BIOAVAILABILITY OF SOME SELECTED HEAVY METALS AS AFFECTED BY AMENDMENTS UNDER VARYING DEPTH AND GROWING STAGE OF MAIZE IN SUDAN SAVANNAH OF NIGERIA

[1] Aliyu Abdulkadir, [1] Sufiyanu Sani, [2] Mansur Usman Dawaki, [3] Sani Mahmud, [4] Muazu Salisu,[1] Yakubu Muhammad Abdullahiand, [1] Firdausi Haruna Dalhat

[1] Department of Soil Science, Federal University Dutsin-Ma, Katsina State, Nigeria
[2] Department of Soil Science, Bayero University Kano, Kano State, Nigeria
[3] Department of Agronomy, Federal University Gashua, Yobe State, Nigeria
[4] Centre for Dryland Agriculture, Bayero University Kano, Nigeria

ABSTRACT

An experiment was conducted to study the effects of amendments on the bioavailability of some selected heavy metals under varying Depths and Growing Stages of Maize in Sudan Savannah of Nigeria. The experiment was conducted at Bayero University Kano teaching and research farm. Three type of amendments were used; the amendments are NPK fertilizer, compost and biochar with additional plot as control. The solution was sampled in all the plots at three different depths (10, 20 and 30cm) in three different growth stages (Seedling, vegetative and tasseling) of maize. The experiment was laid out in randomized complete block design (RCBD). The amendments were found to show a significant effect on the bioavailability of Cu^{2+} *in all the stages and depths while both* Co^{2+} *and* Pb^{2+} *were found to show significant effect with advancement in the growth stage of the test crop.*

1. INTRODUCTION

Soil solution is the most important exchange medium for the chemical elements that are essential to life and it differs from aqueous solution in that it is not electrically neutral(Bohn *et al.,* 2003). Soil solution composed of dissolved solids most important of which are those that dissociate into ions called electrolytes(Sparks, 2003). Its composition might vary considerably for a given horizon through the year as a result of variable composition of infiltration water, climatic conditions and biological activity(Mulder and Cresser, 1994). Most of the solutes in the soil solution are ions, which occur either as free hydrated ions (e.g., Al^{3+} which is expressed as $Al(H_2O)_6^{3+}$) or as various complexes with organic or inorganic ligands (Sparks, 2003). Plants absorbs nutrients from the soil solution(Havlin *et al.,* 2012) to meet their nutritional requirement, its indeed the source nutrients for all terrestrial organisms and is absorbed directly or indirectly(Bohn *et al.,* 2003), as it is constantly replenished, it also serve as the most important supplier of dilute nutrient to the plant roots (Brady and Weil, 1999). The concentration is affected by several factors that either add or remove solutes but its composition is controlled by the mineral phase of the soil(Lindsay, 1979). The actual concentration of the solutes in the soil solution varies with changes in soil moisture content(Wolt, 1994). Not all soil water is available to the plants, rather the soil solids attract and held water strongly in such way that some moisture remains in the soil even after the plants dried and wilted (Brady and Weil, 1999) this form of water is not available to the plants. pH of soil solution is very important phenomena in its study, as several chemical and biological reactions greatly depends on the concentration of H^+ and OH^+

ions in the soil (Brady and Weil, 1999). The solubility and the availability of many essential nutrients to plants is affected by its pH (Dawaki et al., 2019, Brady and Weil, 1999). The total ionic concentration of the soil solution provides important information on the quantities of ions available for uptake by the plants and transport through the soil profile (Sparks, 2003).

There is the need to increase and improve biochar production as the research in its field application shows increased ability in most soil properties such as water holding capacity, fertilizer conservation, storm water and roof drain filter media, remediation and/or protection against particular environmental pollution, animal feed supplement and carbon sequestration (Fuchs *et al.,* 2014). It proved to be successful in the remediation of soil contaminated with heavy metals.

An important and useful feature of biochar is its ability to holds nutrients in soil and this helps to reduce nutrient leaching. increase in nutrient uptake by plants with leads to higher crop yield has also been reported(Prins *et al.,* 2007). Its use as soil amendment was found to increase soil pH, soil organic C, total N, and decreased soil bulk density(Abdulkadir et al., 2020, Zhang *et al.*, 2010 Sani et.al., 2019, 2023). The soil concentration of Phosphorus, K, Ca, and magnesium (Mg) was not affected with use of biochar as amendment(Laufer and Tomlinson, 2013). Biochar has the ability to help in climate change mitigation, by means of its high carbon sequestration ability(Woolf *et al.,* 2010), as such it might be added to the soils with the aim of enhancing the soil functions in the reduction of GHG emissions from biomass that would otherwise be degraded (IBI, 2016). The transformation of Carbon in biomass to Biochar Carbon leads to sequestration of around 50% of the initial Carbon in contrast to 3% retained after burning and <10–20% after 5–10 years after biological decomposition(Noma and Sani 2008, Lehmann *et al.*,2006a).

Composting is a microbial decomposition of organic materials in a controlled way with aim of producing a material that is stable and used either as soil amendment or organic fertilizer(Manu *et al.,* 2016), it involves the manipulation of the natural biological aerobic decomposition so as to speed up the rate of decomposition(Evanylo *et al.,* 2009) through creating suitable condition for them to grow and reproduce (Campbell, 2012). The process of composting is carried out by successive population of microbes that function with increase in temperature to produce carbondioxide, water, minerals and stable organic matter as a product of decomposition of biomass(Evanylo *et al.,* 2009). The piling up of biomass and allowing it to decompose cannot be regarded as Composting(Evanylo *et al.,* 2009). This processes reduces the release gases such as methane into the atmosphere which contrary to the anaerobic decomposition in landfills (Evanylo *et al.,* 2009).

This research is aimed at studying the influence of amendments (NPK, biochar and compost) on the bioavailability of three selected heavy metals in a maize field with varying growth stage and depth.

2. Materials and Methods

2.1. Experimental Site and Materials

The research was conducted at Faculty of Agriculture Bayero University Kano research farm, Kano state. The site is located in the Sudan savannah zone of northern Nigeria, having latitude of 11^{0}59’N and longitude of 8^{0}25’E. Three set of amendments; biochar, compost and an inorganic fertilizer (NPK) were used as experimental materials. 2009 EVDT maize variety was used for the experiment.

2.2. Soil Sampling, Preparation and Analysis

Prior to the establishment of trial 10 soil samples were collected from the field in zigzag manner using Auger.Samples were air dried, gently crushed and sieved through a 2 mm sieve mesh and stored in an air tight container prior to soil analysis.

The pH of the soil was determined in soil : water of 1:2.5 using glass electrode pH meter as described in Estefan *et al.;* (2013). Soil EC was determined in soil : water ratio of 1:5 soil : water as described by Bower and Wilcox, (1965), Estefan *et al.*,(2013) and then converted to EC_e by using Slavich conversion factor(Slavich and Petterson, 1993). The heavy metals were extracted using 0.1M HCl and read using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP), (Estefan *et al.*, 2013; IITA, 1979)

Organic Amendments Production and Analysis

The Biochar used was produced based on the description of Johannes Lehmann (2007) using grinded and well dried wood in a fabricated pyrolysis Kiln in the Department of soil science Bayero University, Kano. While bin composting was adopted for the production of the compost used in the experiment as described in USDA (2010).

The pH and EC of both the biochar and the compost were determined in amendment: water ratio of 1:10as described by McLaughlin (2010) and USDA (2010) respectively. Available forms of Cu^{2+},Co^{2+} and Pb^{2+} were extracted using 0.1M HCl and read using Atomic Organic Spectrophotometer (Buck Scientific Model 210 VGP), (Estefan *et al.*, 2013; IITA, 1979)

2.3. Amendments Incorporation

All the organic amendments were incorporated into the soil before planting by surface broadcasting and then using hoe to mix it for proper incorporation into the soil.

3. SOIL SOLUTION SAMPLING AND ANALYSIS

3.1. Lysimeter Installation

Three ceramic suction Lysimeters were installed in each plot 1 week after sowing. The soil was drilled with an auger to install the suction cup of the lysimeter at the required depth. The depths at which the Lysimeters were installed were 10, 20 and 30cm randomly distributed within each plot.

3.2. Solution Collection

The solution samples were collected at three different growth stages of maize (seedling, vegetative and tasseling). Prior to sample collection a suction pressure was applied to the lysimeters using a hand operated vacuum pumpand then allowed to stand for 24 hours. The solution inside the cup was collected using a hand operated evacuation syringe.

3.3. Soil Solution Analysis

The samples of the solutions werecollected and taken to the laboratory for analysis. Nitrate,pH, and ammonium were determined on reaching the laboratory. The samples were then stored at a low temperature for further analysis. pH was determined using a glass electrode pH meter as described by Estefan *et al.,* (2013), NO_3^- and NH_4^+ were determined using Steam distillation technique as described in Estefan et al. (2013), EC was determined using glass electrode EC meteras described by Bower and Wilcox (1965). Cu^{2+}, Co^{2+} and Pb^{2+} were read using AAS (BUCK SCIENTIFIC MODEL 210 VGP).

3.4. Statistical Analysis

The data was analysed using Genstat 17th edition. Analysis of variance (ANOVA) was carried out to determine if there is significance difference between the concentration of the selected heavy metals with respect to amendments and sampling depth in all the three sampling stages.

4. RESULTS AND DISCUSSION

4.1. Experimental Soil and Organic Amendments

Table 1 shows the chemical characteristics of the soils of the experimental site. The soil has mean pH and $EC_e$of 6.63 and 1.90dS/m respectively which is agreement with the findings of Abdulkadir et al., (2022). The mean concentrations ofCu, Pb and Co were6.38, 0.83 and 0.97mg/kg respectively.The results of the soil in the experimental site as described above shows that the soil is neutral and falls within the optimum range for the growth of the experimental crop as described by Havlin *et al.,* (2012). The Electrical Conductivity (EC_e) of the soil shows that it is non-saline based on FAO rating (FAO, 1999).

It shows that the pH of the compost was 6.490 while that of the biochar used was 7.717. The EC(1:5) of the compost was 1.78dS/m and that of the biochar was 0.62dS/m. The concentration of available form of Cu, Co and Pb in the compost was found to be 10.67, 0.83 and 0.85mg/kg respectively while in the biochar it was 17.67, 0.72 and 1.46mg/kg respectively.

Table 1: Experimental soil and Organic Amendments

	Soil	Biochar	Compost
pH	6.57	6.42	7.31
EC (dSm^{-1})	1.93	1.84	0.58
Cu ($mgkg^{-1}$)	6.38	10.67	17.67
Pb ($mgkg^{-1}$)	0.83	0.85	1.46
Co ($mgkg^{-1}$)	0.97	0.83	0.72

4.2. pH and EC of the Soil Solution

The response of the soil solution pH and EC as well as its variability with sampling depth and stage is presented in table 2. From the table it can be seen that there is significant difference in the pH values ($p = 0.001$) as influenced by amendments, however, it can be deduced that there is no significant variation with respect to sampling depth but it varies significantly with sampling stage ($p < 0.001$). It can also be deduced that the EC responded statistically to the amendments ($p < 0.001$) but there was no statistical variation with respect to both sampling depth and stage.

The highest soil solution pH response to the amendments was obtained in the biochar amended soil with the least in the compost amended soil. The high increase in the biochar amended soil could be attributed to the ability of the biochar to increase soil pH and partly to the crop uptake as reported by (Gaskin *et al.,* 2010; Major *et al.,* 2010; Zhang *et al.,* 2010, 2012)while the low pH in the compost treated soil may be as a result of dissociation of the carboxyl and phenolic groups(Bohn *et al.,* 2003) in the composted materials which lead to the release of H^+ which decrease soil pH as described in the equation:

Organic C $\rightarrow$ R-COOH $\rightarrow$ $RCOO^- + H^+$ (Havlin *et al.,* 2012)

The general increase in the solution pH compared to that of the experimental soil could be explained by the high demand of maize to NO_3^- which ultimately results in the release of OH^- in order maintain electrical neutrality with higher uptake of more anions than cations, this is subsequently followed by an increase in the soil (Havlin *et al.,* 2012). As the crop grows, the net uptake of nutrients increases which is followed by an increase in the solution pH of the soil, The soils followed this trend with least and its peak values recorded during the seedling and the tasselling stages respectively.

The EC of the soil solution was found to be higher in the solution of NPK amended soil which is as a result of the dissolution of the added inorganic fertilizer which increases the net soluble salts in the soil solution. The difference obtained in the biochar and the compost amended soils could be explained by the ability of the two amendments to increase the soil CEC which increases the adsorption sites for the cations as well as the release of the cations with decomposition.

4.3. The Heavy Metals

Table 3 represents the response of the selected heavy metals to amendments as well as their variability with change in sampling depth and stage. From the table it shows that the concentration of Cu^{2+} is statistically different under the influence of the amendments ($p = 0.045$). It also varies with sampling depth ($p = 0.011$) and sampling stage ($p < 0.001$).

Amendments and sampling stage were both found to significantly affect the concentration of Pb^{2+}(<0.001), however, it was affected by sampling depth. Addition of biochar leads to immobilization of Pb^{2+}*(Li et al., 2016)*to decline in the concentration of Pb^{2+} in the soil solution, this is in accordance with findings of *Li et al.,* (2016). Soil pH is an important critical factor affecting the amount of Pb^{2+} in the soil. The concentration of Co^{2+} was found to vary significantly with sampling stage ($p < 0.001$) but not affected by amendments and sampling depth. The concentration of $Cr^{2+}$and Pb^{2+} decrease with advancement in sampling stage, whereas the concentration of Co^{2+} increases with advancement in sampling stage.

The decrease in the concentration of Cu^{2+} is governed by plant uptake, increase in the solution pH and adsorption onto clay and organic matter surfaces. Microbial assimilation and complexation could also contribute to this decrease. The pH dependent relationship between Cu^{2+} is represented below:

$Cu^{2+} + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H^+$(Havlin *et al.,* 2012)

Increase in the concentration of Co^{2+} could be explained by waterlogging conditions which favour its availability for plant uptake. .

Table 3: The Concentration of Trace Elements as Influenced by Amendments, Sampling Depth and Stage

	Cu^{2+}	Pb^{2+}	Co^{2+}
	←	mg/l	→
AMM			
CTR	0.840b	0.167b	0.174
BCH	0.683a	0.128a	0.194
CMP	0.790ab	0.190b	0.202
NPK	0.834b	0.165b	0.190
SED	0.061	0.013	0.016
Depth(cm)			
10	0.746a	0.162	0.199
20	0.882b	0.163	0.191
30	0.733a	0.163	0.179
SED	0.053	0.012	0.014
SST			
Seedling	0.901b	0.181b	0.156a
Vegetative	0.867b	0.190ba	0.144a
Taselling	0.592a	0.116a	0.269b
SED	0.053	0.012	0.014
Interactions			
AMM*Depth	NS	NS	NS
AMM*SST	NS	*	*
SST*Depth	NS	NS	NS
AMM*Depth*SST	NS	NS	NS

BCH = Biochar, CMP = Compost, CTR = Control and means followed by the same letter are statistically the same at 5% level of probability using Fischer's protected LSD

The interaction of amendments and the sampling stage on the concentration of Pb^{2+} in the soil solution were presented in table 4. The table shows that there is significant difference between the amendments during both the vegetative and the tasseling stage but there is no significant difference obtained during the seedling stage.

Table 4: Interaction between Amendments and Sampling Stage on the Concentration of Pb^{2+}(mg/l)

	SEEDLING	VEGETATIVE	TASELLING
CTR	0.17cdef	0.18bcde	0.12fg
BCH	0.16defg	0.22ab	0.12fg
CMP	0.25g	0.20abcd	0.11g
NPK	0.15efg	0.22abc	0.11g
SED		0.024	

BCH = Biochar, CMP = Compost, CTR = Control and means followed by the same letter are statistically the same at 5% level of probability using Fischer's protected LSD

Table 5 shows the interaction effect of amendments on the sampling stage of the soil solution Co^{2+}. The results shows that there is no significant influence of the amendment on the stage during both the seedling and vegetative stage, however, it was found to vary significantly during the tasseling stage.

Table 5: Interaction between Amendments and Sampling Stage on the Concentration of Co^{2+}(mg/l)

	SEEDLING	VEGETATIVE	TASELLING
CTR	0.14c	0.15c	0.22b
BCH	0.15c	0.14c	0.23b
CMP	0.13c	0.15c	0.31a
NPK	0.19bc	0.15c	0.33a
SED		0.029	

BCH = Biochar, CMP = Compost, CTR = Control and means followed by the same letter are statistically the same at 5% level of probability using Fischer's protected LSD

5. CONCLUSION

The results of the experiment showed that both biochar and NPK fertilizer have the ability to increase the soil solution pH and EC whereas compost decreases pH and increases EC. Biochar has the ability to reduce the concentration of Cu^{2+} and therefore making it less available. The concentration of Cu decreases downward indicating lower leaching potential of the specie. It is also found that the concentration of Co^{2+} increases with advancement in growth stage of the test crop indicating that the species tend to be more available for the crop as it mature. Also, the concentration of Cu^{2+} and Pb^{2+} decreased, showing that the species tend to be less available as the crop becomes matured.

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AUTHOR

Abdulkadir Aliyu was born in Makarfi local government area of Kaduna state, Nigeria. He had his basic and post basic education in the same place. He obtained his bachelor degree from Alexandria University Egypt and his Master of science in Soil Science from Bayero University Kano. He is currently doing his PhD in Bayero University Kano and working with Federal University Dutsin-Ma, Katsina state, Nigeria.