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Fate and Form of Nitrogen under Different Soil Redox Status

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***Abstract*— The experiment sets out to investigate the effect of oxidation-reduction on nitrogen formsin soil. The trial was a 3 x 2 factorial experiment laid out in a Randomized Complete Block Design (RCBD) and replicated three times. Treatment consisted of two variables which are poultry manure at three levels (0t/ha, 6t/ha and 8t/ha) and water regime at two levels (field capacity and waterlogged).The combinations resulted into six (6) treatments resulting into three oxidation-reduction potential range [oxidized (>300), moderately reduced (-100 to 300), reduced (<-100)]. Data collected pH, Eh, Total nitrogen, Organic matter,NO_3^-–N and NH_4^+-N. Data collected were subjected to Analysis of variance (ANOVA) while mean were separated using Tukey Honesty Significant Difference (HSD) Test. Graphs were generated using Microsoft excel. The result showed that nitrogen under oxidize condition is majorly in nitrate form while under reduced condition is ammonia. However, moderately reduced soil had the highest total nitrogen content. This is attributed to the fact that both forms of nitrogen are present in the soil as a result of accumulation of NH_4^+ and progress of nitrification process. It was concluded that the forms and fate of nitrogen in soil also depends on the oxidation-reduction status of the soil.*

Keywords— **Ammonia, Oxidized, Reduced, Nitrate.**

I. INTRODUCTION

Nitrogen (N) is the most abundant element in the atmosphere and is usually the most limiting crop nutrient (USDA, 2014). Nitrogen fixation are necessary to convert N into forms which plants can use. Some of these processes can lead to nitrogen losses such as leaching or volatilization (Aczel, 2019). Nitrogen is added to soil naturally from N fixation by soil bacteria associated with legumes and through atmospheric deposition in rainfall (Brady and Weil, 2010). Additional nitrogen is typically supplied to the crop by fertilizers, manure, or other organic materials. Because nitrogen is so dynamic, it can easily be lost to the environment, making it difficult to determine adequate nitrogen levels throughout the growth cycle of crops. Soil nitrate-N is an excellent indicator of N-cycling in soils, whether carryover nitrogen was used by the previous crop and whether additional nitrogen is needed. Excessive application of N fertilizer can result in leaching of nitrates below the root zone and into groundwater at a shallow depth (Yadav, 1997). Factors such as soil drainage, soil texture, and slope steepness influence N-transport and N-transformation processes that limit availability of crops. Climatic factors such as rainfall and temperature as well as site condition such as moisture, soil aeration (oxygen levels) and salt content (electrical conductivity) affect the rate of N mineralization from organic matter decomposition, nitrogen cycling and nitrogen losses through leaching, runoff, or denitrification (USDA, 2014). The potential for leaching is dependent on soil texture and soil water content among other things (Domnariu*et al*., 2020). Organic matter decomposes releasing nitrogen more quickly in warm humid climate and slower in cool dry climates. This nitrogen release is also quicker in well aerated soils and much slower on wet saturated soils. Soils that have poor drainage and are saturated with water causes denitrification to occur resulting in loss of nitrogen as a gas resulting in emission of potent greenhouse gases, yield reduction and increased nitrogen fertilizer expense (USDA, 2014).

As both $NO_3^-$and NH_4^+ are soluble, pH mainly influence the form under which N is assimilated by plants (Hinsinger*et al.,* 2003). The form of N assimilated by plants also has a marked effect on cellular regulation of pH (Marschner, 1995). Furthermore, as plants use NH_4^+ to synthesize proteins, the assimilation of NO_3^- N inducesa considerable energy cost for the plant to reduce NO_3^--N to NH_4^+-N (Marschner,1995). In addition, as NO_3^- is highly soluble, there is a risk of loss, and pollution. The form of nitrogen assimilated by plants has a marked effect on rhizospheric pH and on the assimilation by plants of other cations and anions (Hinsinger *et al.*, 2003). This forms of nitrogen is greatly affected by the prevailing conditions in the soil such as aeration and moisture content both of which are function of oxidation-reduction potentials. However, very little is known about how soil redox status affect the forms of nitrogen in the soil. Hence the necessity of this research.

II. MATERIALS AND METHODS

The study was carried out at the screen house of the Department of Crop, Soil and Pest Management, Federal University of Technology Akure, Ondo State, Nigeria.

The experiment was a 3 x 2 factorial experiment laid out in a Randomized Complete Block Design (RCBD) and Replicated 3 times. The two factors were poultry manure at 3 levels (0tha^{-1}, 6tha^{-1} and 8tha^{-1}) and water regimes at two levels (waterlogging and field capacity). Five kilogram homogenous soil was put inside each bucket after which levels of poultry manure was applied. Treatments subjected to field capacity were perforated underneath to allow for easy drainage of water from the bucket.Soil samples were collected, mixed together from which a composite sample was taken for pre-experimental analysis. Subsequent samples were collected based on treatments applied at an interval of 3 weeks (3WAI, 6WAI and 9WAI) samples collected were taken to the laboratory for analysis.

Analysis was done to determine the chemical properties of the soil, some of the properties considered are pH, Eh, organic carbon content, organic matter contents, Total nitrogen, Nitrate and Ammonium content.

pH

In determining the pH, 10g of soil was weighed and 20ml of distilled water was added to it. It was stir and allowed to stand for 30 minutes after which it was measured by using a pH meter.

Determination of Organic Matter

Soil organic matter content was determined using the Walkley-Black oxidation method which measures the active or decomposable organic matter in the soil. The soil sample was ground into fine powder from which 1g soil sample was taken and placed in a 250ml conical flask and 10ml of 0.167M $K_2Cr_2O_7$ was added. Twenty ml of conc. H_2SO_4 was rapidly added to the mixture and the swirled gently until the soil and the reagents mixed properly. The mixture was then allowed to cool for about 30 minutes, 3 drops of ferroin indicator was added and titrated against 0.5M Iron (II) ammonium sulphate. The end product is a brownish red or maroon color solution. Also a blank titration was done without soil.

Calculations

% Organic Carbon= (B-T) x M x 0.003 x 1.33 x 100/wt

Where:

B= Blank titre value

T= Sample titre Value

M= Molarity of $Fe (SO_4)_2$

Wt= Weight ofdriedsample

Percentage Organic Matter is then further calculated as

%OM= % Organic Carbon x 1.724

Soil Redox potential (Eh) determination

Redox potential was measured using the method described by (Rabenhorst*et al.*, 2009). Twenty gram of the soil samples were collected, soaked in water from bottom to top so as to prevent entrapment of air during saturation and allowed to mix for 30 minutes after which 50 ml of the solution was collected and taken to the laboratory for reading. In the laboratory, redox potential (Eh) was measured using a pH/Redox combined meter. Voltage was measured every 10 seconds for 60 seconds and the mean values of the collected measurements were calculated.

AMMONIUM

Five gram of soil was weighed, 50 ml of sodium acetate was added to it allow to stand for 2 hours then filter through filter paper. Then 5 ml of the filtrate was taken and 10 ml of sodium hydroxide was added to it then 25 ml of water. Distillate so that the steam will go to the conical flask where 5 ml of boric acid with 3 drop of ferroin indicator was. The color changes to green as the steam was dropping and make it up to 25 ml. then titrated against 0.01M hydrochloric acid (HCL).

NITRATE

Five gram of soil was weighed, 50 ml of potassium chloride was added to it allow to stand for 30 minutes then filter through filter paper. Then 5 ml of the filtrate was taken and add 10 ml of sodium hydroxide, 25 ml of distilled water then set up distillation steam, the receiving flask 5 ml of boric acid with 3 drop of ferroin indicator was added. The color changes to green as the steam was dropping and make it up to 25 ml. It was then titrated against 0.01M hydrochloric acid (HCL).

NITROGEN

One gram of soil was weighed into conical flask and 20 ml of concentrated H_2SO_4 with one kjeldahl catalyst tablet was added. It was heated on digestion stand until the solution becomes clear and white. It was then allowed to cool after which 50 ml of distilled water was added. Mixed well then filtered through filter paper. 10 ml sodium hydroxide and 25 ml of distilled water was added to 10ml of the filtrate in a conical flask. To the receiving flask, 5ml of boric acid with 3 drops of ferroin indicator was added. Distillation steam was set up, 25ml of the distillate was collected inside the receiving flask and was titrated with 0.01M hydrochloric acid (HCL).

Statistical Analysis

Data collected were subjected to analysis of variance (ANOVA) using SPSS version 17 and means were compared with Tukey HSD test to verify significant differences among treatment at 5% probability level. Graphs and charts were generated using Microsoft excel 2013 edition.

III. RESULT

Pre Experimental Soil Analysis

Table 1 shows the pre experimental soil analysis of the soil used for the experiment. The soil is a sandy clay loam having a sand content of 64.82%, silt content of 15.14% and clay content of 20.04%. It has a pH of 4.61 making it a strongly acidic soil, the Eh value is 78 mV making it a moderately reduced soil, nitrogen content is 0.19%, organic matter content is 1.77%, nitrate content is 0.04% and ammonium content is 0.06%. Hence the soil can be considered moderately fertile.

Table 1: Pre experimental Soil Analysis

Parameters	Values
Sand (%)	64.82
Silt (%)	15.14
Clay (%)	20.04
Textural class	Sandy loam clay
pH	4.61
Eh (mV)	78
Eh class	Moderately reduced
Nitrogen (%)	0.19
Organic Matter (%)	1.77
NO^{-}_3 (%)	0.04
NH_4^+ (%)	0.06

Effect of Soil Oxidation-Reduction Potential on N-forms and Other Chemical Properties

Table 2 shows the effect of soil oxidation-reduction on N-forms and other chemical properties. At 3WAI the pH values range from 4.82 to 5.68 which is strongly acidic. Treatment 6 had the highest value of pH 5.68 while treatment 4 (reduced soil) had a pH value of 4.82. Nitrogen content range from 0.10 to 0.28, treatment 5 (oxidized soil) had a nitrogen content of 0.28 while treatment 2 (reduced soil) had a nitrogen content of 0.10.Nitrate content was highest at T1 (oxidized soil) having a nitrate value of 0.22 while T2 (reduced soil) had a nitrate content of 0.04. Ammonium content was highest at T3 and T5 (moderately reduced soils) while the lowest value was recorded at T2 which is 0.02. Organic matter was highest at T6 having an organic matter content of 4.88 the lowest value for organic matter was recorded at T1 (oxidized soil) having an organic matter content of 2.07. At 6WAI T6 recorded the highest value of pH having a value of 5.88 while T1 (oxidized soil) has the lowest of pH 5.03. Nitrogen content was highest on T5 having a value of 0.24 and was lowest on T2 (reduced soil) having a value of 0.07. Nitrate content was highest on T1 having a value of 0.22 and lowest on T2 having a value of 0.02. Ammonium content was highest on T5 having a value of 0.31 (moderately reduced soil) and lowest on T2 (reduced) having a value of 0.04. Organic carbon and organic matter was highest on T4 (reduced) having a value of 2.62 of organic carbon and 4.51 of organic matter and the lowest was recorded at T1 (oxidized) having a value of organic carbon 1.00 and organic matter 1.74. At 9WAI the pH value was highest on T6 (reduced) having a pH value of 6.05 while the lowest was on T1 (oxidized) having a pH value of 5.00. Nitrogen content was highest on T5 (moderately reduced soil) having a value of 0.27 and lowest on T2 (reduced) having a value of 0.04. Nitrate content was highest on T1 (oxidized) having a value of 0.17and lowest on T2 and T4 both having a nitrate content of 0.00. Ammonium content was highest on T5 (moderately reduced soil) having a value of 0.38 and lowest on T2 (reduced) having an ammonium content of 0.02. Organic matter was highest on T4 (reduced) having organic matter content of 4.44 the lowest organic matter was recorded at T1 (oxidized) having organic matter content of 1.49.

Table 2: Effect of Soil Oxidation-Reduction Potential on N-forms and Other Chemical Properties

Treatments			**3WAI**		
	pH	N	NO_3^-	NH_4^+	OM
T1	5.03d	0.12e	0.22a	0.07b	2.07e
T2	5.10c	0.10f	0.04e	0.02c	2.13e
T3	5.44b	0.26b	0.11d	0.33a	4.64c
T4	4.82f	0.18d	0.09e	0.06bc	4.76b
T5	4.92e	0.28a	0.12c	0.33a	4.41d
T6	5.68a	0.20c	0.19b	0.09b	4.88a
			6WAI		
T1	5.03f	0.11d	0.22a	0.07c	1.74e
T2	5.15e	0.07e	0.02d	0.04c	2.06d
T3	5.76b	0.22b	0.13c	0.30a	3.98c
T4	5.22d	0.15cd	0.03d	0.11b	4.51a
T5	5.42c	0.24a	0.17b	0.31a	3.91c
T6	5.88a	0.17c	0.13c	0.16b	4.31b
			9WAI		
T1	5.00e	0.08c	0.17a	0.05d	1.49e
T2	5.18d	0.04c	0.00c	0.02d	1.57e
T3	5.90b	0.24a	0.16a	0.32a	3.91c
T4	5.74c	0.12b	0.00c	0.11c	4.44a
T5	5.80c	0.27a	0.15a	0.38a	3.76d
T6	6.05a	0.12b	0.09b	0.18b	4.24b

Means followed by the same alphabet are not significantly ($p < 0.05$) different from each other according to Tukey HSD.

Effect of Soil Redox Potential on Nitrogen Forms

Figures 1-6 Show the effect of redox potential on nitrogen forms in soil. T1 (oxidized soil) had a nitrate range from 0.22%, 0.22% and 0.17% and ammonia range from 0.07%, 0.07% and 0.05% at 3WAI, 6WAI and 9WAI respectively. T2 (reduced soil) had a nitrate range from 0.04%, 0.02% and 0.00% and ammonia range from 0.02%, 0.04% and 0.02% at 3WAI, 6WA1, and 9WAI respectively. T3 (moderately reduced soil) had a nitrate range from 0.11%, 0.13%, and 0.16% and ammonia range from 0.33%, 0.30% and 0.32% at 3WAI, 6WAI and 9WAI respectively. T4 (reduced soil) had a Nitrate range from 0.33%, 0.30% and 0.32% and ammonia range from 0.33%, 0.30% and 0.32% at 3WAI, .6WAI and 9WAI respectively. T5 (moderately reduced soil) had a nitrate range from 0.12%, 0.17%, 0.15% and ammonia range from 0.33%, 0.30% and 0.32% at 3WAI, 6WAI and 9WAI respectively. T6 (reduced soil) had a nitrate range from 0.19%, 0.13% and 0.09% and ammonia range from 0.09%, 0.16% and 0.18% at 3WAI, 6WAI and 9WAI respectively.

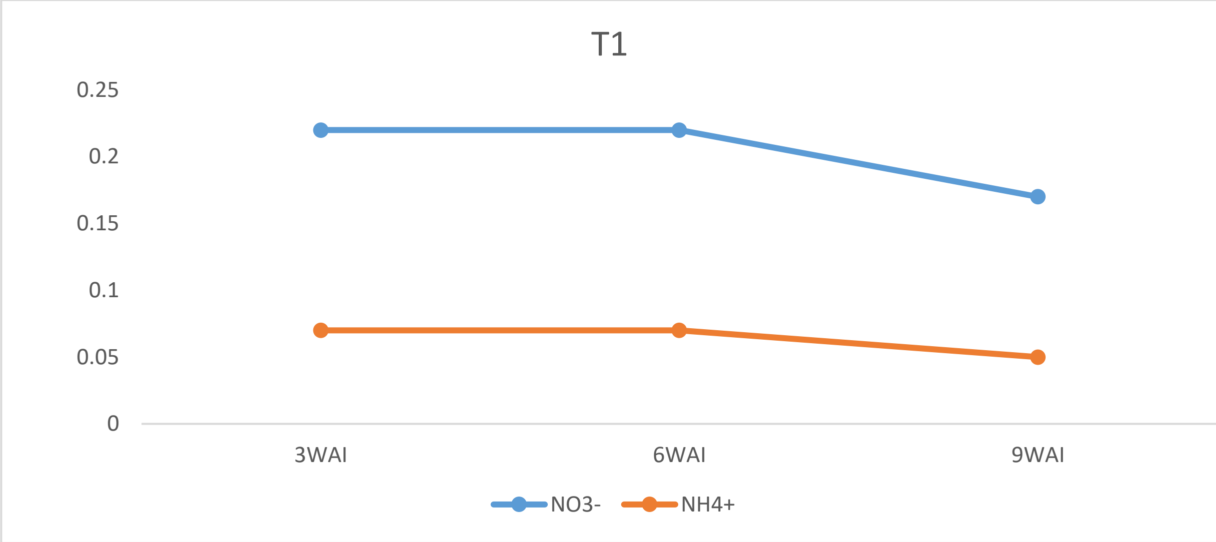

Fig.1: Effect of redox potential on nitrogen forms (oxidized)

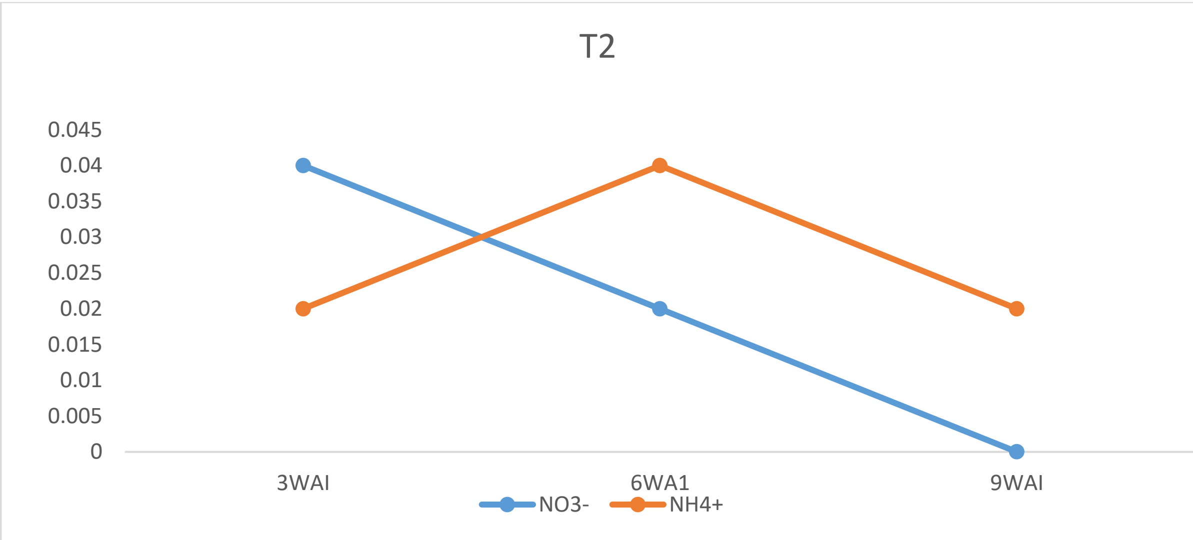

Fig.2: Effect of redox potential on nitrogen forms (reduced)

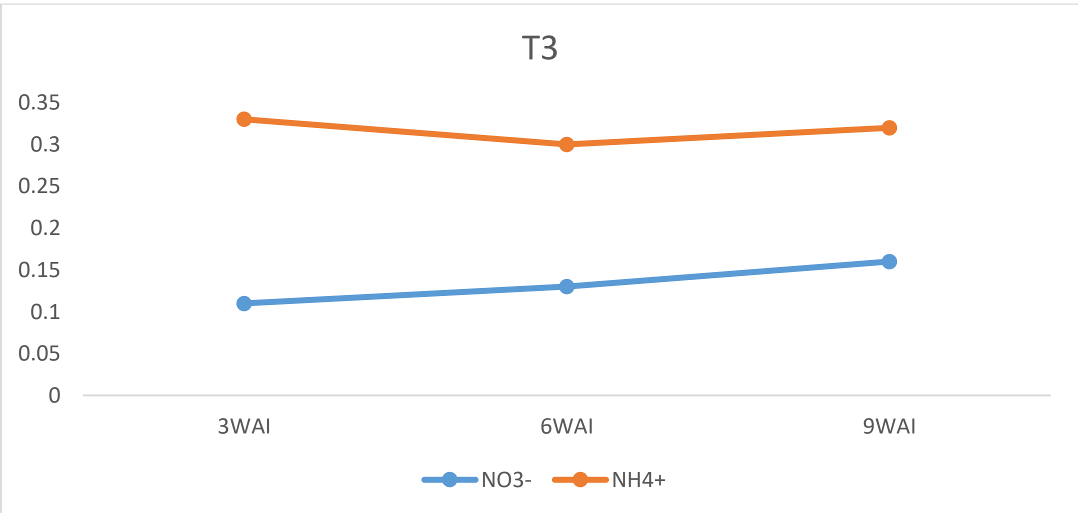

Fig.3: Effect of redox potential on nitrogen forms (moderately reduced)

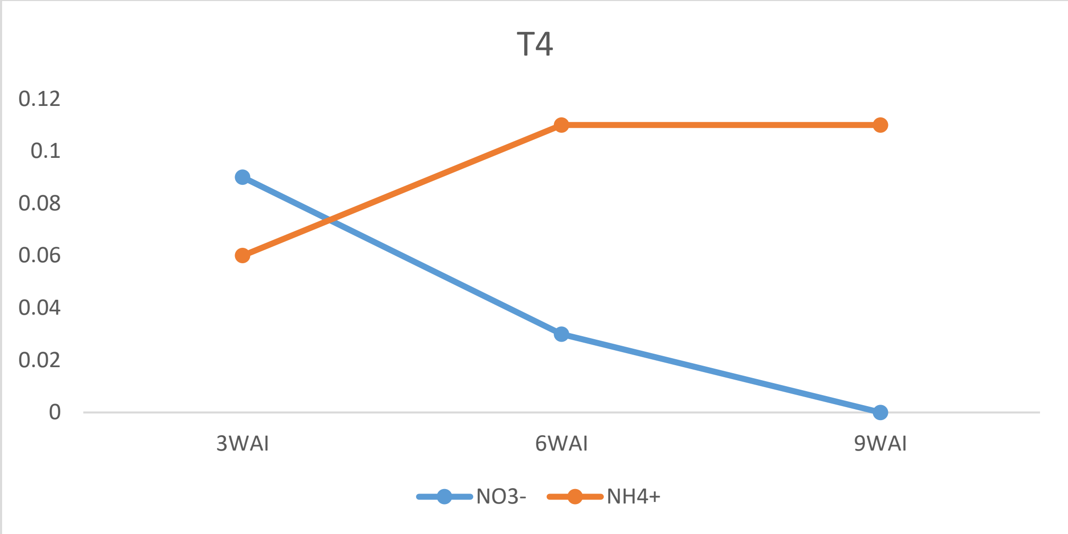

Fig.4: Effect of redox potential on nitrogen forms (reduced)

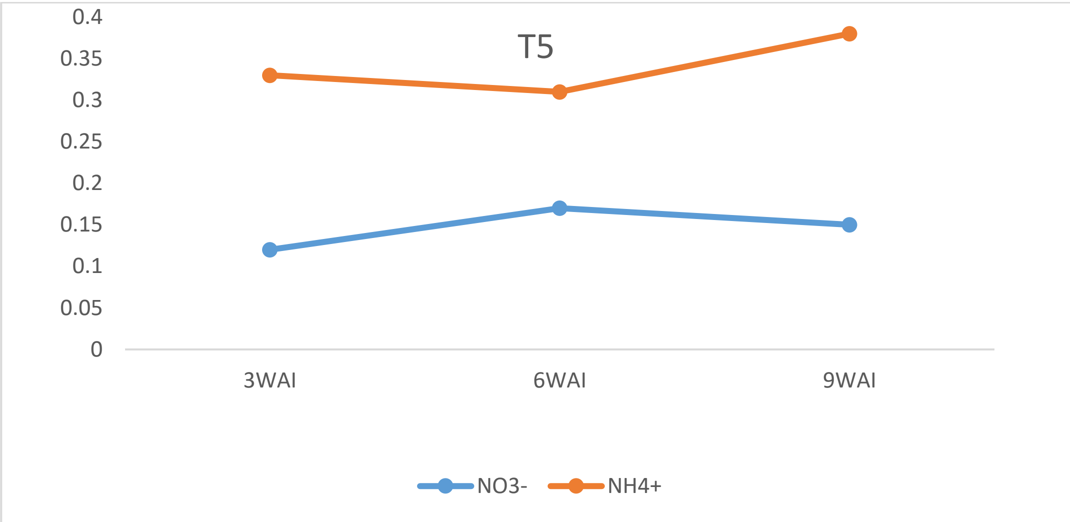

Fig.5: Effect of redox potential on nitrogen forms (moderately reduced)

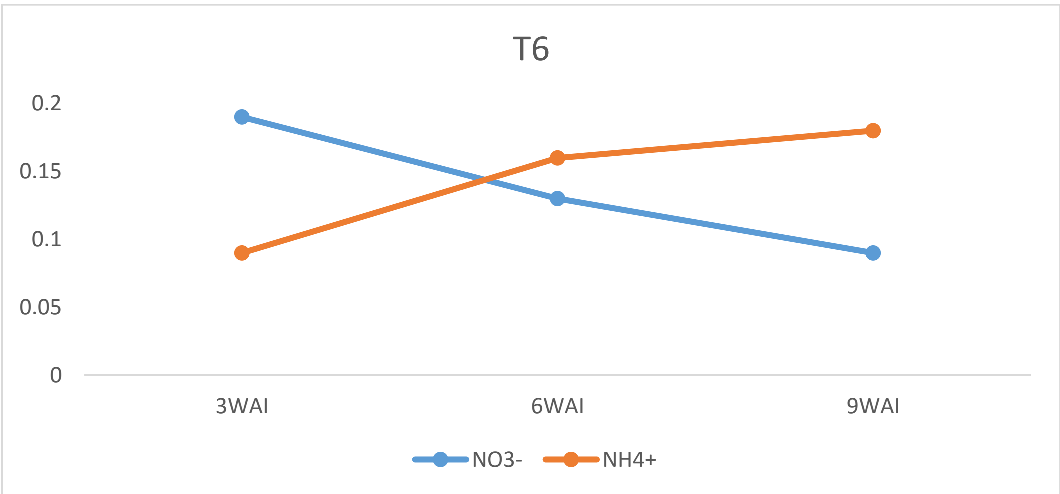

Fig.6: Effect of redox potential on nitrogen forms (reduced)

IV. DISCUSSION

The results from these research has been able to show that redox status of the soil can affect chemical properties of the soil as well as N-forms. The pH of T1 which is oxidized soil reduced across the trial period. (3WAI, 6WAI and 9WAI). It went from 5.03 to 5.00 i.e. it became more acidic. Reduced soil T2, T4 and T6 increase in pH from 5.10 to 5.18, 4.82 to 5.74, 5.68 to 6.05 at 9WAI, T3 and T5 which is moderately reduced soil there had an increased in pH also. Reduction of pH of oxidized soil T1 from 5.03 to 5.00 at 9WAI could be due to nitrification process. In oxidized soil nitrification process progresses and there is conversion of ammonia to nitrite and from nitrite to nitrate. This process is induce by nitrosomonas and nitrobacter respectively. The first step which involves the oxidation of ammonia to nitrite releases four molecules of hydrogen ion into the system and hydrogen ion is an acid forming ion. Hence, the net effect is a reduction in pH or acidification of the soil.

$$2NH_4^+ + 3O_2 \xrightarrow{\text{nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+ \text{ (oxidation)}$$

There was an increase in the pH of reduced soils and this could be attributed to the fact that the nitrification process is hindered since majority of the organism that are responsible for nitrification are aerobic in nature when the environment becomes reduced they cannot perform or function very well or can even die out. Also, reduction process according to Ojanuga, (1996) consumes hydrogen ion,since hydrogen ion is used up, the environment becomes less acidic. This process of hydrogen ion consumption is common in denitrification process where twelve (12) molecules of hydrogen ion is consumed to produce atmospheric nitrogen and six molecules of water.

$$2NO_3^- + 10e^- + 12H^+ \longrightarrow N_2 + 6H_2O \text{ (Denitrification)}$$

There is continuous reduction of nitrogen in oxidized soil and this can be attributed to the loss of nitrate through leaching as the major form of nitrogen in oxidize soil is nitrate (Powlson and Addiscott, 2005). In moderately reduced soil there was reduction in nitrate formation and later increased at 9WAI this could be attributed to the fact that both nitrate and ammonia are present in the soil. Ammonia content was highest under reduced condition because there is accumulation of ammonia in the system resulting from a halt in nitrification process, this causes a build-up of ammonia in the system as nitrate formation from NH_4^+ is hindered. Also under reduced conditions many other processes can lead to accumulation of ammonia, one of such is hydrolysis of urea in the presence of urease to form ammonium and carbon dioxide (Guillermina and Kenneth, 2004). The net effect of all this is a build-up of ammonia in reduced soil. This could account for the high ammonia content in reduced soils (T2, T4 and T6).

$$(NH_2)_2CO + H_2O \xrightarrow{\text{urease}} CO_2 + 2NH_3$$

V. CONCLUSION

Nitrate was found to be more in redox potential greater than 300 compared to other levels of oxidation or reduction while ammonium was more in reduced condition < -100. It was concluded that the fate and forms of nitrogen in the soil environment is also a function of the oxidation- reduction status of the soil.

REFERENCES

[1] Aczel, M. (2019) What is Nitrogen Cycle and why is it key to life. *Young minds.*Vol 7:41

[2] Brady, N.C., Weil, R. R. (2010). The nature and properties of soils.

[3] Domnariu, H. Paltineanu, C., Marica, D.,Lăcătușu, A.,Rizea, N., Lazăr, R. Popa, G. A., Vrinceanu, A.AndBălăceanu, C. 2020. Influence of Soil-Texture on Nitrate Leaching From Small-ScaleLysimetersToward Groundwater in Various Environments.*Carpathian Journal of Earth and Environmental Sciences*, Vol. 15, No. 2, p. 301 - 310; Doi:10.26471/cjees/2020/015/130

[4] Guillermina Estiu and Kenneth M. Merz. 2004. The Hydrolysis of Urea and the Proficiency of Urease. *Journal of the American Chemical Society* Vol 126 (22), 6932-6944. DOI: 10.1021/ja049327g

[5] Hinsinger, P., Plassard, C., Tang, C., Jaillard, B. (2003) Origins of root-mediated pH change In The rhizosphere and their responses to environmental constraints: a review. *Plant Soil* 248:43–59

[6] Marschner, P. (1995) Mineral nutrition of higher plants, 2nd edn. Academic, London

[7] Ojanuga, A.G., Okusami, T.A. and Lekwa, G. (1996). Wetland Soils of Nigeria: Status of Knowledge and Potentials. *Soil Science Society of Nigeria Monograph* No 2

[8] Powlson D.S. and Addiscott T.M. 2005 NITROGEN IN SOILS | Nitrates. *Encyclopedia of Soils in the Environment, Elsevier*,Pages 21-31,ISBN 9780123485304,https://doi.org/10.1016/B0-12-348530-4/00905-X.

[9] Rabenhorst, A.C., Hively, W.D and James, B.R. (2009) Measurements of soil redox potential. *Soil Science Society of America Journal* 73: pp 668–674

[10] USDA, United State Department of Agriculture. (2014) Soil Nitrogen. *Guide for educators*

[11] Yadav S.N. (1997) Formulation and estimation of nitrate-nitrogen leaching from corn cultivation. *Journal of Environmental Quality*. Vol 26: pp 808-814