Toxic Metal Concentration In Soils: A Case Study Of A Cocoa Research Field in Ibule, Ondo State, Nigeria

Elijah O. Openiyi,[1] Okiki N. Quadri, [1] *Wasiu B. Tomori [1]
1Department of Chemistry, Federal University of Technology Akure
*wb.tomori@futa.edu.ng, #elijahopeniyi@gmail.com

Abstract— Environmental pollution of the natural environment by heavy metals is a global concern. These metals are not degradable and can bioaccumulate in reservoirs and biomagnify along the food chain thereby having toxic effects on living organisms. Many ailments and birth defects have been linked to the ingestion of heavy metals which can occur by inhalation, leaching into our foods and water from the soil and many other routes. This study seeks to investigate the physicochemical parameters and heavy metals (Cu, Zn, Cd and Pb) concentration of soil samples from an abandoned cocoa research field operated by the Cocoa Research Institute of Nigeria (CRIN) located at Ibule, Ondo State. The abandoned field and its environs is fast becoming a residential area. A total of twenty-four soil samples from the study site was analyzed using standard analytical methods and Atomic Absorption Spectroscopy followed by descriptive statistics. Results showed some evidence of accumulation of heavy metals in the studied area. The heavy metals concentration was seen to be in the order Zn>Cu>Pb>Cd. Cd and Pb are in small concentrations while Zn and especially Cu may have accumulated probably from extensive experimental agricultural practices on the site (the use of copper fungicides in the cocoa plantation).

Keywords— heavy metals, soil contamination, agriculcural soil

INTRODUCTION

Cocoa is a major export crop that is of key economic importance to Nigeria. There are more than 650,000 ha of land being cultivated with cocoa in Nigeria. The highest percentage of cocoa exports from Nigeria comes from Ondo State. Cocoa export is important to the rural economy of the state, the industry is dominated by a lot of peasant farmers whose means of livelihood is tied to the crop (Acquaah, 1999; Appiah, 2004).

One of the objectives of Cocoa Research Institute of Nigeria (CRIN), established in 1964, is to identify the ecology and ways for control of pests and diseases that affects Cocoa (Adejumo 2004). Fulfilling this objective led to the establishment of experimental stations around the country; one of such experimental station was located at Ibule, Ondo State. The infection of cocoa pods with *Phytophtora sp.* (black-pod disease) which in turn affect the quality of the beans inside the pod is the main source of economic loss to farmers. Combating this menace of *Phytophtora sp.* on Cocoa pods made the farmers rely solely on the use of copper-based fungicides that were known to be effective at controlling the black pod disease (Aikpokpodion et al, 2013). On average, the farmers applied the copper-based fungicides for about eight times in a year. Application is done once in every three weeks starting from the rainy season in April to about the first week of November. Both frequency and timely application are reported to be necessary for the fungicide to be effective These frequent applications of the copper-based fungicides are expected to lead to the accumulation of copper which is a heavy metal in the soil (Adegbola, 1993). The main matrix for pesticide/fungicides disposition is the soil, a large percentage of applied pesticides/fungicides are retained in the upper topsoil. Researchers have established that only about 15% of applied fungicides reach the target of interest, the remaining 85% are expected to end up in the soil (Aikpokpodion. et al, 2013).

There are other sources of heavy metal contamination that may be present in the cocoa field. One of such is the use of Phosphate based fertilizers on the fields. Phosphate based fertilizers are known to contain heavy metals especially cadmium (Aikpokpodion et al, 2012). The irrigation processes on the cocoa field may be another source of metal contamination. The water used on these fields may likely be contaminated with heavy metals, this is especially true if they are wastewater or runoffs. The water used on this field were not pre checked before they were used for irrigation purpose.

Environmental pollution of the natural environment by heavy metals is a global concern. These metals are not degradable and can bioaccumulate in reservoirs and biomagnify along the food chain thereby having toxic effects on living organisms. (Aikpokpodion et al, 2012). The capabilities for these metals to form complex ion pose enormous health risks. Heavy metals like Zn, Pb, Cd, and Cu are known environmental contaminants whose continuous presence in the environment (soils) have been reported to have some toxic effects in humans (Aikpokpodion et al, 2012). Acute and chronic effects such as damage to the liver, central and peripheral nervous system, lungs, kidney and in some cases, deaths can be the result of constant exposure to high levels of these toxic metals. Children are more susceptible to these toxicities.

The cocoa field used for this study on heavy metal accumulation is a CRIN experimental station that has been abandoned for decades which is now being apportioned for residential purpose. Several houses can be spotted within and around the field and its environs. It is on record worldwide the catastrophe that attend such "human invasion" of such abandoned industrial/experimental sites. An example of such catastrophe is the love canal located in the Niagara Falls, New York, USA (Clapp Richard, 2009).

MATERIALS & METHODS

Study Area

Ibule is a town on the outskirt of Akure, the Ondo state capital. Ibule lies about 7° 18′ North of the equator and 5° 7′ East of the Meridian. The proximity of the town to the Federal University of Technology, Akure and Elizade University, Ilara-Mokin is fast making the town of Ibule to become a residential district for university students and employees. The town is in the tropical rain forest zone in Nigeria.

The soil samples used for this research were collected from a cocoa plantation belonging to CRIN along Akure Ilesha expressway way, Ibule, Ondo state, Nigeria. The selected site for this study had a lot of cocoa trees on it. Some part of the field has been left fallow while some other parts are being used to cultivate other agricultural crops (notable among these crops is corn).

Sample collection and processing

Soil sample for this research were taken from ten different points within the plantation at about 100 meters away from each other. Each sampling point was sampled to depth of 90 cm in 30 cm segments. The soil samples were collected using cutlass, stainless steel soil probe and a meter rule. The collected soil samples were stored in clean polyethylene bags and were labelled accordingly. Soil samples taken at the 30 cm depths were labeled "SD"; hence, we had SD1-SD10 while samples taken at the 90 cm depths were labelled "SL"; hence we had SL1-SL10. Control samples were taken from the vicinity of Federal University of Technology, Akure (FUTA), specifically from the school crop farm at Obanla and the school animal farm at "Malu" road, Obanla. The control samples were labelled CD1-CD2 and CL1-CL2 respectively. A total of 24 soil samples were collected for analysis within a two-day period.

The collected soil samples were air dried in the environmental chemistry lab at FUTA, Obanla campus. The air dried soil-samples were ground with a ceramic mortar and pestle and the large particles were separated with a 20 mm sieve. The samples were stored in airtight containers until analysis were done. Precautions were taken to avoid contamination during sampling, drying and storage. Analysis for metal content was done on the soil samples following standard methods (US-EPA 1996). Atomic Absorption Spectroscopy (AAS) was used for the measurement of metal concentration. Calibration standards were prepared through serial dilution of standard stock solution of multi elements concentrations of 1000 mg/L. Validation of the analytical method was done using the standard solutions. The extractions and analysis were done in triplicate, the mean values were reported.

Determination of physicochemical parameters

The methods described by (Allison 1960 and Ibitoye 2006) were used to determine physiochemical properties of the soil samples. The physicochemical parameters of the soil samples are reported in Table 1.

Toxic metals extraction using 0.5M HNO_3 (aq) extractant.

2.0 grams of the soil sample was weighed into an extraction cup and 10 ml of 0.5M HNO_3(aq) (Lob Chemie Pvt. Ltd, India) was added to the sample. The soil-extractant solution was shaken for 24 hours at 5 hours interval using stirrer and then filtered into a 25 ml volumetric flask using whatmann filter paper (№. 42) and marked up to the level with distilled water. The filtrate was poured into the sample bottle, labelled, and stored for metal analysis. A blank sample was also prepared. Metal content (Cu, Pb, Cd and Zn) of the soil sample (filtrate) were determined by AAS. The distribution characteristics of heavy metals in the study area and control sites are reported in Table 1 and 2 respectively.

Toxic metals extraction using 1M $NaNO_3$ (aq) extractant.

2.0 grams of the soil sample was weighed into extraction cup and 5 ml of 1M HNO_3(aq) (Lob Chemie Pvt. Ltd, India) was added to the sample. The soil-extractant solution was shaken for 24 hours at 5 hours interval using stirrer and then filtered into a 25 ml volumetric flask using whatmann filter paper (№. 42) and marked up to the level with distilled water. The filtrate was poured into the sample bottle, labelled, and stored for metal analysis. A blank sample was also prepared. Metal content (Cu, Pb, Cd and Zn) of the soil sample (filtrate) were determined by AAS. The distribution characteristics of heavy metals in the study area and control sites are shown in Table 1 and 2 respectively.

Data Analysis

Data and statistical analysis for this research work were performed using Microsoft Excel 2010 (www.microsoft.com) on an IBM-PC computer. The mean, standard deviation and sample variance were some descriptive statistics performed.

RESULTS DISCUSSION

Physicochemical analysis and toxic metals results

The concentration of metals (mean, standard deviation and sample variance) and the physicochemical parameters in soil samples (study site and control sites) of this research are presented in Table 1 and 2. The heavy metal concentration were seen to be in the order Zn>Cu>Pb>Cd.

From the tables below, the mean value of pH for the topsoil (30 cm) on the study site was 5.84 which is quite low compared with that (6.04) of the bottom soil (90 cm). (Table 1) The value obtained shows the soil is slightly acidic. This is within the range (6.03) reported by Ololade et al., (2010). The pH of soil is an indication of nutrients availability, toxic substances potency and the physical properties of the soil. The effect of soil pH is profound on the solubility of minerals and nutrients. It is regarded as a useful indicator of other soil parameters. Particularly, pH provides useful information about the availabilities of exchangeable cations (e.g., $Ca^{2+,}$ Mg^{2+}, K^{+}, etc.) in soils. Most minerals and nutrients are more soluble or available in acid soils than in neutral or slightly alkaline soils.

Table 1: Descriptive Statistical data obtained from the physicochemical analysis and toxic metals concentration at the study site.

Parameters		Sample depth	Mean (mg/kg)	Standard deviation	Sample variance	Median	Mode
*p*H		30cm	5.84	0.93	0.78	6.03	0.00
		90cm	6.04	0.76	0.52	5.83	0.00
Electrical conductivity		30cm	328.1	570.01	292423.1	161	0.00
		90cm	81.6	52.62	2492.04	58	0.00
Total organic carbon		3ocm	2.11	0.65	0.3765	2.18	0.00
		90cm	1.53	0.48	0.21	1.38	0.00
Cl^{-}		30cm	0.07	0.02	0.0002	0.07	0.00
		90cm	0.08	0.02	0.0003	0.08	0.00
NO3-		30cm	3.49	1.71	2.6351	3.82	1.59
		90cm	4.11	2.16	4.20	3.68	4.17
S042-		30cm	4.99	2.13	4.09	5.00	5.45
		90cm	6.36	5.68	2.24	5.68	6.36
Cu	HNO_3	30cm	34.15	9.06	73.90	31.92	0.00
		90cm	31.51	5.92	31.54	29.98	0.00
	$NaNO_3$	30cm	2.40	0.84	0.63	2.56	0.00
		90cm	1.76	0.69	0.43	1.52	0.00
Pb	HNO_3	30cm	1.18	0.19	0.03	1.21	0.00
		90cm	1.08	0.38	0.13	1.13	0.00
	$NaNO_3$	30cm	0.73	0.09	0.00	0.72	0.00
		90cm	0.63	0.22	0.04	0.68	0.00
Cd	HNO_3	30cm	0.03	0.00	0.00	0.03	0.00
		90cm	0.03	0.00	0.00	0.03	0.00
	$NaNO_3$	30cm	0.00	0.00	0.00	0.00	0.00
		90cm	0.00	0.00	0.00	0.00	0.00
Zn	HNO_3	30cm	62.26	17.23	267.30	55.01	0.00
		90cm	39.43	12.65	144.13	43.41	0.00
	$NaNO_3$	30cm	3.85	2.02	3.66	3.26	0.00
		90cm	2.25	0.88	0.70	2.24	0.00

The mean value of the Total Organic Carbon (TOC) for the topsoil (30 cm) on the study site was 2.11 mg/kg while that of the bottom soil (90 cm) on the study site was 1.53 mg/kg in the study area. (Table 1). These values are quite different from the mean value (1.7 mg/kg) gotten by Ololade et al., (2010). The difference in these TOC values may be as a result of the long abandonment of the study area from agricultural purposes. The mean electrical conductivity of 328 μs/cm^{-1} is quite high as observed on the topsoil (30 cm) of the study site while 81.6 μs/cm^{-1} is low as seen for bottom soil (90cm) (Table 1). As observed in Table 1, this can be an indication of excess nitrogen-based fertilizer in the soil or a high level of exchangeable sodium (Ololade et al, 2010). Electrical conductivity can almost be viewed as the quantity of available nutrient in the soil.

The mean values of the chloride ions obtained on the study site are 0.073 and 0.080 for 30 cm and 90 cm depth, respectively. (Table 1). The mean value obtained for the nitrate ions are 3.48 and 4.10 for 30 cm and 90 cm depth, respectively. (Table1). The mean value obtained for the sulphate ions are 4.99 and 5.22 for 30 cm and 90 cm depth, respectively. (Table 1). From the above, it can be incurred that the anions occured in the following sequence, Cl^{-} < NO_3-< SO_4^{2-}. The nitrate content in the soil is quite high which is also noticed for the sulphate.

This may be because the rate of the uptake of nitrate by the plant is more than the rate the plant reduces it; hence, it is being accumulated. Most nitrate accumulates in the leaves which fall off and decay inside the soil matrix. Activities such as burning which was noticed on the study area can lead to accumulation of sulphate ion inside the soil (Ololade et al, 2010).

The results from table 1 showed that the mean concentration of toxic metals extracted with HNO_3 and $NaNO_3$ extractant for the study site were in the sequence Zn> Cu >Pb> Cd which also conform to the standard deviation value obtain in the statistical data (Table 1 and 2). For all metals studied, it was

Table 2: Descriptive Statistical data obtained from the physicochemical analysis and toxic metals concentration at the control site.

Parameters		Sample depth	Mean (mg/kg)	Standard deviation	Sample variance	Median	Mode
*p*H		30cm	6.19	0.35	0.06	6.19	0.00
		90cm	6.21	0.38	0.06	6.21	0.00
Electrical conductivity		30cm	64.00	1.41	1.00	64.00	0.00
		90cm	53.50	26.16	342.25	53.50	0.00
Total organic carbon		30cm	1.30	0.44	0.10	1.30	0.00
		90cm	0.78	0.00	0.00	0.78	0.00
Cl$^-$		30cm	0.06	0.00	0.00	0.06	0.00
		90cm	0.07	0.00	0.00	0.07	0.00
NO3-		30cm	2.44	0.35	0.06	2.44	0.00
		90cm	2.49	1.27	0.80	2.49	0.00
S042-		30cm	7.68	3.15	4.96	7.68	0.00
		90cm	6.82	2.85	3.97	6.82	0.00
Cu	30	11.23	0.94	0.44	11.23	0.00	0.00
	90	12.62	6.33	20.01	12.62	0.00	0.00
	30	5.80	0.06	0.00	5.80	0.00	0.00
	90	4.38	1.02	0.52	4.38	0.00	0.00
Pb	30	0.06	0.00	0.00	0.06	0.00	0.00
	90	0.05	0.01	0.00	0.05	0.00	0.00
	30	0.05	0.00	0.00	0.05	0.00	0.00
	90	1.76	2.40	2.89	1.76	0.00	0.00
Cd	30	0.06	0.00	0.00	0.06	0.00	0.00
	90	0.04	0.01	0.00	0.04	0.00	0.00
	30	0.03	0.00	0.00	0.03	0.00	0.00
	90	0.03	0.00	0.00	0.03	0.00	0.00
Zn	30	28.22	17.29	6.38	28.22	0.00	0.00
	90	33.54	19.67	7.59	33.54	0.00	0.00
	30	21.48	12.01	5.52	21.48	0.00	0.00
	90	31.26	17.85	7.01	31.26	0.00	0.00

observed that the mean concentration of each metal was higher in the study site than in the control sites. This sequence is in order with the sequence obtained by (Khan et al, 2008) but varies differently from the sequence (Zn>Pb>Cu>Cd) obtained by Holmgren et al (1993). The same sequence Zn> Cu >Pb> Cd was also observed for the control samples though the concentration of the metals are lower in the control. (Table 2). The results in Table 1 and 2 also revealed that HNO_3 is more suitable than $NaNO_3$ for the extraction of the heavy metals studied in this research.

Zinc has the highest concentration in the studied area, which affirms the fact that a lot of industrial (mechanized farming) activities may have occurred in the said environment during the time it was used as an experimental station by CRIN. Zinc occurs naturally in the soil, however most Zn is added during industrial activities, such as mining, waste combustion and mechanized farming (Davies and Jones, 1988).

Copper has the second highest concentration of all the heavy metals studied which confirms the fact that a lot of copper-based fungicides may have been used during the operation of the experimental station by CRIN on the study area (Aikpokpodion et al, 2013).

Lead seems not to be too concentrated in the study area; however, the smallest level of lead can cause toxicity. Eliminating

all lead exposures in our environment is our best course of action; hence, its presence in the soil of the study area is a threat to human life and livestock. Lead has no physiological role in the body (Wani and Usmani, 2015).
Cadmium is the least concentrated of all the four metals tested for in the studied area. The presence of Cadmium can be said to be due to the use of phosphate-based fertilizers in the study area which may have been prevalently used during the operation of the experimental station by CRIN on the study site (Aikpokpodion et al, 2013).

CONCLUSION

The results from this research work showed some evidence of accumulation of heavy metals in the studied area. Cadmium and Lead are in small concentrations while Zinc and Copper may have accumulated probably from extensive experimental agricultural practices on the site (the use of copper fungicides in the cocoa plantation). A few regions with low enrichment in Cadmium or Lead were identified. No matter how minute these contaminations might be, they should be avoided since these metals are highly toxic.

REFERENCES

Acquaah, B. (1999) Cocoa Development in West Africa (The Early Period with particular reference to Ghana), Ghana Universities Press, Accra, Ghana. 273.

Adegbola M.O.K, G.A Filani (1984) Response of the Amelonado and Amazon varieties of cacao to control of the Phytophthora black pod disease by fungicides. 9th International Cacao Research Conference Report, Lome, Togo; 379-383.

Adegbola M.O.K (1993) Determination of the most suitable frequency and time of fungicide spraying schedule for the adoption in the control of Phytophthora black pod (pod rot) disease of cacao. Proceedings of the 11th International Cocoa Research Conference, Yamoussoukro, Cote d'Ivoire; 273-285.

Adejumo T. O. (2004) Crop protection strategies for major diseases of cocoa, coffee and cashew in Nigeria. African Journal of Biotechnology. 4 (2) 143-150.

Adeyemi .A .A (2000) Effective management of cocoa farms in Nigeria for profitability. Cocoa Growers' Bulletin, 52; 21-31.

Aikpokpodion P.E, L. Lajide and A.F. Aiyesanmi (2012) Assessment of Heavy Metals Mobility in Selected Contaminated Cocoa Soils in Ondo State, Nigeria. Global Journal of Environmental Research, 6 (1); 30-35.

Aikpokpodion Paul E, Atewolara-Odule O. C, Osobamiro T, Oduwole O. O and Ademola S. M. (2013) A survey of copper, lead, cadmium and zinc residues in cocoa beans obtained from selected plantations in Nigeria. Journal of Chemical and Pharmaceutical Research, 5(6); 88-98.

Allison LE (1960) Wet-combustion apparatus and procedure for organic and inorganic carbon in soil. Soil Sci. Soc. Am. Proc. pp. 36 - 40

Appiah, M. R. (2004) Impact of Cocoa Research Innovations on Poverty Alleviation in Ghana. Ghana Academy of Arts and Sciences Publication. 1, 17-19.

Clapp R. (2009) The love canal story is not finished. *Environmental health perspectives*, *117*(2), A54. https://doi.org/10.1289/ehp.12310.

Davies B.E. and Jones L.H.P. (1988) "Micronutrients and heavy elements," in Russell's Soil Conditions and Plant Growth, a wild edition; 11th edition. John Wiley & Sons; Inter-science, New York, NY, USA. 781–814.

Holmgren G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. (1993) Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils of the United States of America. J. Environmental quality journal l2: 62-74.

Ibitoye A.A (2006) Laboratory Manual on Basic Soil analysis. 2nd edition. Foladave Nig. ltd. Pp. 32 – 36.

Khan. S, Q. Cao , Y.M. Zheng , Y.Z. Huang , Y.G. Zhu(2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. An Environmental Pollution journal. 152; 686-692.

Ololade I.A, Ajayi I.R, Gbadamosi A.E, Mohammed O.Z and Sunday A.G (2010) A Study on Effects of Soil Physico-Chemical Properties on Cocoa Production in Ondo State. Modern Applied Science Journal. 4(5); 16-22

US-EPA (1996) Report: recent Developments for In-Situ Treatment of Metals contaminated Soils, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

Wani, A. L., Ara, A., & Usmani, J. A. (2015) Lead toxicity: a review. *Interdisciplinary toxicology*, *8*(2), 55–64. https://doi.org/10.1515/intox-2015-0009