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Assessment of the Environmental Impact of Fly Ash on the Concentration of Heavy Metals around Cement Company of Northern Nigeria

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Abstract

This study assessed the impact of Coal Fly Ash on the concentration of Heavy metals in water, soil, and vegetables (moringa and spinach) in the environment of Cement Company of Northern Nigeria. The samples collected were digested, and analysed for heavy metals concentration using Atomic Absorption Spectroscopy. The concentrations of heavy metals obtained in water samples were higher than the WHO/SON permissible limit, except for Cu and Zn which are below the standard limits. The average concentration of Pb, Mn, Cd, and Ni in all plant samples was higher than the permissible limit, except Cd in spinach sample. The roots of the spinach accumulate higher concentrations of heavy metals than the leaves and stem, while leaves of moringa accumulate higher than the roots and stem. The concentration of heavy metals in soil sample was below the WHO limit. Comparatively the plants samples have the highest concentrations of heavy metals than the water and soil samples. The coal fly ash from the Cement Company must have contributed to the significant concentration of Heavy metals in the environment making the water and plants from the study area unfit for human and animal consumption.

Keywords: Fly ash, heavy metals, vegetable, soil, plant

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Introduction

Heavy metals pollution is a menace to our environment as they are foremost contaminating agents of our food supply, especially vegetables. Vegetables get contaminated by absorbing heavy metals from polluted air, soil, and water [1]. Heavy metals pollution in soil and water adversely affect the public health, agricultural production, and environmental health and hence a cause for concern [1]. The soil pollution mostly results from the disposal of industrial and urban wastes as well as usage of agrochemicals, whereas water pollution could be trigger by industrial wastes, sewage disposal, petroleum contamination, and agricultural drainage water [1]. Some areas of the developing countries are prone to air pollution because heavy metals containing aerosols are always deposited on soil surface and get absorbed by vegetables and other plant leaves. Factors like application of agrochemicals, solubility of heavy metals, soil pH, soil type, and plant species affect the uptake of heavy metals by the plants from the soil [1]. Leafy vegetables accrue higher amounts of heavy metals in roots and leaves than stems and fruits. The heavy metals at exceedingly higher concentrations than the required physiological demand of vegetables can cause lethal effect in them as well as human health through food chain [1].

Vegetables make up the most important daily diets in many of the households worldwide. However, the consumption of leafy vegetables is reported to increase in the urban community, various researches revealed heavy metals like Cu, Zn, Fe, Pb, Cd, Mn, Hg, and Cr to be significant contaminants of vegetables in urban agriculture. Heavy metals like Cu, Zn, and Fe play a significant role in plant physiology but heavy metals such as Pb, Cd, Cr, and Hg are exceptionally toxic and dangerous environmental pollutants and the consumption of vegetables is the main route of heavy metal toxicity to humans [1]. In small quantities, certain metals such as Fe, Cu, Mn, Cr, Co and Zn are nutritionally essential for a healthy life [2] but the ingestion of heavy metal contaminated vegetables may lead to various long-term lingering diseases; for instance, continuous exposure of above certain concentration.

Fly ash or flue ash, also known as pulverised fuel ash in the United Kingdom, is a coal combustion product that is composed of the particulates (fine particles of burned fuel) that are driven out of coal-fired boilers together with the flue gases. Depending upon the source and composition of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) and calcium oxide (CaO), the main mineral compounds in coal-bearing rock strata. The minor constituents of fly ash may include one or more of the following elements or compounds found in trace concentrations (up to hundreds ppm): arsenic, beryllium, boron, cadmium, chromium, hexavalent chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium, along with very small concentrations of dioxins and PAH compounds also has unburnt carbon [3-5].

Coal ash contains many toxic substances that can negatively impact the human body. Employees working in coal-fired power plants or near coal ash waste sites are at major risk of inhaling coal ash dust [6]. Coal ash dust is generally known as particulate matter (particle pollution) and the dust particles can harm the lungs when inhaled [4]. Workers increase their risk of harmful side effects when they inhale the smallest coal ash dust particles [6]. The smaller the coal ash dust particle, the deeper the particle will be inhaled into the lungs [6]. As a result, the toxic particles can inflame the lungs causing severe damage to the body [6]. Furthermore, coal ash dust can enter the body through the nose causing damage to the brain directly [6]. However, regardless of particle entry, the toxicity from coal ash can cause harm to major body parts such as the brain, lungs, heart, liver, kidneys, stomach and intestines [5, 6]. Thus, individuals working near coal ash surface impoundments or landfills are at increased risk for many serious health problems.

The effect of fly ash on the environment can vary based on the thermal power plant from which it is produced, as well as the proportion of fly ash to bottom ash in the waste product [7]. This might also be due to the composition of the coal which is based on the geology of the area the coal is found and its burning process in the power plant. When the coal is combusted, it creates an alkaline dust. This alkaline dust can have a pH ranging from 8 to as high as 12 [8]. Fly ash dust deposited on topsoil increase the pH and affects the plants and animals in the surrounding ecosystem [7]. Trace elements, such as, iron, manganese, zinc, copper, lead, nickel, chromium, cobalt, arsenic, cadmium, and mercury, can be found in Fly ash at higher concentrations compared to bottom ash and the parent coal [7]. Fly ash usually leaches toxic constituents that can be greater than the federal standard for drinking water [7]. It contaminate surface water through erosion, surface runoff, airborne particles landing on the water surface, contaminated ground water moving into surface waters, flooding drainage, or discharge from a coal ash pond [7]. Fish can absorb the toxins from Fly ash through their gills [7]. The sediment in the water can also become contaminated which in turn contaminate the food sources for the fish and all other organisms that consume these fish, such as, birds, bear, and even human beings [7, 9]. Once exposed to fly ash contaminating the water, aquatic organisms have had increased levels of calcium, zinc, bromine, gold, cerium, chromium, selenium, cadmium, and mercury [10]. Soils contaminated by fly ash showed an increase in bulk density and water capacity, but a decrease in hydraulic conductivity and cohesiveness [10]. The aim of this study was to determine the concentration of trace heavy metals from coal fly ash on soil, water, and plant. The significance of this study is to identify the risk and effect of coal fly ash on water, soil, and plant responses by assessing the level of trace heavy metals which are highly toxic to human, animal, and plants. The results of such a study can be a basis to identify the risk and provide recommendations that could help in controlling and minimizing present and future contaminations of the environment.

Material and Methods

Sample collection

All the samples were collected from Gansari Village where Cement Company of Northern Nigeria located in Wamakko Local Government, Sokoto State. Surface water samples were collected from four different portion of Gansari River using rinsed and dried polyethylene bottle sand combined to form a composite labelled A. Soil samples were collected from North, South, East, and West of Gansari Farming area at 15 cm depth using clean polyethylene bags and combined to form one composite sample labelled B. Root, Stem, and Leaves of Moringa (*Moringa oleifera*), and Spinach (*Spinacia oleracea*) plants were collected from Gansari Farm and labelled C and D, respectively. Atomic Absorption Spectroscopy was used to determine the heavy metals concentration and data were analyzed using SPSS/10.0 with the results expressed as mean ± SD of five determinations. Statistical evaluations were done using One-way Analysis of Variance (ANOVA) and values were regarded as statistically significant at $p < 0.05$.

Study area

Sokoto State is located in the extreme Northwest of Nigeria, near to the confluence of the Sokoto River and the Rima River which has an estimated population of more than 4.2 million. Gansari village is in Wamakko LG of Sokoto state, the host of the Cement Company of Northern Nigeria located at approximately 20 – 30 meters from the village (Fig. 1 and Plate 1).

Figure 1: Map of Sokoto State showing Cement Company of Northern Nigeria and Gansari Village

Plate 1: Sample location

Samples preparation

All the collected samples were processed and digested in the Laboratory using HCl-HNO_3 mixtures. 50 ml of water sample was measured into the conical flask, 10 ml of Nitric acid (HNO_3) was added and the solution was heated at 95°C to a reduced volume reduced volume and cooled, and then filtered using filter paper. The filtrate was made up with distilled water to 50 ml and stored for further analysis (Plate 2).

A 2 g of soil sample was weighed into the conical flask to which 10 ml of Nitric acid (HNO_3) and 2 ml of hydrochloric acid (HCl) was added and the mixture was heated at 95°C to a reduced volume and cooled, and then filtered using filter paper. The filtrate was made up with distilled water to 50 ml and stored for further analysis.

Plate 2: Prepared samples ready for analysis

The vegetable samples (spinach and lettuce) were thoroughly rinsed under running tap water and then with distilled water to eliminate dusts, pesticides, fertilizers, mud and any airborne pollutant that may be present. The roots, stem, and leaves of the plant samples were cut into pieces separately and 2 g of each plant samples (*Moringa oleifera* and *Spinacia oleracea*) was mixed with 10 ml of Nitric acid (HNO_3)and heated at 95°C to a reduced volume and cooled, and then filtered using filter paper. The filtrate was made up with distilled water to 50 ml and stored for further analysis (Plate 2).

Sample analysis

All the digested samples were analysed using Atomic Absorption Spectroscopy (Model: AA6300, Shimadzu Product) in the Energy Research of Usmanu Danfodio University Sokoto. The analyses were done in triplicate.Total of nine (9) heavy metals were determined in Water Samples; Pb, Cr, Mn, Fe, Se, Cd, Zn, Ni, and Cu. Total of six (6) heavy metals were determined in the Soil and Plants Samples; Pb, Cr, Mn, Cd, Ni, and Cu.

Data were analyzed using SPSS/10.0 with the results expressed as mean ± SD of five determinations. Statistical evaluations were done using One-way Analysis of Variance (ANOVA) and values were regarded as statistically significant at $p < 0.05$.

Results and Discussion

The Concentrations of heavy metals in Gansari water sample compared with the World Health Organisation (WHO) and Standards Organisation of Nigeria (SON) standards were presented in Table 1.

Table 2 indicates the actual concentrations of heavy metals in Gansari soil sample compared with the World Health Organisation (WHO) standards.

Table 1: Concentration of heavy metals in Gansari water sample in mg/l

Parameter	Pb	Cr	Mn	Fe	Se	Cd	Zn	Ni	Cu
Water	0.155±0.045	0.063±0.011	0.176±0.013	1.921±0.068	102.571±1.173	0.063±0.011	0.134±0.012	0.103±0.038	0.235±0.042
Average	0.1	0.04	0.09	0.99	51.87	0.04	0.07	0.07	0.14
WHO	0.01	0.05	0.4l	0.30	0.04l	0.003l	0.3	0.02	0.5l
SON	0.01l	0.0l	0.05	0.30l	---	0.003l	3l	0.02	1.0l

Source: WHO/SON Standards [11]

Table 2: Concentrations of heavy metals in Gansari Soil Sample in mg/kg

Parameter	Pb	Cr	Mn	Cd	Ni	Cu
Soil	0.146± 0.062	0.030± 0.013	0.119± 0.059	0.014 ±0	0.156± 0.055	0.170± 0.036
Average	0.12	0.04	0.09	0.01	0.11	0.10
WHO	85	100	850	0.8	35	36

Source: WHO Standards [12]

The Concentrations of heavy metals in Spinach (*Spinacia oleracea*) compared with the World Health Organisation (WHO) and Food and Agriculture Organisation (FAO) standards are given in Table 3.

Table 4 showed the Concentrations of heavy metals in Moringa (*Moringa oleifera*) compared with the World Health Organisation (WHO) and Food and Agriculture Organisation (FAO) standards.

Table 3: Concentrations of heavy metals in Spinach in mg/kg

Parameter	Pb	Cr	Mn	Cd	Ni	Cu
Leaves	0.204± 0.020	0.351± 0.036	0.353± 0.017	0.015± 0.009	0.153± 0.06	0.138± 0.027
Stem	0.141± 0.018	0.016± 0.002	0.224± 0.027	0.014± 0.002	0.128 ±0	0.138± 0.023
Roots	0.134± 0.117	0.467± 0.006	0.365± 0.054	0.265± 0.42	0.058± 0.005	0.174± 0.027
Average	0.32	0.4	0.5	0.4	0.3	0.3
WHO/FAO	0.3	2.3	0.2	0.2	0.1	0.8

Source: WHO/FAO Standards [12]

Table 4: Concentrations of heavy metals in Moringa (*Moringa oleifera*) in mg/kg

Parameter	Pb	Cr	Mn	Cd	Ni	Cu
Roots	0.162± 0.031	0.400± 0.090	0.326± 0.044	0.015± 0.005	0.092± 0.016	0.089± 0.013
Stem	0.166± 0.017	0.027± 0.023	0.211± 0.022	0.011± 0.002	0.045± 0.044	0.074± 0.001
Leaves	0.168±0	0.310± 0.019	0.327± 0.046	0.155± 0.068	0.343± 0.005	0.132± 0.015
Average	0.4	0.4	0.5	0.1	0.2	0.2
WHO/FAO	0.3	2.3	0.2	0.2	0.1	0.8

Source: WHO/FAO Standards [12]

Table 5: Average concentrations of heavy metals in the three parts of plants samples

Samples/HM (mg/kg)	Pb	Cr	Mn	Cd	Ni	Cu
Spinach roots	0.13	0.23	0.21	0.34	0.03	0.10
Moringa roots	0.09	0.25	0.18	0.01	0.05	1.0
Spinach leaves	0.11	0.19	0.18	0.01	0.11	0.08
Moringa leaves	0.16	0.16	0.18	0.11	0.17	0.07
Spinach stem	0.13	0.01	0.13	0.01	0.13	0.08
Moringa stem	0.09	0.03	0.12	0.01	0.04	0.04
WHO/FAO	0.3	2.3	0.2	0.2	0.1	0.8

The average concentrations of heavy metals in the three parts of plants samples to determine which part of the plants accumulates higher concentration of heavy metals, and also compared with the WHO/FAO standards are shown in Table 5.

Table 6 indicated the comparison of the total concentrations of heavy metals in all the four (4) samples (water, soil, spinach, and moringa) in other to determine which of the samples has the highest and lowest concentrations of heavy metals.

Table 6: Comparison of heavy metals concentrations in water, soil, and plant samples

Parameter	Pb	Cr	Mn	Fe	Se	Cd	Zn	Ni	Cu
Water samples	0.1	0.04	0.09	0.99	51.87	0.04	0.07	0.07	0.14
Soil samples	0.12	0.04	0.09	-	-	0.01	-	0.11	0.10
Spinach (*S. oleracea*)	0.32	0.4	0.5	-	-	0.4	-	0.3	0.3
Moringa (*M. oleifera*)	0.4	0.4	0.5	-	-	0.1	-	0.2	0.2

Heavy metal levels in water

Lead

From Table 1 the average concentration of lead in water sample is 0.1 mg/l which is above the WHO/SON permissible limit of 0.01 mg/l. Lead is a dangerous element, it is harmful even in small amount and enters into human body in many ways [13]. High concentration of lead can cause death or permanent damage to the central nervous system, brain, and kidneys [14]. In the similar study conducted by Kacholi and Sahu, concentration of lead in water samples was also found to be above the WHO/SON permissible limit of 0.01 mg/l [1]. According to Chanchal *et al.* [15], the lead concentration of the water samples obtained from Kagini, Damangaza, Pigbakasa, Durumi and Apo villages ranged between 0.03 and 0.31 mg/L. Which were found to have exceeded the standard limits of 0.015 set by WHO, EPA and NSDWQ. The possible sources of heavy metals like Pb could be road runoff and atmospheric deposition [16, 17]. The Fly ash from the cement company of northern Nigeria would have been a major contributor to the concentration of Pb in the water obtained from Gansari River.

Selenium

The average concentration of selenium in water sample obtained from the river is 51.87 mg/l which is much higher than the WHO standard limit of 0.04 mg/l. This may be due to the dissolved fly ash in the water. Potential health effects of water contaminated selenium are hair and fingernails changes, damage to the peripheral nervous system, fatigue and irritability [9].

Copper

The average concentration of copper in water sample is 0.14 mg/l and is lower than the WHO (0.5 mg/l) and SON (1.0 mg/l) standard limits, similar result was obtained from a study conducted by [1] where the concentration of copper (0.1 mg/l) in water sample was found to be below the standard limit.

Chromium

The average concentration of chromium in water sample is 0.04 mg/l which is below the WHO/SON standard limit of 0.05 mg/l, this may be due to the effect of coal fly ash from the cement company behind the sampling site. In as similar study carried out by Jibrin [18], the chromium concentration of the water samples obtained from the five villages within FCT were mostly above the standard limit of 0.05 set by WHO, EPA and NSDWQ Excess amount of chromium in water can cause kidney and liver damage and can damage circulatory and nerve tissue [14].

Manganese

The average concentration of manganese in water sample is 0.09 mg/l which is greater than the SON (0.05 mg/l) standard limits but lower than the WHO (0.4 mg/l). Higher concentration of manganese in water is reported to cause neurological impairment and manganese [13]. Metal ions in water can occur naturally from leaching of ore deposits and from anthropogenic sources, which mainly include industrial effluents and solid waste disposal [18].

Iron

The average concentration of the iron from the water sample is 0.99 mg/l which is higher than the WHO/SON permissible limit of 0.30 mg/l. Iron is found in both soil and water. Coal and ash are rich source of iron in water. Liver cirrhosis is found to be related to drinking water contaminated with iron [14].

Cadmium

The average concentration of cadmium in water sample is 0.04 mg/l and is above the WHO/SON standard limit of 0.003 mg/l. water contaminated cadmium can be toxic to human in both short term and long term of exposure. Jibrin [15] concluded that all the water samples obtained from Durumi, Pigbakasa, Kagini, Damangaza and Apo villages in FCT exceeded the maximum limit ranging from 0.07 to 0.25 mg/L which is similar to the result obtained in this work. High concentration of cadmium could be caused by commercial use of fertilizers and disposal of sewage sludge. The short-term diseases resulting from high

Cadmium concentration includes nausea, diarrhea, liver injury and so on, while long term disease includes kidney, blood, bone, and liver damage [9].

Zinc

The average concentration of zinc in water sample is 0.07 mg/l which is below the WHO (0.3 mg/l) and SON (3.0 mg/l) permissible limits. A study conducted by [1] found the concentration of zinc (0.8 mg/l) to be lower than the standard limit in water samples. Zinc is an essential nutrient for body growth and development; however drinking water containing high levels of zinc can lead to stomach cramps, nausea and vomiting [19].

Nickel

The average concentration of nickel in water sample was 0.07 mg/l which is higher than the WHO/SON standard limit of 0.02 mg/l. [14] conducted a similar study and the concentration of Nickel (0.024 – 0.087) was found to be above the standard limit. Nickel is regarded as essential trace metal but toxic in large amount to the health by causing hair loss and can be related to dermatoxicity in hypersensitive human [14].

Heavy metal levels in soil

The average concentration of lead, chromium, manganese, cadmium, nickel, and copper in soil samples are 0.12, 0.04, 0.09, 0.01, 0.11 and 0.10 mg/kg, respectively. The concentrations of heavy metals in soil sample are below the targeted values proposed by World Health Organisation (WHO). However due to the presence of these heavy metals in the soil, the plants samples absorbed heavy metals at high concentrations into their organs depending on the defense mechanism developed by the plant species and the heavy metal tolerance.

Heavy metal levels in plants

Heavy metals were determined from each of the plant samples (roots, stem, and leaves) to determine which of the plant part accumulates higher and lower heavy metals depending on the heavy metal tolerance of the plants and the result is as presented in Table 6. The bioaccumulation differs from the plant samples, it was discovered that in spinach sample, the roots has the highest concentration of 0.13, 0.23, 0.21, 0.34, 0.03 and 0.10 for Pb, Mn, Cd, Ni and Cu, respectively. Followed by leaves which have 0.11, 0.19, 0.18, 0.01, 0.11 and 0.08 for Pb, Mn, Cd, Ni and Cu, respectively and lowest concentration of the metals in stem. In moringa, leaves have the highest concentration of heavy metals then the roots and lowest in stem. The average concentrations of Pb, Mn, Cd, and Ni in spinach are higher than the permissible limits, while Fe and Cu are lower than the standard limits. The average concentrations of Pb, Mn, and Ni in Moringa are higher than the standard limits, while Cd, Fe, and Cu are below the standard limits. When the two plant samples were compared it was shown that spinach has the higher concentrations of Cd, Ni, and Cu than moringa, while moringa has the higher concentrations of Pb. The two plant samples have the same concentrations of Cr and Mn. The bioaccumulation of the plant samples differs and the heavy metals are distributed in all parts of the plants samples, this may be due to the presence of these heavy metals at higher concentrations in the soil and water that the plants are absorbing at the sampling site. Fly ashes coming out from the cement company are the main source of these heavy metals contamination in water, soil, and plants at the sampling site.

Comparison of heavy metals concentrations in the samples

Plant, water, and soil samples were compared to determine which of the sample has the highest heavy metal concentrations and it was shown from the result in Table 6 above that the plant samples have the highest concentration of the heavy metals compared with the two samples. The orders of the heavy metals from the samples are as follows;

Pb – Plants > Soil > Water
Cr – Plants > Soil >Water
Mn – Plants > Soil >Water
Cd – Plants > Water > Soil
Ni – Plants > Soil > Water
Cu – Plants > Water > Soil

Conclusion

The results from this study have shown that the concentrations of heavy metals Pb, Cd, Se, Ni, Fe in water samples were higher than the WHO/SON permissible limit, while the concentrations of Cu and Zn were below the WHO/SON standard limits, Mn in water was higher than the SON but lower than the WHO standards. In plants samples, the heavy metals accumulate in plant organs at different concentrations depending on the antioxidants defense mechanism developed by the plant cells and the level of their metal tolerance. The bioaccumulation of the plant samples differs and the heavy metals were distributed in all parts of the plants samples, the roots of the spinach accumulated higher concentrations of heavy metals than the leaves and stem, while in moringa leaves accumulated higher than the roots and stem. The average concentrations of Pb, Mn, Cd, and Ni in all plant samples were higher than the permissible limit, while Cd was higher only in spinach sample. The concentrations of heavy metals in soil sample were below the targeted values proposed by World Health Organisation (WHO). The heavy metals concentrations in water, soil, and plants samples were compared and it was shown that the plants samples had the highest concentrations of heavy metals than the water and soil samples. This showed that the water and plant samples from the study area have heavy metals concentrations above the permissible limit. These maybe due to the effect of the coal fly ash from Cement Company of Northern Nigeria, Sokoto that is nearby the study area, and with this it was concluded that the water and plants from the study area are unfit for human use.

Conflict of interest: There is no conflict of interest among the authors.

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