

Effects of Urea and Di-Ammonium Phosphate Application on Acidification of three Burundi representative Soils

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ABSTRACT

An 8-week incubation study was conducted under controlled laboratory conditions to evaluate the potential acidifying effect of urea and Di-Ammonium Phosphate (DAP) on three Burundi representative soils, namely two acidic high altitude soils (Nyabisindu and Kajondi) and a saline sodic soil from the Imbo plain (Gihanga). Urea was applied at equivalent rates of 40 and 80 kg ha⁻¹, while Di-Ammonium Phosphate (DAP) was applied at 100 and 200 kg ha⁻¹. At the completion of the study, the acidifying effect of urea and DAP increased with the increasing original soil pH values. In comparison with the unfertilised control treatments, soil pH decreased by - 0.18 to - 0.217 pH units in Nyabisindu soil (pH = 5.07), whereas in Kajondi soil (pH = 5.2) and Gihanga (pH = 7.40), it decreased by - 0.073 to - 0.286 and - 0.367 to - 0.470 pH units, respectively. Furthermore, results highlighted that each soil-applied kg of N as urea and each soil-applied kg of N as DAP requires 3.6 kg and 5.4 kg of CaCO₃ to neutralize their respective residual acidity. The study revealed a helpful approach of using CaCO₃ as a rational N fertilizers management that the agriculture extension services and farmers can undertake in order to reduce soil acidity, improve soil fertility and increase crop production in Burundi and beyond under similar soil conditions.

Key Words: Soil Acidification, Urea, Di-Ammonium Phosphate, Residual Acidity, Neutralization, Lime.

1. INTRODUCTION

Soil acidification is a natural soil degradation process aggravated by intensification of agriculture in response to rapidly growing populations in need of adequate food supply. The soil acidification process is essentially common in all parts of the globe, where precipitations are high enough to leach base-forming cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) from the top soil layers [1].

The soil acidification process is depicted by changes in soil pH, and these changes are due to numerous natural and anthropogenic processes which controls soil pH including : (i) change in soil redox conditions; (ii) acidic atmospheric depositions resulting from industrial activities and pollution; (iii) release of H⁺ protons during microbially-mediated oxidation of C, N and S compounds in soils; (iv) CO₂/H₂CO₃ system; (v) weathering or reverse weathering of minerals; (vi) reserve acidity associated with exchangeable H⁺ and Al³⁺; (vii) weak acid groups associated with clay minerals,

Al, Fe hydroxides and soil organic matter; (viii) imbalance of cation over anion uptake, as in the case of NH_4^+ as the major source of N in soil; (ix) natural leaching of base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+); (x) repeated successive and intensive cropping systems; (xi) ionic selectivity of soil erosion leading to base cations losses from soil and subsequent accumulation of Al^{3+} ; and (xii) N- and S-bearing chemical fertilizers [2-6].

Soil pH is the major yield-limiting factor in tropical and heavily N-fertilized soils of the World [7]. It controls the solubility of soil chemical compounds and their plant availability or toxicity to plants and soil biota [5, 8].

The acidifying effect of NH_4^+ , S, P and Cl containing chemical fertilizers has been demonstrated by Pierre in 1933[9]. While this investigator considered half of the N in fertilizers as contributing to soil acidity, Andrews (1954) indicated latter that the entire amount of N contributes to soil acidity [10]. However, both authors agree on the fact that all S and Cl and one third of P contained in chemical fertilizers generate residual acidity.

In most of agricultural systems, soil acidification due to excessive use of inorganic N fertilizers is a major factor contributing to environment degradation [11-13]. According to FAO, the world consumption of chemical fertilizers was estimated at 150 in 2008 and 200 millions tons in 2018, an increase of 25 % for the periode of ten years [7]. Consequently, this ever increasing use of chemical fertilizers and its consequences on soil acidification and pollution of water and soil resources are major environmental constraints that impede the agricultural production worldwide. Like many other developping countries, Burundi is among minor consumers of chemical fertilizers. As indicated below (Table 1), the average fertilizer consumption per year is less than 10 kg ha^{-1} per year, realistically insignificant compared to some selected world countries [14].

Table 1. Chemical fertilizers consumption in selected world countries in 2015

Country	Amount of fertilizer consumed ($\text{kg ha}^{-1}\text{year}^{-1}$)
Burundi	8.3
Tanzania	8.8
Rwanda	19.7
Kenya	28.6
South Africa	58.5
USA	137
Brazil	163.7
Belgium	283.9
China	2334.3

Nevertheless, Burundi yearly consumption of chemical fertilizers has recently increased from 10,000 tons per year in 2013 to 52,000 tons per year in 2018 [15]. This trend has raised concerns of Government and farmers alike on the risk of soil acidification by Dia-Ammonium Phosphate (DAP) and urea, the two major fertilizers used in the country. Annually, the rate of consumption of these fertilizers is estimated at 67 % for DAP and 30% for urea. The remaining 3% represent KCl and NPK fertilizers [15].

It is the responsibility and mission of researchers to assess and alleviate the risk of soil acidification associated with urea and DAP on Burundi soils. Hence, this study attempts to evaluate the potential acidifying effect of DAP and urea applied to three Burundi representative soils: two soils from the high altitude zone (Kajondi and Nyabisindu) and one soil from the Western Imbo plain (Gihanga). Additionally, the study illustrates the major chemical reactions occurring in soil following urea and DAP application and, from there, estimates the quantity of lime (CaCO_3) required to neutralize their associated residual acidity.

2. MATERIAL AND METHODS

2.1. Soils

The clay soils used (0 -15 cm depth) in the study were collected from Kajondi, Nyabisindu and Gihanga sites. The first two sites are government farms for seed production located at 70 and 120 km East of Bujumbura City, in Kayokwe and Rutovu Communes, respectively. The Gihanga site is located 20 km North of Bujumbura. The soils were crashed, sieved with a 2-mm sieve. Physical and chemical soil analyses included particle size, pH, % C, % N, electrical conductivity, exchangeable, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} and H^+ . Mechanical analysis of the soils was performed by the hydrometer method [16]. Soil pH was measured using a 1:1 soil-water mixture. Organic C was determined using the Walkley-Black method [17]. Organic N was measured as described by Bremner and Mulvaney (1982) [18]. Exchangeable cations were determined by ICP spectrophotometry after extraction by the Mehlich III [19]. Electrical conductivity (E.C) was determined using the 2:1 water: soil extract [20]. Selected physical and chemical properties of the soil are presented in Table 2.

2.2. Fertilizers used

Fertilizers used in this study were urea [$\text{CO}(\text{NH}_2)_2$] and Di-Ammonium phosphate [$(\text{NH}_4)_2\text{HPO}_4$] which are the two most used chemical fertilizers in Burundi [15]. DAP was applied at equivalent rates of 100 and 200 kg per hectare, whereas urea was applied at 40 and 80 kg per hectare. These applied amounts were based on fertilizer application rates recommended for common crops grown in Burundi, such as common beans (*Phaseolus vulgaris* L.), potatoes (*Solanum tuberosum* L.) and rice (*Oryza sativa* L.) [21].

2.3. Incubation procedure

The laboratory incubation was conducted at room temperature ($27\pm 1^\circ\text{C}$) in the Soil Laboratory Facility of the Faculty of Agriculture and Bio Engineering, University of Burundi. The soils were air dried at room temperature until they could be crashed and sieved through a 2-mm sieve. Soil samples (100 g dry weight basis) from the top-layer (0-15 cm) of cultivated fields were mixed with fertilizers in open 250-mL pots. The mixtures soil-N-fertilizers were incubated under aerobic conditions for 8 weeks. Soil samples were set at 60 % water-holding capacity at the start of the incubation process.

2.4. Experimental design and statistical analyses

The incubation study was conducted in a completely randomized design (CRD). Soils samples without chemical fertilizers were used as controls. Experimental treatments consisted of a control (soil only) urea or DAP applied treatments. Each treatment was replicated three times making a total of 15 experimental units for each soil. Fertilizers were thoroughly incorporated into soils at two rates: 40 and 80 kg ha^{-1} for urea and 100 and 200 kg ha^{-1} for DAP. Statistical analyses (ANOVA) were performed with GenStat and treatment means were separated using the Least Significant Difference method (LSD) [21]. Values of general means, test of Fischer, probability and coefficient of variation were also evaluated.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the soils used in the study

The table 2 below shows physical and chemical properties of the soils used in the study.

Table 2: Selected physical and chemical characteristics of the soils used in the study

Parameter	Kajondi Soil	Nyabisindu Soil	Gihanga Soil
pH	5.20	5.05	7.40
% C	2.02	2.86	0.50
% N	0.14	0.25	0.04

C/N	14.43	11.44	12.00
CEC (cmol _c /kg soil)	11.02	12.20	28.38
Ca ²⁺ (cmol _c /kg soil)	6.22	4.88	12.00
Mg ²⁺ (cmol _c /kg soil)	2.33	3.19	11.83
K ⁺ (cmol _c /kg soil)	0.65	1.22	0.09
Na ⁺ (cmol _c /kg soil)	0.01	0.03	4.55
Al ³⁺ (cmol _c /kg soil)	1.53	1.83	-
H ⁺ (cmol _c /kg soil)	0.52	0.27	-
E.C (dS/m)	0.035	0.028	4.20
Clay (%)	59.79	77.61	47.09
Silt (%)	11.47	10.88	8.82
Sand (%)	28.74	11.51	44.09

Nyabisindu and Kajondi soils were acidic (pH < 5.5), while Gihanga soil was saline (E.C > 4 dS/m) with a sodic tendency (ESP > 15 %). This information will be of interest when discussing the results of our experiment in the following paragraphs.

3.2. Effects of Urea and DAP on soil pH

The effects of urea and DAP applications on Nyabisindu, Kajondi and Gihanga soils are indicated in table 3. Means with the same letter are not significantly different at the 5 % level of probability.

Table 3: Effects of Urea and DAP on soil pH in three Burundi representative soils

Treatments	Nyabisindu soil	Kajondi soil	Gihanga soil
Control	5.320a	4.903a	8.180
DAP 100 kg ha ⁻¹ (18 kg N)	5.103b	4.830ab	7.813
DAP 200 kg ha ⁻¹ (36 kg N)	5.117b	4.617c	7.710
Urea 40 kg ha ⁻¹ (18.4 kg N)	5.133b	4.743bc	7.790
Urea 80 kg ha ⁻¹ (36.8 kg N)	5.140b	4.710bc	7.760
LSD	0.137	0.132	0.453
General Mean	5.163	4.761	7.851
Test F	4.210	6.930	1.710
Probability	0.030*	0.006**	0.223 NS
C.V (%)	1,5	1,5	3,2

On Nyabisindu soil, all the four fertilizer application rates showed significantly lower pH values as compared to the control, but no significant difference was observed between them. Soil pH values declined by - 0.18 to - 0.217 units in comparison with the control soil. Moreover, no urea or DAP application rate effect was observed.

On the other hand, on Kajondi soil, 100 kg DAP per hectare was not significantly different from the control, whereas the other three fertilizer applications (DAP 200 kg ha⁻¹, 40 and Urea 80 kg ha⁻¹) showed significantly lower pH values as compared to the control soil. The lowest pH value was observed with DAP 200kg ha⁻¹. Overall, observed pH values followed the statistical order: DAP 200 kg ha⁻¹ ≤ Urea 40 kg ha⁻¹ ≤ Urea 80 kg ha⁻¹ ≤ DAP 100 kg ha⁻¹ ≤ Control. In comparison with the control soil, pH values decline was of -0.073 for DAP 100 kg ha⁻¹, - 0.160 for Urea 40 kg ha⁻¹, - 0.193 for Urea 80 kg ha⁻¹ and -0.286 for DAP 200 kg ha⁻¹. The application rate effect was only observed with DAP where 200 kg ha⁻¹ significantly acidified the Kajondi soil (pH=4.617) compared to the 100 kg DAP ha⁻¹ application rate (pH=4.830).

Although differences in pH values decline observed with the fertilizer treated Gihanga soil were high (- 0.367 to - 0.470) in comparison with the control soil, no statistical differences were observed among all treatments including the control.

Results obtained in our study are in agreement with those reported by other investigators. For example, a linear decrease of pH was observed with the application of ammonium sulfate fertilizer accompanied by a decrease in Ca^{2+} and Mg^{2+} saturation and an increase in Al and acidity saturation with increasing rates of N applications [23]. In the same line, long-term fertilizer application of ammoniacal N fertilizer increased exchangeable acidity, decreased Cation Exchange Capacity (CEC), decreased base saturation and exchangeable Ca^{2+} and Mg^{2+} [24][25]. In China, a decrease in rhizosphere pH and an increase in Cd uptake and in phyto-toxicity due to higher solubility of Aluminium (Al) and Manganese (Mn) was reported following ammonium-based fertilizers application to soil [26]. Similarly, an investigation performed on Alfisol and Ultisol from Southern Nigeria and Oxisol from Colombia observed that application of 50 and 100 kg ha⁻¹ of ammonium sulfate, urea and calcium ammonium nitrate was characterized by decreases in soil pH in the order: Ammonium Sulfate > Urea > CAN [27]. Lower decreases were observed on the Oxisol (- 0.41 to - 0.36 pH unit), the same Order of soils as the Nyabisindu and Kajondi soils used in our experiment.

A soil pH decline as high as 1.2 unit of pH was reported in soils treated with NH_4NO_3 during a 9-year experiment, possibly because of partial nitrification of NH_4^+ and plant uptake of NH_4^+ with its subsequent replacement by protons (H^+) in the soil [5]. On the other side, residual acidity following 9 annual applications of N fertilizers was in the order: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{Anydrous } \text{NH}_3 > \text{NH}_4\text{NO}_3 > \text{Urea}$ [28]. Comparatively, our short-term incubation study did not show a clear difference between urea and DAP in neither tested soils.

The acidifying effect of chemical fertilizers is not only due to their chemical nature, but is also controlled by their rates of application. Generally, soil pH decreases with increasing N application rates [29][30][31].

In our study, the only treatment where a similar conclusion could be drawn was with DAP in the Kajondi soil: application of 200 kg of DAP significantly decreased soil pH compared to 100 kg of DAP (Table 3).

3.3. Mechanisms of action of Urea and DAP in soil

Urea and DAP fertilizers applied to soil undergo chemical changes controlled by soil pH and/or microbial oxidation. The following paragraphs illustrate the different reactions undergone by urea and DAP when applied to soils of different pH.

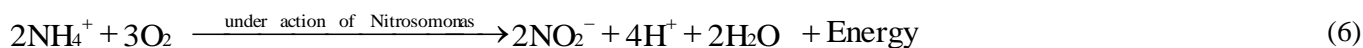
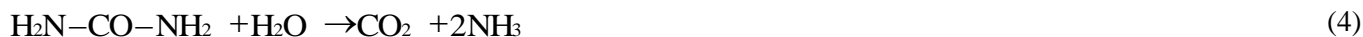
3.3.1. Urea reactions in soil

In the soil, urea undergoes first an enzymatic hydrolysis and nitrifying bacteria are then involved in the transformation of NH_4^+ and NO_2^- to NO_3^- . As the nitrification is a process based on aerobic metabolism, oxygen behaves like an electron acceptor whereas NH_4^+ and NO_2^- behave like electron donors.

The half-equations which describe the involved redox couples $\text{O}_2/\text{H}_2\text{O}$, $\text{NO}_2^-/\text{NH}_4^+$ and $\text{NO}_3^-/\text{NO}_2^-$ are presented below [32].



In view of these different half-equations (equations 1, 2 and 3) involved in urea transformation processes, the following successive equations describe urea reactions in soil:



Whereas the enzymatic hydrolysis is described by equation (4), the bacterial activities by Nitrosomonas and Nitrobacter which are autotrophic bacteria are described by equations (6) and (7), respectively. These bacteria groups (Nitrosomonas and Nitrobacter) involved in ammonium oxidation to NO_3^- (nitrification) are very sensitive to soil acidity [33]. Under low soil pH (< 6), such as in the case of Nyabisindu and Kajondi soils, the nitrification process is slowed and the production of H^+ alike [33]. This explains the limited acidification observed in Nyabisindu soil with an original pH = 5.07 and, to some extent in Kajondi soil with an original pH value slightly higher (pH = 5.2).

This observation is in accordance with results reported by other researchers [4] in a N mineralization study conducted in two soils of contrasting pH: Leadvale soil (pH = 4.6) and Taloka soil (pH = 5.9). These investigators reported that in the more acidic Leadvale soil, only 41.5 % of mineral N was in the NO_3^- form. On the contrary, almost all mineral N (95 %) in the Taloka soil was in the NO_3^- form, indicating a near complete nitrification in this particular soil of pH close to 6.

Similar complete nitrification was expected to have occurred in the Gihanga soil with an alkaline soil pH. However, nitrification might not have been the sole process that controlled the variation of soil pH in the Gihanga soil, but also in the Nyabisindu and Kajondi soils fertilized with DAP.

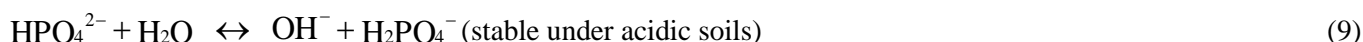
3.3.2. Di-Ammonium Phosphate (DAP) reactions in soil

The dissociation of DAP in soil with the release of HPO_4^{2-} and NH_4^+ proceeds as follows:



The effect of P fertilizers on soil pH is dependent on the ionic form of P fertilizer added and on the pH range of the soil [33]. The form of P in DAP is HPO_4^{2-} which makes acidic soils more alkaline (equation 9), but has no effect on soils with a pH > 7.2. Under neutral to alkaline soils, HPO_4^{2-} is stable and no pH change occurs [34]. Consequently, in the Gihanga soil, DAP through its HPO_4^{2-} component did not affect the pH, whereas the NH_4^+ component presumably nitrified and released protons (H^+) with a subsequent decrease in soil pH (Table 3).

Under acidic soils as in the Nyabisindu and Kajondi soils, the following reaction leading to OH^- production and pH increase occurs.



In other words, the pH dynamic in the acidic Nyabisindu and Kajondi soils was under two controlling and counterbalancing processes: acidification due to the somehow limited nitrification (equations 2, 3, 6 and 7) yielding protons (H^+) and the release of OH^- following the hydrolysis of HPO_4^{2-} (equation 9). Apparently, the first process of nitrification dominated, because in the end, soil pH values in fertilised treatments were lower than the controls in both Nyabisindu and Kajondi soils.

As it was previously stressed out, the HPO_4^{2-} component of the DAP is stable under the alkaline Gihanga soil (pH > 7.2) and did not generate any change in soil pH. Therefore, it is the NH_4^+ component of the DAP which affected the

change in soil pH observed in this particular soil, through the nitrification process. However, NH_4^+ either from urea or DAP might not have fully realised its acidification potential in the Gihanga soil ($\text{pH} > 7$), because of the potential loss of N from the soil by NH_3 volatilization [23].

At the completion of the 56-day incubation study, the Gihanga soil was characterized by a substantial increase in soil pH (+ 0.8 pH unit) when compared to the original soil. From its analytical data (Table 2), the Gihanga soil was a saline and sodic soil. Under such soil conditions, Na compounds in soil solution and on the exchange sites undergo hydrolysis with a release of OH^- ions and a subsequent soil pH increase, as described by equations 10 and 11 below.

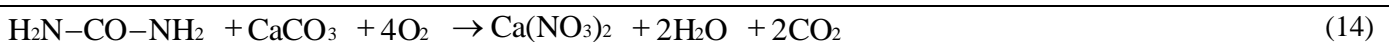


Thus, the pH change in the Gihanga saline and sodic soil was controlled by the acidifying nitrification process of NH_4^+ from urea and DAP counterbalanced by the hydrolysis of Na soluble and exchangeable compounds yielding OH^- in soil solution. Consequently, the pH change in the Gihanga soil is a result of the two contrasting chemical processes.

3.4. Neutralization of Urea and DAP residual acidity

Residual acidity associated with chemical fertilizers can be controlled. For example, Cai *et al.* (2015) reported that in a 18-year experiment with application of 300 kg ha^{-1} per year of chemical and organic fertilizers, it appeared that (pig) manure inhibited the acidification process due to NPK fertilizers. These investigators noted that application of sole chemical fertilizers increased soil exchangeable acidity and decreased soil exchangeable base cations. On the contrary, application of pig manure alone or combined with NPK fertilizers increased or stabilised soil pH and, at the same time increased soil exchangeable base cations: in essence a reverse soil acidification process [35].

Another solution to soil acidification due to chemical fertilizers is lime (CaCO_3) application. Quantity necessary to neutralize the acidity resulting from application of chemical fertilizers can be calculated based on Pierre and Andrews's methods [10]. A general equation (14) obtained by combining equations (4, 5, 12, et 13) is used to calculate the amount of CaCO_3 necessary to neutralize the acidity resulting from application of urea as fertilizer.



The general equation (14) shows that each kg of N in the form of urea is neutralized by 3.6 kg of CaCO_3 . Therefore, 100 kg of urea is neutralized by 165 kg of CaCO_3 in a ratio of 1:1.65. Application of a similar approach to DAP fertilizer indicates that each soil-applied kg of N in the form of DAP requires 5.4 kg of CaCO_3 to neutralize its residual acidity. Hence, 100 kg of DAP would require 100 kg of CaCO_3 in a ratio of 1:1. It could be noted that urea is theoretically 65 % more acidifying than DAP fertilizer due to its high NH_4^+ content.

The above calculations extended to chemical fertilizers consumption in Burundi, based on 2018 Ministry of Agriculture data as indicated above, show that quantities of CaCO_3 required to neutralize the amount of consumed DAP (34 840 T) would be equal to 34 840 T per year. Similarly, the quantity of CaCO_3 needed to neutralize the residual acidity associated with the quantity of urea consumed nationwide in 2018 (15 600 T) is estimated at 25 740 T of CaCO_3 per year. It is our conviction that this information could be helpful to extension personnel in charge of chemical fertilizers sale to Burundi farmers and even beyond under similar soil conditions.

4. CONCLUSION

This study focused on the potential acidifying effects of urea and DAP which make over 90 % of the total amount of chemical fertilizers consumed in the Burundi. A short-term incubation study conducted on two acidic soils (Nyabisindu and Kajondi) and a saline sodic soil (Gihanga) indicated that, overall, application of urea 40 kg ha⁻¹, urea 80 kg ha⁻¹, DAP 100 kg ha⁻¹ and DAP 200 kg ha⁻¹ has a decreasing effect on the soil pH, as compared to the control soils without fertilizers addition. In Nyabisindu soil (pH = 5.07) and Kajondi (pH = 5.2), the soil pH decreased by - 0.18 to - 0.217 and - 0.073 to - 0.286 pH units, respectively. Likewise, the results highlighted the same trend in Gihanga (pH = 7.40) with values decreasing from - 0.367 to - 0.470. However, no statistical differences were observed among the fertilized treatments or between fertilizer applied rates, except for DAP in Kajondi soil, where application of DAP 200 kg ha⁻¹ significantly acidified the soil in comparison with DAP 100 kg ha⁻¹. It could be noted that the acidifying effect of urea and DAP increased with increasing pH of the soils used in the study, presumably because of the oxidation process of NH₄⁺ to NO₃⁻ (nitrification), itself controlled by soil pH. This residual acidity associated with urea and DAP could be neutralized by concomitant lime (CaCO₃) application, based on Pierre's method revised by Andrews. Hence, 100 kg of urea is neutralized by 165 kg of CaCO₃ in a ratio of 1:1.65, and 100 kg of DAP would require 100 kg of CaCO₃ in a ratio of 1:1. In the context of agriculture, this could be a helpful approach of using CaCO₃ as a rational N fertilizers management that the agriculture extension services and farmers can undertake for reducing soil acidity, improve soil fertility and increase crop production in Burundi and even beyond under similar soil conditions.

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