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Determination of Some Essential and Toxic Metals in Low Grade Coal and drinking water in Chilga, Amhara region, Ethiopia

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ABSTRACT: The levels of selected essential (Ca, Fe, Zn, Mn, Cr and Cu) and potentially toxic (Cd and Pb) metals were analyzed using flame atomic absorption spectrophotometer (FAAS) from low grade coal and drinking water collected from Chilga, Ethiopia using composite sampling technique by developing an optimized digestion procedure and recovery tests. The average concentrations from the digests were found as Ca (3176.6 ± 12.3 µg/g), Fe (704 ± 3.2 µg/g), Zn (365 ± 5.8 µg/g), Mn (120.2 ± 0.6 µg/g), Cr (53 ± 0.33 µg/g), Cu(167 ± 0.1 µg/g), Pb (14.5 ± 0.12 µg/g) and Cd (0.8 ± 0.04 µg/g) in low grade coal and Ca (142.81 ± 0.05 µg/mL), Fe (9.632 ± 0.06 µg/mL), Zn (18.08 ± 0.4 µg/mL), Mn (3.21 ± 0.3 µg/mL), Cr (3.01 ± 0.02 µg/mL) and Cu(4.165 ± 0.004 µg/mL) in drinking water composite samples. While Pb and Cd were both not detected (ND) for the method used in drinking water sample located in Chilga near the coal area selected. Fe and Zn were obtained predominantly in coal and drinking water respectively.

KEYWORDS: Low grade coal, water, digestion, optimization procedure, % recovery test, toxic metals, essential metals, FAAS.

1 INTRODUCTION

The economic significance of coal is for electricity generation through underground coal gasification and coal clean technology. Energy plays an important role in the industrial and economic growth bringing prosperity to the nations [1]. Coal is a sedimentary rock containing more organics than inorganics [2]. Coal composed chiefly of rings of six carbon atoms joined together in an extremely complex composition of layered arrangement containing oxygen and nitrogen with varying amounts of sulfur and other environmental pollutants [3]. Coal contains a wide variety of metallic elements generally enriched by sequestration from ground water by humic acid compounds at the peat or sub-lignite stage of the coalification. Almost all naturally occurring elements, including major elements (C, H, O, N, S, Na, K, Ca, Mg, P, Si, Al, Fe, and Ti) and 74 trace elements, have been reported to be present in different coal types using a number of modern analytical techniques [4].

Environmental pollution has become a key focus of concern for all the nations worldwide, as not only the developing countries but developed nations as well are affected by and suffer from it. Contaminations of the environment with toxic metals are from mining discharges that are mostly coal enriched deposits eroded by runoff or artificially by man activities during mining [4, 5]. To accurately determine the total concentrations of trace metals in environmental matrices, such as urban residential particles, dust, airborne particulate matter, soils, water, and sediments is a significant challenge. This has led to the development and continuous improvement of various analytical methods for sample digestion or pre-concentration. In addition, new instrumental techniques have been developed to obtain exhaustive chemical information in a relatively short time. Determining the concentrations of essential and toxic elements allows for the study of their distributions, the pollution level, and the risks they pose to the investigated ecosystems [6].

Quantitative study of metal content can give information concerning the origin, depositional environment, organic matter content and maturation of the coal [7]. Naturally, trace metals can be resided in mineral deposits as well as in volcano areas. As the result of deposition, the trace metals can be distribute to rivers, soils of agricultural areas through anthropogenic activities [8]. The disruption of the strata of the coal below ground by mining and naturally by runoff causes metals to be oxidized and mobilized in to water and agricultural discharges near the coal strata. These contaminated water sources and agricultural irrigated lands can seep in to quality water veins and aquifers [7-9].

Leaching of elements from different substrates, including coal ash, can be influenced by different factors such as pH or complexing capability of the reagent. One of the mechanisms of heavy metal mobilization is due to changes of ionic strength, whose variations in the aquatic environment will necessarily cause ionic exchange reactions. It should be expected that the increase of ionic strength of the extractant will enhance ion-exchange processes [10].

Diverse amounts of heavy metals may be found everywhere; in soils, water, sediments and plants. Heavy metals may chemically or physically interact with the natural compound, which changes their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate. They may be bound or sorbed by particular natural substances, which may increase or decrease mobility [11]. Heavy metals even at their trace level can disrupt the metabolic function of humans by accumulating in their body, and thus disturb the functions of the vital organs and glands such as heart, brain; kidney, bone, liver etc or they dislocate vital nutritional minerals from their original place and thus hinder their biological function [12].

Metals can be determined nicely by a variety of methods, with the choice often depending on the precision and sensitivity required flame atomic absorption spectrometer (FAAS) [13], hydride (HGAAS) or electro thermal atomization (ETAAS) [14], graphite furnace atomic absorption (GFAA) [15, 16], inductively coupled argon plasma optical emission spectrometry (ICP-OES) [17] and inductively coupled atomic emission spectrometry (ICP-AES) [18,19] are most commonly used for the determination of metals in water and coal materials because of their inherent selectivity, sensitivity, precision and accuracy.

Many techniques employed for elemental analysis require the conversion of the sample matrix into a solution form. The selection of an appropriate treatment for sample dissolution depends on the nature of the sample and different approaches are required for predominantly inorganic and organic matrices. Geological, geochemical, and soil samples generally contain silicate, metal oxides, carbonates, and, in many cases, organic matter. Such samples must be dried and ground to a fine powder to facilitate dissolution [20]. Frequently, the sample is not soluble in water and must be treated with acids or mixtures of acids to facilitate solubilization. The type of acid treatment must be given careful consideration, since particular acids may or may not oxidize the sample, and may be incompatible with certain elements.

Microwave assisted sample decomposition with HNO_3 or its mixtures with HCl or H_2SO_4 (with or without added H_2O_2) is these days predominantly used for fast and efficient decomposition of a variety of inorganic and organic materials [20, 21]. Today, Ultrasound (US) assisted sample decomposition procedures are considered as alternatives for solid sample pre-treatments. They were found to be superior in facilitating and accelerating such sample preparation steps as dissolution, fusion and leaching [21].

Ethiopia, has a low grade coal (lignite) deposits that are recently studied their heating value to generate electric power. In this particular area of study in Chilga, this low grade coal is sometimes used for home kitchen supplements by the rural residents. Furthermore, the geographical location of the coal area is highly exposed to water runoff. The naturally occurring metals bound in the coal structure may migrate toward the soil agricultural fields and drinking water through leaching behaviours of the metals due to man activities. Trace and toxic metals have a bioaccumulation and biomagnifications behaviour in which they incorporate into our food chain system. Assessment on these selected metals is then an important role to know the concentration levels which may pose toxic effect to human being beyond their dosage.

The literature survey revealed that there is no report on the levels of metals in low grade coal located in Chilga, Ethiopia. Thus, this paper includes (i) development a feasible working procedure coal and drinking water sample (ii) development of an optimized procedure for digestion of coal and drinking water sample to determine some selected metals by FAAS (iii) determination of levels of essential metals (Ca, Fe, Zn, Mn, Cr & Cu) and toxic (Pb and Cd) in the samples from coal and drinking water (iv) comparison of the level of concentration of metals determined for coal and drinking water in the study area and (v) to compare the levels of the selected metals in Chilga low grade coal and drinking water samples taken with the levels of metals analyzed from the other part of the world in literatures.

2 EXPERIMENTAL

2.1 DESCRIPTION OF THE STUDY AREA

Collection of coal, soil, cow's milk and drinking water samples were from Chilga, Gondar. Chilga is located 52 kms southwest of Gondar and the basin is found between 1900 and 2100 m above sea level, 12 boreholes were drilled in the central part of the basin. The reason for selection of this place from other sites of coal deposits was based on the availability of the sample needed and societal problems with unknown non-point source pollution but that might be related to unbalanced nutrient composition of the coal deposits that may enter to the food chain. The Chilga basin is situated $12^0$25'N and $37^0$03' - $37^0$11'E latitude and longitude respectively as it is mapped in Fig 1.

2.2 APPARATUS AND INSTRUMENT

A polyethylene (PE) plastic bags and bottles, open beakers, sieves (0.125 mm diameter size), volumetric flask, whatmann No.542 (90mm) filter paper, mortar and pestle, drying oven (DIGITHEAT, J. P. SELECTA, S. Spain), A refrigerator (Hitachi, Tokyo, Japan) were used in the site and laboratory. A 250 mL necked round bottom flasks fitted with reflux condenser on digestion block (Gerhardt apparatus) and micropipettes (20-100 µL and 100-1000 µL), Digital analytical balance (Mettler Toledo, Model AG 204, Switzerland) with a precision of ± 0.0001 g and BUCK SCIENTIFIC MODEL 210 VGP (East Norwalk USA) AAS equipped with deuterium background corrector using air- acetylene flame, were used for analysis of the metals.

2.3 CHEMICALS AND REAGENTS

Analytical reagent grade chemicals, reagents, distilled and de-ionized water were used throughout the study. All glassware and plastic containers used were washed with detergent solution followed by soaking in 0.5 M HNO_3 and then rinsed with de-ionized water. HNO_3 (69-72%, Spectrosol, BDH, England) and $HClO_4$ (70% Reagent, Qialikems Pvt. Ltd. New Delhi) were used to digest the matrix samples. Calibration standard solutions of each metal (Ca, Mn, Fe, Cu, Zn, Cr, Cd and Pb) were prepared from stock solutions by appropriate dilution of 2% HNO_3 prepared with de-ionized water to plot the calibration curves for their respective metals.

2.4 SAMPLE COLLECTION AND HANDLING

A total of six coal samples were collected and stored in PE plastic bags from site selected of the coal area. The coal samples collected were allowed to be air dried and prevented from direct sun light exposure for two weeks. A 200g from each crushed and ground of the six coal samples was homogenized and kept in oven at room temperature prior to analysis of levels of metals.

Drinking water samples were collected with 0.5M HNO_3 acid sterilized 500 mL PE plastic bottle sampling containers from around the coal area. A total of eight PE plastic bottle water samples were collected from the available drinking water supplies. The sampling bottles were pre-soaked overnight with 0.5 M HNO_3, rinsed with de-ionized water and rinsed using water sample itself before samples were collected. Equal volume of water sample from each was taken and homogenized to be used as a composite sample. Preservation of water samples was done by adding two drops of conc. HNO_3 to each water sample before storage below 4°C.

2.5 OPTIMIZATION OF WORKING PROCEDURES

Before applying the digestion procedure for the analysis of samples, digestion time, reagent volume ratio and temperature were optimized by varying one parameter at a time for the digestion of low grade coal and drinking water. Thus, for the complete digestion of 0.5 g of homogenized coal composite sample 8 mL conc.HNO_3 and 2 mL conc. $HClO_4$ for a total of 2.5 hrs at 250^{o}C was selected as optimized procedure while for 200 mL drinking water composite sample, 3 mL HNO_3 and 2 mL conc. $HClO_4$ for 1.5 hrs at 250^{o}C. The final solution of the digest obtained was a clear colorless with no suspended and residue within the solution which was transferred to a 50mL volumetric flask and diluted with de-ionized water to its mark.

Digestion of a reagent blank was also performed in parallel with the samples keeping all digestion parameters the same for each type of sample. For the analysis of reagent blank, nine samples were prepared and the digested samples were stored in refrigerator until analysis using FAAS.

2.6 INSTRUMENT CALIBRATION AND METHOD DETECTION LIMIT

The standard deviation of the nine reagent blanks was calculated. The detection limits were obtained by multiplying the standard deviation of the reagent blank by three. The wavelengths at which analysis was done, the correlation coefficients of the calibration curve for each of the metals and method detection limits of each metal are given in Table 1 & 2. The results clearly show that the calibration curves with good correlation coefficients and lower method detection limits were obtained during the analysis.

2.6.1 PRECISION

The precision of the results of this analysis is reported with corresponding standard deviation of nine measurements for a bulk sample of triplicate reading per sample and percent relative standard deviation.

2.6.2 RECOVERY TEST

The method validation was checked by spiking experiments of only one sample which costs small time, temperature and smaller reagent volume of the acid during digestion. The spiked samples were prepared by adding a small known amount of metal standard solutions depending on the concentration of the unspiked sample obtained. Because of high concentration standard solution that is to spiked may have a problem during digestion, 30-70% of the concentration of the un-spiked sample and the cumulative volume of the known standard solutions added were less than 1 mL. The spiked and non-spiked samples were digested and analyzed in similar conditions.

3 RESULT AND DISCUSSION

3.1 RECOVERY TEST

The efficiency of the optimized procedure was checked by adding known concentration of each metal to a 200 mL water sample. The results of percentage recoveries for the studied metals were lie within the acceptable range (100±10) in water sample except for chromium as shown in Table 3. The lower recovery of chromium was found to be due to the strong matrix-analyte interaction. This indicates that contamination was not a trouble during the digestion procedure and the recovery results were in good agreement with the expected values. Therefore the recovery test and precision of the method were found satisfactory to validate the experimental practice. Recovery test for Pb and Cd have not carried out because these metals were not detected (ND).

3.2 LEVELS OF METALS IN COAL AND DRINKING WATER SAMPLES

The accuracy and precision of the method were tested by spiking the samples with a standard solution of the analyte metals. Thus, in the present work, the concentration of eight selected essential (Ca, Fe, Zn, Mn, Cr & Cu) and toxic (Cd & Pb) metals in the digested coal and drinking water samples were analyzed by FAAS. The result indicates that the concentrations of metals determined are found in agreement within the acceptable range (100 ± 10%) for all metals except Cr. Among the analyzed metals Cd and Pb were lie below the MDL in water except in coal and soil samples but the rest metals shown with their respective percent relative standard deviation (% RSD) in Table 4.

3.3 DISTRIBUTION PATTERN OF METALS IN DIFFERENT SAMPLES

The levels of the metals show considerable variation among different samples between the same metals. Mineral levels of coal is depend on the pH, cation exchanging capacity, ion strength, organic matter content and the age or rank of the coal itself as it can be shown from Table 4 and Fig. 2a.

The composite sample of coal contains high levels of Ca (3164.3 – 3188.9 µg/g) due to the fact that Ca is one of the macronutrients available for plants, animals and human being as well for their health in large amounts. The other probable reason for higher level of Ca is due to coal is formed by degradation of plants in swamp areas and the earth's layers and rocks at various depths are primarily composed of lime and phosphate rocks.

Fe (700.8 – 707.2 µg/g) was the most predominant trace metal followed by Zn (359.2-370.8µg/g), Mn (119.6-120.8 µg/g), Cu (166.9 – 167.1µg/g),Cr (52.66 – 53.33µg/g) and the toxic metals, Pb (14.62 – 14.38µg/g) and Cd (0.76 – 0.84µg/g). The considerable high concentration of Mn is also coal pH dependence has its own effect on Mn availability on the composition of the coal.

The water sample collected from eight drinking water supply of the residents around the coal sampling site were found some detectable metal contents of Ca, Fe, Zn, Mn, Cr and Cu and the toxic metals Pb and Cd were below MDLs of the method used in the water composite sample. Fig. 2b showed that high amount of Ca when it is compared to the trace elements as it is expected and from the trace metals Mn is the predominant followed by Fe and Cu.

The composition of water varies widely with local geological conditions. Neither ground water nor surface water has ever been chemically pure water, since water contains small amounts of minerals of natural origin. The total concentrations of substances dissolved in fresh water considered to be of good quality can be hundreds of mg/L [22]. The extreme levels of Ca obtained are due to hardness arising from neighboring limestone deposit that is sticked along in the soil layers as well as in the coal deposit.

3.4 COMPARISON OF LEVEL OF METALS BETWEEN DRINKING WATER AND COAL SAMPLES

Surface drinking water supplies are influenced by higher level of trace metal levels containing in coal or in soil through natural leaching. Generally there is a direct relation in the levels of metals in drinking water and coal. Zn contains 365µg/g and 18.08µg/mL in analysis of coal and water samples respectively. These indicate that, large levels of metals in coal, makes higher the levels of metal in water. Coal pH has also a critical reason for the degree of mobilization of trace metals from their sources.

3.5 COMPARISON OF AVERAGE METAL LEVELS OF THIS STUDY WITH OTHER LITERATURES AND GUIDELINES

As listed and compiled in Table 5, average levels of coal composite samples of this study (ETH) is compared with other reports from five coal deposits of South Africa (SA), United states geological survey (USGS), Nigeria coal (Nig), West Virginia Geological and Environmental Survey (WVGES), Australian thermal exports coal (AU), and average range of global value (Ave.R.G) is depicted in Fig.3. The average levels of metals determined in Chilga, Ethiopia is found to be in the lower boundaries of the average global ranges except for Australian thermal export coals and some of the Nigerian coal. The abundance of these metals with their high concentration indicates that those coal samples are coupled with their coal beds could be a good sources of these metals [23, 24].

Except Pb and Cd that were not detected, the other trace metals found to be exceeded from their drinking water guidelines. This is due to solubility and leaching behaviors of metals from their active deposits. This solubility and distribution of metals mainly depend on redox potential, cation exchange capacity and pH of the background component from which it is leached [25, 26].

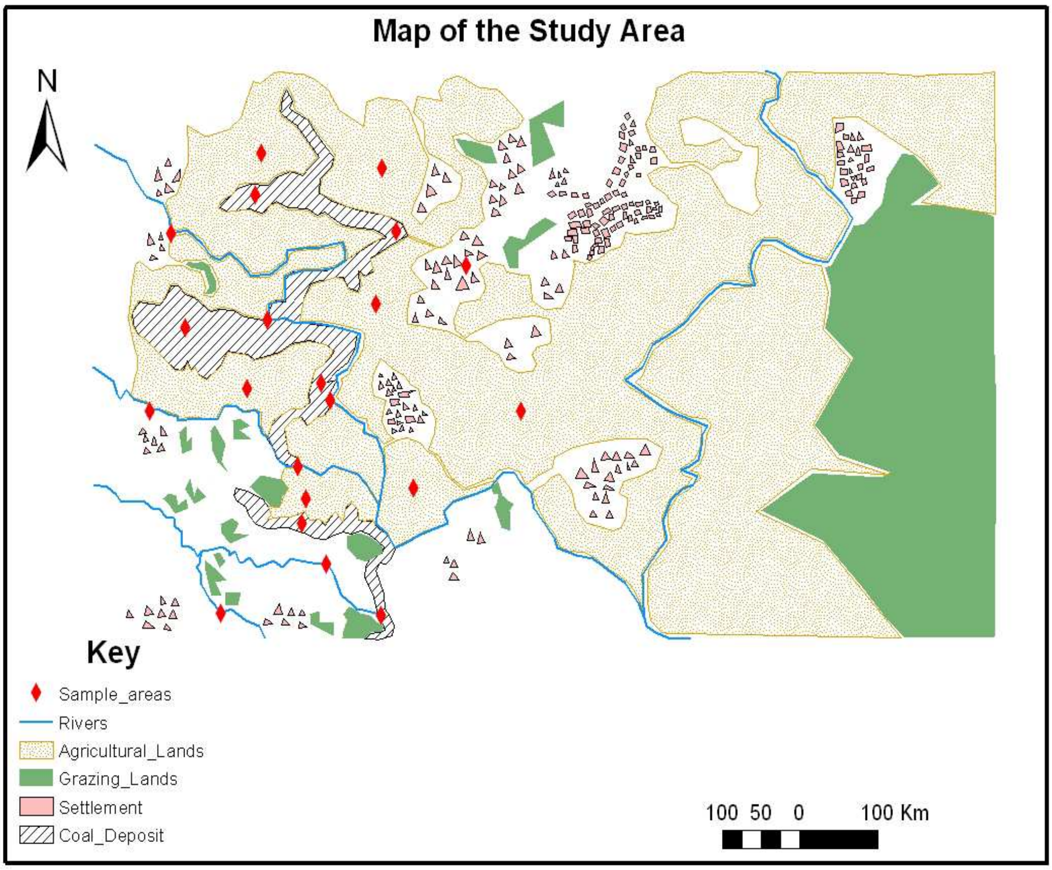

Fig. 1. Map of the study area

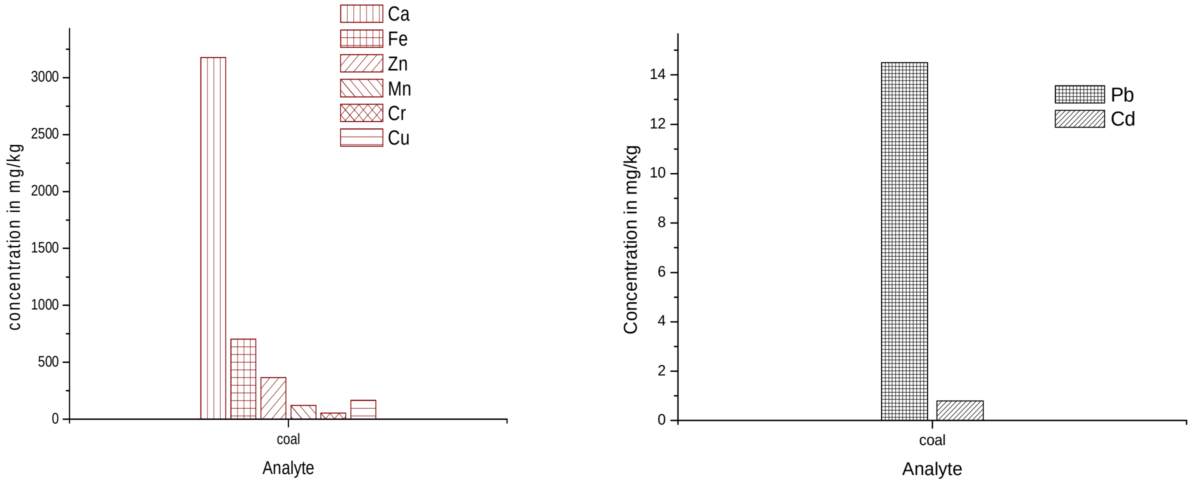

Figure 2a Comparison of levels between Ca, Fe, Zn, Mn, Cr, Cu, Pb and Cd in low grade coal composite sample

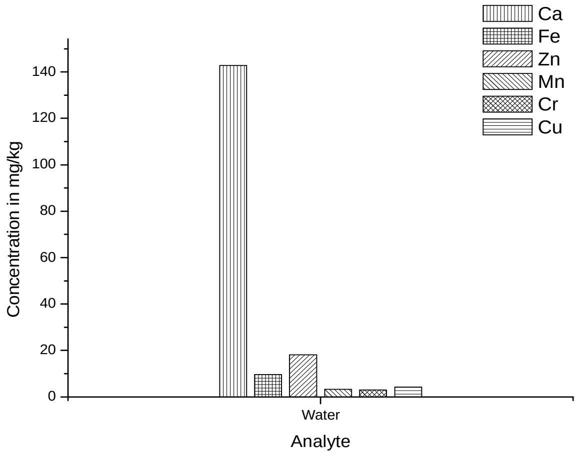

Figure 2b Comparison of levels between Ca, Fe, Zn, Mn, Cr, Cu, Pb and Cd in water sample

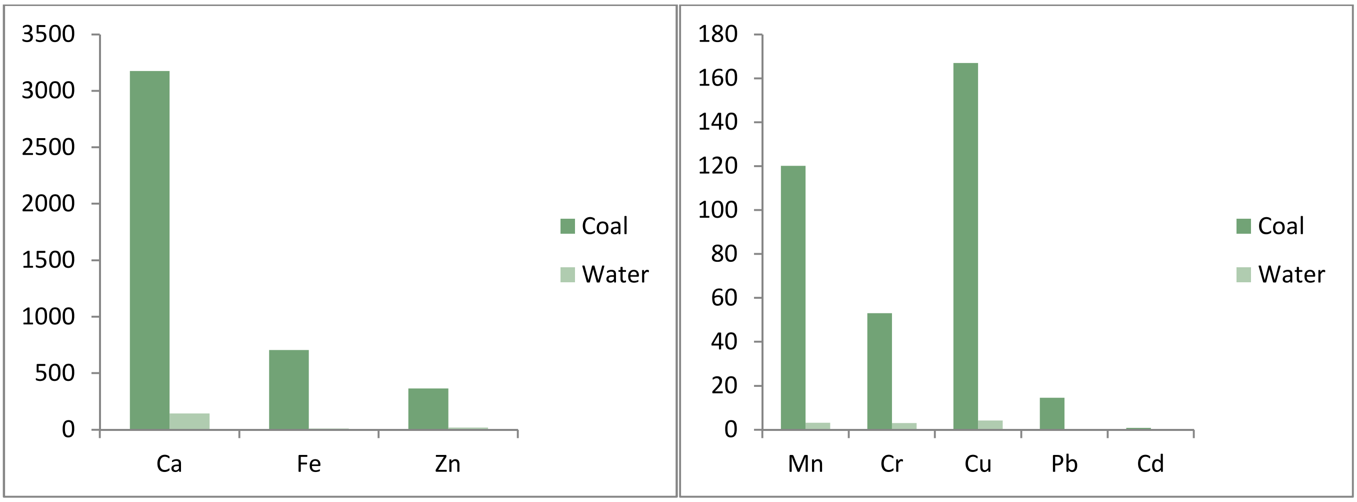

Figure 3 Comparison of average levels of essential and toxic metals in coal and drinking water samples.

Table 1. Concentration of working standard solutions for FAAS instrument calibration and correlation coefficient of calibration curves

Element	Wavelength(nm)	Concentrations of working standard solutions in (mg/L)	Correlation coefficients (R^2)
Ca	422.7	1.0, 2.0, 4.0, 8.0	0.9990
Zn	248.3	0.5, 1.0, 2.0, 4.0	0.9965
Cu	213.9	0.2, 0.4, 0.8, 1.6	0.9996
Fe	279.5	0.5, 2.0, 4.0, 8.0	0.9969
Cr	357.9	1.0, 2.0, 4.0, 8.0	0.9968
Mn	324.8	0.2, 0.4, 0.8, 1.6	0.9996
Pb	283.3	0.2, 0.4, 0.6, 0.8	0.9989
Cd	228.9	0.02, 0.04, 0.08, 0.16	0.9983

Table 2. Method detection limits for coal, soil, water and milk samples

Metal	Instrumental detection limit (IDL) in (ppm)	MDL of coal in (ppm)	MDL water in (ppm)
Ca	0.0100	4.0950	4.9890
Fe	0.0300	0.3520	0.1400
Zn	0.0050	1.7540	1.7690
Mn	0.0100	0.0230	0.0195
Cr	0.0500	0.5240	0.4710
Cu	0.0500	0.0970	0.0620
Pb	0.1000	0.1910	0.1180
Cd	0.0050	0.0076	0.0076

Table 3. Recovery tests for the optimized procedure of water sample

Metal	Conc. in unspiked sample(mg/L)	Amount added(mg/L)	Conc. in spiked sample(mg/L)	% Recovery
Ca	35.703 ± 0.0123	10.711	45.758 ± 0.017	93.88 ± 1.38
Fe	2.408 ± 0.014	1.445	3.826 ± 0.009	98.13 ± 4.62
Zn	4.520 ± 0.096	2.26	6.869 ± 0.012	103.93 ± 0.97
Mn	0.802 ± 0.0074	0.4812	1.312 ± 0.0034	105.91 ± 0.7
Cr	0.752 ± 0.005	0.4514	1.106 ± 0.002	78.25 ± 7.86
Cu	1.041 ± 0.001	0.729	1.726 ± 0.001	93.90 ± 0.2
Pb	ND	-	-	-
Cd	ND	-	-	-

Table 4. Average concentration (mean ± SD, N = 9, µg/g dry weight basis for coal and µg/mL for samples taken as liquids) and % RSD of essential and toxic metals in the specified samples

Metal	Average conc. ± standard deviation		% of relative standard deviation	
	Coal	Water	Coal	Water
Ca	3176.60 ± 12.30	142.81 ± 0.05	3.24	2.91
Fe	704.00 ± 3.20	9.63 ± 0.06	8.68	10.14
Zn	365.00 ± 5.80	18.08 ± 0.40	7.19	10.03
Mn	120.20 ± 0.60	3.21 ± 0.30	2.21	4.07
Cr	53.00 ± 0.33	3.01 ± 0.02	15.79	18.75
Cu	167.00 ± 0.10	4.17 ± 0.004	1.92	0.46
Pb	14.50 ± 0.12	ND	14.26	-
Cd	0.80 ±0.04	ND	10.45	-

Table 5. Comparison of average metals concentrations of this study in coals with the global range (in mg/L) unless specified.

Metals	**ETH[a] (µg/g)**	**SA(2005) [b]**	**Nig(µg/g)**	**USGS(2004)[c]**	**WVGES(2002)**	**AU(µg/g)[d]**	**Ave. R.G [e]**	
							1990	2004
Cd	365±5.80	0.05 - 0.51	-	0.47	0.1	0.067	0.1-3	0.6
Zn	53±0.33	23 - 69	0-13.53	15.0	17.85	15.9	0.5-60	10
Cu	167±0.10	9 - 16	60.33-83.51	16.0	20.4	9.8	0.5-50	15
Pb	14.5±0.12	4.2 - 11	-	11.0	8.19	6.8	2.80	25
Mn	120.2±0.60	84 - 117	12.11-206.7	0.11	21.29	51.4	5-300	50
Cr	0.8±0.04	8-19	28.2-65.43	53.0	14.97	12	5-300	50

Table 6. Recommended metal levels for drinking water quality criteria from different organizations and countries (in ppm)

Metals	WHO	EU	Canada	USA	South Africa	this study
Fe	0.3	NG	NG	NG	NG	9.63±0.06
Zn	3.0	0.1- 5.0	5.0	5.0	0 – 3.0	18.08±0.4
Mn	0.4	0.05	0.05	0.05	0 – 0.05	3.21±0.3
Cr	0.05	0.05	0.05	0.1	0 – 0.05	3.01±0.02
Cu	2	0.1 – 3.0	1	1	0 – 1.0	4.165±0.004
Cd	0.003	0.005	0.005	0.005	0 - 0.005	ND
Pb	0.01	0.05	0.05	0.015	0 – 0.02	ND

4 CONCLUSION

Coal contains appropriate amount of metals (essential and non- essential) but Pb and Cd were not identified in water because they are below the method detection limit of the validated method used. Only calcium is selected from the major metals which was present in larger concentration. The levels of trace metals analyzed have showed an elevated increase except Pb and Cd as they compared to the quality baseline concentration in water. There was also a difference on the levels of average concentration of coal as compared to literatures of other countries. The trace metals identified here were almost in lesser levels when compared to the literatures given in the industrialized western countries but greater than the ranges of quality guideline criteria.

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