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Comparative potential effects of biochar, compost and inorganic fertilizer on major nutrient ions mobility and stability in screen-house irrigated maize in the drier savannas of Nigeria

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ABSTRACT

A screen-house experiment was conducted in the dry season of 2017 to evaluate the potential effect of organic and inorganic soil amendments on the mobility and stability of significant plant nutrient ions. 5 t ha-1 compost or Biochar were applied to pot-grown maize to compare their effect with NPK at the rate of 120: 60: 60 kg ha-1 and a control. Soil solution was sampled with lysimeters at varying depths of 10, 20, and 30 cm at the seedling, vegetative and tasselling stages of growth. Ions mobility was evaluated by concentrations at the stages and depths while stability was measured as a function of Gibb's free energy of formation. Results revealed variable, often non-significant, and non-interactive effects on cations except Biochar on K+; NPK and compost on NH4+ across growth stages and depths. More significant variations were recorded with concentration and stability of significant anions with all the amendments across depths and growth stages, especially NPK and compost on NO3-. Increasing concentration was noted to be associated with an increase in ΔG and hence higher stability due to approach to equilibrium. It is concluded that the effect of the amendments in the short term may be unpredictable and unreliable.

1.0. Introduction

The soil solution is the immediate source of nutrients to growing plants and the medium through which materials move through the soil. It is an aqueous phase consisting of dissolved ions that move freely or form complex and ligand associations with various other ions in the solution (Sparks, 2003).

The soil solution is in constant transition in terms of composition and stability of its ionic constituents both under natural and managed conditions. For example, weathering of minerals in soils' parent materials has been found to alter the composition and the chemistry of the ionic constituents of the soil solution (Sposito, 2008). Under field conditions, agronomic practices such as fertilizer addition may have a significant influence on the nature of the soil solution. Auxtero *et al.* (2012) postulated that liming and changing organic carbon content might strongly influence Al solubility and other chemical features of the soil solution.

Biochar and compost are gradually becoming important bio-resources with multiple environmental use advantages, especially for amending potentially problematic soils. Although increasing evidence suggests that organic amendments addition to soil may enhance plant production in a variety of natural and agricultural environments (Atkinson *et al.* (2012); Jeffery et al. (2011)).The direct influence of the additions of such materials on soil nutrient cycling and

other chemical behaviour of the soil are inconsistent and remain somewhat poorly understood.

In the drier savannas of Nigeria, availability of moisture is a critical set back to production, and therefore irrigation to supplement soil moisture and extend growing season is a commonplace activity both at small and large scale levels.

There is a scarcity of empirically-based literature to aid the understanding of the potential effect the addition of amendments, especially in the organic form may have on the chemistry of the soils of the drier savannas of the country. It is a region of intense agricultural activities but of declining soil fertility and therefore, exploration of better and sustainable production approaches that may enhance soil fertility and nutrients availability is direly needed. Bearing this in mind, therefore, this research was aimed at evaluating the potential effect of the addition of amendments on the mobility of ions in soil solution extracted from different depths in the soil and at different stages within a growing period of irrigated maize.

2.0. Materials and Methods

2.1. Experimental site

The research was conducted in the screen-house facility of the faculty of agriculture Bayero University Kano, Nigeria, during the dry season of 2017. The site is located in the Sudan savannah of northern Nigeria, having latitude of '$11^0$59'N and longitude of $8^0$25'E.

2.2. Treatments and experimental design

The experiment consisted of four sets of treatment: Biochar and compost at the equivalent rate of 5 t ha^{-1}(being the minimum rate at which significant effect was recorded) [6], inorganic fertilizer (NPK) at the rate of 120:60:60 kg ha^{-1} and control that had neither organic amendment nor compost. The experiment was laid out in Complete Randomized Design (CRD) replicated three times.

2.3. Growing media

Surface 0-20 cm soil was excavated from a fallow field in the research farm and used to fill to 50 cm mark, a 40 cm wide and 60 cm deep plastic planting pots that had drainage holes at the bottom. The pots with soil content were weighted and the equivalent of 5 t ha^{-1} biochar or compost using the 2, 000, 000 kg furrow slice weight as the basis, was incorporated and worked in with hand trowel to 5 cm depth. Half of the Nitrogen and all of phosphorus and potassium fertilizers were applied using side drilling as basal application. The fertilizer used was NPK 15:15:15 at the rate of 60:60:60 kg ha^{-1} at sowing. The remaining nitrogen was applied three weeks after sowing (WAS) using urea (46% N) to supply the remaining 60 kg N ha^{-1} at 4 WAS. The pots are saturated with water before planting and every three days after seedling emergence due to the predominantly sandy nature of the soil. The pots were planted to an early maturing maize variety (EVDT2009). Two seeds each were sown in two 5 cm deep holes at opposite edges of the containers. The holes were made 7.5 cm from the edges and 25 cm apart. The seedlings were thinned to one at 2 WAS. The pots were kept weed-free throughout the experiment by hand pulling.

2.4. Soil sampling and analysis

Before excavation, 5 soil samples were collected from the field in an M-shaped zigzag manner by auguring to 20 cm depth. Samples were air-dried, gently crushed, and sieved through a 2 mm sieve mesh and stored in an airtight container before analysis. The samples were used for the characterization of the soil.

Particle size distribution was determined using the principles of Boyoucous Hydrometer as described by Gee and Or (2002). The textural class of the studied soil was determined using the USDA textural triangle.

The Bulk density was determined by the core sampler method, where an undisturbed soil sample was collected using a stainless steel cylinder and then oven-dried at 105^oC to constant weight as described by Campbell and Henshall (1991). It was expressed as a mass of dry soil per unit volume of moist soil.

The pH and EC of the soil were determined in soil: water ratio of 1:2.5 and 1:5 respectively using glass electrode pH and EC meters as described in [9]. EC values were then converted to EC_e by using the Slavich conversion factor (Slavich and Petterson, 1993). Soil Organic Carbon (SOC) was determined using the Walkley-Black wet oxidation method (Walkley and Black, 1934).

Neutrally buffered ammonium acetate was used in the extraction of exchangeable bases (Anderson and Ingram, 1993). Ca^{2+} and Mg^{2+} were read using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP), while Na^+ and K^+ were read using a flame photometer (Jenway PFP 7). Exchangeable acidity was extracted using the IM KCl solution and determined by titration with NaOH as described in Anderson and Ingram (1993). Cation Exchange Capacity was determined by the summation method as described by Chapman (1965).

Total nitrogen was determined using the Micro Kjeldahl method as described in Bremmer (1996). The soil available phosphorus was extracted using Bray 1 method (Bray and Kurtz, 1945) and determined using the Blue method (Drummond and Maher, 1995).

2.5. Organic amendments production

The Biochar used was produced from sun-dried (moisture content, MC < 10%) and crushed maize cobs using a fabricated pyrolysis Kiln in the Department of soil science Bayero University, Kano. The kiln consisted of an airtight cylindrical metal drum and butane combustion burners. The material was heated to 350 - 400 ^oC for 3 hours. The material was allowed to cool overnight before evacuation to prevent re-ignition. Before addition to the experimental pots, the material was ground and sieved to pass through 2 mm sieve.

Compost was produced from dried herbages and assorted animal manure from the University's livestock shade. The materials were laid in pens in a layered manner of 3:1 herbage: manure height ratio to a height of 1 m. Setup was watered with an average of 1 litre of water to 5 kg material at an interval of 7 to 10 days. Turning was done every 2 weeks from the first 10 days of setup. The setup was main-

tained for 3 months and the material was cured under shade for 2 weeks after harvesting before application.

2.6 Amendments sampling and analysis

Portions of the two amendments were taken, sieved using 2mm sieve, and preserved for analysis. The pH and EC of the Biochar and compost were determined using amendment: water ratio of 1:10 as described by McLaughling (2010) and USDA (2010) respectively. Bulk density in all materials was determined by the gravimetric method. Biochar and compost's volatile matter, resident matter, particle density, and porosity were determined by the methods of McLaughlin (2009). Their total nitrogen was determined using the micro Kjeldahl method as described in Bremmer (1996). Total carbon in both of the amendments was determined by the ignition method as described by Shuttle (1995). Available phosphorus was extracted using Bray 1 method (Bray and Kurtz, 1945) and then read using a spectrophotometer(22PC MODEL) at a wavelength of 860nm (Murphy and Riley, 1962).

Exchangeable bases were extracted using the NH_4Ac saturation method as described in Anderson and Ingram, (1993). Ca^{2+} and Mg^{2+} were determined using AAS (BUCK SCIENTIFIC 210 MODEL) while Na^+ and K^+ were determined using a flame photometer (JENWAY PFP 7). Exchangeable acidity was extracted using IM KCl and then determined by titration with NaOH as described by Anderson and Ingram, (1993). The Effective Cation Exchange Capacity was determined by the summation method as described by Chapman (1965).

2.7 Soil solution sampling and analysis

2.7.1 Lysimeter installation

Three ceramic suction Lysimeters were installed in each pot one week after sowing at three varying depths of 10, 20, and 30 cm. The soil was drilled with an auger to install the suction cup at the required depth. The lysimeters were placed in a row starting at 5 cm from the edge where there was no growing plant and place 10 cm apart passing through the 25 cm gap separating the seedlings.

2.7.2 Solution collection

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

2.7.3 Soil solution analysis

The samples of the solutions collected were taken to the laboratory for analysis. pH, nitrate, and ammonium were determined on reaching the laboratory. The samples were then refrigerated throughout the analysis. pH was determined using a glass electrode pH meter (JENWAY 3520 MODEL) as described by [9]. NO_3^- and NH_4^+ were determined using the Steam distillation technique as described in Estefan et al. (2013). EC was determined using a glass electrode EC meter (DDS-307 MODEL) as described by Estefan et al. (2013). Phosphate was determined by the Blue method (Murphy and Riley, 1962) and then read using a spectrophotometer at 860nm (22PC MODEL). Na^+ and K^+ were read using a flame photometer (JENWEY PFP7 MODEL). Ca^{2+}, Mg^{2+}were read using AAS (Buck Scientific MODEL 210 VGP). $SO_4^{2-}$was determined using the Gelatin Barium Chloride method and read using a spectrophotometer (DDS-307 MODEL).

2.8 Thermodynamic calculations

The following thermodynamic parameters were calculated as described below

2.8.1 Ionic strength

The ionic strength of the solution was determined using the Equation below:

$$I = 0.013EC$$ (Griffin and Jurinak, 1978)---------- (1)

Where I = Ionic strength

EC = Electrical conductivity of soil solution (dSm^{-1})

2.8.2 Activity coefficients

The activity coefficients used were determined using the Davies equation as described below:

$$\text{Log}\gamma_i = -AZ^2 \left(\frac{I^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} - 0.3I \right)$$ (Sposito,2008)….. (2)

Where γ = single-ion activity coefficient of specie i

A = dielectric constant of water (0.511)

Z is the ionic charge of the specie i

I = the ionic strength of the solution of the specie I is the chemical species

2.8.3 Ion activities

The activity of the chemical species in the soil solution was determined using the Equation:

$\alpha_i = \gamma_i m_i$ (Sposito, 2008) ---------- (3)

where α_i = single-ion activity of specie i

γ_i = single-ion activity coefficient of specie i

m_i = concentration of specie i

2.8.4 Change in free energy

The change in free energy was calculated using the Equation

$\Delta G = 5.71 \log \alpha_i$ (Bohn et al, 2003)---------- (4)

Where: α_i is the activity of the ion under consideration.

2.9 Statistical Analysis

Data analyses for the work was done using Genstat 17th edition. Analysis of variance was carried out to determine if there is a significant difference between chemical properties of the soil solution as well as changes in free energy to amendments, sampling depth, and time. Significant

differences were separated from Tukey's HSD.

3.0. Results

3.1. Characteristics of the Experimental Soil and the Organic Amendments

Table 1 shows the chemical characteristics of the soils of the experimental site and the organic amendments used in the experiment. The soil and the compost were very slightly acidic, while Biochar was very slightly alkaline. Nutrients content in the soil was characteristically low, typical of the predominantly sand textured soils of Nigeria's drier savannahs. Variation in nutrient contents was, however, observed in the organic amendments with higher values occurring in compost than in Biochar. Both materials were physically light and porous with Biochar being lighter and more porous. Biochar also had a higher carbon content, thereby more fixed matter than compost.

3.2 Effect amendments on pH and EC

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 a significant difference in the pH values ($p = 0.001$) as influenced by amendments and growth stages. The pH was significantly more alkaline under the influence of Biochar and with the advance in the growth stage. The EC varied significantly only due to the amendments ($p < 0.001$) with the highest value recorded under the influence of mineral fertilizer.

3.3Effect of amendments on nutrient anions (NO_3^-, SO_4^{2-} and PO_4^{3-})

The effect of the amendments, sampling depth, and stage on the concentration of nitrate is presented in Table 2. NO_3^- concentration was significantly higher in compost, and

Table 1: Physical and chemical characteristics of the experimental soil and the organic amendments

	Soil	**CMP (dry weight)**	**BCH (dry weight)**
pH	6.63	6.49	7.72
EC (dSm^{-1})	1.90	1.78	0.62
TN (gkg^{-1})	0.13	12.8	10.1
OC (%)	0.32	26.8	65.6
K ($cmolkg^{-1}$)	0.46	5.06	3.81
Na ($cmolkg^{-1}$)	0.20	0.9	0.08
Mg ($cmolkg^{-1}$)	1.15	1.60	1.39
Ca ($cmolkg^{-1}$)	2.72	2.06	1.39
EA ($cmolkg^{-1}$)	0.17	0.85	0.51
ECEC ($cmolkg^{-1}$)	4.69	10.47	7.18
Av. P ($mgkg^{-1}$)	7.17	171.76	33.06
CN ratio		25.24	60.18
Sand (%)	84		
Silt (%)	7		
Clay (%)	9		
Textural Class	Loamy sand		
Bulk Density ($g\ cm^{-3}$)	1.5	0.31	0.21
Porosity (%)		69.09	87.54
Moisture content (%)		26.28	1.01
Volatile matter (%)		18.00	15.50
Fixed matter (%)		52.50	82.50

Spatio (Soil Depth) and Temporal (Growth Stage) Variations of Soil Solution Characteristics as Affected by Amendment Type

mineral fertilizer treated soils. Its values also significantly fluctuated with sampling depth and expectedly decreased with the advance in the growth stage. The concentrations of phosphates and sulphates in the soil solution were only significantly affected with variation in the sampling stage as $SO_4^{2-}$was found to decrease linearly with the advance in growth stage while PO_4^{3-} fluctuated overgrowth stage with the highest value occurring at vegetative stage

3.4. Effect of amendments on nutrient cations (basic cations and NH_4^+)

Table 2: Variation of soil solution pH, EC, and anions as influenced by amendment types

	pH	EC dSm^{-1}	NO_3^-	SO_4^{2-} mg/l	PO_4^{3-}
AMM					
CTR	6.97bc	0.40c	77.53b	26.74	7.35
BCH	7.11a	0.48b	70.63b	32.14	8.42
CMP	6.88c	0.51b	87.86a	26.77	7.44
NPK	7.064ab	0.62a	94.11a	24.13	6.39
SED	0.0613	0.037	3.79	6.599	1.149
Depth(cm)					
10	7.007	0.49	74.08b	27.43	7.83
20	7.005	0.48	93.89a	26.62	8.15
30	7.002	0.55	79.63b	28.28	6.23
SED	0.0531	0.032	3.28	5.715	0.995
SST					
Seedling	6.504c	0.53	98.20a	46.90a	4.79b
Vegetative	7.165b	0.50	82.21b	19.22b	9.00a
Taselling	7.344a	0.47	67.19c	16.20b	8.42a
SED	0.0531	0.032	3.28	5.715	0.995
Interactions					
AMM*Depth	NS	NS	NS	NS	NS
AMM*SST	NS	NS	NS	NS	NS
SST*Depth	NS	NS	NS	NS	NS
AMM*Depth*SST	NS	NS	NS	NS	NS

Table 3 shows the influence of amendments, sampling depth, and stage on the concentration of basic cations and ammonium in the soil solution of the experimental soil. The concentration of $Ca^{2+}$was not affected by the amendments. It, however, significantly varied with sampling depth ($p = 0.014$) and growth stage ($p<0.001$). It progressively increased with depth and decline with advancing stage of growth. The concentration of Mg^{2+}only varied significantly with the growth stage ($p < 0.001$) where it was found to be declining with the advancement in growth just like its counterion (Ca^{2+}). The concentration of K^+ was found to be significantly highest in Biochar treated pots in amendments and at the seedling and vegetative stages of growth ($p < 0.001$). Na^+ concentration only varied statistically with sampling stage ($p < 0.001$). Unlike the other cations, Na^+ concentration was highest at the tasselling stage of the crop. Unlike the other metallic cations, it also showed a significant interaction between the amendments and the stage of growth with the highest concentration occurring at the tasselling stage under the influence of mineral fertilizer (Table 4). The trend of NH_4^+ was similar to that of its counterpart inorganic N (NO_3^+) with the highest values under the influence of NPK and compost. Its values fluctuated with depth and progressively declined with the advancement in the growth stage (Table 3).

3.5. Effect of amendments on the free energy of formation

3.5.1 The Change in free energy of formation of nutrient anions

Table 5 represents the change in free energy of the formation of the significant nutrient anion forms in the soil solution. The general trend of the result was similar to the concentration of the ions in solution. The results show that the change in free energy of formation of NO_3^- was found to be affected by the amendments ($p < 0.001$), sampling depth ($p < 0.001$) and stage ($p < 0.001$). Similar to the trend in concentration, the higher free energy of formation values were recorded under the influence of NPK and compost at 20 cm depth during the seedling stage of growth. The free energy of formation for $SO_4^{2-}$was only statistically different from the advancement in the sam-

Table 3: Variation of soil solution's nutrient cations as influenced by amendment types

	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+
	← mg l^{-1} →				
AMM					
CTR	4.27	8.98	12.44b	2.65	11.20b
BCH	3.91	6.52	18.69a	2.09	10.45b
CMP	4.29	7.58	13.22b	2.43	12.88a
NPK	4.36	7.75	12.86b	2.76	13.80a
SED	0.288	1.414	2.074	0.331	0.710
Depth					
10	4.01b	7.25	15.08	2.42	10.60b
20	3.97b	7.19	15.08	2.57	13.92a
30	4.64a	8.68	12.74	2.46	11.73b
SED	0.250	1.225	1.796	0.287	0.615
SST					
Seedling	5.85a	18.83a	17.14a	1.02c	14.30a
Vegetative	4.43b	3.61b	16.21a	2.71b	11.92b
Taselling	2.34c	0.69c	9.56b	3.73a	10.03c
SED	0.250	1.225	1.796	0.287	0.615
Interactions					
AMM*Depth	NS	NS	NS	NS	NS
AMM*SST	NS	NS	NS	*	NS
SST*Depth	NS	NS	NS	NS	NS
SST*AMM*Depth	NS	NS	NS	NS	NS

Table 4: Interaction between Amendment and Sampling Stage on the Concentration of Na+(mgl-1) in the soil solution

	SEEDLING	VEGETATIVE	TASELLING
CTR	1.209de	3.638b	3.097bc
BCH	0.973e	2.183cd	3.127bc
CMP	0.865e	2.714bc	3.717b
NPK	1.023e	2.300cd	4.966a
SED		0.573	

Means followed by the same letter are statistically the same at 5% level of probability using 'Fischer's protected LSD

pling stage with values decreasing with the advancement in growth. The change in free energy of formation of PO_4^{3-} was however found to statistically vary with variation in sampling depth ($p = 0.041$) and advancement in sampling stage ($p < 0.001$), fluctuating with depth and increasing with growth stage.

3.5.2. Free energy of formation for nutrient cations

Table 6 shows the influence of amendments, sampling depth, and stage on the change in free energy of the formation of basic cations in the soil solution of the experimental soil. Similar to the anions, the trend shows the tendency of ΔG to increase with the increase in the concentration of the ions. As with its concentration, Ca^{2+} was found to differ statistically to sampling depth ($p = 0.000$) and the sampling stage ($p<0.001$). High concentration at 30 cm depth and vegetative stage of growth resulted in high value for ΔG. The ΔG of Mg^{2+} however only varied significantly with variation in the sampling stages ($p < 0.001$) in which the highest value corresponded with the period of the highest labile concentration of the element. The ΔG values for K^+ were significantly higher than all the other treatments ($p = 0.029$), and this was more so at the seedling and the vegetative ($p < 0.001$) stages of growth. Similar to the effect on the concentration, The Change in free energy of formation of Na^+ was found to be significantly affected with the advancement in the growth stage ($p < 0.001$), and the amendments significantly interacted with the growth stage to influence the ΔG of Na^+ (Table 7). As with its concentration, the ΔG value for NH_4^+ was also found to be significantly affected by all three factors ($p <0.001$) with the highest values corresponding to the highest concentrations shown in Table 5.

4.0, Discussion

4.1. Description of the experimental soil

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 the FAO rating (FAO, 1999). The soil exhibits the typical characteristics of the tropical dry savanna soils (Esu, 2010) in terms of its low organic carbon, available phosphorus, total nitrogen; and medium CEC, calcium, and sodium. Magnesium and potassium were however high probably due to the effect of localized minerals

The texture of the soil in the study area is sandy loam using USDA textural triangle. The Bulk density of the soil

Table 3: Variation of soil solution's nutrient cations as influenced by amendment types

	$\Delta G_{NO_3^-}$ ←	$\Delta G_{SO_4^{2-}}$ kJmol^{-1}	$\Delta G_{PO_4^{3-}}$ →
AMM			
CTR	-16.82b	-22.02	-25.76
BCH	-17.22c	-21.41	-25.51
CMP	-16.54a	-22.02	-25.68
NPK	-16.41a	-22.36	-26.15
SED	0.134	0.522	0.339
Depth			
10	-16.97b	-21.66	-25.70ab
20	-16.38a	-21.94	-25.44a
30	-16.89b	-22.26	-26.19b
SED	0.116	0.452	0.294
SST			
Seedling	-16.28a	-20.44a	-26.97b
Vegetative	-16.73b	-22.54b	-25.10a
Taselling	-17.23c	-22.88b	-25.26a
SED	0.116	0.452	0.294
Interaction			
AMM*Depth	NS	NS	NS
AMM*SST	NS	NS	NS
SST*Depth	NS	NS	NS
AMM*Depth*SST	NS	NS	NS

Table 6: Variation in cationic Gibb's free energy of formation (ΔG) as influenced by amendment types

	$\Delta G_{Ca^{2+}}$	$\Delta G_{Mg^{2+}}$ ←	ΔG_{K^+} kJmol^{-1}	ΔG_{Na^+} →	$\Delta G_{NH_4^+}$
AMM					
CTR	-23.64	-22.50	-21.46b	-23.22	-18.57b
BCH	-23.96	-23.10	-19.37a	-23.73	-18.99c
CMP	-23.85	-22.89	-21.20b	-23.39	-18.24ab
NPK	-23.83	-23.09	-21.30b	-23.58	-18.14a
SED	0.172	0.305	0.781	0.372	0.185
Depth (cm)					
10	-23.94b	-22.83	-20.70	-23.64	-18.76b
20	-23.95b	-23.06	-20.67	-23.29	-18.09a
30	-23.57a	-22.80	-21.13	-23.51	-18.60b
SED	0.149	0.264	0.677	0.322	0.160
SST					
Seedling	-22.84b	-18.82a	-20.20a	-25.19c	-17.99a
Vegetative	-23.48a	-22.95b	-19.68a	-23.05b	-18.54b
Taselling	-25.13c	-26.92c	-22.62b	-22..21a	-18.92c
SED	0.149	0.264	0.677	0.322	0.160
Interactions					
AMM*Depth	NS	NS	NS	NS	NS
AMM*SST	NS	NS	NS	*	NS
SST*Depth	NS	NS	NS	NS	NS
SST*AMM*Depth	NS	NS	NS	NS	NS

Table 7: Interaction between the amendment and sampling stage on the change in free energy of formation of Na+

	SEEDLING	**VEGETATIVE**	**TASELLING**
CTR	-24.69efg	-21.96ab	-23.05bcd
BCH	-25.30fg	-23.51cde	-22.38abc
CMP	-25.57g	-22.68abc	-21.21.90ab
NPK	-25.20fg	-23.def	-21.51a
SED		0.644	

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

was found to be from medium to high.

4.2. Effect amendments on pH and EC

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 as reported by Gaskin et al. (2010); Zhang et al., (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 R-COOH $RCOO^-$ + H^+ (Havlin *et al.,* 2012)

The overall increase in the solution pH in comparison to that of the experimental soil could be explained by the high demand of maize to NO_3^- which 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 pH(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 have its peak in the solution of NPK amended soil which is 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 thereby reducing the total soluble salts that may be formed by the basic cations.

4.3. Effects of amendments on forms of nitrogen in the soil solution

The highest concentration of both $NO_3^-$and NH_4^+in the soil solution of the amended soils were found in NPK amended soil which was not different statistically with compost amended soil while the least value was in Biochar amended soil which was statistically the same with the control. Inorganic nitrogenous fertilizers are highly soluble and have the immediate ability to enrich the solution with plants absorbable nitrogen forms through the transformation of urea to ammonia then to ammonium as well as the subsequent conversion of ammonium to nitrate with the help of nitrifying bacteria (Poss and Saragoni, 1992). To a lesser extent, nutrient-rich compost may also exert a similar effect through biological mineralization in the form of proteolysis and ammonification (Auxtero et al., 2012). The low values recorded in the solution of Biochar amended soils may be attributed to the lower nutritive value (Table 2) of the material (Jones et al., 2012)as well its ability to retain both forms in both positively and negatively charged sites on the material (Abukari, 2014) thereby reducing the leaching potential of the ions. It may also be attributed to its effect on reducing the rate of ammonification (DeLuca et al., 2009). Biochar has also been noted to decrease the potential for NH_3volatilizationby reducing the amount of available NH_4^+ in the soil solution and raising the pH of the soil; both of which do not support the formation of NH_3 as well as its volatilization (Abukari, 2014). The combined effect of its uptake and leaching are two major processes that govern the decrease in its concentration in the soil solution with depth and especially with the advancement in the growth of the experimental crop. Maize is mainly known for its heavy demand for nitrogen all through its life cycle, and especially at vegetative growth stage

4.4. Effects of amendments on phosphates and sulphates in the soil solution

The progressive decrease in the concentration of SO_4^{2-} with an increase in sampling time signifies significant uptake of the nutrient and the fact that its adsorption decreases with increasing pH (Mulder and Cresser, 1994) as a result of the amphoteric character of some adsorbing surfaces (oxides). The adsorption sites on the oxide surfaces become negatively charged upon de-protonation resulting in sulphate repulsion, thereby forcing more of the ion into a solution for uptake and leaching. This might also explain the lack of significant effect of all the amendment forms on the concentration of the ion.

Phosphates are comparatively slower forming ions due to the low solubility of P minerals and their rapid change from soluble forms to fixed or more complicated forms especially in coarse-textured soils with relatively high Ca content (Al-Rohily et al., 2013). This, therefore, makes the element less available to the growing plant even with the use of mineral fertilizers. The solubility of P may progressively increase with rising pH (Huang et al., 2005) as the activity of P-binding elements such as Fe and Mn deceases. As pH values become buffered especially with the application of amendments such as compost (Latifah et al., 2018) and provision of enhanced sorption sites by amendments such as Biochar; the concentration further decreases as noted during the tasselling stage of the crop. Therefore there is the tendency for organic amendments to decrease the spontaneous release of P-ions and encouraging gradual releases, thereby reducing its leaching and runoff vulnerability. This may thereby enhance its continuous availability throughout the crops' growth stages as opined by Al-Rohily *et al*. (2013).

4.5. Effects of amendments on **b***asic cations*

The only significant effect of amendments noted in the concentration of the ions in solution was to Biochar on K^+. The unusually high amount recorded in the treatments may be due to the inability of the ion to compete for adsorption sites against such ions as Mg^{2+} and Ca^{2+} because more abundant ions show higher significant polarization potential (Evangelou, 1998). Higher valence ions, especially when hydrated are generally better attracted to exchange sites in the soil, thereby displacing lower valence ions into solution. Because of its high sorptive capacity, therefore, Biochar treated soil may likely have a lesser affinity for K^+. The sorption mechanics in biochars derived from grass and non-woody plant materials are predominantly regulated by ion exchange and physical sorption because of their

high CECs caused by O contents and acidic surface sites (Harvey et al., 2011). The concentration may also have been enhanced by the relatively high amounts of the element in the material (Table 1) as K and P have been established to be significantly high in biochars due to thermal mineralization and subsequent retention in the product (Knicker, 2010). Although it may also be argued that both NPK and compost (Table 1) may also be rich in the element, but yet sorption and ion exchange may be less prominent phenomena regulating ion concentration in the soils amended with both. Furthermore, K release by Biochar has also been demonstrated to be from 'major' to 'complete' (Angst and Sohi, 2013).

The concentration of basic cations in soil solution across treatments progressively decreased with crop growth as a result of uptake by the crop. Exceptionally, however, Na^+ showed an increasing trend, thereby signifying its lesser significant physiological role in the life cycle of the crop. The behaviour of the ions here is similar to the findings of (Carmona et al., 2010) in Brazilian soils, who additionally proposed accelerated leaching especially in coarse-textured soils as is the case with the experimental soil (Table 1) as another reason for the cation loses in irrigated soils and soils of high rainfall areas.

The result generally portrays cation availability in solution across amendments, sampling depth, and time to be in the order of $K^+ > Mg^{2+} > Ca^{2+} > Na^+$.

4.6. Effect of amendments on the free energy of formation

The general trend of the results obtained with the free energy of formation for the various ions as shown in Tables 5 - 6 showed that as ionic concentration increases, there was a corresponding increase in free energy. Bearing in mind that concentration of an ion is directly related to its activity in solution as shown by equation (3) Sposito, (2008), it, therefore, implies that the higher the activities of ions in solution, the higher their approach to equilibrium.

According to (Liu et al., 2013) the relative stability of the chemical system in the soil solution or other words the tendency of the system to react or change is determined by the Gibbs free energy also simply called free energy. It is a quantity derived from the relationships between heat and work in thermodynamics of the chemical system. As a rule, systems change toward minimum free energy (Sposito, 2008). The Fundamental Equation of the Gibbs energy is as shown below:

$G = H - TS$ (Jeffery et al., 2011)

where, G = the Gibbs free energy (kJ); H = the enthalpy (kJ); T = the absolute temperature (°K); and S = the entropy (kJ °K-1). According to Angst and Sohi (2013 for the three variables in soil solution, Equation (1) can be rewritten as follows:

$\Delta G = G_{products} - G_{reactants} = \Delta H - T\Delta S$ (Situmeang et al., 2015)

where, ΔG = the difference in the Gibbs free energy between products ($G_{products}$) and reactants ($G_{reactants}$) in the chemical system. ΔH and ΔS = the differences in enthalpy and entropy between the products and reactants. The spontaneity of chemical species interactions in the solution may lead to the formation of new products as predicted by equation 6.

As a rule; if $\Delta G < 0$, then reactions will occur (spontaneous), $\Delta G < 0 = 0$, then the system is at equilibrium, while $\Delta G > 0$, no reaction will occur . In the soil solution, it has been shown that ΔG is strongly related to the log of activities of ions in solution as portrayed by equation (4) (Bohn et al., 2003).

It could be noted that there was an increase in the ΔG of NH_4^+ with an increase in that of NO_3^- and vice versa which may be attributed to the microbially mediated nitrification process as reported by Poss & Saragoni (1992). While the noted increase in the ΔG of NO_3^- with the increase in that of SO_4^{2-} could be attributed to the concurrent formation of the two ions from the decomposition of organic matter. ΔG values of $NO_3^-$was also noted to move closer to zero at the same condition as the values of those of Ca^{2+}, Mg^{2+}, and K^+ which is in agreement with the findings of Poss & Saragoni (1992) and maybe. As a result of the transformation of organic matter N and the applied urea into NO_3^- which lead to the release of those ions from the exchange complex. During the conversion of NH_4^+ to NO_3^- two protons would be released which displace the cations from the exchange sites. Although increasing ΔG values indicate the potential for the stability of ions, the tendency for the ions in solution to be leached or exhausted via uptake by plants is equally high. Therefore in the long term, the situation observed in the NPK and compost treatments may not be favourable for crops' growth and environmental safety. The situation in the biochar field may, therefore, serves better in these directions where the ions are gradually formed and released into solution.

An increase in the ΔG value of PO_4^{3-} may be explained by the fact that proton is consumed during the conversion of NH_3 to $NH_4^{+,}$ which tends to increase soil pH. This condition favours the solubilization of PO_4^{3-}(Al-Rohily et al., 2013) which will eventually lead to an increase in its activity; this means the more the NH_4^+ is produced via this process, the higher the activity of PO_4^{3-}.

5.0. Conclusions

In conclusion, it could be said that despite the variability of the effects of the different treatments on the features of the ions examined in the short period of the experiment, there is the distinct potential that in the long term the decrease observed in the concentration and the net change in free energy of formation of especially essential ions like NO_3^- and NH_4^+in the Biochar treated pots; may lead to decrease in the leaching potential of the two species thereby retaining them for further uptake, while compost and NPK fertilizer may increase the leaching potential of the species.

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