0.9002	0.9612	0.9147	-0.8728	0.9614	0.8122	0.7611	1	-0.3466	0.9725
Hg	0.3240	-0.1850	-0.3933	-0.4099	0.1039	-0.0431	-0.1423	-0.3140	-0.3996	0.3742	-0.4131	-0.2218	-0.0952	-0.3466	1	-0.3947
As	-0.9486	0.9171	0.7833	0.8511	-0.3654	0.4072	0.8713	0.9416	0.9601	-0.8671	0.9497	0.8305	0.7455	0.9725	-0.3947	1

Impact of Trace Elements on Human Health

The trace elements present in coal directly or indirectly cause air pollution. The impact of trace elements on human health can't be absolutely termed as toxic or carcinogenic, as effects of trace metal depends upon the organism, dosage and chemical form. Many trace elements are, in fact, essential for the metabolism of the man, but may be toxic if they are in excess amount required by the body. These have been classified by level of concern based on known adverse health effects or because of their abundances in coal (Hermine Nalbandian, 2012).

Major Concern: Arsenic (As), Boron (B), Cadmium (Cd), Lead (Pb), Mercury (Hg), Molybdenum (Mo) and Selenium (Se) are of major concern. Arsenic, cadmium, lead and mercury are highly toxic to most biological systems at concentrations above critical levels. Selenium is an essential element but is also toxic above certain levels. High levels of molybdenum and boron in plants are of concern. Molybdenum affects the lactation of cows and boron is phytotoxic.

Moderate Concern: Chromium (Cr), Vanadium (V), Copper (Cu), Zinc (Zn), Nickel (Ni) and Fluorine (F) are of moderate concern. These elements are potentially toxic and are present in coal combustion residues at elevated levels. Bio-accumulation is of some concern. Fluorine has an adverse effect on forage.

Minor Concern: Barium (Ba), Strontium (Sr), Sodium (Na), Manganese (Mn), Cobalt (Co), Antimony (Sb), Lithium (Li), Chlorine (Cl), Bromine (Br) and Germanium (Ge) are of minor concern. These elements are of little environmental concern. They are classified mainly on the basis that they are present in residues. The low level of Beryllium, Thallium, Silver, Tellurium have negligible impact.

The information about the concentration and distribution of trace elements in coal may assist people to use in a secured manner which has high concentration of these elements.

CONCLUSIONS

It has been found that trace elements such as Mn, Cr, Zn, Cd, Co, Ni, Cu and Pb are present in high concentrations in the coal samples. The average concentrations of these elements are much higher than the published average values for USA coal and world coal. The high concentration of trace elements in the coals may be attributed to the nature of parent plant material and the physico-chemical condition viz. climatic condition, environment of deposition, nature of associated rocks etc. Further, It has been observed that the matrix correlation coefficient with percentage of ash indicates Fe and Na in coal show positive correlation with ash, hence it can be regarded to have an inorganic association. Since, the other elements show negative correlation with ash, they are regarded to have an organic association. With extensive mining and combustion of coal, these elements disperse into the surrounding environment and contaminate the air, soil and surface as well as the ground water resources of the region. The better knowledge of coal quality parameters may help to minimize some of the health problems caused by coal use. Information on the concentration and distribution of elements in coal may help people to avoid those areas of coal deposit having high concentration of toxic elements.

Conflict of Interest

Conflict of interest none declared

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