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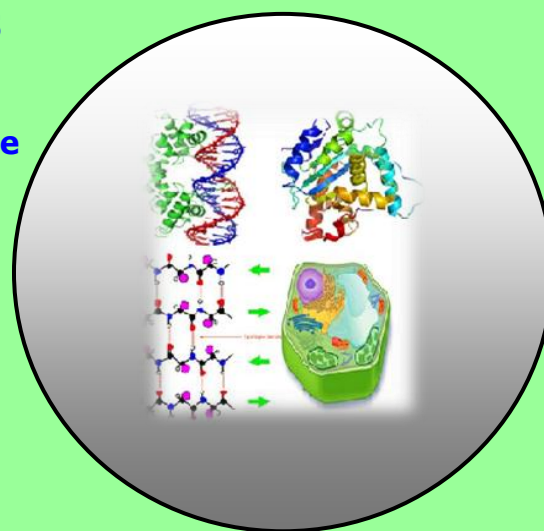
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RESEARCH PAPER

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Assessment of the Effects of Cadmium and Copper on pH and Cation Exchange Capacity of Soil under Different Plant Canopy in the Tropical Wet and Dry Climate

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ABSTRACT

The importance of food security in this era of environmental pollution can not be over emphasize. To estimate the effect of heavy metal on pH and Cation Exchange Capacities of soil on incubation, relationships between availability of metals in soil after contamination were investigated for a range of soils and metals. Three concentrations (0 mg/kg, 2 mg/kg and 5 mg/kg) of copper and cadmium were added as sulphate solution as single and combine treatments to six soil samples under different plant canopy. The soils-metal were incubated at field capacity for 8 weeks under 25⁰C. The exchangeable bases in soils were determined in IM ammonium acetate (pH 7.0) extract by FAAS and pH by pH meter with a combination electrode. The treatment is arranged in randomised complete design each in triplicates. The pH decreased from 7.02 to 6.65. Cation Exchange Capacities decreased from range of 5.97 to 4.26 and 3.75 C mol kg⁻¹ under single and combined treatments respectively for the six locations. These results enable us to understand natural attenuation of metal contamination and also to assess the risk of soil contamination by determining effects of metals reactions with CEC and pH in 8-weeks incubated soils after artificial contamination.

Keyword: Heavy Metals, Incubation Process, pH and CEC.

INTRODUCTION

Metals are often present in soil in mixtures of two to five, depending on the source of pollution (Spurgeon et al. 1994). Environmental effects of combined heavy metals may be quite different from those of individual pollutants due to interactions between heavy metals (MacFarlan nd Burchett 2002). Experiments on the toxicity of mixtures of pollutants may reflect the actual toxicity to ecosystems in a more realistic way than experiments in which

toxicants are tested individually (Spurgeon et al. 1994: Alloway, 1995.), and several studies have investigated the combined effects of heavy metals in soil. Heavy metals mobility is closely related to metal solubility, which is further regulated by adsorption, precipitation and ion exchange reactions in soils. It is very important to investigate the process of soil contamination itself with special attention to available fractions because it directly relates to the management and prevention of soil contamination. However, such predictions under field conditions suffer from much uncertainty. This is partially due to the difficulty in assessing the effects of dynamic soil solution chemistry on trace metal speciation (Thornton, 1991.). However, changes in soil solution chemistry, such as pH, redox potential and ionic strength, may also significantly shift the retention processes of heavy metals by soils (Gerringa et al., 2001). These effects may be further complicated by ligand competition from other cations (Norrstrom and Jacks, 1998: Amrhein et al, 1994). Soil redox status varies temporally and spatially. In a surface soil, it is influenced by rainfall, bioactivity, and in particular changes in land use. The importance of maintaining an adequate soil nutrition supply to crops in order to maximize agricultural output has long been recognized and the routine application of plant residue to agricultural land have become an integral part of agriculture in developing countries (Spurgeon et al 1994:). However, continued long term application of plant residue can lead to accumulation of organic nutrients in surface horizons which will likely influence of soil properties on kinetics of heavy metals release under different land use. Therefore, a better understanding of the the effect of heavy metal on soil pH and CEC under incubation seem to be an important issue of present day research on risk assessments.

MATERIAL AND METHODS

Experiment was undertaken to observe the effect of incubation period of cadmium and copper for single and combined treatments. The study was conducted at the Federal University of Agriculture along Alabata road, Abeokuta (Latitude 7° 15'N, Longitude 3° 25'E) within a forest savanna transition zone (Salako *et al.*, 2007) in the tropical wet-and dry climate, South Western Nigeria. Preliminary analysis of the soil samples were collected randomly from locations under different plant canopy at 0-20cm depth. The locations included cashew plantation, Fadama area, Maize cultivated area, grass area, orange farm and Forest reserve site. All the six location were cleared and plant residue left on land till about 80% of plant residue were no longer visible on site. The soil samples in these locations were air-dried, sieved in 2mm diameter mesh and analyzed for soil physiochemical properties using appropriate analytical methods.

Incubation experiment

The laboratory incubation study involved one-hundred grams each of soil samples from the locations, weighed into cellophane. The heavy metals (cadmium and copper) treatments consisted of three rates (0 mg/kg (R₀), 2 mg/kg (R₁) and 5 mg/kg (R₂)) randomised in a complete design each in triplicates. The treatments were incubated for eight weeks at field capacity under 25⁰c . After eight-weeks of soil-metal incubation, the soil-metal samples were grounded with a ceramic coated grinder and sieved through a nylon sieve. The final samples were kept in labeled polypropylene containers at ambient temperature.

The digested soil samples from the six locations were analysed pH mixing the soil samples with distilled water in a 1-2 ratio, stirred on mechanical shaker for 5 minutes and measure with pH meter.

The exchangeable bases in soil such as sodium, potassium, calcium and magnesium were determined by flame Atomic Absorption Spectrophotometer (FAAS) in IM ammonium acetate (pH 7.0) extract. Cations exchange capacity (CEC) was estimated by summing the exchangeable bases. Data collected were subjected to analysis of variance (ANOVA) . Mixed model procedure in Statistical Analysis System(1999). The sources of variation for the ANOVA were rep, pH and ECEC. The significance of the main and interaction effects was determined and significant means were separated using multiple range test at 5 % level of probability (Duncan, 1955).

RESULT AND DISCUSION

The preliminary analysis of morphological examination of the soil samples from the locations as presented in table 1 shows that the soils generally contain weak aggregates which is probably related to the presence low clay and organic matter content. The surface texture of the soils indicated that the surface soils are loamy sand texture on the surface and the organic carbon was within the the range of 0.78 % to 4.49 % with the highest at the Fadama site. The total nitrogen ranged between 0.8% and 1.36 % and the available phosphorus (determine by Bray-1- method) ranged between 1.20 to 3.95 mg kg⁻¹ with the highest value for cashew plantation and fadama respectively.

Table 1. Some initial properties of experimental soils sample from the six locations.

Sample	Fadama	Maize area	Grass area	Forest -site	Orange farm	Cashew plantation
pH	7.02	7.02	7.02	7.01	7.01	6.99
O.C(%)	4.49	0.91	1.72	1.21	1.15	0.78
AV. P(mgkg ⁻¹)	3.95	2.72	1.65	1.52	1.20	1.55
CEC cmol ⁻¹ kg ⁻¹	5.33	6.60	6.34	6.30	6.29	6.62
O.M (%) mg g ⁻¹	7.74	1.60	2.96	2.09	1.98	1.34
T. N (%)	1.36	1.20	0.10	1.40	1.22	8.0
Sand (%)	83.1	68.6	75.6	74.8	73.8	74.6
Clay (%)	11.3	17.2	10.1	11.6	11.7	11.4
Silt (%)	5.5	13.4	13.8	13.6	13.8	13.6
Textural class	Loamy sand	Sandy loam	Sandy loam	Loamy sand	Loamy sand	Loamy sand

O.C= Organic Carbon, T.N= total nitrogen AV. P= available phosphorus, CEC= Cation Exchange Capacity, O.M= Organic matter

Tables 2 show the pH values of the soils under different plant canopy for 0 mg/kg treatments which indicated that they were under neutral conditions which was within the optimal range for plant growth. Ojanuga and Awujoola (1981) attributed this range of neutral pH level especially on the surface horizon of the locations to low humus, pollution by acidic gases and annual addition of small quantity of carbonates present in form of harmattan dust.

Adetunji and Bamiro (1994) however stated that the neutral pH is generally most favourable for plant growth because most plant nutrients are readily available within this range. Single application of these metals significantly reduced the pH from 7.01 to 6.70 (from neutral to slightly acidic pH irrespective of the plant canopy. The individual treatments of cadmium or copper at different concentration that is 2 mg/kg and 5 mg/kg after eight weeks of incubation indicated a concentration dependent which implies that increase in the concentration of metals leads to increase in acidity of the soil surface. This can be attributed to ion exchange reaction of the cadmium or copper with the soil substrates releasing small hydrogen ion concentration to soil surface that makes the soil to be slightly acidic. According to Kalavrouziotis, *et al* (2009) metal reacts and held to the negative charge on the soil surface by electrostatic, covalent, columbic –force, outer and inner-sphere surface complexation (adsorption) and precipitation. The combination of retaining solid phase and retention mechanism determines the bioavailability and thus potential toxicity of metal ions (Gerringa et al., 2001; Tessier and Campbell, 1987). Combine treatment of copper and cadmium with soils under different plant canopy still showed increase in acidity after incubation indicating that the two metals still react with the negative charge on the soil surface and release more hydrogen ion on the soil surface thus increasing the soil acidity which may be harmful to soil microorganisms.

Table 2. Effects of cadmium, copper on pH of soil under different plant canopy after 8 weeks of incubation.

Treatments (mg/kg)	Fadama	Maize area	Grass area	Forest site	Orange farm	Cashew plantation
Cd 0	6.99 ^a	7.02 ^a	7.02 ^a	6.97	7.01 ^a	6.98 ^a
2	6.82 ^b	6.81 ^b	6.80 ^b	6.80 ^b	6.90 ^a	6.80 ^b
5	6.72 ^c	6.80 ^b	6.77 ^b	6.70 ^c	6.81 ^b	6.73 ^c
Cu 0	6.95 ^a	7.02 ^a	7.02 ^a	6.90 ^a	7.01 ^a	6.98 ^a
2	6.89 ^a	6.85 ^b	6.81 ^b	6.85 ^b	6.89 ^b	6.86 ^{ab}
5	6.84 ^b	6.83 ^b	6.82 ^b	6.80 ^b	6.84 ^b	6.84 ^b
Cd, Cu						
0 0	6.95 ^{abc}	7.02 ^a	7.02 ^{ab}	6.90 ^{bcd}	7.01 ^a	6.98 ^{ab}
2	7.01 ^a	7.00 ^a	7.08 ^a	7.06 ^a	7.03 ^a	7.03 ^a
5	6.96 ^{abc}	6.97 ^{ab}	6.91 ^{bc}	6.96 ^{abc}	6.98 ^{ab}	6.92 ^{abc}
2 0	6.87 ^{bcde}	6.83 ^{bcd}	6.87 ^{bcd}	6.88 ^{bcd}	6.69 ^e	6.84 ^{bcd}
2	6.83 ^{cd}	6.80 ^{dc}	6.74 ^{cde}	6.83 ^{cd}	6.82 ^{cd}	6.84 ^{bcd}
5	6.87 ^{bcde}	6.81 ^{dc}	6.84 ^{cd}	6.87 ^{bcd}	6.76 ^{de}	6.80 ^{bcd}
5 0	6.98 ^{abc}	6.92 ^{abc}	7.10 ^a	6.98 ^{abc}	6.73 ^{de}	6.98 ^{ab}
2	6.77 ^e	6.76 ^{d=}	6.68 ^e	6.77 ^d	6.67 ^e	6.73 ^d
5	6.81 ^{de}	6.72 ^d	6.71 ^{ed}	6.83 ^{cd}	6.66 ^e	6.76 ^{cd}

Means with the same superscript are not significantly different at $P \leq 0.05$.

The cation exchangeable capacities of all the soils for the 0 mg/kg treatments for the metals under different canopy in the areas as shown in table 3 are generally moderate and in line with the classification by Kparmwang *et al.* (1998) that soils with CEC less than 4, range of 4 to 10 and greater than 10 $\text{cmol}^{-1} \text{kg}^{-1}$ are low, medium and high respectively.

The moderate CEC level of these soils can be attributed to clay content (though low potassium). It is therefore important that the organic matter of the soils be well maintained for the CEC to be improved to a large extent. The effects of single application of cadmium or copper at 2 and 5 mg/kg significantly reduce the CEC from range of 7.02 to range of 6.70 under high concentration. The significant reduction of CEC is due to reaction of cadmium or copper with the with clay or organic matter content in soil substrate by isomorphic substitution reaction this will make heavy metal to form complex with the exchangeable base elements (Na,Mg,Ca, and K).These effects may be deu to ligand competition from the copper or cadmium cations (Norrstrom and Jacks, 1998:Amrhein et al, 1994).These exchangeable base elements are micro element should be available at the soil surface for plant absorption but would have reacted with heavy metals (copper or cadmium).Combined cadmium and copper treatments gave more significant reduction on CEC than single application so the effects of two metal is higher than one metal.effect most expecially under high concentration 5 mg/kg. This agrees with work of Stathi *et al* (2010)that deduce that surface complexation model describe successfully adsorption of ions on charged surfaces by assuming that adsorption involve both coordination reaction at specifics. The combination of retaining solid phase and retention mechanism determines the bioavailability and thus potential toxicity of metal ions.

Table 3. Effects of cadmium, copper on CEC of soil under different plant canopy after 8 weeks of incubation.

Treatments (mg/kg)	Fadama	Maize area	Grass area	Forest site	Orange farm	Cashew plantation
Cd 0	5.33 ^b	6.60 ^a	6.34 ^a	6.29 ^a	6.30 ^a	6.62 ^a
2	6.17 ^a	5.68 ^b	6.09 ^a	6.16 ^a	6.15 ^{ab}	4.54 ^b
5	5.40 ^b	4.71 ^c	5.18 ^c	5.40 ^b	5.43 ^b	4.88 ^b
Cu 0	5.33 ^b	6.60 ^a	6.34 ^a	6.29 ^a	6.30 ^a	6.62 ^a
2	5.81 ^{ab}	4.84 ^b	5.78 ^a	5.82 ^a	5.66 ^b	3.99 ^b
5	5.82 ^{ab}	4.81 ^b	5.30 ^a	5.41 ^b	5.54 ^b	3.98 ^c
Cd ,Cu						
0 0	6.41 ^{ab}	5.70 ^b	6.40 ^a	6.30 ^{ab}	6.40 ^{ab}	5.50 ^b
2	5.80 ^c	5.60 ^b	5.80 ^{bc}	5.70 ^{bd}	5.80 ^{bc}	5.10 ^c
5	5.04 ^d	4.70 ^c	5.00 ^e	5.10 ^c	5.00 ^c	4.00 ^e
2 0	7.00 ^a	6.60 ^a	6.80 ^a	7.00 ^a	7.00 ^a	6.00 ^a
2	5.68 ^{cd}	4.60 ^c	5.10 ^{bcd}	5.60 ^{bc}	5.70 ^{cd}	3.70 ^g
5	5.85 ^{bc}	4.90 ^{bc}	5.90 ^b	5.90 ^{bc}	5.90 ^{bc}	3.90 ^f
5 0	5.53 ^{cd}	5.00 ^{bc}	5.30 ^{cde}	5.60 ^{bc}	5.50 ^d	4.20 ^d
2	5.36 ^{cd}	4.20 ^c	5.20 ^{de}	5.10 ^c	5.30 ^{cd}	3.10 ^h
5	5.31 ^{cd}	4.90 ^{bc}	5.00 ^e	5.60 ^{bc}	5.30 ^{cd}	4.00 ^e

Means with the same superscript are not significantly different at $P \leq 0.05$.

CONCLUSION

The effect of cadmium- copper treatment in soil incubation changes the pH from neutral to slightly acidic. The acidity increases in combine treatment than single treatments. There was a significant reduction effects on the CEC of the soil of different crops canopy.

The combined treatment of cadmium and copper produced more reduction in CEC in all the treatments of different plant canopy. The showed a concentration dependent.

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