

Full Length Research Paper

Intermittent leaching of copper from copper based fungicide through a saturated soil profile

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Copper is a micronutrient required for plant growth. However, it can have negative effect on plant growth if the concentration is too high. The aim of this study was to examine copper concentrations of leachate from soil columns treated with copper based fungicide. A 2 × 4 factorial arrangements consisting of two soil types (0 to 60 cm sample depth) and four rates of copper based fungicide concentrations (0, 1.88, 3.75 and 7.50 g/L) was used with three replications. The column leaching experiment was conducted by saturating the soil profile with water at 5 mm/h rate of water flow for 1 day. After saturation, the fungicides was applied and the soil columns kept completely saturated with water by maintaining ponding by continuously applying de-ionized water at a rate of 10 mm/h throughout the experimental period. The process was repeated three more times. Leachate samples were collected every 6 h for 7 days and analyzed for copper using Atomic Absorption Spectrophotometer. The results indicated that drainage time, soil type and fungicide concentrations significantly ($p < 0.01$) effected copper concentration in the leachate. Highest metal concentration in the leachate was obtained between 2.5 to 3.25 days. On the average, the concentration of copper in the leachate during the first fungicide application and leaching was 1.94 mg/L. This concentration reduced to about 1.12 mg/L during the second application. It was also observed during the experiment that the flow rate of water decreases during the leaching of the second fungicide application. The concentration then increases to 1.85 and 2.83 mg/L for the third and fourth applications, respectively. Repeated application of the metal through the fungicide leads to the accumulation of the metal in the soil.

Key words: Leaching, copper, saturated soil profile.

INTRODUCTION

Pesticide application is essential for pest control in agricultural production in order for pesticides to be effective; especially pre-emergence herbicides must be able to move within the soil profile to reach the germinating weed seeds. However, too much movement

can move a pesticide away from the target pest and this could lead to reduced pest control, injury of non-target species including humans, and contamination of surface and groundwater (Arnold and Briggs, 1990). Pesticides can be transferred in five ways: volatilization, runoff, crop

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removal, absorption, and leaching (Arnold and Briggs, 1990). Volatilization is the conversion of a solid or liquid into a gas. Once volatilized, a pesticide can move away from the treated soil surface. Runoff occurs when the rate of water application exceeds percolations or bound to eroding soil particles.

Pesticide leaching depends in parts on the chemical and physical properties of the pesticide (Kordel and Kleim, 1992). A pesticide strongly adsorbed to the soil particles is less likely to be leached. Solubility is another factor that affects the leaching of pesticides (Kordel and Kleim, 1992). A pesticide that dissolves in water can move with water in the soil. The pesticide longevity influenced the likelihood of it being leached down the soil profile (Kordel and Kleim, 1992). A pesticide that is rapidly broken down by a degradation process is less likely to be leached because it may remain in the soil only a short time. Soil factors that influence pesticide leaching include texture, organic matter content, soil moisture content and availability, soil pH, and microbial community. These factors influence leaching because of their effect on pesticide adsorption (Arnold and Briggs, 1990). Soil permeability, or how readily water moves through the soil may also be important. The more permeable a soil is the greater potential for pesticide to leach down the soil profile. Therefore, pesticides that are highly water soluble, not readily adsorbed and not rapidly degraded are the most likely to leach. Pesticide leaching down the soil profile is of great concern both in relation to environmental contamination and pesticide efficiency (Peoples et al., 1980; Weaver et al., 1983). Low pesticide concentrations in the soil effectively control pest. On the other hand, high pesticide concentration due to excess application is wasteful and could potentially lead to environmental pollution.

The use of metal based fungicides such as copper sulphate could be more detrimental if not properly managed. This is due to increased potential risk of pollution from the chemical and the heavy metal. Unlike organic chemicals, which are eventually broken down to simple non-toxic compounds, the addition of metals and other potentially toxic elements to soil leaves a residue, which is permanent unless leaching occurs (Logan, 1990). Contamination of agricultural soils by toxic heavy metals is one form of chemical degradation of soils (Logan, 1990). Environmental hazards derived from heavy metals are closely link to metal mobility, and therefore concentrations of the metals in soil solution. The mobility of heavy metals in terms of leachability depends not only on the total concentration in soil but also on soil properties and environmental factors (Li and Shuman, 1997). Most of them are associated with pollution of soil and water environment, though some of them are essential to plant and animals at low levels.

The movement of heavy metals in soil profiles has received considerable attention, since even a slow transport through soil and subsoil materials may result in an increased content of heavy metal in the groundwater.

Dowdy and Volk (1983) suggested that the movement of heavy metals in soils would occur in sandy, acid, and low - organic matter soil, subjected to heavy rainfall or irrigation. However, some investigators have reported that metal movement was low in soil treated with sludge (Williams et al., 1987; Dowdy et al., 1991). The low mobility of metal in sludge - treated soils was attributed to the retention of organic matter on the soil in the upper layers (Giusquiani et al., 1992) because most of the heavy metals in the organic wastes were associated with colloidal organic matter (Sposito et al., 1982; Sims and Kline, 1991).

Generally, the metal content of soils is low, at least in soils that are not adjacent to main roads or zones of high industrial or mining activity (Greppi and Preti, 1999). On agricultural land, however, the application of agrochemicals, wastewater, sewage sludge or compost (for disposal and/or fertilization) can introduce significant amount of metals. Most metal mobility studies have concentrated on pollution and movement of waste - borne heavy metals and not pollution associated with pesticide application especially copper based fungicides. Copper is one of the heavy metals which can be detrimental to plant growth if excessively present in the soil. Therefore, it is important to understand the impact copper based fungicides applied in agriculture lands, could potentially have in the soil and environment. This study was established to determine the copper concentrations in leachate from soil columns treated with copper fungicide.

MATERIALS AND METHODS

Soil description

The experiment was conducted using soils collected from the Obafemi Awolowo University Teaching and Research Farm at 0 to 60 cm soil depth. The soils were air-dried at 25°C, gently crushed to pass through a 2 mm diameter sieve and stored. All soil had been under secondary forest and did not have any history of fungicide application. The soils are classified at the series level as *Apomu* and *Egbeda* series (Smyth and Montgomery, 1962). The *Egbeda* series classified as *Oxic Tropudalf* (Ojanuga, 1975; Soil Survey Staff, 1992) was derived from granite and gneiss parent rock, while the *Apomu* series classified as *Oxisol* (Soil Survey Staff, 1992) was derived from sedimentary sandstone parent rock. According to the FAO/UNESCO terminology, *Egbeda* and *Apomu* soils are classified as *Nitisol* and *Luvisol*, respectively (FAO, 1988). Some physico-chemical properties of the two soils are shown in Table 1. For metal mobility experiment, the columns were prepared in three replicates with disturbed soil samples.

Leaching experiment and management

The soil column method used in this study represents a simplification of the natural processes. The movement of the metals in the field will be much slower than in the soil columns due to the heterogeneity of soils. Collected soils were homogenized, air-dried, stems and roots removed by hand and sieved through a 2 mm sieve. Plastic cylinders (40 cm internal diameter and 60 cm long) were used. The columns were perforated at the base for drainage of leachate and wire mesh screen placed at the base of the

Table 1. Some physical and chemical properties of the soils.

Description	Apomu series		Egbeda series	
	0 - 15 cm	15 - 30 cm	0 - 15 cm	15 - 30 cm
Textural classification	Loamy sand	Loamy sand	Sandy clay loam	Sandy slay loam
pH	4.98	4.65	5.82	5.64
Cation exchange capacity (cmol/kg)	7.75	5.75	13.25	7.00
Electrical conductivity (mmhos/cm)	0.058	0.029	0.04	0.034
Organic carbon content (%)	1.72	1.16	2.10	1.85
Sand (%)	78.5	82.5	68.0	70.0
Silt (%)	12.0	7.0	10.0	10.0
Clay	9.5	10.5	22.0	20.0
Copper ion (mg/kg)	0.008	ND	0.020	ND
Manganese ion (mg/kg)	34.29	23.56	87.98	54.87
Lead ion (mg/kg)	ND	ND	27.21	6.83
Zinc ion (mg/kg)	0.178	0.170	0.037	0.244
Calcium ion (cmol/kg)	1.45	0.88	2.12	1.64
Magnesium ion (cmol/kg)	1.21	1.19	1.58	0.72
Potassium ion (cmol/kg)	0.35	0.22	0.41	0.33
Sodium ion (cmol/kg)	0.34	0.31	0.39	0.39

columns to prevent the blockage of the drainage holes and to prevent large clumps of soil from falling off the perforated holes of the soil columns. For each soil type, four soil columns (soil packed to 1.5 g/cm³ bulk density) with 0, 1.88, 3.75 and 7.50 g/L fungicides concentration rates replicated three times was established. All the columns were packed with 103.67 kg of the two soil types to a height of 55 cm. The columns were then raised of about 30 cm from the ground surface. Basins were put at the base of the columns for water samples collection during the leaching experiment (Figure 1). This led to a total of 24 soil columns for the entire experiment, 12 columns for each soil type.

The soil columns were then saturated with water at the rate of about 5 mm/h using perforated bowl placed directly above the soil columns for 1 day (A preliminary experiment was conducted before the commencement of the experiment to determine the flow rate from the perforated bowl). After saturation, the fungicides (at the above mentioned rates) were applied at the top of the soil columns. The columns were then kept completely saturated with water by maintaining ponding through continuous application of de-ionized water at a rate of about 10 mm/h for the entire duration of the experiment.

The volume of outflow was measured as a function of time during the experiment to confirm the steady flow conditions in all the columns. The outflow rate remains relatively constant for each of the two soils. The experiment was conducted for 7 days after which the bowl supplying the columns with the de-ionized water was removed. Leaching activities were then allowed to cease for 24 h to permit adsorption of the metals in the fungicides left in the columns to the soils. During this time all columns were covered with plastic to prevent surface evaporation. After the 24 h "adsorption" period, the plastic cover was removed, another 250 ml of fungicide solution at the same concentration was added to the surface of the column and the leaching process resumed by placing the bowls back at the top of each of the soil columns and the de-ionized was poured into them for another round of 7 days period of leaching. This process of displacement experiment was repeated three times and for each of the experiments, leachate samples were collected every 6 h for next 7 days and the leachate transferred to the Laboratory for analysis of copper. The concentration of copper in the leachate solution was determined using Atomic Absorption

Spectrophotometer. Analysis of variance (SAS, 1987) was used to test the variation of metal concentrations in the leachate as affected by the fungicide application and time after the commencement of drainage, while Duncan multiple range test was used for the separation of means.

RESULTS AND DISCUSSION

The concentration of copper measured in the leachate after leaching started with de-ionized water from the columns treated with the three different concentrations of the copper fungicide (Kocide 101) are shown in Figures 2, 3, 4 and 5 for the four series of fungicide applications. The concentration of copper in the leachate for the four series of fungicide applications increased with sampling time and reached maximum at 60 h after the commencement of leaching then dropped as the time increases. Soil types and initial fungicide concentration had significant ($p < 0.01$) effects on the concentration of copper in the leachate for the four series of fungicide application. As expected, the concentration of copper in the leachate was at the maximum when 7.5 g/L fungicide concentration was applied for the four series of fungicide applications. On the average, for the two soil types considered in this study, the concentration of copper in the leachate during the first fungicide application and leaching was 1.94 mg/L. Interestingly, this concentration reduces to about 1.12 mg/L on the average during the second application and increased to an average concentration of 1.85 and 2.83 mg/L during the third and fourth applications, respectively. It was also observed during the experiment that the flow rate of water decreases during the leaching of the second fungicide application and increased with the third and fourth fungicide applications.

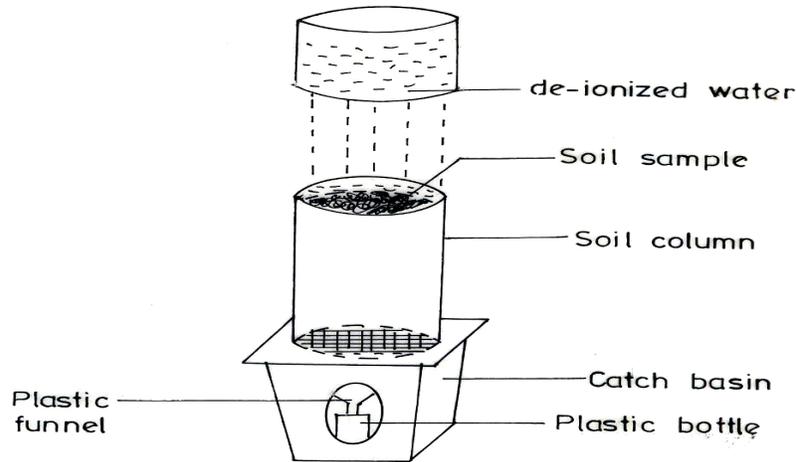


Figure 1. Experimental setup of the soil columns in the laboratory.

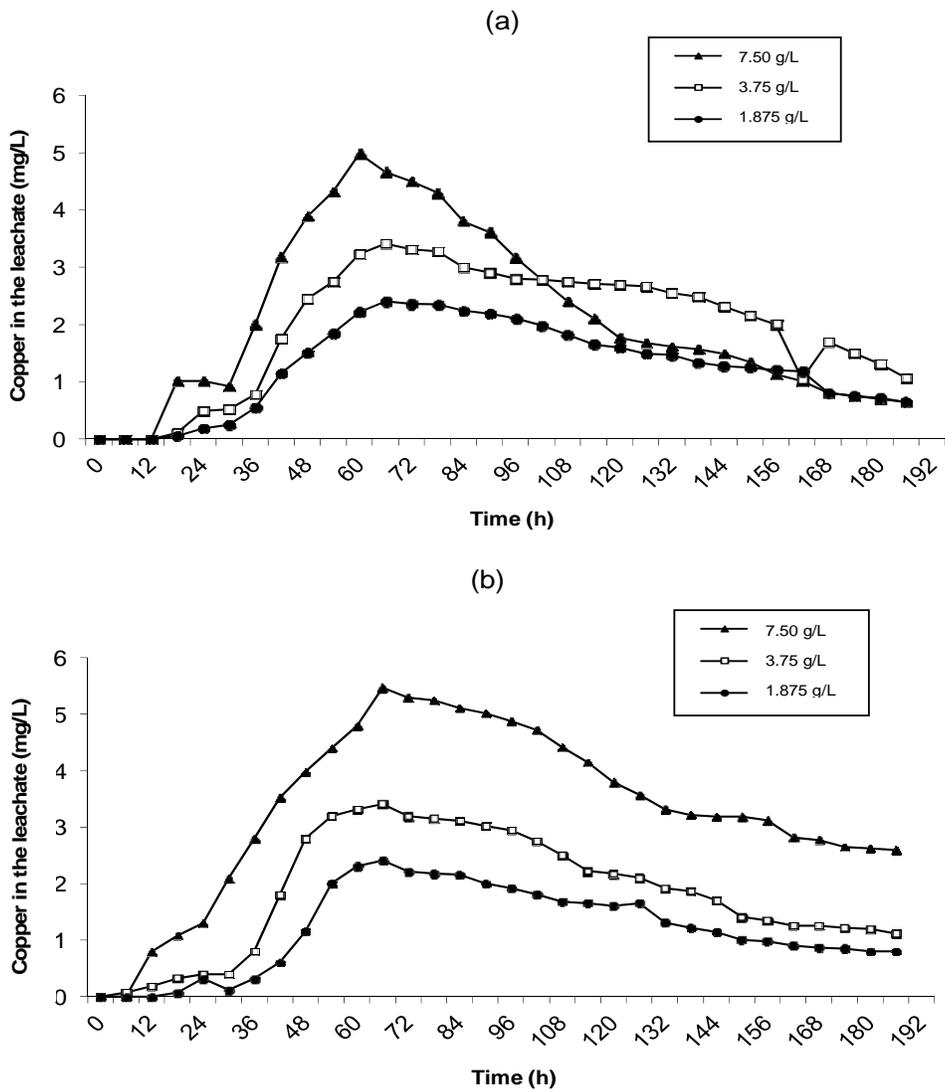


Figure 2. Leaching of copper from Kocide 101 with concentrations of 7.50, 3.75 and 1.875 g/L in (a) Egbeda soil and (b) Apomu soil after the first fungicide application.

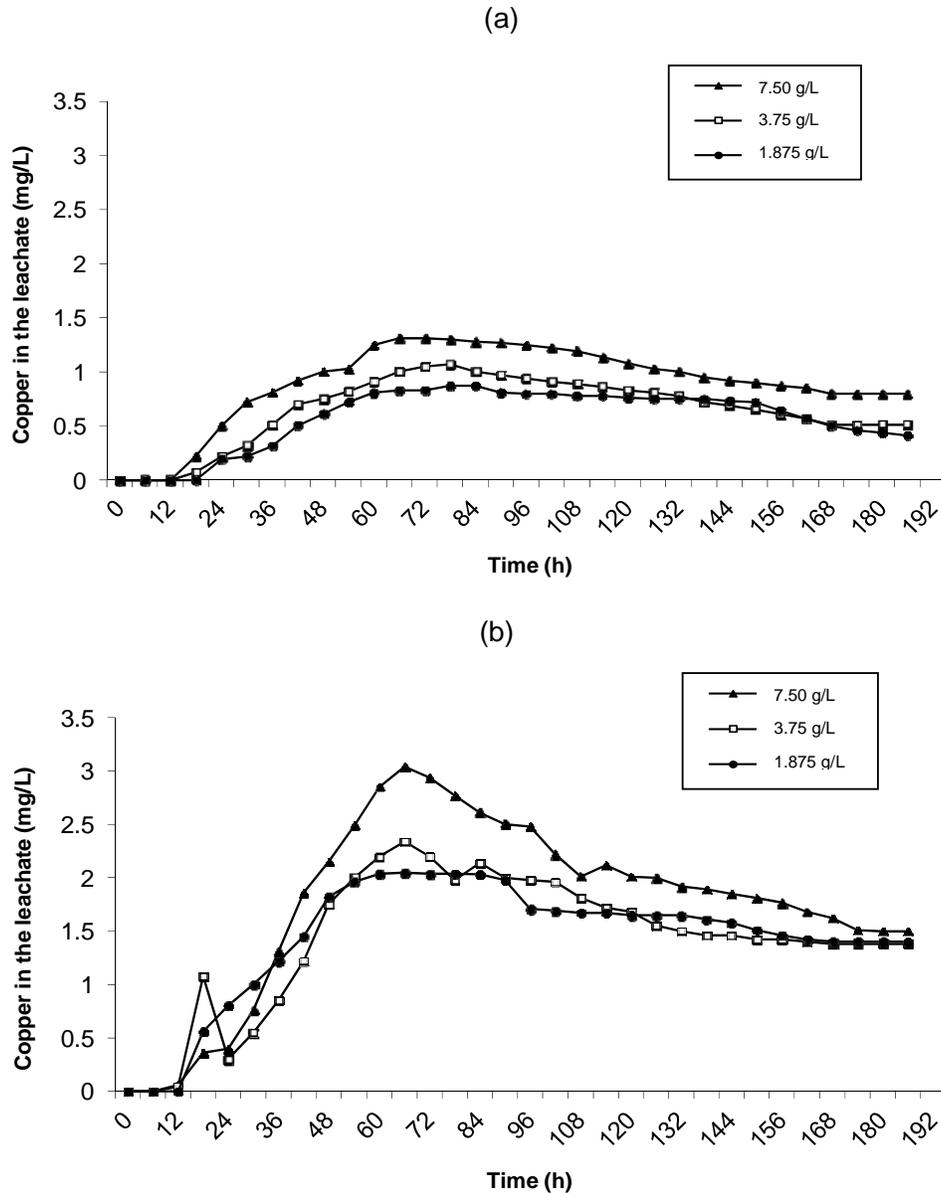


Figure 3. Leaching of copper from Kocide 101 with concentrations of 7.50, 3.75 and 1.875 g/L in (a) Egbeda soil and (b) Apomu soil after the second fungicide application.

Leaching of the columns with first fungicide application

The concentration of copper in the leachate when the soil columns were leached with the three different fungicide concentrations increases from zero at time 0 h to maximum of 3.63 mg/L at the sampling time of 66 h after which the concentration of copper in the leachate begins to decline. Figure 2 shows the concentration of copper in the leachate as a function of time after the commencement of drainage for the first fungicide application. From Figure 2, the concentration of copper in the leachate from both soils increase from 0 mg/L to the

maximum of 3.49 and 3.76 mg/L for *Egbeda* and *Apomu* soils, respectively.

The three factors considered that is, time after the commencement of drainage, soil and fungicide concentrations were all significant in their effects on the copper concentration of the leachate ($p < 0.01$). On the average, the concentration of copper in the leachate from soil columns containing Egbeda soil was 1.77 mg/L, while the concentration was 2.11 mg/L for Apomu soil. This is expected because Apomu soil has more macro pores that will permit mobility of water and solute than Egbeda soil. On the average, the concentrations of copper in the leachate were 1.19, 2.82 and 3.31 mg/L for fungicide

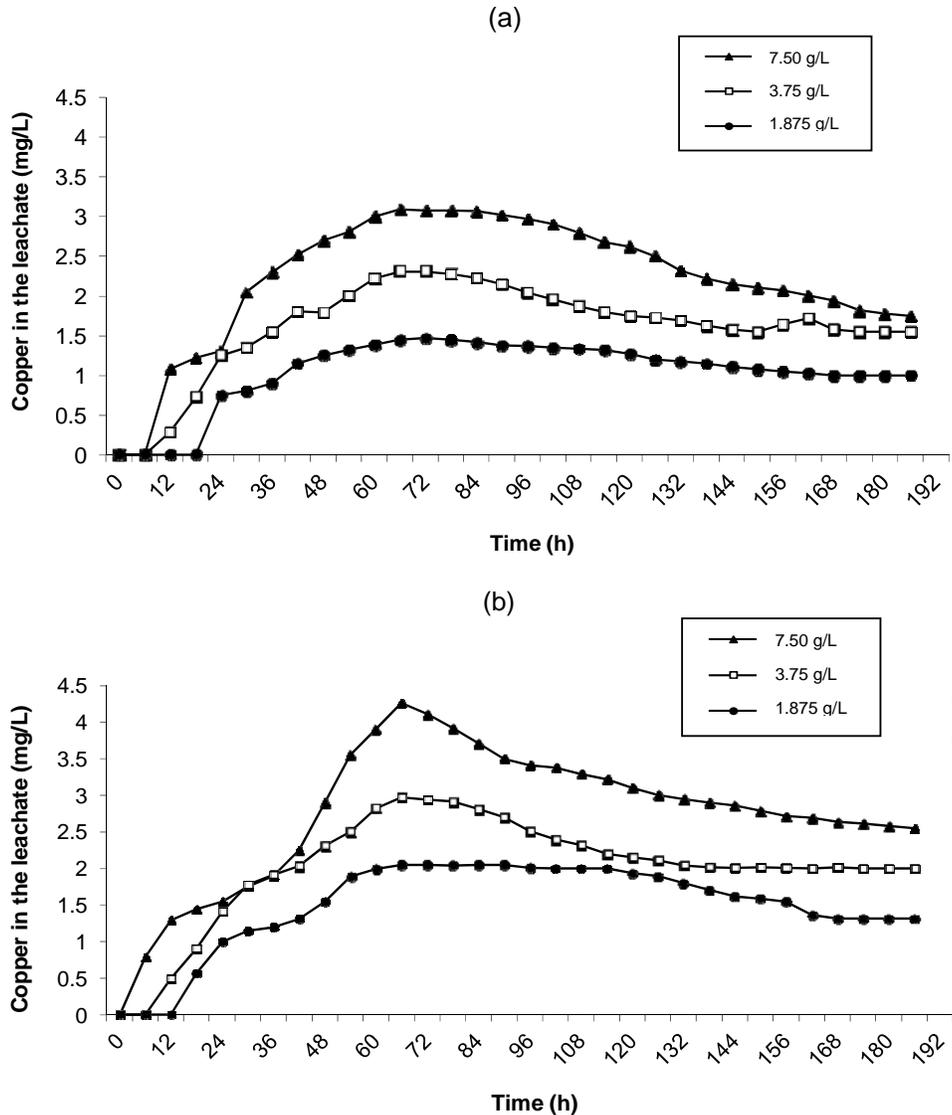


Figure 4. Leaching of copper from Kocide 101 with concentrations of 7.50, 3.75 and 1.875 g/L in (a) Egbeda soil and (b) Apomu soil after the third fungicide application.

concentrations of 1.875, 3.75 and 7.5 g/L, respectively for Apomu soil, while the concentrations of copper in the leachate for Egbeda soil were 1.27, 1.95 and 2.10 mg/L for fungicide concentrations of 1.875, 3.75 and 7.5 g/L, respectively.

According to Duncan multiple range test, these three leachate concentrations of copper as affected by the applied fungicide concentrations were significantly different from one another. These leachate concentrations reduce to 1.27, 1.95 and 2.10 mg/L for the three different fungicide concentrations, respectively when the soil in the columns was Egbeda soil. The concentrations of copper in the leachate when the applied fungicide concentrations were 3.75 and 7.50 g/L are not significantly different ($p < 0.05$). However, these

two leachate concentrations of copper are significantly different from the leachate concentration when the applied fungicide concentration was 1.875 g/L. Moreover, the three fungicide concentrations considered in this work were significantly different in their effect on the concentration of copper in the leachate.

Leaching of the columns with second Fungicide application

Figure 3 shows the concentration of copper in the leachate as a function of time after the commencement of drainage for the second fungicide application. From Figure 3, the concentration of copper in the leachate from

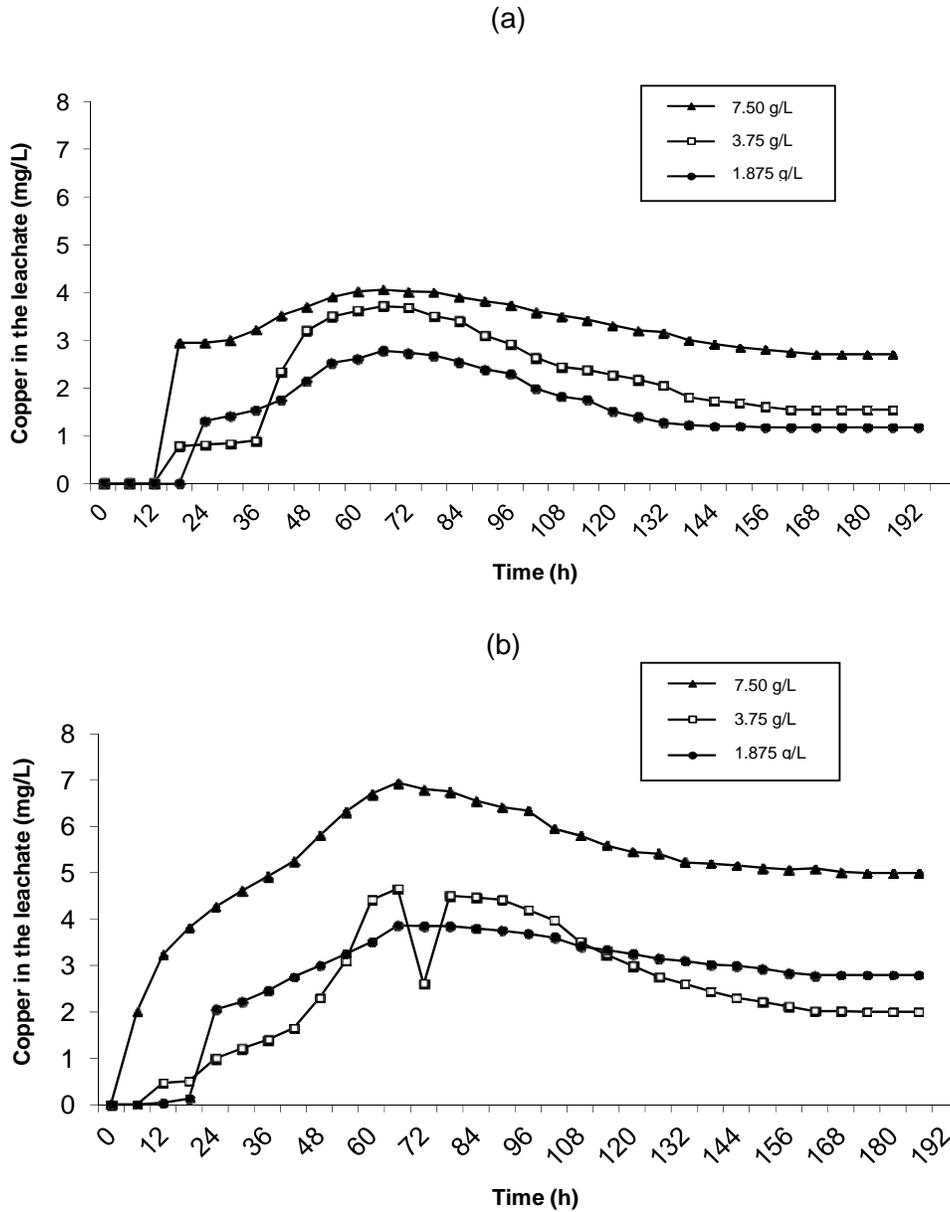


Figure 5. Leaching of copper from Kocide 101 with concentrations of 7.50, 3.75 and 1.875 g/L in (a) Egbeda soil and (b) Apomu soil after the fourth fungicide application.

Egbeda soil columns increases from 0 mg/L at time 0 h to maximum of 1.08 mg/L at 78 h after the commencement of drainage after which the concentration of copper in the leachate begins to drop. For Apomu soil, the maximum concentration of copper in the leachate was recorded at time 66 h after the commencement of drainage.

All the three factors considered that is, time after the commencement of drainage, soil and fungicide concentrations were also significant in their effects on the copper concentration of the leachate ($p < 0.01$). It is interesting to note that on the average, the concentration of copper in the leachate during the second application

fell from 1.77 mg/L for the first fungicide application to 0.70 mg/L of copper in the leachate during the second application for Egbeda soil. The same trend was observed for Apomu soil where the average copper concentration of the leachate was 1.54 mg/L as against 2.11 mg/L observed for the first fungicide application. It was also observed that the amount of leachate collected during the second fungicide application and simulated rainfall was less than that which was collected during the first application. This may likely be as a result of the blockage of soil pores caused by the fungicide particles during the first application which prevents easy flow of

the water and solute through the soil columns.

On the average, the concentrations of copper in the leachate during the second application were 1.42, 1.43 and 1.75 mg/L for fungicide concentrations of 1.875, 3.75 and 7.5 g/L, respectively for Apomu soil. According to Duncan multiple range test; fungicide concentrations 1.875 and 3.75 g/L were not significantly different in their effects on the concentration of copper in the leachate. However, the two concentrations were significantly different in their effects from the fungicide concentration of 7.50 g/L. For Egbeda soil, the concentrations of copper in the leachate as affected by the fungicide concentrations of 1.875, 3.75 and 7.50 g/L were 0.57, 0.65 and 0.89 mg/L, respectively. However, these three concentrations are significantly different ($p < 0.05$).

Leaching of the columns with third fungicide application

Figure 4 shows the concentration of copper in the leachate as a function of time after the commencement of drainage for the third fungicide application. From Figure 4, the concentration of copper in the leachate from soil columns containing Egbeda soil increases from 0 mg/L at time 0 h to maximum of 2.29 mg/L at 72 h after which the concentration begins to decline. For columns containing Apomu soil, the maximum copper concentration of 3.09 mg/L was observed at 66 h after which the concentration began to decline steadily.

All the three factors considered that is, time after the commencement of drainage, soil and fungicide concentrations were significant in their effects on the copper concentration of the leachate ($p < 0.01$). On the average, the concentration of copper in the leachate from soil columns containing Egbeda soil was 1.62 mg/L, while the concentration was 2.08 mg/L for Apomu soil. When the effect of fungicide concentrations on the concentration of copper in the leachate was investigated, it was observed that the concentrations of copper in the leachate from Egbeda soil were 1.03, 1.61 and 2.22 mg/L for fungicide concentrations of 1.875, 3.75 and 7.50 g/L, respectively, while the concentration from Apomu soil for the same three levels of fungicide concentration were 1.49, 2.01 and 2.73 mg/L. According to Duncan multiple range test, these three different leachate concentrations for both soil types are significantly different ($p < 0.05$).

Leaching of the columns with fourth Fungicide application

Figure 5 shows the concentration of copper in the leachate as a function of time after the commencement of drainage for the fourth fungicide application. From Figure 5, the concentration of copper in the leachate from soil columns containing Egbeda soil increases from 0 mg/L at time 0 h to maximum of 3.52 mg/L at 66 h after which the concentration begins to decline. For columns containing

Apomu soil, the maximum copper concentration of 5.15 mg/L was also observed at 66 h after which the concentration began to decline steadily except for column treated with fungicide concentration of 3.75 g/L. For this concentration, after the maximum copper concentration was reached at time 66 h, the concentration of copper in the leachate decreases to 2.59 mg/L at 72 h before increasing to the same value as for time 66 h after which it began to decline.

All the three factors considered that is, time after the commencement of drainage, soil and fungicide concentrations were significant in their effects on the copper concentration of the leachate ($p < 0.01$). On the average, the concentration of copper in the leachate from soil columns containing Egbeda soil was 2.19 mg/L, while the concentration was 3.46 mg/L for Apomu soil. When the effect of fungicide concentrations on the concentration of copper in the leachate was investigated, it was observed that the concentrations of copper in the leachate from columns containing Egbeda soil were 1.54, 2.03 and 3.01 mg/L for fungicide concentrations of 1.875, 3.75 and 7.5 g/L, respectively, while the concentration from Apomu soil for the same three levels of fungicide concentrations were 2.47, 2.74 and 5.18 mg/L. According to Duncan multiple range test, these three different leachate concentrations for both soil types are significantly different ($p < 0.05$).

Conclusion

The following conclusions were drawn from the study:

- 1) Soil type had significant effect on the concentration of the metals in the leachate.
- 2) Time to peak concentration of the metals in the leachate varies between 2.5 to 3.25 days.
- 3) Fungicide concentration had significant effect on the concentration of copper in the leachate. The three fungicide concentrations were significantly different in their effects on the copper concentration in the leachate. However, fungicide concentrations of 3.75 and 1.875 g/L were not significantly different in their effects on the copper concentration in the leachate from the column containing Apomu soil for the second fungicide application. For the columns containing Egbeda soil, fungicide concentrations of 7.50 and 3.75 g/L were also not significant in their effects on the concentration of copper in the leachate for the first fungicide application.

Conflict of Interest

The author(s) have not declared any conflict of interest

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