

Effects of fungicide residues on the physico-chemical characteristics of soils of a major cocoa-producing area of Nigeria

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Abstract

The effects of copper-based fungicide residues on some physico-chemical properties of soils in some cocoa-producing areas of Nigeria were investigated. The results show that the fungicide residues cause significant increases in the soil pH, organic matter and copper concentrations while lowering the concentrations of inorganic nitrogen, available phosphorus, exchangeable potassium and sodium. Slight increases were also observed for the cation exchange capacity (CEC) and exchangeable Ca^{2+} and Mg^{2+} but there are no significant changes in the Zn, Fe and Mn concentrations with fungicide treatment. It is concluded that the copper-based fungicide residues predispose the soils to nitrogen, phosphorus and potassium (N, P and K) deficiencies and perhaps copper toxicity if not properly managed.

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1. Introduction

Cocoa farming is very common in the South-western part of Nigeria. In addition to supplying much-needed raw materials for some local industries, its export is an important source of foreign exchange earnings for the country. The soils on which most of the cocoa are grown in the country have homogeneous depth profile derived from metamorphic and igneous rocks (Egbe et al., 1989; Wessel, 1966).

The major problem encountered by cocoa farmers is the occurrence of “Black-pod” disease on the pods (seeds) caused by a fungus called *Phytophthora palmivora*. The disease can cause as much as 40%–80% loss in production, depending on environmental factors such as rainfall and relative humidity (Opeke, 1982).

Copper fungicides in form of hydrated $\text{CuSO}_4/\text{Ca}(\text{OH})_2$ have been the major fungicides used for the treatment of this disease in most Nigerian cocoa plantations over the years (Maddison and Bickness, 1979; Opeke, 1982). This would have led to considerable accumulation of copper-fungicide residues in the soils of these cocoa plantations, as have been reported in similar situations in the literature (McLaughlin et al., 2000; Merry et al., 1983).

In this paper, we report on the effects of the copper-fungicide residues on the soil nutrients and other physico-chemical properties of the soils in one of the major cocoa-producing areas of Nigeria.

2. Materials and methods

2.1. Sample collection and preparation

Soil samples were collected randomly from two of the major cocoa-producing areas of Ondo State of

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Nigeria. A total of 30 composite samples were taken at depths of 0–15, 15–30, and 30–60 cm from 10 cocoa plantations where copper-based fungicides had been applied. Fifteen composite samples were similarly taken from 5 cocoa plantations with no prior fungicide application, and another 15 from 5 fallow or uncultivated lands with no prior fungicide application.

The soil samples were crushed to pass through 2 mm sieve for all analyses except organic carbon determination for which the samples were ground to pass through 0.5 mm sieve.

2.2. Physico-chemical analysis

The samples were leached with 1 M ammonium acetate. The leachate was used for exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) determination (Schollenberger and Simon, 1945; Sharman et al., 1942) while the residual soil was extracted with 1 M KCl for the determination of the cation exchange capacity (Udo and Uzu, 1972). The trace metals (Cu, Zn, Fe, Mn) were extracted with 0.05 M EDTA (Jackson et al., 1986). Potassium and sodium concentrations were determined by flame photometry (Corning EEL model 100 Flame photometer) while other elements, viz: Ca, Mg, Fe, Cu, Zn were determined by atomic absorption spectrometry (AAS Hitachi model 207). Cation exchange capacity (CEC) was determined by Kjeldahl distillation and titrimetric procedures (Jackson et al., 1986).

Organic matter was determined by dichromate oxidation and titrimetric method (Walkey and Black, 1934) while available phosphorus was determined by extraction with Bray P₁ (Bray and Kurtz, 1945) and vanadomolybdate spectrometric methods. Organic nitrogen

was determined by extraction with 2 M KCl followed by treatment with 50% NaOH solution, Kjeldahl distillation and titrimetric method. pH was determined with a pH meter with glass electrodes in 1:2.5 soil–water suspension. In all cases, blank determination was carried out to ascertain the purity of the chemicals and materials used. All the reagents used were of analytical grade.

3. Results and discussion

The results of the pH, organic matter, inorganic nitrogen and available phosphorus concentrations of soils at the 2 sites are presented in Table 1. The pH of the soils are generally acidic for both fungicide-treated and regular soils. This is normal for this type of humid soils which are subject to leaching by bases (Alloway, 1996, Ch. 14). The pH of soils in the fungicide-treated areas are generally higher than those of the untreated areas at both locations and at all sampling depths. This is due to the presence of calcium hydroxide in the fungicides (hydrated $\text{CuSO}_4/\text{Ca}(\text{OH})_2$). Since pollutant bio-availability depends on soil pH among other soil physico-chemical conditions, the significant variation in pH values of soils of the treated and untreated areas would be expected to alter significantly the bio-availability of pollutants in the fungicide-treated areas.

The inorganic matter contents of the surface soils of the fungicide-treated areas are $4.12 \pm 0.69\%$ and $4.69 \pm 0.06\%$ at sites 1 and 2, respectively, and they decrease progressively with soil depth, being due to phytocycling. They are higher than in the soils of the untreated ($3.14 \pm 0.46\%$ at site 1 and $3.23 \pm 0.14\%$ at site 2) and other control soils, particularly at the sur-

Table 1
Soil pH, organic matter (O. M) content, available P and inorganic N contents of the soils

Depth (cm)	Trt	pH		Organic matter (%)		Inorganic N (%)		Available P (ppm)	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
0–15	A	6.8 ± 0.3	6.5 ± 0.2	4.12 ± 0.69	4.69 ± 0.06	0.24 ± 0.06	0.25 ± 0.02	14.50 ± 3.54	15.38 ± 0.53
	B	6.3 ± 0.4	6.0 ± 0.4	3.14 ± 0.46	3.23 ± 0.14	0.29 ± 0.04	0.34 ± 0.01	18.83 ± 3.50	16.80 ± 3.03
	C	6.0 ± 0.5	6.2 ± 0.01	2.14 ± 0.06	2.69 ± 0.09	0.26 ± 0.03	0.26 ± 0.02	12.38 ± 2.33	16.50 ± 0.001
15–30	A	6.4 ± 0.6	6.2 ± 0.4	2.25 ± 0.10	2.20 ± 0.23	0.08 ± 0.01	0.06 ± 0.02	11.25 ± 4.24	8.62 ± 2.15
	B	5.7 ± 0.1	5.7 ± 0.1	2.19 ± 0.03	1.81 ± 0.03	0.12 ± 0.02	0.07 ± 0.01	14.50 ± 4.70	13.96 ± 0.97
	C	5.4 ± 0.1	5.9 ± 0.4	1.82 ± 0.10	1.52 ± 0.03	0.09 ± 0.01	0.12 ± 0.02	9.50 ± 0.33	15.38 ± 0.53
30–60	A	6.0 ± 0.7	5.5 ± 0.6	1.95 ± 0.10	1.17 ± 0.11	0.06 ± 0.01	0.05 ± 0.02	8.70 ± 0.27	5.63 ± 0.424
	B	4.8 ± 0.2	5.4 ± 0.6	1.55 ± 0.09	1.14 ± 0.03	0.07 ± 0.01	0.06 ± 0.01	12.63 ± 1.76	10.96 ± 2.15
	C	4.2 ± 0.001	5.6 ± 0.4	1.32 ± 0.02	1.03 ± 0.20	0.08 ± 0.02	0.10 ± 0.01	7.88 ± 0.53	12.00 ± 3.18

A = cocoa soil treated with copper-based fungicides.

B = untreated cocoa soil.

C = soil of uncultivated or fallow land.

Trt = treatment.

Table 2

Exchangeable cation concentrations and cation exchange capacity (cmol. kg⁻¹) of the soils

Depth (cm)	Trt	Ca ²⁺		Mg ²⁺		K ⁺		Na ⁺		CEC	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
0–15	A	11.03 ± 1.33	11.55 ± 1.21	3.17 ± 0.29	3.24 ± 0.05	0.29 ± 0.05	0.18 ± 0.02	0.18 ± 0.02	0.17 ± 0.03	19.80 ± 0.42	19.20 ± 0.33
	B	10.25 ± 1.23	10.17 ± 0.89	3.02 ± 0.40	3.07 ± 0.44	0.30 ± 0.03	0.20 ± 0.05	0.19 ± 0.03	0.19 ± 0.05	17.90 ± 0.43	17.90 ± 0.36
	C	10.48 ± 0.90	11.81 ± 0.81	2.99 ± 0.25	3.03 ± 0.51	0.30 ± 0.06	0.19 ± 0.02	0.18 ± 0.01	0.20 ± 0.01	18.40 ± 0.31	18.70 ± 0.34
15–30	A	9.21 ± 0.72	10.08 ± 1.18	2.71 ± 0.19	3.03 ± 0.44	0.24 ± 0.03	0.15 ± 0.04	0.15 ± 0.03	0.12 ± 0.02	15.70 ± 0.24	17.60 ± 0.42
	B	9.08 ± 1.67	9.40 ± 2.12	2.51 ± 0.66	2.63 ± 0.09	0.27 ± 0.05	0.17 ± 0.02	0.16 ± 0.04	0.17 ± 0.02	14.90 ± 0.03	14.80 ± 0.57
	C	8.99 ± 0.43	10.44 ± 1.41	2.34 ± 0.42	2.37 ± 0.75	0.28 ± 0.02	0.17 ± 0.02	0.16 ± 0.01	0.13 ± 0.02	15.30 ± 0.22	16.00 ± 0.05
30–60	A	8.26 ± 0.90	8.12 ± 0.90	2.04 ± 0.56	2.32 ± 0.51	0.21 ± 0.04	0.11 ± 0.05	0.12 ± 0.02	0.11 ± 0.01	12.70 ± 0.16	11.90 ± 0.37
	B	7.83 ± 1.69	7.87 ± 1.13	1.91 ± 0.77	2.19 ± 0.02	0.22 ± 0.001	0.14 ± 0.03	0.13 ± 0.02	0.12 ± 0.02	11.40 ± 0.62	10.80 ± 0.30
	C	7.90 ± 1.21	7.97 ± 0.88	1.55 ± 0.15	1.68 ± 0.23	0.23 ± 0.01	0.15 ± 0.03	0.12 ± 0.02	0.12 ± 0.02	12.30 ± 0.35	10.90 ± 0.29

A = cocoa soil treated with copper-based fungicides.

B = untreated cocoa soil.

C = soil of uncultivated or fallow land.

Trt = treatment.

face. This increase in organic matter content with fungicide treatment is apparently due to the fungicide causing a decrease in the microbial population of the soil, consequently decreasing the degree of decomposition of the organic matter. Thus, the fungicides not only act on the fungi on the cocoa pods, but also on the host soils in a positive sense.

The inorganic nitrogen concentrations decrease slightly with fungicide treatment at both surface and sub-surface levels. This can be attributed to a reduction in the rate of ammonification of organic matter (Deshpande, 1976) and hence loss of ammonium nitrogen, by the Ca(OH)₂ component of the fungicide as well as the deleterious effect of the hydrated CuSO₄ component of the fungicide on the soil-nitrifying bacteria. Similarly, the available phosphorus contents of the soils decrease with fungicide application at both surface and sub-surface layers. This might be due to increasing base

saturation of the soils with lime-containing fungicide residues, probably encouraging fixation or immobilization of available phosphorus (Caudhuri, 1964; William, 1951).

The exchangeable cation concentrations and cation exchange capacity (CEC) of the soils are shown in Table 2. The cation exchange capacities increase significantly with fungicide treatment at all soil levels. This follows the pH pattern of the soils which is expected as cation exchange occurs where a higher concentration of cations is held in the zone of attraction of the negative charges on the soil solution (Alloway, 1996, Ch. 14). The CECs decrease significantly from the surface to sub-surface soils, for both fungicide-treated and untreated areas, following the pattern of decrease in organic matter contents down the soil profile which results in a high degree of unsaturated colloidal complex in the lower surface of the soils, and

Table 3

Extractable copper, zinc, iron and manganese content of the soils

Depth (cm)	Trt	Cu (Mg/kg)		Zn (Mg/kg)		Fe (Mg/kg)		Mn (Mg/kg)	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
0–15	A	7.68 ± 1.23	8.20 ± 1.84	6.20 ± 2.17	6.80 ± 0.99	5.46 ± 0.85	5.03 ± 0.70	6.25 ± 0.12	5.88 ± 0.28
	B	4.95 ± 0.49	4.32 ± 0.64	6.10 ± 0.07	7.50 ± 2.12	5.15 ± 0.48	5.15 ± 0.72	7.00 ± 0.08	6.50 ± 0.13
	C	4.50 ± 0.65	4.03 ± 1.07	5.80 ± 2.31	5.50 ± 0.28	4.71 ± 0.83	5.12 ± 0.78	6.13 ± 0.06	6.37 ± 0.14
15–30	A	7.39 ± 1.39	4.50 ± 1.82	5.20 ± 1.90	4.00 ± 2.08	4.01 ± 0.30	4.19 ± 0.93	3.13 ± 0.15	3.88 ± 0.15
	B	3.21 ± 0.08	3.45 ± 1.07	4.60 ± 1.20	6.50 ± 2.69	4.61 ± 0.04	4.61 ± 0.84	5.75 ± 0.28	4.25 ± 0.04
	C	2.58 ± 0.35	2.34 ± 0.82	4.30 ± 1.72	5.40 ± 0.21	3.68 ± 0.95	4.54 ± 1.07	4.50 ± 0.06	5.31 ± 0.23
30–60	A	7.10 ± 0.52	2.45 ± 0.77	3.70 ± 1.50	3.20 ± 2.03	2.48 ± 1.17	3.39 ± 0.36	3.00 ± 0.06	2.38 ± 0.05
	B	2.17 ± 0.08	2.09 ± 0.53	2.80 ± 2.55	3.30 ± 2.97	3.03 ± 1.29	3.58 ± 0.54	3.00 ± 0.10	3.63 ± 0.11
	C	2.05 ± 0.29	1.42 ± 0.08	2.30 ± 0.25	3.80 ± 1.34	0.29 ± 0.06	0.45 ± 0.64	3.50 ± 0.01	2.38 ± 0.28

A = cocoa soil treated with copper-based fungicides.

B = untreated cocoa soil.

C = soil of uncultivated or fallow land.

Trt = treatment.

hence low exchangeable sites (Devlesschauwer and Lai, 1981).

There are no significant differences in the exchangeable cation concentrations of the fungicide-treated and untreated soils, both Ca^{2+} and Mg^{2+} increasing slightly with treatment while K^+ and Na^+ decrease slightly with treatment.

Table 3 shows that extractable Cu concentration of the soils are significantly increased with fungicide treatment while the concentrations of the other extractable trace metals, Zn, Fe, and Mn do not change significantly with treatment. This is expected since the fungicide has a CuSO_4 component, but no Zn, Fe and Mn components. For site 1, there is not much change in extractable Cu concentration with depth of fungicide-treated soil, but there is significant drop in extractable Cu with depth at site 2 as expected. However, extractable Cu concentration decreases generally with depth at both sites for the control soils (B and C). For other metals viz: Zn, Fe and Mn, the extractable concentrations generally decrease from surface to sub-surface levels at both sites. So in general, extractable metal concentrations decrease with depths for both fungicide-treated and untreated soils.

4. Conclusion

It can be conveniently deduced that copper-based fungicide residues directly increase the pH and the organic matter contents of the soils and the resultant effects bring about variations in the concentrations and distribution of some major and trace elements in the soils.

The agronomic importance of this study is the implication that application of copper-based fungicide to cocoa plantations causes nutrient imbalance as a result of their effects on soil chemical equilibria. The copper-fungicide residues predispose the soils under cocoa plantations to nitrogen, phosphorus and potassium deficiency and increase copper concentration, perhaps to phytotoxic level, which may be reduced by the $\text{Ca}(\text{OH})_2$ component of the copper-fungicide residues. However, if the fungicide application is followed by successive application of N, P, K fertilizer, these nutrients could be replenished back to the soil. Other neg-

ative effects of the residues on the physico-chemical properties of the soil identified during the course of this study can be ameliorated by careful disposal of the fungicide waste (excess liquid or solid $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$).

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