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Forms of Zinc, Cobalt, and Chromium in Soils cultivated to Oil palm and Rubber in the rainforest

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ABSTRACT

The study aimed to determine the status of six forms of Zinc (Zn), Cobalt (Co), and Chromium (Cr) in soils cultivated for Oil palm and Rubber in the rainforest belt of Nigeria.

Soils were collected from 2 (Oil palm and Rubber) plantations using a Randomized complete block design from 4 depths in 3 replications to make a total of 24 soil samples. A Laboratory experiment was conducted in the soil and land management division of the Nigerian Institute for Oil palm Research (NIFOR) between February and September 2018. Some soil properties and forms of Zn, Co, and Cr were determined by 6 steps of sequential fractionation following high-speed centrifugation and decantation at each step. Zn, Co, and Cr in the soil extracts were read using an Atomic adsorption spectrophotometer. Correlation analysis was used to determine the relationship between some soil properties and Zn, Co, and Cr forms. Results showed acidic soil reaction (< 4.91) with Oil palm plantation slightly higher in organic carbon (32.60 g/kg) and available P (18.00 mg/kg) when compared to Rubber plantation. The results also indicated variations in the Zn, Co, and Cr fractions in both plantations. The influence of some soil properties on forms and speciation of Co and Zn was indicated by significant correlation results. The present study indicated that the soils can be continuously used for citrus and teak production since the various forms of Co, Zn and Cr were within permissible levels and thus poses no health risk to the food chain.

1.0 Introduction

Heavy metals are a class of metals with a specific gravity greater than or equal to 5 g cm^{-3} (Orhue and Uzu, 2011). The essential metals including Zn, Co, and Cr are needed by living organisms in trace quantities for optimum performance of life processes, while only Zn and Co amongst others are required by humans (Forstner and Prosi, 1978).

Heavy metals enter the soil through various anthropogenic (Aguilar *et al.,* 2013) and pedo-lithogenic sources (Chlopecka *et al*., 1996). However, human activities have contributed significantly to the occurrence, accumulation, and availability of metals and their salts in the soil (Agbenin, 2020). The accumulation of heavy metals in agricultural soils is of increasing concern because of food safety issues, potential health risks, and its detrimental effects on the soil ecosystem (Cui *et al*., 2004). When these metals enter the soil, their reactions with soil components lead to progressive conversion to insoluble forms such that they are incorporated into soil components through a variety of mechanisms (Navas and Lindhorfer, 2003). These associations with various soil

components determine their mobility and availability (Ahumada *et al.,* 1999). When the capacity of the soil to retain heavy metals is reduced due to accumulation, soils can release heavy metals into the groundwater and or soil solution thus making it available for plant uptake (Rajesh *et al*., 2007). Studies on sequential extraction techniques have increased because they give an idea of the forms and speciation of elements and provide knowledge on metal affinity to soil components (Narwal *et al.,* 1999).

Sequential fractionation of Zn, Co, and Cr in Soils cultivated in Oil palm and Rubber in the rainforest belt of Nigeria will help quantify their distribution, forms, and binding strengths subject to a series of chemical reagents. Many studies have been reported on heavy metals (Orhue and Uzu, 2011; Orhue and Nwaoguala, 2011; Orhue *et al.,* 2014; Musa, *et al.,* 2017) and sequential fractionation (Orhue and John, 2015) in agricultural soils but none have been reported on fractions of Co, Zn and Cr in soils under Oil palm and Rubber plantation in the rainforest belt of Nigeria. Thus the study aimed at assessing the fractions of Co, Zn, and Cr in soils under Oil palm and Rubber plantations in the rainforest belt of Nigeria.

2.0 Methodology

2.1 Description of Study Area

The sequential fractionation study was conducted to understand the forms and speciation of Co, Zn, and Cr in soils planted with Oil palm and Rubber in the rainforest belt of Nigeria. The area has two distinct (rainy and dry) seasons, and falls within the low land rain forest, with average annual temperature and rainfall of 27 ^{0}C and 2000 mm respectively. Mean annual relative humidity ranges between 89 - 75% (NIFOR 2013).

The Oil palm plantation is located opposite Dentistry Quarters, University of Benin, Benin City, Nigeria. And lies between latitude 06.63978N and longitude 005.62778E with an elevation of 113 m., The vegetation in the Oil palm plantation included mainly *Axonopus compressus* (carpet grass), *Elaeis guineensis* (Oil palm), *Eleusine indica* (stubborn grass), etc at the time of sampling.

The Rubber plantation is located at Oghara in Delta state, Nigeria. And lies between latitude 05.58889N and longitude 006.10028E with an elevation of about 20 m. The vegetation in the Rubber plantation mainly included leaf litter, and *Axonopus compressus* (carpet grass) at the time of planting.

2.2 Soil sampling and preparation

Soil samples were collected from a quadrant of 20 m x 30 m in oil palm and Rubber plantations, using a randomized complete block design in 3 replications from 4 depths to make a total of 12 soil samples per plantation. The samples were air-dried, ground, and stored in a labeled polythene bag for analysis.

2.4. Laboratory Analysis

Some physical and chemical properties of the studied soils are presented in (Table 1). Analyses were performed according to standard methods reported by Orhue *et al.* (2021).

2.4.1. Chemical Fractionation of Zn, Co, and Cr in the Soil samples

The sequential fractionation method reported by Chang *et al*. (1984) was adopted to determine the forms of Zn, Co, and Cr. 5 g air-dried soil was weighed into a 50 ml centrifuge tube. 30 ml of the extracting solution for each form was added to the soil sequentially after air drying and respective fractions were extracted. The supernatant of extracted solutions at each step was separated by high-speed centrifugation for 20 minutes and decanted into 120 ml plastic bottles for determination of Zn, Co, and Cr using atomic absorption spectrophotometer.

2.5. Statistical Analysis

Data obtained were analyzed by Genstat statistical package (version 6.1.0234). Means were separated by Duncan Multiple Range Test (DMRT) at a 5% level of probability. While the relationship between some soil properties and forms of Zn, Co, and Cr was determined by correlation analysis.

3.0. Results and Discussion

3.1. Particle-sized distribution of the soils

The particle size distribution describes the relative percentage of sand, silt, and clay in any given soil (Table 1). The sand was the dominant fraction of the soils in the Oil palm and Rubber plantations. The sand and silt content decreased with increased soil depth while clay increased with increased soil depth. The high sand content indicts coarseness and high permeability in the soils (Brady and Weil, 2007). While the increase in clay fraction with an increase in soil depth could be attributed to argilluviation. (Amalu *et al.*, 2001). The silt/clay ratio depicts the degree of weathering occurring in the soil (Van Alphen and Stoorvgel, 2000). The high silt/clay

Table 1. Some physical and chemical properties of the soils

DEPTH (cm)	pH (H_2O)	OC	TN	Av. P	CEC	EA	ECEC	Sand	Silt	Clay	S/C ratio	TC
	←	gkg^{-1}	→	$mgkg^{-1}$ ←	$cmolkg^{-1}$	→	←	$g\ kg^{-1}$	→			
OIL PALM PLANTATION												
0-30	5.36a	41.10a	2.95a	19.00a	2.32a	0.35a	2.68a	864.00a	71.90a	64.10a	1.12a	LS
30-60	5.10a	37.07a	2.60a	21.70a	1.93a	0.36a	2.28a	852.70b	56.70b	90.70a	0.79a	LS
60-90	4.76b	31.73b	1.20a	17.40a	1.64a	0.36a	2.01a	848.00b	47.40b	104.60a	0.46b	LS
90-120	4.60b	20.73b	0.81a	13.60a	1.40a	0.35a	1.75a	845.30b	35.30c	119.10a	0.29b	LS
Mean	4.96	32.66	1.89	18.00	1.82	0.36	2.81	852.50	52.80	94.60	0.67	
RUBBER PLANTATION												
0-30	5.06a	40.10a	2.04a	12.96a	1.85a	0.47a	2.31a	864.00a	71.90a	64.10b	1.12a	S
30-60	5.13a	34.07b	1.55ab	11.40a	1.50ab	0.46a	1.97ab	852.70ab	56.70a	90.70b	0.79a	S
60-90	4.83a	30.67b	0.94	9.59ab	1.28bc	0.57a	1.85c	848.00b	47.40b	104.60a	0.46a	LS
90-120	4.80a	18.60c	0.63	7.78b	1.05c	0.50a	1.55c	845.30c	35.30b	119.10a	0.29a	LS
Mean	4.96	30.86	1.29	10.43	1.42	0.50	1.92	852.50	52.80	94.60	0.67	

OC= organic carbon, TN= total nitrogen, Av. P= available phosphorus, CEC= cation exchange capacity, EA= exchangeable acidity, ECEC= effective cation capacity, S/C= silt/clay, TC= textural classification, LS= loamy sand, S= sand,

ratio in topsoil may be attributed to the coarse texture or resistance of the parent materials to weathering (Nwaka and Kwara, 2000). The textural class of the soils was loamy sand at the Oil palm plantation and sand at the topsoil of the Rubber plantation, depicting the high sand content of the soils studied.

3.2. Chemical properties of the soils

The result of some soil chemical properties (Table 1) in Oil palm and Rubber plantations showed a very strongly acidic pH. The acidity could be attributed to the leaching of basic cations which causes an increased percentage of Al^{3+} and H^{+} resulting in an acidic soil reaction. The organic carbon contents in Oil palm and Rubber plantations were high when compared to critical values reported by Landon (1991). The high organic carbon content in both plantations could be attributed to high litter fall. The mean total Nitrogen content in Oil palm plantations was high while that of Rubber plantations was low when compared to the critical level of 1.5 g/kg recommended for tropical soils by Enwenzor *et al* (1979). The difference in Nitrogen content may be due to differences in litter falling and management practices. The mean available phosphorous was above the lower limit of 10 mg/kg in both plantations, compared with the critical level of 10 - 16 mg/kg recommended by Adeoye and Agboola (1985). The adequate level of available phosphorous in both plantations could be attributed to organic matter mineralization and low phosphorus sorption capacity (Aghimien *et al.*, 2015). ECEC value of the soils in both plantations was below the 15 cmol/kg critical value reported by Udo *et al.*, (2009), for tropical soils.

3.2.1. Forms and speciation of Zn, Co, and Cr

Sequential fractionation of Zn, Co, and Cr (Table 2) showed that carbonate-bound Zn was the predominant form in both plantations, although Zn was present in other forms but in a smaller mean amount. The higher mean value of carbonate-bound zinc reflects the high mobility and bioavailability potentials of zinc. This result is however in contrast with the findings of Emmerich *et al.* (1987) who reported Zn to be predominated in the residual fraction. The high carbonate bound Zn fraction could be due to anthropogenic activities in

Table 2. Forms and speciation of Zn, Co, and Cr in Oil palm plantation (mgkg-1).

Depth (cm)	H_2O sol.	Exch.	Ads.	Org. B.	CO_3 B.	Res.
		ZINC				
0-30	1.13	2.74	0.67	1.15	5.16	3.65
30-60	2.08	3.27	0.16	1.05	5.01	1.83
60-90	1.48	3.11	0.48	2.07	7.42	0.47
90-120	0.63	2.73	0.57	0.41	5.14	0.47
Mean	1.33	2.96	0.47	1.17	5.68	1.61
$LSD_{0.05}$	0.47	1.69	0.12	0.05	0.57	1.15
		COBALT				
0-30	0.03	0.06	0.03	0.03	0.01	0.03
30-60	0.04	0.05	0.03	0.05	0.02	0.04
60-90	0.04	0.07	0.03	0.05	0.02	0.03
90-120	0.05	0.08	0.03	0.07	0.01	0.04
Mean	0.04	0.06	0.03	0.05	0.02	0.04
$LSD_{0.05}$	ns	0.01	ns	0.01	ns	ns
		CHROMIUM				
0-30	0.03	0.05	0.01	0.03	0.01	0.01
30-60	0.04	0.01	0.00	0.01	0.02	0.01
60-90	0.05	0.04	0.01	0.04	0.02	0.01
90-120	0.03	0.05	0.00	0.01	0.01	0.01
Mean	0.04	0.04	0.01	0.03	0.01	0.01
$LSD_{0.05}$	ns	0.03	0.01	ns	ns	ns

H_2O sol.= water soluble, Exch. exchangeable, Ads.= adsorbed, Org.= organically, CO_3= carbonate, Res.= residual, B.= bound, $LSD_{0.05}$= least significant difference at 0.05 significant level, ns= not significant.

line with the findings of Jiang *et al.* (2001) who posited that the distribution of metals in soils is mainly by biological cycling and soil pedogenic processes. Co was highest in the exchangeable fraction and closely followed by organically bound, water-soluble, and residual Co fractions in the Oil palm plantations (Table 2). While the higher mean concentration was recorded for carbonate and organically bound Co in the Rubber plantation (Table 3). This result is contrary to the findings of Osakwe (2010), who reported Co to be predominant in the exchangeable fraction. The high concentration of cobalt in the organically bound, carbonate and residual forms in the rubber plantation reflects the tendency of Co to become available over time depending on soil condition. The highest mean concentration of Cr in Oil palm plantations was associated with the water-soluble and exchangeable form compared to the other forms. This result is contrary to the findings of Venkateswaran *et al.* (2007), who reported that Cr was not detectable in the water-soluble, Exchangeable, and adsorbed forms. The results of Venkateswaran and colleagues could have resulted from the fact that the samples used were not contaminated with Cr. The results in this study suggest that Cr could be available for plants or biota uptake in the soils studied. Although it was found below the critical permissible level of 50 mg/kg recommended for Agricultural soil (MAFF, 1992; EC, 1986). Cr, therefore, poses no health risk to man in these soils. The fractionation scheme revealed that Zn occurred more than Co and Cr in both plantations studied.

Table 3. Forms and speciation of Zn, Co, and Cr in Rubber plantation ($mgkg^{-1}$).

Depth (cm)	H_2O sol.	Exch.	Ads.	Org. B.	CO_3 B.	Res.
		ZINC				
0-30	1.14	2.92	0.37	1.42	2.99	3.48
30-60	2.40	3.76	0.96	2.84	4.04	2.26
60-90	2.85	2.56	2.36	2.66	4.17	2.96
90-120	1.15	2.65	1.95	3.36	4.21	2.97
Mean	1.95	2.97	1.41	2.57	3.85	2.17
$LSD_{0.05}$	0.64	0.71	0.64	0.93	0.85	0.37
		COBALT				
0-30	0.08	0.04	0.06	0.12	0.13	0.11
30-60	0.07	0.04	0.07	0.14	0.12	0.12
60-90	0.08	0.05	0.07	0.11	0.11	0.11
90-120	0.08	0.06	0.07	0.11	0.11	0.11
Mean	0.07	0.05	0.06	0.12	0.12	0.11
$LSD_{0.05}$	Ns	ns	ns	ns	ns	ns
		CHROMIUM				
0-30	0.00	0.01	0.01	0.01	0.01	0.01
30-60	0.01	0.01	0.01	0.01	0.01	0.01
60-90	0.00	0.01	0.01	0.01	0.02	0.00
90-120	0.01	0.00	0.00	0.01	0.01	0.01
Mean	0.01	0.01	0.01	0.01	0.01	0.01
$LSD_{0.05}$	Ns	ns	ns	ns	ns	ns

H_2O sol.= water soluble, Exch. exchangeable, Ads.= adsorbed, Org.= organically, CO_3= carbonate, Res.= residual, B.= bound, $LSD_{0.05}$= least significant difference at 0.05 significant level, ns= not significant.

3.3. The relationship between forms of Zn, Co, and Cr.

A relationship between some soil properties and the forms of Zn and Co was obtained in this study via correlation (Tables 4 and 5). The main soil components influencing the forms and speciation of metal elements in soils are soil properties, and biological and pedogenic processes (Jiang *et al.,* 2001). A significant correlation between some soil properties and forms of Zn and Co in both plantations was obtained in this study. This is in line with reports of Gleyzes and his colleagues that reported forms of metals to be sensitive to pH changes (Gleyzes *et al.*, 2002). However, Cr did not correlate significantly with soil properties under Oil palm and Rubber plantations, which could be attributed to management practices resulting from avoidance of agriculture input that could lead to heavy metal contamination amongst others in both plantations.

Table 5. Relationship between Zn, Co, and Cr forms and some soil properties in Rubber plantation.

Soil properties	H_2O sol	Exch.	Org. B	CO_3 B.	Res.
		ZINC			
Sand	0.147	-0.222	0.069	-0.350	0.988*
Silt	0.373	0.018	0.240	-0.232	0.945*
Clay	-0.291	0.072	-0.178	-0.278	-0.967*
pH	0.396	0.030	0.098	-0.383	0.963*
ECEC	0.345	-0.017	0.186	-0.282	0.961*
		COBALT			
Sand	-0.942*	-0.793	-0.942*	-0.030	-0.425
pH	-0.989*	-0.741	-0.989*	0.104	-0.647
OC	-0.975*	-0.776	-0.975*	0.052	-0.554
Av. P	-0.968*	-0.682	-0.968	-0.140	-0.461

*Correlation is significant at $P \leq .005$ significant level, H_2O sol.= water soluble, Exch. exchangeable, Org.= organically, CO_3= carbonate, Res.= residual, B.= bound, ECEC= effective cation exchange capacity, OC= organic carbon, Av. P= available phosphorus.

4.0 Conclusion

Zn forms were adequate and were not deficient confirming its ready availability for plant uptake in both plantations. Co was found mainly in the exchangeable and organically bound forms in the Oil palm plantation and organically bound and carbonate forms in the Rubber plantation. These forms indicate Co availability for plant uptake depending on management and soil factors over time. While forms of Cr were found in an amount that posed no health risk since they were below the permissible limit. The distributions of these metals studied in the various forms confirm their difference in mobility. The Zn, Co, and Cr content of the soils of both plantations are within tolerance level for agricultural production. The significant correlation obtained indicates a strong relationship between some soil properties and forms, speciation, and availability of Zn and Co. However, the status of these metals should be monitored to prevent toxicity shortly. Toxicity levels could be hazardous to humans who regularly consume products of these plantations.

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