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Comparative Study on The Availability, Impact, Fate and Mobility of Copper in The Soil of Cocoa Plantations in Oyo, Ondo And Ogun States of Nigeria Due to The Use of Boudreaux Mixture

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ABSTRACT

Soil samples from CRIN cocoa plantation in Oyo State where Boudreaux mixture was previously used as pesticides were compared with soil samples from Ondo and Ogun States where the Keywords is currently being used. Depths 0 to 15 cm and 15 to 30 cm were subjected to five-stage sequential extraction and the Cu extracts from the extraction were read with an Atomic Absorption Spectrophotometer (AAS). The total Cu content and the physicochemical parameters of the soils were also determined. The result obtained showed that Cu was bound to the exchangeable, carbonate and organic fractions from the three sites apart from Fe/Mn fraction. The results showed variation in the distribution of the Cu species from one depth to another. Cu from the exchangeable fraction is mostly being transported from the surface to the lower layer. The carbonate bound species is less mobile and is not readily transported down the soil depth. The organic bound Cu has nearly equal distribution between the top and bottom soils and there was little or no transport of the residual Cu species from the top to the bottom. Results showed that all the sites are still been impacted with Cu regardless of when the mixture was used. Moreover, the aim of the study was to find out whether the impact of copper can be eroded from the soil where the mixture was previously used with time. Since it was established that the use of Boudreaux mixture is capable of impacting the soil with copper where the mixture is presently being used. Therefore, plants, human and animal pollution and bioaccumulation are inevitable.

Keywords: Copper speciation, fungicide, Boudreaux mixture, exogenic, lithogenic.

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INTRODUCTION

The use of Copper sulphate in the form of Boudreaux mixture has been of tremendous benefit to the farmers in improving the quality of crop yield. Though there has been a ban on the use of copper sulphate in the treatment of cocoa yet, some farmers still found it useful and effective. The constant and regular usage of this fungicide leads to increased copper pollution in the soil, cocoa bean and even the entire ecosystem. Exposure to high concentration of copper poses a great danger to humans, plants and animals. Copper sulphate, a fungicide, has been used to control diseases in various fruits, vegetables, nuts, and field crops including cocoa. It is used in combination with lime and water as a protective fungicide, referred to as Bordeaux mixture. It is applied on plant leaf and for seed treatment. It can also be used as an algaecide; an herbicide in irrigation and municipal water treatment systems; or as a molluscicide. Though copper is one of 26 essential trace elements occurring naturally in plant and animal tissues, it is moderately toxic at acute exposures. The dose of copper sulphate that has been documented toxic when ingested by humans is 11mg/kg (NIOSH, 1981,1986). A healthy human adult may contain up to 80 mg of copper in total body weight (Lin et al., 2005). Ingestion of copper at a toxic level may cause metallic taste in the mouth, burning pain in the chest and abdomen, intense nausea, vomiting, diarrhea, headache, sweating, shock, discontinued urination leading to yellowing of the skin, injury to the brain, liver, kidneys, stomach and intestinal linings in the case of copper sulphate poisoning (Tapiero et al., 2003; Davanzo et al., 2004; Srivastava et al., 2005; Uriu-Adams and Keen, 2005). For increase in production of cocoa (Theobroma cacao), an economic crop with significant contribution to the Gross Domestic Product (GDP) of several countries, Bordeaux mixture was applied in the past to control cocoa diseases such as Black pod, Monilia, Witches' broom, Vascular streak dieback, Ceratocystis Wilt of Cacao, and Swollen shoot virus among others. This fungicide has been outlawed because of copper toxicity but is still being applied in some cocoa plantations due to the fact that it is readily available at relatively low cost. Also, its persistence over the period after the last application needs to be evaluated.

In recent years, heavy metals (Cu inclusive) have been of serious environmental concern. The reasons for the concern are their toxicity and how they bioaccumulation or bioconcentrate in living organisms. In addition, the heavy metals are being associated with human and animal health failures, which are aggravated by their long-term persistence in the environment and their non-degradable nature (Yoon et al., 2006). Once copper is introduced into the environment, particularly in the soil, it cannot be broken down biologically. It, however, can move into the different fractions of the soil based on the prevailing biogeochemistry of the environment (Ramirez et al., 2005). This is because it happens to be one of the mobile heavy metals. Within the European Community, the 13 elements of highest concern are: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn and Ti. Some of these elements are actually necessary for human in minute amounts (Co, Cu, Cr, Ni) while others are carcinogenic or toxic, affecting among others, the central nervous system CNS, (Hg, Pb, As), the kidneys or liver (Hg, Cd, Pb, Cu) or skin, bone or teeth (Ni, Cd, Cu, Cr) Ron et al. (2001). Therefore, this study is aimed at finding out whether the impact of copper can be eroded from the soil where the mixture was previously used over time. Since, it was established by Olu-Owolabi et al. (2012) that the use of Boudreaux mixture copper-based pesticide is capable of impacting the soil with copper, particularly with copper where the mixture is presently being used.

METHODOLOGY

Site Description

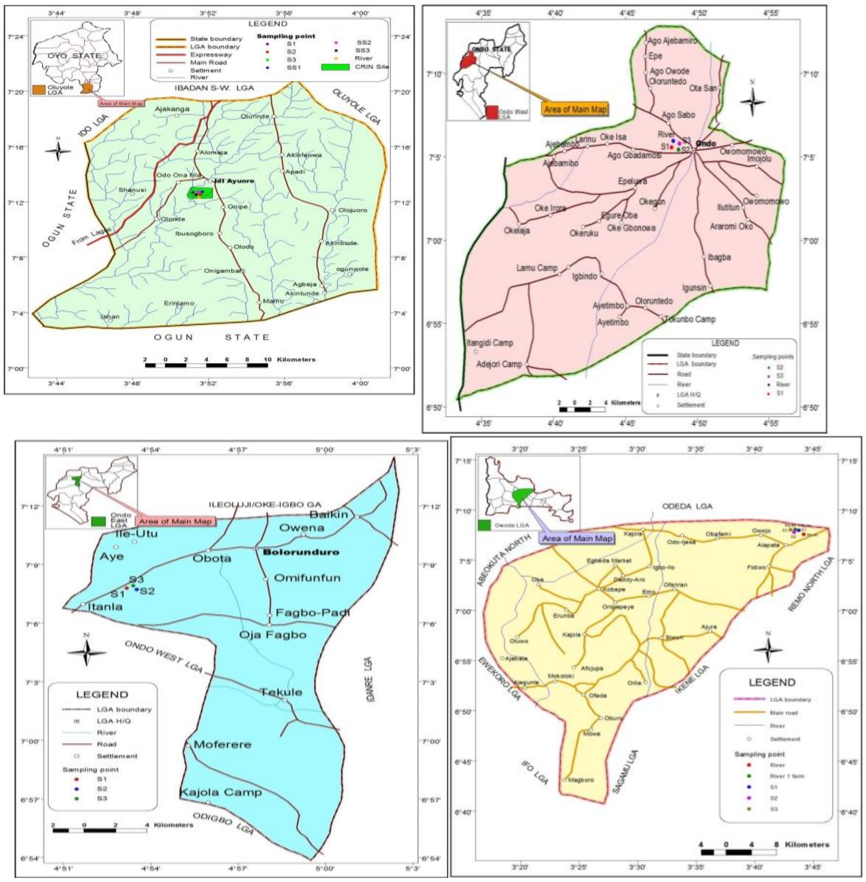
This study was conducted in five cocoa plantations from three different states of south-western Nigeria (Figure 1). The sites are Cocoa Research Institute of Nigeria (CRIN) in Oyo State (CRIN) site 1 and CRIN site 2 which are at Idiayunre, Ibadan, Oluyole local government area (labeled as CR 1 and CR 2, respectively), Ondo site 1, which is at Orimolade Sabo, in the Ondo West local Government Area (labeled OD1). The Ondo site 2 is at Igba, in the Ondo East Local Government Area (labeled OD2) (Figure 2) The sample from Ogun state was collected at Soora Baale, at the Obafemi/Owode Local Government Area (labeled SB). The sampling points from the sites are indicated as S1, S2 and S3 as seen in Figure 1 but on the tables and figures as P1, P2 and P3, respectively. In the sampling sites, there are cocoa plantations where Bordreaux mixture has been applied either in the past or present. The coordinate of the points from which samples were collected was obtained with a Garmin eTrex GPS receiver (Vista H model). The summary of sampling coordinates is presented in Table 1.

Sampling Procedure and Treatment

Each sampling point was stratified into three dues to the heterogeneous nature of soil and the soil samples were collected at each point and composited. In each case, field replicate samples were taken at three different points on the site labeled as points 1, 2, and 3. The soil samples were collected using a soil auger and sampling was carried out at different depths (0 to 15 cm and 15 to 30 cm) at each of the sites to study the soil profile analysis and the fate of the contaminant. The soil samples were kept in polyethylene nylon and were air-dried in the laboratory, then ground in an agate mortar and screened through a 0.05 mm sieve. The analysis was conducted using 1.0 g of each soil sample placed in a 50 ml polyethylene bottle for the extraction. All analyses were carried out in duplicate.

Physicochemical Properties of Soil

The physicochemical properties of the soil determined were pH, particle sizes, organic carbon, exchangeable acidity, and cation exchange capacity (CEC). The pH was determined in a ratio of 1:1 (soil/water ratio) g/ml using a pH meter. Particle size analysis of the soil was carried out with 50 g of oven-dried soil sample mixed with 50 ml of sodium hexametaphosphate reagent in a baffled cup and shaken for 6 to 15 min. The suspension was assessed in a bouyoucos cylinder with a hydrometer after distilled water has been added to the suspension in the cylinder to mark. The particle sizes were measured relative to the time of settling with the hydrometer. The determination of organic carbon content of the soil was carried by a method reported by Hesse (1971). A soil sample weighing 2.0 g was placed in a 250 ml Erlenmeyer flask, 10 ml of potassium dichromate, K2Cr2O7 (0.167M), was added, and the flask was swirled gently to disperse the soil in solution, 20 ml of



Figures 1. Maps of the sampling sites showing the different sampling points and the cocoa plantation in circles.

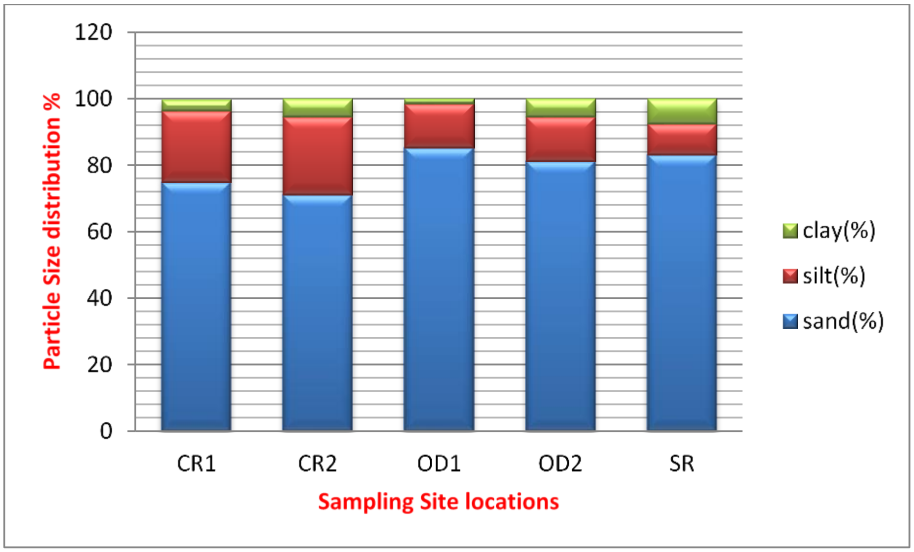


Figure 2. Particle size distribution in CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2 and Soora Baale site.

0.01M concentrated H2SO4, and swirled vigorously for 1 min. The flask was allowed to stand on an insulator for 30 min, after which 100 ml of distilled water and a few drops of diphenylamine indicator were added. The mixture was titrated with 0.4M ferrous ammonium sulphate hexahydrate [Fe (NH4)2 (SO4)2 .6H2 O]. The

Table 1. The coordinates of the points at which soil samples were collected taken with a GPS.

Sampling Points	Latitude (North)	Longitude (East)
CRIN site 1 (Ibadan)	07°12′36.8″	003° 51′37.5″
P1	07°12′36.7″	003° 51′37.6″
P2	07° 12′36.5″	003° 51′37.9″
P3		
CRIN site 2 (Ibadan)		
P1	07 °12′35.9″	003° 51′18.1″
P2	07 °12′35.9″	003° 51′18.0″
P3	07° 12′36.5″	003° 51′17.6″
Ondo site 1 (Orimolade Sabo)		
P1	07° 05′ 30.6″	004° 48′ 11.1″
P2	07° 05′ 30.6″	004° 48′ 11.6″
P3	07° 05′ 30.1″	004° 48′ 11.1″
Ondo site 2 (Igba)		
P1	07° 07′ 57.6″	004° 53′ 22.6″
P2	07° 07′ 57.5″	004° 53′ 22.9″
P3	07° 07′ 56.9″	004° 53′ 23.0″
Ogun site (Soora Baale)		
P1	07° 08′ 01.8″	003° 43′ 22.7″
P2	07° 08′ 01.4″	003° 43′ 22.7″
P3	07° 08′ 01.1″	003° 43′ 22.2″

exchangeable acidity was determined by weighing 2.0 g of the air-dried soil sample into a 50 ml centrifuge tube and adding 30 ml of 1 M KCl and agitating for 1 h on a reciprocating shaker. The content was subsequently centrifuged at 2000 rpm for 15 min and the supernatant separated into a 100 ml volumetric flask. Another 30 ml of 1M KCl was added to the same soil sample and shaken for 30 min and supernatant was also added to the same volumetric flask. 25 ml of KCl extract (the supernatant) was diluted with 100 ml of distilled water and 5 drops of phenolphthalein indicator were added.

The solution was titrated with 0.01M NaOH. The amount of the base used is equivalent to the total amount of acidity (H+ Al) in the aliquot. To the same flask, 1 drop of 0.01M HCl was added to bring the solution to a colorless condition, and 10 ml of 0.01M NaF solution was also added. The solution was then titrated with 0.01M HCl until the color of the solution disappeared. Two drops of the indicator were added to see if the disappeared color will reappear. The value obtained here was subtracted from the value of the first titration to obtain the milliequivalent of exchangeable H. The value was then expressed in Meq per 100 g of soil. The oxides of Fe and Mn were determined in the soil by the citrate-bicarbonate-dithionite extraction method reported by Weaver et al. (1968), while CEC in soil was determined with 2.0 g of the soil sample and 30 ml of 1M NH4 OAC shaken for 2 h. It was then centrifuged at 2000 rpm for 10 min and the supernatant decanted into a 100 ml volumetric flask. Three extractions of such were undertaken, combined, and made up to mark. K, Ca, and Na concentrations in the solution were evaluated with flame photometer while Mg and Mn were determined with Flame AAS, Buck Scientific Incorporated model 205A). The CEC was then calculated by the sum of the exchangeable bases (Ca, Mg, K, Na) and exchangeable Al and H expressed in Meq/100 g (Black, 1965; Jackson, 1962).

Metals Speciation by Sequential Extraction of Soil Samples

Metal speciation achieved by sequential extraction methods based on several modifications of Tessier's method (Welte et al., 1983; Zerbe et al.,1999). The distribution of copper in different phases was determined using the five stages of extraction procedures described as follows: Stage 1:Exchangeable Metal Fraction. 10 ml of 1M ammonium acetate solution was added to 1.0g of the soil samples and brought to a pH of 7. The sample solution was then shaken for 1 h by a horizontal shaker with a thermostat at room temperature. The sample was then centrifuged for 20 min at 3000 rpm. The supernatant was decanted into a 50 ml polyethylene bottle and made up to mark with deionized water. 0.2 ml of nitric acid was used to preserve the extract before instrumental analysis. Stage 2: Metal Bound to Carbonate Fraction. The soil residue from stage 1 was washed with 20 ml deionized water and discarded. 20 ml of 1 M ammonium acetate was added and brought to a pH 5 with acetic acid. The mixture was shaken for 5 h with a horizontal shaker at room temperature. The sample was

Table 2. Mean values of the physicochemical parameters of the soil sample from cocoa plantations from southwestern Nigeria.

Site	Free Oxides (%)							Particle Size Analysis (%)			
	Fe	Mn	Organic Carbon (%)	Organic Matter (%)	Exchangeable Acidity (meg/100 g)	CEC (meg/100 g)	Base Saturation (%)	Sand	Silt	Clay	pH
CRIN 1	0.022	0.137	4.83	8.31	1.0	17.36	94.24	75	21.4	3.4	8.1
CRIN 2	0.100	0.053	4.48	7.71	1.0	17.30	94.22	71.2	23.4	5.4	8.2
OD1	0.02	0.093	4.36	7.54	0.6	8.41	92.87	85.2	13.4	1.4	6.35
OD2	0.025	0.125	5.31	9.18	1.0	16.20	93.83	81.2	13.4	5.4	6.95
SB	0.16	0.068	4.28	7.40	8.6	29.93	71.27	83.2	9.4	7.4	8.05

centrifuged for 20 min at 3000 rpm. The supernatant was decanted into a 50 ml polyethylene bottle. The extract was made up to the mark with deionized water and preserved with 0.2 ml of nitric acid prior to instrumental analysis. Stage 3: Metal Bound to Iron and Manganese Oxides (Reducible). The soil residue from stage 2 was washed with 20 ml of deionized water and the supernatant discarded. 20 ml of 0.04M hydroxylamine hydrochloride in 25%(v/v) acetic acid was added in order to bring the pH to 2.

The mixture was shaken for 5 h at 95◦C with a horizontal shaker. The sample was centrifuged for 20 min at 3000 rpm after cooling. The supernatant was decanted into a 50 ml polyethylene bottle and made up with deionized water. The extract was preserved with 0.2 ml nitric acid before instrumental analysis. Stage 4:Metals Bound to Organic Matter Fraction (Oxidizable). The residue from stage 3 was washed with deionized water and the supernatant discarded. 5 ml of 0.02 M HNO3 and 5 ml 30% H2O2 was then added. The pH of the mixture was adjusted to 2 and shaken for 2 h at 85◦C. Again 5 ml of 30% H2O2 was added to the mixture at pH 2, and the sample mixture was shaken for 3 h at 85◦C. After cooling, 10 ml of ammonium acetate in 20% nitric acid was added and was shaken for 30 min at room temperature. The sample solution was centrifuged and the supernatant collected in a 50 ml polyethylene bottle and made up to mark. The extract was kept for instrumental analysis. Stage 5—Residual Fraction. The soil residue from stage 4 was washed with 20 ml deionized water and the supernatant discarded. The remaining soil residue was transferred into a 100 ml beaker. 2.5 ml of conc. HNO3 and 7.5 ml conc. HCl was slowly added. The mixture was refluxed for 2 h. The condensed solution was rinsed with deionized water, filtered and the filtrate was transferred into a 50 ml bottle for instrumental analysis. The samples were analyzed in triplicates using AAS and the mean value was obtained.

Extract for the Total Copper Concentration

A total of 1g of samples were weighed and transferred into a 100 ml beaker. 2.5 ml of concentrated nitric acid (HNO3) and 7.5 ml concentrated hydrochloric acid (HCl) was added slowly to avoid losses due to violent reactions. The mixture was heated under reflux for 2 h. The condensed solution was rinsed with deionized water and then filtered. The filtrate was transferred into a 50 ml bottle and made up with deionized water and taken for analysis. The values obtained from the determination of total metals concentration were compared with the summation of the various fractions. All reagents used for both the sequential extraction and the extraction for total metals were analytical grade reagents.

RESULTS AND DISCUSSION

Soil Physicochemical Parameters

The physicochemical parameter results of the soils from Table 2 showed that the pH of the soil from CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2 and Soora Baale site are 8.1, 8.2, 6.35, 6.95 and 8.05, respectively.

This shows that the soils at Ondo sites are slightly acidic and the soils at CRIN sites and Soora Baale are alkaline. The pH of the soil is within the normal pH range in soil worldwide (4.0 to 8.5) The influence of pH is displayed in increasing the CEC of soil with every rise in pH, at least up to pH 7.0 (Alloway, 1995). At low pH, most heavy metals are soluble including copper leading to higher leachability, whereas at higher pH they are immobilized. The soil organic carbon for CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2, and Soora Baale sites are 4.83, 4.48, 4.36, 5.31 and 4.28%, respectively.

These relatively high values of organic carbon may cause a large amount of copper to bind to the organic matter fractions of the soil. (Dipalma et al., 2007). Organic matter in the soil consists of a wide variety of plants and animal materials that were generated from various processes of decomposition and synthesis. It is concentrated at the topsoil and decreases with depth. It is important in the transportation and accumulation of metallic ions that are leached from the parent rock materials and various sources during soil formation. The organic matter differs from organic carbon because it includes other elements like nitrogen in the studied organic compound. Thus, the organic matter contents of the studied soils are between 7.40 and 9.18%. Usually, organic matters of most soils lie in the range of 0.1 to 10% but peaty soils in hotter climates tend to contain much lower amounts of organic matter than soils in cooler, humid regions (Rowel, 1994). It was previously reported that pH and organic matter were the key parameters that regulated the distribution of metals in soils (Schramel et al., 1998). Copper was documented to be mostly bound to organic matter fraction in marine sediments in a highly polluted area of Villifranche Bay (Rapin et al., 1983).

The high content of organic matter in this soil is an indicator of the bounding nature of copper to the oxidizable fractions because organic matter favors the entry of Cu into the oxidizable fraction through the formation of organic complexes of this element (Morillo et al., 2004; Dipalma et al., 2007). In addition, the rate at which organic matter is decomposed depends on its chemical composition and environmental conditions. Many factors such as temperature, pH, available nutrients, and carbon to nitrogen (C: N) ratio may interact to control the size and turnover rate of soil organic matter (Alvarez et al., 1998; Takejiro et al., 2010). Another important soil parameter that influences reactions in soil is the exchangeable bases in soils which are Ca, Mg, Na, and K, presented in Table 2. The soil samples on which the exchange was carried out contained a relatively high content of the exchangeable bases. From the five sites, Ca has the highest concentration, ranging from 5.93 to 16.38 meq/100 g. Soora Baale had the highest Ca, which may be accounted for in high pH. It was followed by CRIN 2 with 11.35 meq/100 g, CRIN 1 with 11.31 meq/100 g Ondo site 2 with 9.77 meq/100 g, while Ondo site 1 had the least with 5.93 meq/100 g. The high Ca may be from the additional contribution from the lime in the applied pesticide. Mg ranked next and had the highest value in Ondo site 2 with 4.53 meq/100 g, followed by CRIN 1 site with 4.15 meq/100 g, Soora Baale site 3.80 meq/100 g, CRIN2 site with 3.72 meq/100 g and 1.13 meq/100 g at Ondo site 1. Ondo site 2 had the highest Na with 0.71 meq/100 g while Soora Baale, CRIN 2, Ondo site 1and CRIN 1 had 0.61,0.59, 0.60 and 0.55 meq/100 g, respectively. For K, CRIN 2, Soora Baale, CRIN 1, Ondo site 2 and Ondo site 1 had 0.64, 0.57, 0.35, 0.19 and 0.15 meq/100 g, respectively. This work agrees with the result reported by Banjoko et al. (1983), Sha'ato (1996), Igwe et al. (1999), where Ca was the highest exchangeable base followed by Mg.

Exchangeable Acidity (EA) values from Table 2 showed that the soil at Soora Baale has 8.6 meq/100 g exchangeable acidity while CRIN site 1, CRIN site 2, Ondo site 2 and Ondo site 1 are 1.0, 1.0, 1.0 meq/100 g and 0.6 meq/100 g, respectively. From these results, it is obvious that exchangeable acidity at the Soora Baale site has the highest from all the sites.

The CEC of the Soora Baale site is reasonably high with 29.0 meq/100 g; next to this is CRIN site 1, CRIN site 2, Ondo site 2 and Ondo site 1 with 17.36 meq/100 g, 17.30 meq/100 g ,16.20 meq/100 g, and 8.41 meq/100 g, respectively. A high CEC in Soora Baale, CRIN site 1 and CRIN site 2, respectively support the claim that an increase in pH enhances CEC (Alloway, 1995). Soil with high CEC takes a longer time to acidify as well as to recover from an acidified status than soil with low CEC (assuming similar base saturation). Closely related to cation exchange capacity is the base saturation, which is the fraction of exchangeable cations that are base cations (Ca, Mg, Na, and K). The higher the amount of exchange base cations, the more acidity can be neutralized within a short time. Since the base saturation contents are high in those sites (CRIN site 1, CRIN site 2, Ondo site 2, Ondo site 1 and Soora Baale with 94.24, 94.22, 93.85, 92.87 and 71.27%, respectively), the soils could therefore, have the tendency of getting their acidic nature neutralized within a short time. Particle size analysis was used to determine the soil texture of the sampled soils. The particle size determination from Table 2 showed a higher amount of sand with 75, 71.2, 85.2, 81.2, and 83.2% for CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2, and Soora Baale site, respectively. The silt content has the next higher values in the soil sampled. The clay content is very low when compared with the silt and sand contents. The clay contents for CRIN site1, CRIN site 2, Ondo site 1, Ondo site 2, and Soora Baale sites are 3.4, 5.4, 1.4, 5.4, and 7.4%, respectively. Clay soil is often known for its high-water retention capacity, metal adsorption capacity, and nutrient storage (Miroslay et al.,1999). The low clay content in the soils in comparison with the silt and sand may imply that a small amount of metal retention such as copper will likely be witnessed in the soils. The free oxide of Fe in CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2 and Soora Baale soils are 0.022, 0.100%, 0.02, 0.025, and 0.16%, respectively. Also, free oxides of Mn are 0.137, 0.053, 0.093, 0.125, and 0.068% for CRIN site 1, CRIN site 2, Ondo site 1, Ondo site 2, and Soora Baale, respectively. The free oxides of Fe and Mn in the soils are very little. Oxides of Fe and Mn are surface-active objects that can adsorb metals. The low concentrations of Fe and Mn oxides imply the tendency of less bounding of copper with Fe-Mn oxides fraction in the speciation of copper in the soils. The Cu speciation form in the soil from these three sites may be controlled by the higher organic matter content, carbonate content, and CEC compared to other soil parameters. These results were in agreement with previous reports (Takejiro et al., 2010).

Table 3. Mean concentration of copper in the various fractions in soil samples from all sites at different depths after speciation.

CRIN Site 1	**CR1P1 (0 to 15) cm**	**CR1P1 (15 to 30) cm**	**CR1P2 (0 to 15) cm**	**CR1P2 (15 to 30) cm**	**CR1P3 (0 to 15) cm**	**CR1P3 (15 to 30) cm**
Ex	ND	ND	ND	0.150±0.2	0.175±0.3	0.150±0.2
Car	3.875±0.1	2.350±0.0	3.425±0.0	3.625±0.0	5.625±0.0	4.850±0.1
Fe/Mn	ND	ND	ND	ND	ND	ND
Org	4.100±0.0	6.300±0.2	3.900±0.11.625±0.0	3.575±0.1	5.025±0.0	
Res	2.590±0.0	1.890±0.1	1.205±0.0	1.915±0.0	1.275±0.0	4.125±0.0
CRIN Site 2	CR2P1 (0 to 15) cm	CR2P1 (15 to 30) cm	CR2P2 (0 to 15) cm	CR2P2 (15 to 30) cm	CR2P3 (0 to 15) cm	CR2P3 (15 to 30) cm
Ex	0.350±0.1	0.175±0.3	ND	ND	0.150±0.2	0.525±0.0
Car	5.650±0.1	5.475±0.0	4.625±0.1	5.450±0.1	6.425±0.0	6.375±0.0
Fe/Mn	ND	ND	ND	ND	ND	ND
Org	8.175±0.16.925±0.0	5.025±0.0	4.875±0.0	8.250±0.1	9.350±0.1	
Res	2.650±0.1	5.905±0.1	3.415±0.1	3.590±0.0	5.880±0.1	4.555±0.0
Ondo Site 1	OD1P1 (0 to 15 cm)	OD1P1 (15 to 30 cm)	OD1P2 (0 to 15 cm)	OD1P2 (15 to 30 cm)	OD1P3 (0 to 15 cm)	OD1P3 (15 to 30 cm)
Ex	5.9 ± 0.2	11.6 ± 0.1	11.5 ± 0.8	10.1 ± 1.6	0.7 ± 0.1	0.1 ± 0.01
Car	64.0 ± 5.7	38.6 ± 2.7	99.2 ± 12.7	31.9 ± 3.5	17.9 ± 1.45	16.2 ± 1.3
Fe/Mn	ND	ND	ND	ND	ND	ND
Org	16.2 ± 2.2	9.7 ± 2.9	21.2 ± 1.6	8.4 ± 0.25	8.8 ± 0.61	11.6 ± 0.51
Res	6.4 ± 0.4	3.7 ± 0.3	1.2 ± 0.09	2.3 ± 0.23	3.1 ± 0.5	3.0 ± 0.25
Ondo Site 2	OD2P1 (0 to 15 cm)	OD2P1 (15 to 30 cm)	OD2P2 (0 to 15 cm)	OD2P2 (15 to 30 cm)	OD2P3 (0 to 15 cm)	OD2P3 (15 to 30 cm)
Ex	1.2 ± 0.1	1.6 ± 0.04	ND	0.7 ± 0.1	0.1 ± 0.02	0.8 ± 0.04
Car	55.3 ± 3.0	59.8 ± 3.2	26.3 ± 3.5	22.0 ± 3.4	15.7 ± 1.5	7.7 ± 1.6
Fe/Mn	ND	ND	ND	ND	ND	ND
Org	22.6 ± 0.7	22.3 ± 2.8	11.2 ± 1.9	12.0 ± 2.8	12.3 ± 1.7	4.3 ± 0.07
Res	4.20 ± 0.41	4.30 ± 0.50	2.30 ± 0.21	3.10 ± 0.30	2.0 ± 0.12	1.4 ± 0.07
Soora Baale Site	SRP1 (0 to 15 cm)	SRP1 (15 to 30 cm)	SRP2 (0 to 15 cm)	SRP2 (15 to 30 cm)	SRP3 (0 to 15 cm)	SRP3 (15 to 30 cm)
Ex	0.20 ± 0.03	ND	0.4 ± 0.05	0.4 ± 0.04	ND	0.5 ± 0.07
Car	14.1 ± 0.39	10.3 ± 1.1	4.2 ± 0.39	3.3 ± 0.12	7.5 ± 0.11	10.1 ± 0.11
Fe/Mn	ND	ND	ND	ND	ND	ND
Org	11.3 ± 1.4	7.8 ± 0.3	7.1 ± 0.71	4.7 ± 0.28	7.6 ± 1.2	13.5 ± 1.5
Res	6.1 ± 0.07	6.1 ± 0.14	4.5 ± 0.4	4.2 ± 0.51	4.5 ± 0.07	8.2 ± 0.57

Soil Speciation for Copper

Speciation of an element involves the individual different physiochemical forms of that element that together make up the total element concentration. The results of the speciation of Cu in the soil samples of the studied areas are presented in Table 3. Cu was not detected in the Fe/Mn bound fraction. This trend may be attributed to the low free Fe and Mn oxide in the soils from these plantations. The reasons for speciation relate to environmental or human health concerns, where the ultimate impact on biological systems is of interest (Long et al., 1997).

The observed results are due to the transformation of chemicals species that may occur in the natural environment or are introduced by anthropogenic activities through processes such as hydrolysis,

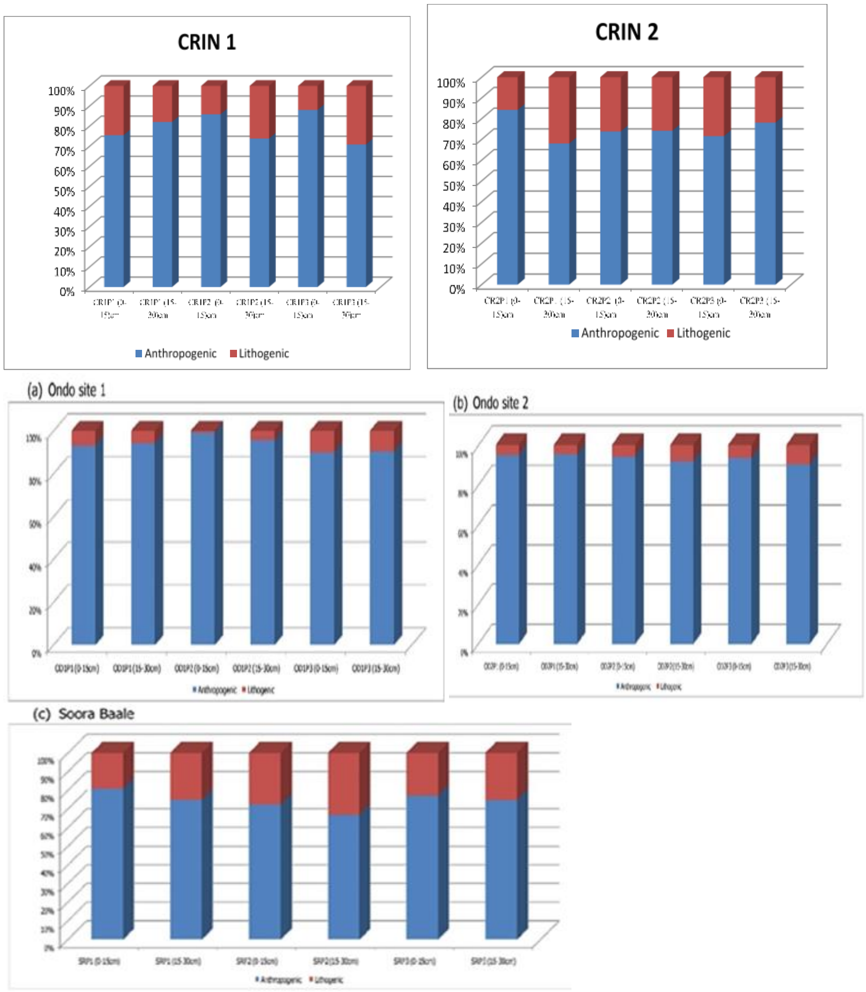


Figure 3. Graphs of the relative abundance of the anthropogenic Cu fraction compared to the lithogenic fraction from the sites.

photolysis, chemical and biological degradation, depending on the biogeochemistry of the environment. The bioavailability and possible toxicity of these forms is the major focus of speciation studies. Thus, the results of Cu speciation from the cocoa plantation were formulated into relative abundance based on the lithogenic and anthropogenic divide and the results are presented in Figures 3. The lithogenic species is the least bioavailable, least mobile and toxic species, which is contributed by the geological structure of the environment and is therefore natural. It is measured by the residual fraction in the sequential extraction. The other species are classified as exogenic or from anthropogenic sources. The exogenic species are more bioavailable than the lithogenic. The results clearly indicated that the more mobile exogenic species are far more abundant than the lithogenic, which is the less mobile fraction. CRIN 1, CRIN 2 and Soora Baale soil exhibited a high relative abundance of the lithogenic species, ranging from 20 to 40% of the total copper concentration in the soil. It may be inferred that the soil of the cocoa plantation in these three sites are least impacted and may have less exposure risk tendency based on the observed concentrations of Cu (Table 3). This is because the speciation, or chemical form, of metals, governs its fate, toxicity, mobility, and bioavailability in contaminated soils, sediments, and water.

The results of the comparative study also showed that despite the fact that the two sites (CRIN 1 and CRIN 2) had stopped the use of Boudreaux mixtures over 13 years, the soil remained contaminated with copper? This is owing to the fact that heavy metals are non-biodegradable. Also, the speciation study carried out showed that copper is mostly bound to the organic oxidizable fraction. The high concentration of the organic bound species (Table 3) may be attributed to the complexation of Cu to the high organic matter in the soil samples from the plantations (Morillo et al., 2004). The results correspond to the findings by Rapin et al. (1983), Ramos et al. (1999), and Li et al. (2009), which reported that Cu was mostly bound to organic matter fraction (70

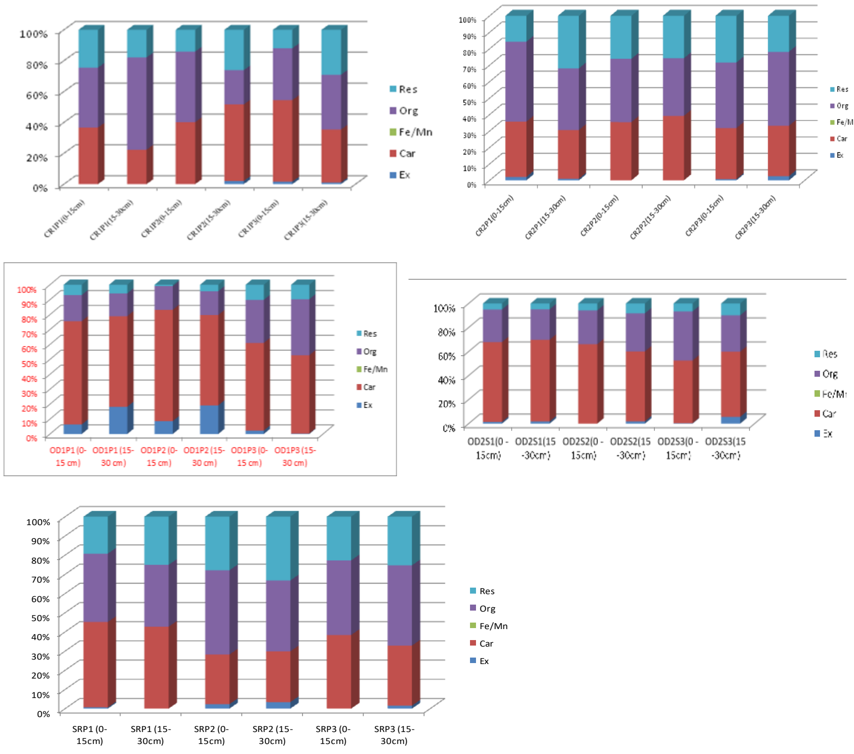


Figure 4. Relative abundance of the sites.

to 80%) in marine sediments in the highly polluted areas. Also, these findings are consistent with the findings of Turki (2007), who reported that Cu is mainly bound to organic matter and sulphides. The highest percentage was found in the oxidizable fraction (71.7%) in sediment from Al Shabab Lagoon, Jeddah, Saudi Arabia. Organically bound copper becomes available under certain environmental conditions such as changes in temperature and pH. Consequently, copper then bioaccumulates in plants which could include the cocoa bean. Next to the organic bound fraction in concentration is the carbonate bound fraction, this could be as a result of the lime component of the Boudreaux mixture used in the spraying of the cocoa plantations. This also accounts for the high content of calcium in the exchangeable bases from the physicochemical parameter values. The Cu bound to this fraction could become available when there is a fall in the pH of the soil. The concentration of copper bound to the exchangeable fraction is very little while at some other points are indeterminate. At some points at the exchangeable fraction, no concentration was recorded while other points had little concentrations. This could be due to the geographical location of the points. Also, since the exchangeable fraction is the water-soluble fraction, the copper at the points with no concentrations could have been washed down the lowland. Conversely, the results at the other three sites namely: Ondo site 1, Ondo site 2 and Soora Baale site showed that Cu is mostly bound to the carbonate fraction. Results from Figure 4 showed that copper was mostly bound to the carbonate and organic fractions. Since the carbonate bound fraction is more stable and less bioavailable, the risk of exposure may be less except when the pH is lowered (that is, under acidic condition). The same applies to the organic or oxidizable fraction which is also less bioavailable but under the action of organic microbes, the organically bound fraction will be made available. However, the exchangeable fractions are most mobile and as such, during rainfall, are easily washed from the topsoil to the subsoil. Consequently, copper is made available to the cocoa plant through the root by adsorption.

CONCLUSION

The results obtained revealed that regardless of whether copper had been used in some parts of the sites, it does not disprove that the soil had been impacted upon with copper due to the use of the pesticide. Considering the various fractions (exchangeable, carbonate and organic) where copper was mostly bound from the research, it could be said that the soil plantations have some level of pollution. Also, the soils, the plants and living organisms from all the plantations are prone to the risk of copper metal pollution due to the bioaccumulation and accumulation of copper. Hence, under the same conditions of low temperature, variation of pH and oxidation by organic micro bacteria, copper has free mobility in the environment.

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REFERENCES

Alloway BJ (1995). Heavy metals in soils. 2nd ed. Backie Academic and professional, Glasgow.UK. pp. 310- 325.

Alvarez R, Lavado RS (1998). Climate organic matter and clay content relationships in the Pampa and Chaco soils, Argentina.Geoderma.83:127- 141.

Banjoko VA, Ojo AJ, Olomu E (1983). Morphology, mineral and classification of Ferrallitic soils in Southwestern Nigeria. Nigeria Journal of Soil science.4:38-52.

Black CA (1965). Methods of Soil Analysis. ed. Agronomy no 9. Part 2. American Society of Agronomy. Madison. Wisconsin.

Dipalma P, Ferrantelli C, Merli EP, Pitzolu I (. 2007). Influence of soil organic matter on complex extractions from contaminated soil. Journal of soil and sediment contamination. 16: 323- 335.

Hesse PR (1971). A textbook of soil chemical analysis. Chemical publishing co. inc. New York.

Igwe CA, Akamigbo FOR, Mbagwu JSC (1999). Chemical and mineralogical properties of Soils in South – eastern Nigeria in relation to aggregate stability.Geoderma 92: 111- 123.

Long ER, Field LJ, McDoland DD (1997). Predicting toxicity in marine sedimentquality guidelines. Environmental and Toxicological Chemistry. 17 (4): 714-727.

Morillo J, Usero J, Garcia I (2004). Heavy metals distribution in marine sediments fromthe southwest coast of Spain. Chemosphere, 55: 431-442.

National Institute for Occupational Safety and Health (NIOSH) (1981-1986). Registry of toxic effects of chemical substances (RTECS). Cincinati. OH: NIOSH.

Olu-Owolabi BI, Agunbiade FO, Ogunleye IO, Adebowale KO (2012). Fate and Mobility of Copper in Soil of Cocoa Plantations in two South-Western States of Nigeria treated with Copper-Based Fungicides. An International Journal of Soil and Sediment contamination. 21.918-936.

Ramirez M, Serena M, Frache R, Correa J (2005). Metal speciation and environmentalimpact on sandy beaches due to El Salvador copper mine.Chile Marine Pollution Bulletin. 50: 62-72.

Ramos l, Gonzalez MJ, Hernandez LM (1999). Sequential extraction of copper, lead, cadmium and zinc in sediments from Ebro River Spain: Relationship with levels detected in Centre of Disease Control and Prevention. http://www.cdc.gov(Retrieved 6 June 2009)

Rapin F, Nembrini GP, Forstner U, Garica JL (1983). Heavy metals in marine sediment phases determined by sequential extraction and their interaction with interstitial water. Environ. Technol. Lett. 4: 314-318.

Ron Z, Pia K (2001). Control of pollutants in flue Gases and fuel Gases. TKK, Espoo 2001.

Rowel DL (1994). Soil Science: method and applications. Longman group limited.UK. pp 1- 108.

Schramel O, Michalke B, Kettrup A (1998). Study of the copper distribution in contaminated soil of hop fields by single and sequential extraction procedures. Journal of the science of the total environment. 263(2000):11-22.

Sobczynski T, Elbanowska H, Zerbe J, Siepak J (1996). Digestion of Samples of Bottom Sediments Prior to theDetermination of Total Contents of Heavy Metals. Gospodarka Wodna. 6 (570):173.

Soon YK, Bates TE (1982). Chemical pools of cadmium, nickel and zinc in polluted soils and some preliminary indications of their availability to plants. Journal of soil science. 33: 477-488.

Takejiro T, Mirai W, Masami KK, Tomoyoshi M, Shigeki Y, Seiji H (2010). Pollution of Montane soil with Cu, Zn, As, Pb,Sb and nitrate in Kanto,Japan. Journal of science of the total environment. 408: 1932- 1942.

Tessier A, Campbell PG,Bisson M (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Analytical Chemistry. 51 (7): 844.

Turki AJ (2007). Metals Speciation(Cd, Cu,Pb and Zn) in Sediments of Al Shabab Lagoon, Jeddah, Saudi Arabia. Journal of King Abdulaziz University, Marine Science, 18: 191- 210.

Weaver RM, Syers JK, Jackson ML (1968). Determination of silica in citrate-Bicarbonate Dithionite extracts of soil. SSSAP 32:437-501.

Welte B, Bles N, Montiel A (1983). Studies of different methods of speciation of heavy metals in sediments II. Applications. Environ. Technol. Lett. 4:223.

Welte B, Bles N, Montiel A (1983). Studies of different methods of speciation of heavy metals in sediments. Bibliographic studies. About. Technol. Lett. 4: 7988.

Yoon Y, Cao X, Zhou Q, Ma LQ (2006). Accumulation of Pb, Cu and Zn in antive plants growing on a contaminated Florida site. Science of the total environment.368: 456- 464.

Zerbe J, Sobczynski T, Elbanowska H, Siepak J (1999). Speciation of heavy metals in bottom sediments of Lakes. Journal of Environmental Studies. 8(5):331- 339.