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Effects of Copper Fungicides Spray on Nutrient Contents in Soils of Cocoa Growing Areas of Southwestern Nigeria

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Abstract

The present study aimed at evaluating the effects of copper fungicides spray on physical and chemical properties of soils of cocoa growing areas of southwestern Nigeria. Samples were collected from selected cocoa farms and adjacent plots across three states (9 samples from Osun State, 9 samples from Ondo State and 7 samples from Ekiti State), within rainforest zone of Nigeria. The physical and chemical properties of the soil samples were determined. Copper contents of the cocoa plantation soils were significantly higher (16.23 mg Cu/kg) than the adjacent plots (6.31 mg Cu/kg) indicating accumulation of Cu in the soil because of long-term Cu fungicides spray. Other chemical properties determined (pH, Zn, % organic matter, % total N, Ca, Mg and Na) also had higher values in cocoa plantations compared to adjacent plots. Significant decrease was observed in available P in soil samples from cocoa plantations (24.05 mg P/kg) when compared with adjacent plots (30.36 mg P/kg). Management practices like applications of K and P fertilizers are highly recommended for viable cocoa growth and optimum yield in the study areas. Reduction of canopy formed by cocoa trees will allow easy penetration of sunlight into cocoa plantation thereby increase the rate of organic matter decomposition.

Keywords: Copper, fungicide spray, cocoa farms, black pod disease.

Introduction

Cocoa is a crop of economic importance with more than 650,000 ha being cultivated in Nigeria (Sanusi and Oluyole 2005) thus making the country the fourth largest cocoa producer in the world (Aikpokpodion 2010). In Central and West African countries, cocoa is one of the most important cash crops. More than two million farmers grow cocoa on smallholdings in these regions resulting in approximately 70% of the world's cocoa (Lass 2004). However, black pod disease is a major constraint to profitable cocoa production due to the infections of the pods which in turn affect the quality of the beans within the pods (Flood et al. 2004). Similar observation was recorded among cocoa farmers in Ghana where the single most important fungal disease of cocoa in Ghana is *Phytophthora megakarya* black pod and some farmers have described it as a strange disease, apparently because of the extreme harmful and the heavy losses associated with the pathogen (Opoku et al. 2000). According to Evans (1998), *Phytophthora* pod rot or black pod disease causes the largest loss of cocoa production world-wide and has remained the major limiting factor of cocoa production in Nigeria. Guest (2007) observed that the disease probably causes more production losses globally than any other disease of cocoa with annual losses of up to 90% of pod production, depending on the environmental conditions (Nyassé et al. 1995, Bowers et al. 2001).

In Nigeria, cocoa farmers make use of copper-based fungicides which are believed to be the fastest and most reliable in controlling black pod disease. The use of Bordeaux mixture which is made by mixing copper sulfate and calcium hydroxide (hydrated lime) was popular among the farmers in Nigeria. Recently, the Cocoa Research Institute of Nigeria (CRIN) recommended Ridomil gold plus 66wp with active ingredient content: 6% metalaxyl-M and 60% copper (in form of cuprous oxide), which is widely adopted by all farmers in all cocoa producing states in Nigeria. The use of these chemicals has undoubtedly resulted in increased crop production; hence it has been popular among farmers because of its quick and relatively effective action. Notwithstanding, runoff from heavy rainfall, common in cocoa growing regions of West Africa, may lead to soil and water pollution.

Aikpokpodion (2010) reported that an average Nigerian cocoa farmer apply Cu-based fungicide at least eight times in a year thus leading to gradual accumulation of copper in the soil irrespective of the fungicides used. Fungicides are effective crop protection chemicals in modern agriculture. However, they can also exert toxic effects on non-target organisms, including soil-dwelling microbes. In a previous study, the tested fungicide inhibited the activity of dehydrogenases, catalase, urease, acid phosphatase and alkaline phosphatases (Jastrzębska and Kucharski 2007). Copper is not mobile in the soil thus accumulates in the surface horizon and affects the activities of soil microorganisms. The long term use of copper fungicides to treat the high incidence of *Phytophthora* pod rot and mirids in cocoa plantation has resulted to Cu accumulation in soil which affects the availability of some nutrients (Zn, Fe, and P) and some traces of toxic metals (Aikpokpodion 2010, Azeez et al. 2015). The buid-up of Cu in soils can lead to its undue absorption and translocation to various vegetative parts of the tree including the beans, which is the economic part of the crop. According to Toselli et al. (2009), accumulation of copper in Italian soils was due to repeated applications of fungicides to control fungal diseases of pears and grapes. A study conducted by Savithri et al. (2003) in India also revealed that high levels of Bordeaux mixture application resulted in significant accumulation of copper in surface and subsurface soils.

This further shows that horticultural operations with long history of copper fungicide applications often have significant accumulation of copper in surface horizons (Alva et al. 2000). There is increased awareness that toxic metals, present in soil apart from affecting the resource base also have negative consequences on human health and the environment (Ali et al. 2019, Selinus et al. 2005). Pollution of natural environment by heavy metals is a serious global problem because of hazardous effects of these elements in the soil and water bodies (Dalman et al. 2006). Little information is available on the extent to which Cu accumulation in soil affects the availability of other essential elements.

Therefore, this study was carried out to examine the effects of copper fungicide spray on nutrient contents in soils of cocoa growing areas of southwestern Nigeria.

Materials and Methods

Soil samples were collected randomly from three of the major cocoa producing states of southwestern Nigeria. The three states are Ondo (7°11' N– 7°12' N, 4°58' E–5°2' E), Osun (8°50' N–8°92' N, 03°21' E–03°42' E) and Ekiti (7°15' N–7°41' N, 5°8' E–5°20' E) . The three states fall within the rainforest zone and are the major cocoa producing areas in southwestern Nigeria. The mean annual temperature and rainfall in the sampling areas are 25.5–26.6 °C and 1500–2000 mm, respectively. The sampling sites (9 from Osun, 9 from Ondo and 7 from Ekiti States) were randomly selected across the three states as shown in Figure 1. In southwestern Nigeria, Ondo and Osun States are the two dominant producers of cocoa and that could explain higher sampling sites selected in those States. Composite samples (0–20 cm depth) were taken from twenty-five cocoa farms alongside their corresponding adjacent plots as controls. The choice of sampling depth (20 cm) was because Cu is relatively immobile in soil, thus, it accumulates on the surface horizon and rarely leaches to deeper soil layers. The soil samples were air dried, crushed and the soil particles less than 2 mm fraction were retained for laboratory analysis.

The particle size analysis was carried out using the hydrometer method by Bouyoucos (1962). Soil pH in 0.01 M $CaCl_2$ was determined using the soil–solution ratio 1:2 (Schofield and Taylor 1955). The soil organic matter content was determined using the chromic acid digestion method by Walkley and Black (1934) as reviewed by Allison (1965), while total nitrogen was determined using macro-Kjeldahl digestion and distillation procedure (Bremner and Mulvaney 1982). Exchangeable basic cations (Ca, Mg, K and Na) were extracted with 1 N NH_4OAc at pH 7 (Thomas 1982). The trace metals (Cu and Zn) were extracted with 0.1 N HCl (Wears and Sommer 1948). Potassium (K) and sodium (Na) concentrations were determined by flame photometry (Corning EEL model 100 flame photometer), while Ca, Mg, Cu and Zn were determined by Atomic Absorption Spectrophotometry (AAS Hitachi model 207). Available phosphorus was determined by Bray1 method, as described by Bray and Kurtz (1945).

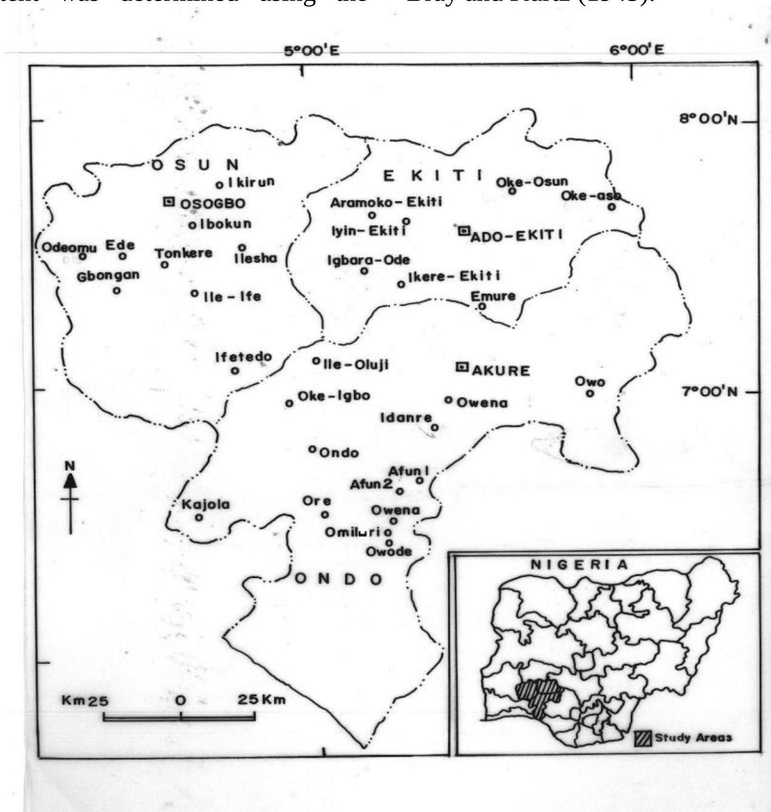

Figure 1: Map of study areas (Ondo, Ekiti and Osun States) showing sampling sites.

Statistical analysis

All analyses were carried out using SAS software version 9.4 (SAS Institute 2013). Data generated were subjected to Analysis of Variance and differences in mean were separated using the Tukey's Honest Significant Difference (HSD) test at 95% confidence interval. Pearson correlation coefficients between pairs of variables were also performed.

Results and Discussion

The results of particle size analysis of soil samples collected at twenty five (25) sites from cocoa farms and their adjacent plots in all the three States are presented in Table 1. Generally, soil samples from all the three States under cocoa plantations and their corresponding adjacent plots ranged in texture from sandy loam to sandy clay loam. The soil textural classes in the study areas were found to be suitable for optimum cocoa production, as these soil textures will permit movement of water and nutrients in the soil. This is similar to previous work on cocoa growing soils of Boki, Cross River State in Nigeria, where textural classes of the study areas ranged between sandy loam to clay loam and found to be adequate for viable cocoa production (Kekong and Ndifon 2020).

Table 1: Particle size analyses of soils in Osun, Ondo and Ekiti States (%)

States	Locations	Cocoa soils				Adjacent plot			
		Sand	Silt	Clay	Textural Class	Sand	Silt	Clay	Textural Class
Ondo	Kajola	53	16	31	SCL	59	12	29	SCL
	Afun1	67	16	17	SL	71	14	15	SL
	Afun2	81	10	9	L S	63	16	21	SCL
	Omiluri	73	12	15	SL	63	16	21	SCL
	Idanre	65	12	23	SCL	66	7	27	SCL
	Akure	51	28	21	SCL	62	15	23	SCL
	Owena	73	10	17	SL	59	18	23	SCL
	Oke-igbo	67	10	23	SCL	81	8	11	L S
	Ore	69	16	15	SL	59	16	25	SCL
Ekiti	Oke-osun	59	24	17	SL	61	20	19	SL
	Aramoko	65	20	15	SL	78	11	11	SL
	Ikere	65	16	19	SL	67	14	19	SL
	Oke-aso	59	22	19	SL	53	24	23	SL
	Iyin	54	24	23	SCL	50	23	27	SCL
	Emure	36	37	27	Loam	42	29	29	CL
	Igbara-odo	53	18	29	SCL	43	16	41	Clay
Osun	T&RFOAU	73	7	20	SL	61	10	29	SCL
	Ilesha	75	7	18	SL	80	2	18	SL
	Ifetedo	71	5	24	SCL	69	6	25	SCL
	Osogbo	71	7	22	SCL	61	10	29	SCL
	Ikirun	67	6	27	SCL	61	10	29	SCL
	Gbongan	61	10	29	SCL	67	6	27	SCL
	Tonkere	57	6	37	SCL	65	6	29	SCL
	Odeomu	61	6	33	SCL	73	5	22	SCL
	Ede	67	6	27	SCL	65	8	27	SCL

SCL = Sandy Clay Loam, SL = Sandy Loam, LS = Loamy sand, CL = Clay Loam.

The results of the chemical properties of soil samples collected from the three States are presented in Tables 2, 3 and 4. The pH values of the soil samples from cocoa plantations and adjacent plots in all the three states ranged from 5.70 to 6.50 (Ondo); 6.20 to 6.80 and 6.00 to 6.80 (Ekiti), respectively, while 4.70–7.10 and 4.30–6.40 were observed in Osun States. According to Enwezor et al. (1988) in a review of soil and fertilizer use research in Nigeria, a good Nigerian cocoa soil should have a pH of 6.0. All the sampling sites in the three States fell within this pH except Ore, Ikirun, Gbongan, Tonkere, Odeomu and Ede. However, no significant ($p > 0.05$) difference was observed in soil pH of soil samples from cocoa plantations and adjacent plots (Table 5), though higher values were observed in soil samples from cocoa plantations over adjacent plots which could be attributed to impacts of fungicides spray in cocoa plantations.

The Cu contents of soil samples collected from the three States ranged between 5.13–46.19 mg/kg (cocoa plantation) and 0.65–31.51 mg/kg (adjacent plots) in Ondo States, 3.19–18.87 mg/kg (cocoa plantation) and 1.42–7.85 mg/kg (adjacent plots) in Ekiti States, while 1.21–14.05 mg/kg and 0.41–7.95 mg/kg were recorded for samples from cocoa plantation and adjacent plots, respectively in Osun State. Extractable copper content of most of the soil samples from cocoa plantations in Ekiti and Osun States were lower than the values obtained for most of the soil samples from Ondo States despite the use of copper-based fungicides by the farmers to control *Phytophthora* pod rot disease. The higher Cu contents recorded in Ondo State could be explained by higher frequency of Cu fungicide applications (Ondo often receives higher rainfall in southwest Nigeria) compared to Osun and Ekiti, as revealed by the farmers in the study areas during farmers' interviews. However, significant increases ($p < 0.05$) in Cu contents of soil samples from cocoa plantations compared to adjacent plots were noticed in all the sampling sites except Odeomu and Owena where slight decrease was recorded thus confirming report from previous work done. Aikpokpodion (2010) reported that soil samples collected from cocoa plantations which had received applications of copper-based fungicides over the years in Ondo State were reported contaminated with copper, which had led to decrease in soil fertility as most of the soils in the study areas were deficient in soil available P and Mg contents.

The Zn contents in cocoa plantations and adjacent plots respectively ranged between 4.74–28.40 mg/kg and 7.14–22.99 mg/kg (Ondo), 5.43–18.14 mg/kg and 2.77–27.92 mg/kg (Ekiti) and 0.04–22.77 mg/kg and 0.03-16.18 mg/kg (Osun). It was also observed that no significant ($p > 0.05$) difference was found in Zn contents of soil samples from cocoa plantations and adjacent plots (Table 5). Significant decrease was observed in Zn contents for samples from cocoa plantations. Presence of humic substances from decomposition of leaf litters in cocoa plantations played significant roles with regard to nutrient availability, for instance, Zn contents.

Available P contents of soil samples across the three States ranged between 13.92–26.18 mg/kg (cocoa) and 11.08–53.54 mg/kg (adjacent) in Ondo States, 11.56–35.61 mg/kg (cocoa) and 19.10–44.10 mg/kg (adjacent) in Ekiti States, while soil samples from Osun States ranged between 11.56–48.35 mg/kg and 13.92–55.90 mg/kg for cocoa and adjacent plots, respectively. The available P contents of soil samples from adjacent plots were significantly ($p < 0.05$) higher than the contents in soil samples in cocoa plantations (Table 5). This might be due to the reasons advanced by Caudhuri (1964) and William (1951) that increasing base saturation of the soils with lime-containing fungicide residues encourage the fixation or immobilization of available P. Ogunlade et al. (2006) reported that leaf litter fall in cocoa plantation was not sufficient to supply the P required for optimal yields. This could be attributed to the complexation of humic substances with P in cocoa soil which resulted in reducing the availability of P in soil. The supply of P fertilizers may therefore be necessary to achieve good cocoa growth in the soil.

The calcium contents of soil samples from cocoa plantations and adjacent plots ranged between 6.82–12.45 cmol/kg and 6.15–11.81 cmol/kg in Ondo States, 7.23–12.15cmol/kg and 6.74–11.03 cmol/kg in Ekiti States. In Osun States, it ranged between 7.72–10.94 cmol/kg and 3.91–10.73 cmol/kg for cocoa plantations and adjacent plots respectively. The Ca contents in all the soil samples from cocoa plantations in the study areas were higher than critical values as reported by Wessel (1971) that when the exchangeable soils Ca is lower than 5 meq/100g soil, deficiency of the element is indicated. The results showed that the Ca contents were adequate for ideal cocoa productions in the study areas. No significant

($p > 0.05$) difference was observed between cocoa plantations and adjacent plots (Table 5), though, the Ca contents of most of soil samples in cocoa plantations were slightly higher than in the adjacent plots.

The magnesium contents in soil in Ondo State ranged between 1.73–3.40 cmol/kg and 1.38–2.87 cmol/kg for soil samples in cocoa plantations and adjacent plots, respectively. They ranged between 1.66–2.80 cmol/kg (cocoa plantaion) and 1.67–3.03 cmol/kg (adjacent plot) in Ekiti State and 0.71–2.85 cmol/kg and 1.09–2.53 cmol/kg for cocoa plantations and adjacent plots, respectively in Osun State. Most of the soil samples in cocoa plantations and adjacent plots had Mg values above the critical value of 2.0 cmol/kg; though no significant ($p > 0.05$) difference was observed between cocoa plantations and adjacent plots (Table 5). Magnesium contents for most of the samples in cocoa plantations were slightly higher than adjacent plots. The slight differences recorded may be attributed to presence of high leaf litter accumulation in cocoa plantations occasioned by Cu fungicide spray on cocoa pods.

The exchangeable potassium contents in Ondo State ranged between 0.07–0.30 cmol/kg (cocoa plantation) and 0.06–0.41 cmol/kg (adjacent plot). In Ekiti and Osun States, the K contents ranged between 0.07–0.40 cmol/kg (cocoa) and 0.11–0.63 cmol/kg (adjacent); and 0.06–0.34 cmol/kg (cocoa plantation) and 0.08–0.53 cmol/kg (adjacent plots), respectively. The K contents showed no significant difference ($p > 0.05$) between the cocoa plantations and adjacent plots (Table 5). The K contents in soil samples under cocoa plantations were below the critical value (0.30 cmol/kg) similar to observation in adjacent plots, but the K contents of soil samples from adjacent plots were higher for almost all the sampled sites. The K fertilizer may therefore be needed for optimum cocoa production.

Sodium concentrations ranged between 0.15–0.20 cmol/kg (cocoa plantations) and 0.13–0.19 cmol/kg (adjacent plots) in Ondo State, 0.15–0.21 cmol/kg (cocoa plantation) and 0.02–0.21 cmol/kg (adjacent plots) in Ekiti State, while ranges of 0.17–0.21 cmol/kg and 0.02–0.20 cmol/kg were observed in Osun State in cocoa plantations and adjacent plots, respectively. No significant ($p > 0.05$) difference in Na contents was observed between cocoa plantations and adjacent plots (Table 5). The concentrations of these exchangeable cations (Ca, Mg, K and Na) were adequate for normal cocoa production though no significant difference was observed in cocoa plantations over adjacent plots across the three States. Generally, the concentrations of exchangeable cations were slightly higher in cocoa plantation than adjacent plot except K. Therefore, the annual Cu fungicide application on cocoa pods had no significant impact on exchangeable cations in cocoa plantations.

Table 2: Chemical properties of the soil samples from cocoa plantation and adjacent farms in Ondo State

Locations	Cocoa soils										Adjacent plots									
	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn
			cmol/kg				%		mg/kg				cmol/kg			%			mg/kg	
Kajola	6.40	12.45	3.40	0.24	0.20	3.69	0.74	17.22	40.14	12.77	6.00	11.81	2.87	0.29	0.15	2.95	0.67	17.22	31.29	10.72
Afun1	6.20	9.95	2.59	0.29	0.19	3.56	0.63	22.41	46.14	28.40	6.10	7.55	1.68	0.06	0.13	1.81	0.35	31.84	2.86	8.62
Afun2	6.40	8.44	2.75	0.30	0.17	2.82	0.88	17.69	43.13	12.80	6.50	6.28	2.42	0.30	0.19	2.41	0.67	29.01	11.76	20.56
Omiluri	6.50	7.63	2.04	0.13	0.17	2.35	0.70	26.18	46.19	9.47	6.50	8.08	2.26	0.21	0.18	3.82	0.63	24.06	31.51	22.99
Idanre	6.50	6.82	2.03	0.21	0.17	2.95	0.91	18.16	38.45	7.14	6.10	9.07	2.24	0.38	0.18	2.75	0.60	11.08	3.22	7.14
Akure	6.40	8.78	2.20	0.11	0.17	1.88	0.91	13.92	26.82	6.31	6.40	8.31	2.49	0.19	0.18	4.02	0.74	24.81	2.15	8.51
Owena	6.30	7.66	1.73	0.22	0.15	1.95	0.60	18.63	5.13	15.68	6.40	7.58	2.06	0.41	0.18	3.09	1.26	31.37	5.28	9.99
Oke-Igbo	6.00	9.01	1.91	0.13	0.17	3.49	1.02	24.76	21.07	4.74	6.10	6.15	1.38	0.22	0.16	2.21	0.74	37.03	0.65	10.06
Ore	5.70	8.82	2.33	0.07	0.19	4.76	1.44	22.88	12.13	16.35	5.70	7.78	2.12	0.09	0.19	2.15	0.91	53.54	4.96	11.02
Mean	6.27	8.84	2.33	0.19	0.18	3.05	0.87	20.21	31.02	12.63	6.20	8.07	2.17	0.24	0.17	2.80	0.73	28.88	10.41	12.18

Table 3: Chemical properties of soil samples from cocoa plantation and adjacent farms from Ekiti State

Locations	Cocoa soils										Adjacent plots									
	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn
			cmol/kg				%		mg/kg				cmol/kg			%			mg/kg	
Oke-Osun	6.40	9.02	2.33	0.26	0.16	3.42	0.63	35.61	6.35	10.99	6.30	8.40	2.40	0.24	0.17	3.49	0.60	44.10	1.42	10.46
Aramoko	6.80	7.23	2.43	0.26	0.18	2.75	0.91	16.27	3.30	11.81	6.40	6.74	1.91	0.11	0.16	2.08	0.56	29.95	1.75	6.51
Ikere	6.30	8.46	1.66	0.40	0.16	2.82	0.70	21.93	3.19	6.11	6.40	8.64	2.01	0.20	0.18	2.55	0.56	28.07	2.61	2.77
Oke-Aso	6.30	8.90	2.37	0.32	0.17	3.69	0.46	11.56	18.87	5.43	6.00	11.03	1.67	0.33	0.18	4.83	0.81	25.71	6.10	9.03
Iyin-Ekiti	6.30	10.33	2.47	0.29	0.15	3.69	1.05	25.71	7.68	12.69	6.80	9.62	2.69	0.09	0.02	2.88	0.49	30.90	7.54	27.92
Emure	6.50	12.15	3.27	0.07	0.21	6.44	1.30	22.41	7.40	18.14	6.70	10.99	3.03	0.63	0.02	5.77	1.30	21.46	7.30	13.61
Igbara-Odo	6.20	10.95	2.80	0.07	0.20	4.23	1.40	23.82	5.69	11.01	6.40	8.25	2.22	0.59	0.21	2.01	1.05	19.10	7.85	4.23
Mean	6.40	9.58	2.48	0.24	0.18	3.86	0.92	22.47	7.50	10.88	6.43	9.10	2.28	0.31	0.13	3.37	0.77	28.47	4.94	10.65

Table 4: Chemical properties of soil samples from cocoa plantation and adjacent farms from Osun State

Locations	Cocoa soils										Adjacent plots									
	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn	pH	Ca	Mg	K	Na	OM	N	Av. P	Cu	Zn
			cmol/ kg				%		mg/kg				cmol/kg				%		mg/kg	
T$R OAU	6.90	10.53	2.33	0.26	0.21	4.49	1.19	14.86	8.90	22.77	6.40	9.61	2.11	0.13	0.20	3.96	0.63	36.56	1.70	16.18
Ilesha	6.60	10.94	2.85	0.34	0.20	4.49	1.12	11.56	10.62	12.94	6.20	7.93	1.44	0.22	0.15	2.35	0.60	48.82	4.81	9.09
Ifetedo	6.40	9.15	1.43	0.12	0.20	1.88	0.67	21.46	12.33	1.73	5.60	8.86	1.21	0.08	0.20	2.15	0.88	22.88	5.38	1.16
Osogbo	7.10	10.86	2.81	0.06	0.19	4.09	0.74	32.31	14.05	21.54	6.10	10.73	2.36	0.24	0.02	4.23	0.63	22.88	1.47	15.99
Ikirun	5.20	7.81	0.71	0.07	0.19	2.08	0.60	32.78	7.94	0.37	6.00	9.90	2.53	0.24	0.20	4.23	0.60	13.92	1.69	0.35
Gbongan	5.60	9.46	1.41	0.08	0.17	1.81	0.74	21.93	6.68	1.70	5.10	8.34	1.26	0.10	0.20	3.02	0.67	31.37	0.52	1.28
Tonkere	4.70	7.92	1.32	0.10	0.19	1.95	0.63	48.35	5.62	3.76	5.40	8.51	1.15	0.53	0.20	3.49	0.49	24.29	0.41	3.29
Odeomu	4.90	8.74	1.13	0.21	0.19	2.95	0.35	32.78	1.21	0.25	4.30	3.91	1.09	0.06	0.17	2.62	0.56	43.16	7.95	0.03
Ede	5.00	7.72	0.78	0.06	0.21	2.68	0.63	45.99	6.71	0.04	6.00	10.00	2.50	0.27	0.21	3.22	0.88	55.90	5.45	4.42
Mean	5.82	9.24	1.64	0.14	0.19	2.94	0.74	29.11	8.23	7.23	5.68	8.64	1.74	0.21	0.17	3.25	0.66	33.31	3.26	5.75

Table 5: Effect of copper residues on Cocoa plantation and adjacent sites in all the three States

Sites	pH	Mg	Ca	K	Na	%OM	% Total N	Avail. P	Cu	Zn
Cocoa	6.14a	2.12a	9.19a	0.19a	0.18a	3.24a	0.83a	24.05b	16.23a	10.19a
Adjacent	6.07a	2.04a	8.56a	0.25a	0.16a	3.12a	0.72a	30.36a	6.31b	9.43a
Means	6.11	2.08	8.88	0.22	0.17	3.18	0.77	27.20	11.27	9.82
P	NS	NS	NS	NS	NS	NS	NS	*	*	NS

NS= Not significant at 5% level of probability, * = significant at 5% level of probability. Means with the same letter within the same column are not significantly different while means with different letters within the same column are significantly different.

The organic matter contents ranged between 1.88–4.76% (cocoa plantations) and 1.81–4.02% (adjacent plots) for soil samples in Ondo State, 2.75–6.44% (cocoa plantations) and 2.01–5.77% (adjacent plots) in Ekiti State, while a range of 1.81–4.49% (cocoa plantations) and 2.15–4.23% (adjacent plots) was observed in Osun State. No significant ($p > 0.05$) difference was observed in cocoa plantations and adjacent plots (Table 5). This can be attributed to the high humidity in cocoa plantations due to the canopy formed by cacao trees which reduces the rate of organic matter decomposition.

Total nitrogen contents ranged between 0.60–1.44% and 0.35–1.26% for samples under cocoa plantations and adjacent plots, respectively. In Ekiti State, the total N contents ranged between 0.46–1.40% (cocoa plantations) and 0.49–1.30 % (adjacent plots), while ranges of 0.35–1.19% (cocoa plantations) and 0.49–0.88% (adjacent plots) were observed for samples in Osun State. In all the sampling sites across the three States, no significant ($p > 0.05$) effects were observed in cocoa plantations over adjacent plots (Table 5).

Correlation of added Cu from the fungicide spray on soil properties

The results showing the effects of Cu fungicides residues on physical and chemical properties of cocoa and adjacent plot are presented in Tables 6 and 7. Positive correlation existed between soil Cu contents and percentage sand and silt (Table 6), while negative correlation was observed in adjacent plots (Table 7) though not significant. A negative correlation existed between soil Cu contents and % clay for all soil samples in cocoa plantations, but this was not significant (Table 6), while Table 7 shows a positive correlation in adjacent plots in all the sampled sites across the three States.

However, Koka et al. (2011) reported a significant negative moderate correlation between water soluble Cu and clay in cocoa soil in Ghana. This suggests that more soil Cu would be adsorbed on the clay while persist for long period of time in the soil. The available copper was positively correlated with pH; though not significant ($p > 0.05$) with r values of 0.292 (cocoa soil) and 0.131 (adjacent plots). In all the twenty-five farms visited, more than 80% of the farms had higher pH (Tables 2, 3 and 4) probably due to the presence of OH group in the fungicides. A significant effect of pH on available Cu was reported by Li and Mahler (1992). The H^+ from humic substances (HS) reduces the amount of Cu available to crops. Copper concentrations in soil solution decrease as the soil pH increases and this behaviour was explained based on stronger Cu adsorption at higher pH (Lindsay 1972, Cui et al. 2016). Negative correlation was observed between Cu and P in the soil samples from cocoa and adjacent farms though not significant. Copper and phosphorus have been found to have antagonistic effects on each other (Azeez et al. 2015). Copper as a divalent element forms complex with phosphate ion thus reducing its availability. This implies that accumulation of Cu in soils of the study areas because of Cu fungicides spray on cocoa pods may have had negative effects on P, which may be attributed to the presence of humic substances that tend to reduce the P contents as Cu accumulates in the soil and this agrees with earlier observation.

There was a negative correlation between soil Cu and organic matter contents in cocoa soil, while a positive correlation was observed in adjacent plots; though not significant. This can also be linked to the presence of humic substances in organic matter which has strong affinity for divalent elements like Cu, and therefore reduces the impacts of copper fungicide spray in the soil. The negative relationships indicate that the availability of Cu decreased with increase in organic matter accumulation. A negative correlation has been reported between organic carbon and extractable Cu where soil organic matter was above 6.0% (Sillampaa 1982). Tisdale et al. (2003) had also reported that micronutrients form stable complexes with soil organic matter. Organic matter binds Cu more tightly than any other micronutrients because Cu forms stable complexes with phenolic and carboxyl groups of soil organic matter (Ogunleye et al. 2020). They further reported that humic and fulvic acids as two ligands for copper (II) binding with the fulvic acids being the more soluble than humic acids with simple aliphatic acids, amino acids, and aromatic acids as chelating agents for copper (II). In fact, copper deficiency has been associated with organic soils where OM accumulation was very high. The results from several studies showed that copper preferentially associates with soil organic matter (Liu and Wang 2004, Boudesocque et al. 2007, Jacobson et al. 2007, Strawn and Baker 2008). In the Liu and Wang (2004) speciation study, 50% of copper in the contaminated soil was associated with organic matter, 28% formed $CuCO_3$, 11% Cu_2O, and 11% CuO. Boudescque et al. (2007) reported that the copper associated with soil organic matter is formed via inner sphere complexes, which occur when copper ions adsorb directly to the organic particles in the soil. Because of the strength of such complexes, organic matter plays an important role in determining the degree of mobility and bioavailability of copper (Boudesocque et al. 2007). Total nitrogen contents correlated negatively with soil Cu contents, but the relationship was not significant ($p > 0.05$) and less pronounced than that with phosphorus.

A positive correlation existed between Cu and Zn in all the sampled sites in the three states (Table 6) but only significant in adjacent plots (Table 7). Significant increase in Cu application may induce availability of Zn in cocoa plantations. Zinc being a divalent element has strong affinity for humic substances in the soil; therefore, as Cu forms complexes with humic substances, the Zn content is also reduced. Copper was positively correlated with Mg in cocoa plantations and adjacent plots; though not significant. Negative correlation existed between available Cu and exchangeable Ca, though not significant ($r = -0.008$), while positive correlation was observed in adjacent plots ($r = 0.173$). The negative r value is tending towards zero which implies that high accumulation of Cu because of Cu fungicide spray may lead to availability of Ca contents in soils. Positive correlation existed between available Cu and exchangeable K in cocoa plantations and adjacent plots, though not significant. This suggests that accumulation of Cu in the study areas may affect the concentrations of K in the soil as the mean values were lower than critical value of 0.39 cmol/kg for soils in cocoa plantations. Copper correlated negatively with Na in both cocoa plantations and adjacent plots. Accumulation of Cu would lead to decrease in Na contents in soil. This is expected as mean pH in cocoa plantations and adjacent plots were below 7.00 and Na generally becomes more available when the pH is above 7 (alkaline). It can be inferred from the results in the study areas that exchangeable Na cannot pose any danger to the plants and soil microorganisms.

Table 6: Correlation matrix of cocoa plantation

	Sand	Silt	Clay	pH	Mg	Ca	K	Na	OM	N	P	Cu	Zn
Sand													
Silt	-0.740**												
Clay	-0.549**	-0.156											
pH	0.117	0.341	-.596**										
Mg	-0.243	0.547**	-0.323	0.720**									
Ca	-0.416*	0.309	0.229	0.340	0.680**								
K	0.231	0.099	-0.456*	0.362	0.276	0.007							
Na	-0.105	-0.198	0.389	-0.130	0.094	0.443*	-0.377						
OM	-0.321	0.444*	-0.080	0.360	0.690**	0.692**	0.056	0.424*					
N	-0.176	0.341	-0.162	0.343	0.529**	0.412*	-0.181	0.267	0.644**				
P	-0.090	-0.294	0.500*	-0.678**	-0.538**	-0.235	-0.468*	0.150	-0.215	-0.328			
Cu	0.209	0.026	-0.343	0.292	0.358	-0.008	0.146	-0.096	-0.066	-0.068	-0.304		
Zn	0.081	0.266	-0.448*	0.612**	0.717**	0.478*	0.232	0.128	0.593**	0.408*	-0.327	0.270	

**= Correlation is significant at 0.01 level of probability; *= Correlation is significant at 0.05 level of probability.

Table 7: Correlation matrix of adjacent plots

	Sand	Silt	Clay	pH	Mg	Ca	K	Na	OM	N	P	Cu	Zn
Sand													
Silt	-0.748**												
Clay	-0.737**	0.103											
pH	-0.368	0.582**	-0.040										
Mg	-0.627**	0.598**	0.331	0.678**									
Ca	-0.561**	0.326	0.509**	0.368	0.550**								
K	-0.557**	0.331	0.498*	0.285	0.303	0.327							
Na	0.294	-0.425*	-0.008	-0.333	-0.391	-0.315	-0.062						
OM	-0.521**	0.459*	0.314	0.193	0.419*	0.595**	0.400*	-0.335*					
N	-0.521**	0.417*	0.356	0.195	0.265	0.192	0.554**	-0.017	0.287				
P	0.340	-0.153	-0.353	-0.211	-0.238	-0.371	-0.399*	0.133	-0.278	-0.009			
Cu	-0.206	0.182	0.123	0.131	0.347	0.173	0.074	-0.023	0.044	0.050	-0.211		
Zn	-0.314	0.511**	-0.050	0.623**	0.502*	0.165	-0.030	-0.537**	0.197	-0.044	0.007	0.401*	

** = Correlation is significant at 0.01 level of probability; *= Correlation is significant at 0.05 level of probability.

Conclusion

The effects of copper fungicides spray on physical and chemical properties of soils of cocoa growing areas of southwestern Nigeria were determined in the laboratory. The results from the 25 cocoa plantations and their adjacent plots in the study States (Ondo, Ekiti and Osun States) ranged in texture from sandy loam to sandy clay loam. The mean Cu contents of the cocoa plantation soils were significantly higher than the adjacent plots which clearly indicated the accumulation of Cu in the soil due to Cu fungicides spray on cocoa pods. Most of the other chemical properties determined were higher in cocoa soil than adjacent plots except available P and exchangeable K. The Cu contents of the soil showed positive correlations with % sand, % silt, soil pH, Zn, Mg and exchangeable K and negatively correlated with % clay, available P, organic matter, total N, Ca and Na. Management practices such as applications of K and P fertilizers are highly recommended for good cocoa growth and optimum yields in the study areas. Reduction of canopy formed by cocoa trees will allow easy penetration of sunlight into cocoa plantations thereby increase the rate of organic matter decomposition.

Declaration of interest

The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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