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Full Length Research Paper

Proton consumption capacity, ash alkalinity and chemical characterization of travertine from different sources in Rwanda

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Soil acidification is among the major factors limiting the sustainability of agricultural production systems throughout the world and more specifically in Rwanda. Travertine samples collected from different deposits in Rwanda were examined for their chemical compositions. Calcium oxide (CaO) content, ash alkalinity and protons consumption capacity were determined as potential indicators to predict the efficiency of travertine. The results found revealed that the studied travertine deposits (Rwaza, Mashyuza, Gishyita and Mpenge) in Rwanda had 35 to 71.1 wt% CaO. Magnesium Oxide (MgO) ranged between 3.1 and 12.7 wt%. Travertine had micronutrients Cl, Zn, Cu, Mo and Co that can offset deficiency encountered in highly weathered Rwandan acidic soils. In addition, these travertine deposits had higher proton consumption capacity and ash alkalinity as compared to other liming materials. The study revealed positive linear correlations among all the investigated indicators, which could serve as a model for predicting proton consumption capacity and ash alkalinity of any liming material when its pH and CaO content are known. It was recommended that travertine from Rwanda could be used for soil acidity amelioration and a potential source of micronutrients for agricultural production.

Key words: Rwanda, travertine**,** proton consumption capacity, ash alkalinity, chemical characterization, soil acidity.

INTRODUCTION

Travertine is limestone rock deposited by hot springs. It is formed by a process of rapid precipitation of calcium carbonate ($CaCO_3$), often at the mouth of a hot spring or in a limestone cave. Travertine is one of the most frequently used rock in modern architecture. It is commonly used for façades, wall cladding, and flooring (Fouke, *et al*., 2000; Pentecost, 2005). Travertine can also be used as liming material in agriculture for acid soil reclamation as well as source of nutrients for crop production due to its high content in calcium carbonate. Rwanda has several travertine deposits located in Northern (Musanze District) and in Western provinces (Karongi and Rusizi Districts). Several studies indicated that Rwanda has relatively good sources of travertine that can be used as liming material for agricultural production (Beernaert, 1999; SOFRECO, 2001; Van Straaten, 2002; Sirikare *et al*., 2012; Nduwumuremyi *et al.,* 2013). Most travertine deposits in Rwanda are found in the Rift Valley area in western Rwanda and the amount is estimated to be more than 10 million tonnes reserve (Sirikare *et al*., 2012; Nduwumuremyi, *et al.,* 2013).

In Rwanda, soil fertility and agricultural productivity are limited in most parts of the country by soil acidity which is mainly linked with highly weathered and old soils (Crawford *et al*., 2008). Therefore, developing liming materials from local travertine will largely contribute to raise and maintain the soil pH above 5.5 and keep extractable Al concentrations low as a desirable soil management technique.

The use of the locally available travertine resources will be an important low-cost sustainable management technique for providing food security to farmers in Rwanda (Crawford *et al*., 2008). Rwandan travertine has not yet been well characterized, especially for agriculture purpose. Hence,

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*Corresponding author. E-mail:sirikasy@yahoo.fr the purpose of this characterization was to investigate the spectrum of chemical composition of travertine found in Rwanda and their potential in proton consumption capacity as well as ash alkalinity for ameliorating soil acidity.

MATERIALS AND METHODS

Source of Travertine

This study was conducted in Rwanda specifically in Rwaza site (Longitude: $1^0$32' S; Latitude $29^0$41'E) and; Mpenge site (Longitude: 1^0 31'S; Latitude: 29^0 39' E) located in Musanze district in Nothern province of Rwanda. Other travertine samples were collected at Mashyuza site (Longitude: $2^0$18' S, Latitude: 29^0 01'E) in Rusizi district and Gishyita site (Longitude: $2^0$10'S; Latitude: 29^0 18'E) in Karongi district in Western province of Rwanda.

Sampling and Laboratory Analysis

Samples were selected randomly based on the active sites mined by the cooperatives. Samples were collected at different depth (0.2-0.5, 0.5-1 and 1-1.50m) and were grounded and sieved to pass a 2 mm mesh size. Chemical analysis was conducted in Dodoma Tanzania at the Geological Survey Laboratory. Twenty gram of powdered sample at <180 microns, air dried at 26 ^{0}C , was hand pressed into XRF sample cups mounted with PANalytical BVX-Ray film polyesterpetp. Samples cups were placed in PANalytical Minipal 4 Energy Dispersive X-Ray Fluorescence Spectrometer, (ED-XRF) model PW4030/45B. Elements in travertine were determined by XRF Machine using Mini pal mini Mate Software package.

Determination of Travertine pH, Ash Alkalinity and Proton Consumption Capacity

Travertine composite samples from each site were used for pH, ash alkalinity and proton consumption capacity measurement. Travertine pH was measured in a 1:2.5 travertine solution ratio in water using a glass electrode. Ash alkalinity was determined by heating a 2 g sample at 500°C for 4 hours in muffle furnace until complete ashing had occurred.

Ashed samples were dissolved in 20 ml of a standardized solution of 1 M hydrocloric acid (HCl) and three 5-ml aliquot was titrated against a standardized solution of 0.25 M sodium hydroxide (NaOH). For each of titration, a 5mL aliquot of the standardized solution 1M (HCl) was also titrated against a standardized solution of 0.25 M sodium hydroxide (NaOH) to know the maximum volume of NaOH required to reach the neutrality.

For the Ash Alkalinity, the following equation was used to calculate ash alkalinity (A) ($\text{kmol}_c\,\text{kg}^{-1}$)

A= (Bt-St) x [HCl] x sample wt x 5 x10^{-5} / [NaOH] (Slattery *et al*., 1991)

Where Bt is the volume of NaOH required to neutralize 5ml of 1mol/L HCl; and St is the volume of NaOH required to neutralized 5mL of 1mol/L HCl plus the ashed sample. Proton consumption capacity was measured in a suspension of 1.5g travertine sample in 30 ml of 2mM Calcium Chloride ($CaCl_2$), which has been used to measure the initial pH of travertine. The suspension, in which a pH indicator has been introduced, has been then slowly titrated from their natural pH values down to pH 4.0 with 0.05M sulfuric acid (H_2SO_4) to determine their proton consumption capacities in that pH range (Wong *et al.*, 1998). Proton consumption capacity was determine by the product of the amount of sulfuric acid required per one kg of travertine by the unit pH change (dpH).

STATISTICAL ANALYSIS

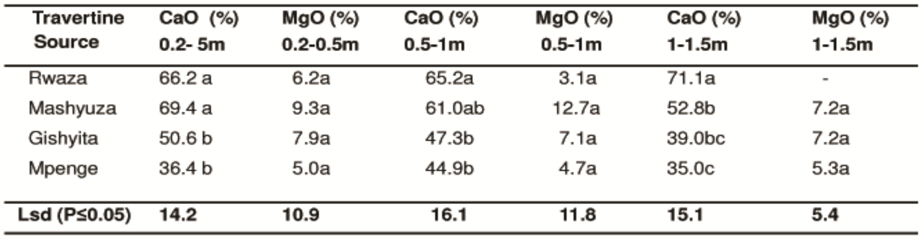
The statistical significance was determined by subjecting the data to analysis of varience (ANOVA) using the Genstat XIV package and least significant differences were calculated at the 5% level.

RESULTS AND DISCUSSION

Calcium Oxide and Magnesium Oxide

Chemical characterization results revealed that the travertine deposits have high concentration of calcium oxide (Table 1). Travertine from Rwaza and Mashyuza were found to have the highest contents ranging from 65.2 to 71.1 and 52.8 to 69.4 wt% CaO, respectively and were significantly ($P \leq 0.05$) different from Gishyita and Mpenge which had contents ranging from 39 to 50.6 and 35 to 44.9 wt% CaO respectively. Applying this travertine in acidic soil will increase calcium carbonates content that may neutralize exchangeable aluminum toxicity. According to Franco and Munns (1982); Hardy *et al*. (1990); Bell and Bessho (1993), the base enrichment especially of Ca^{2+} ions and carbonate in acidic soil neutralizes exchangeable Al thus enhancing root growth of crops. In all travertines however, there were no significant ($P \leq 0.05$) differences when comparing their magnesium oxide content (table 1). Mashyuza and Gishita had contents ranging from 7.2 to 12.7 and 7.1 to 7.9 wt% MgO respectively while Mpenge and Rwaza had contents ranging from 4.7 to 5.3 and 3.1 to 6.2 wt% MgO respectively. The presence of small amount of MgO in all sites may still have a positive impact when combined with calcium carbonate to alleviate the aluminum toxicity, but also to increase the release of calcium in the soil. In their study, Anda et al. (2008), found that in highly weathered soil calcium cations remained on top of the soil but when magnesium amendment are applied, some Ca moved deeper into the soil profile, hence

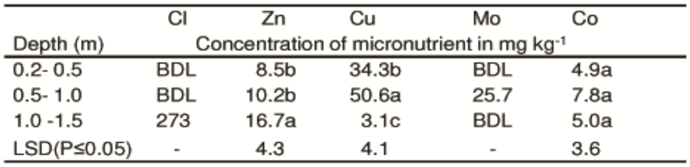
Table 1. Some selected chemical properties of different sources of travertine found in Rwanda**.**



Travertine Source	CaO (%) 0.2- 5m	MgO (%) 0.2-0.5m	CaO (%) 0.5-1m	MgO (%) 0.5-1m	CaO (%) 1-1.5m	MgO (%) 1-1.5m
Rwaza	66.2 a	6.2a	65.2a	3.1a	71.1a	-
Mashyuza	69.4 a	9.3a	61.0ab	12.7a	52.8b	7.2a
Gishyita	50.6 b	7.9a	47.3b	7.1a	39.0bc	7.2a
Mpenge	36.4 b	5.0a	44.9b	4.7a	35.0c	5.3a
Lsd ($P \leq 0.05$)	**14.2**	**10.9**	**16.1**	**11.8**	**15.1**	**5.4**

Means in column with similar letter are not significantly different.

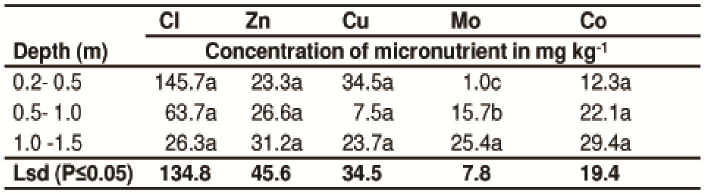
Table 2. Concentration of micronutrients in travertine from Rwaza.



	Cl	Zn	Cu	Mo	Co
Depth (m)	Concentration of micronutrient in mg kg^{-1}				
0.2- 0.5	BDL	8.5b	34.3b	BDL	4.9a
0.5- 1.0	BDL	10.2b	50.6a	25.7	7.8a
1.0 -1.5	273	16.7a	3.1c	BDL	5.0a
LSD($P \leq 0.05$)	-	4.3	4.1	-	3.6

Means in column with similar letter are not significantly different.
BDL: below the detection limit.

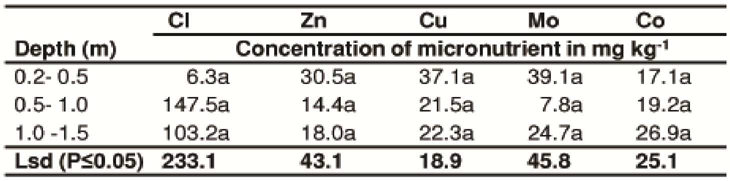
Table 3. Concentration of micronutrients in travertine from Mashyuza.



	Cl	**Zn**	**Cu**	**Mo**	**Co**
Depth (m)	**Concentration of micronutrient in mg kg^{-1}**				
0.2- 0.5	145.7a	23.3a	34.5a	1.0c	12.3a
0.5- 1.0	63.7a	26.6a	7.5a	15.7b	22.1a
1.0 -1.5	26.3a	31.2a	23.7a	25.4a	29.4a
Lsd ($P \leq 0.05$)	**134.8**	**45.6**	**34.5**	**7.8**	**19.4**

Means in column with similar letter are not significantly different.

Table 4. Concentration of micronutrients in travertine from Gishyita.



	Cl	**Zn**	**Cu**	**Mo**	**Co**
Depth (m)	**Concentration of micronutrient in mg kg^{-1}**				
0.2- 0.5	6.3a	30.5a	37.1a	39.1a	17.1a
0.5- 1.0	147.5a	14.4a	21.5a	7.8a	19.2a
1.0 -1.5	103.2a	18.0a	22.3a	24.7a	26.9a
Lsd ($P \leq 0.05$)	**233.1**	**43.1**	**18.9**	**45.8**	**25.1**

Means in column with similar letter are not significantly different.

ameliorating the subsoil calcium contents.

Micronutrients Contents in the Studied Travertines

Chemical characterization also revealed the presence of micronutrients such as Chlorine (Cl), Zinc (Zn), Copper (Cu), Molybdenum (Mo) and Cobalt (Co) in the studied travertines. In Rwaza travertine deposit, Cl was found in bottom layer (1-1.5m depth) while the top layer and the middle layer (0.2-0.5 to 0.5- 1m depth) chlorine was below the detection limit (table 2). Mo was found in the middle layer (0.5-1m depth) while the top layer and bottom layer (0.2- 0.5 to 0.5- 1m depth) Mo was below the detection limit (table 2).The level of Cu in the middle layer was significantly ($P \leq 0.05$) different to level of Cu in the top layer and in the bottom layer (table 2). Zn level in bottom layer was highly significantly ($P \leq 0.05$) different to level of Zn in the top layer and in the middle layer while Co was present in all layers but there was no significant ($P \leq 0.05$) differences among the studied layers (table 2). Mashyuza travertine deposit had Cl, Zn, Cu, Co micronutrients in all layers (0.2 - 0.5, 0.5 -1 and 1-1.5m depth) Generally, there was no significant ($P \leq 0.05$) differences among the studied layers except for Mo level in the bottom layer which was highly significant ($P \leq 0.05$) different to the level of Mo in the middle layer and the top layer (table 3). Gishyita travertine deposit

Table 5. Concentration of micronutrients in travertine from Mpenge.

	Cl	Zn	Cu	Mo	Co
Depth (m)	**Concentration of micronutrient in mg kg^{-1}**				
0.2- 0.5	194.8a	37.5a	17.1a	3.9a	91.0a
0.5- 1.0	45.3a	22.7a	22.1a	11.5a	59.9b
1.0 -1.5	37.7a	34.8a	21.4a	24.5a	51.7b
Lsd(P≤ 0.05)	385.7	60.9	56.3	33.5	22.1

Means in column with similar letter are not significantly different.

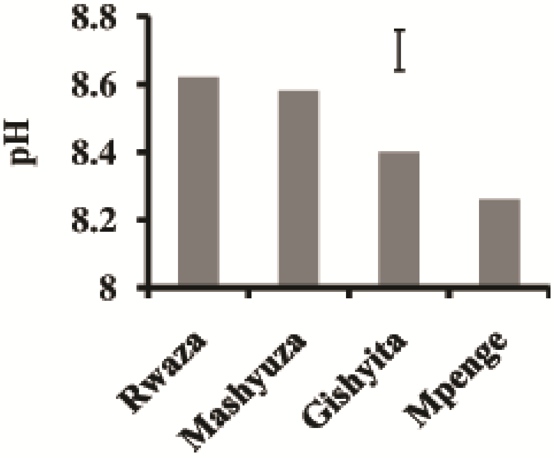


Figure 1. pH of travertine from Rwaza, Mashyuza, Gishyita and Mpenge deposits. LSD shown

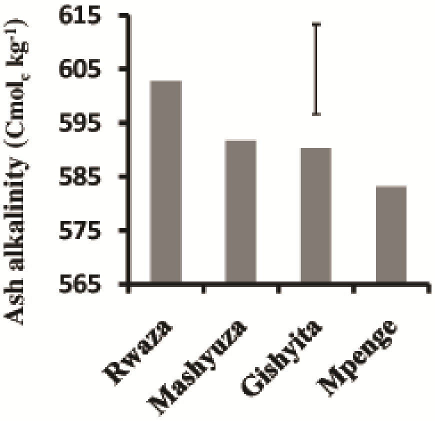


Figure 2. Ash alkalinity of travertine from Rwaza, Mashyuza, Gishyita and Mpenge deposits. LSD shown

had Cl, Zn, Cu, Mo and Co micronutrients in all layers (0.2-0.5, 0.5-1 and 1-1.5m depth) and there was no significant (P≤0.05) differences among the studied layers (table 4).

Mpenge travertine had Cl, Zn, Cu and Mo micronutrients in all layers (0.2 -0.5, 0.5 -1 and 1-1.5m depth) and there was no significant (P≤0.05) differences generally among the studied layers except for Co level in the top layer which was highly significant (P≤0.05) different to the level of Co in the middle and the bottom layers (table 5).

Many research activities have shown the relationships between micronutrient provision to plants and associated crop growth, and trace elements such as zinc, manganese and copper are increasingly recognized as

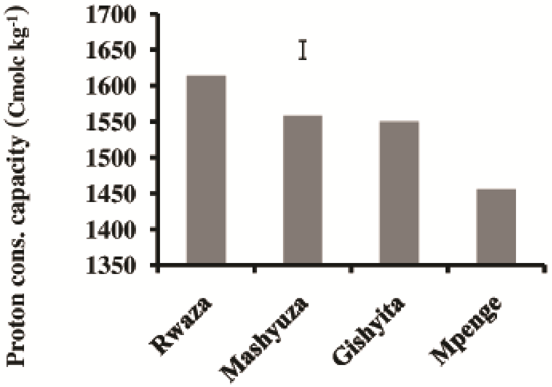


Figure 3. Proton consumption capacity of travertine from Rwaza, Mashyuza, Gishyita and Mpenge deposits. LSD shown

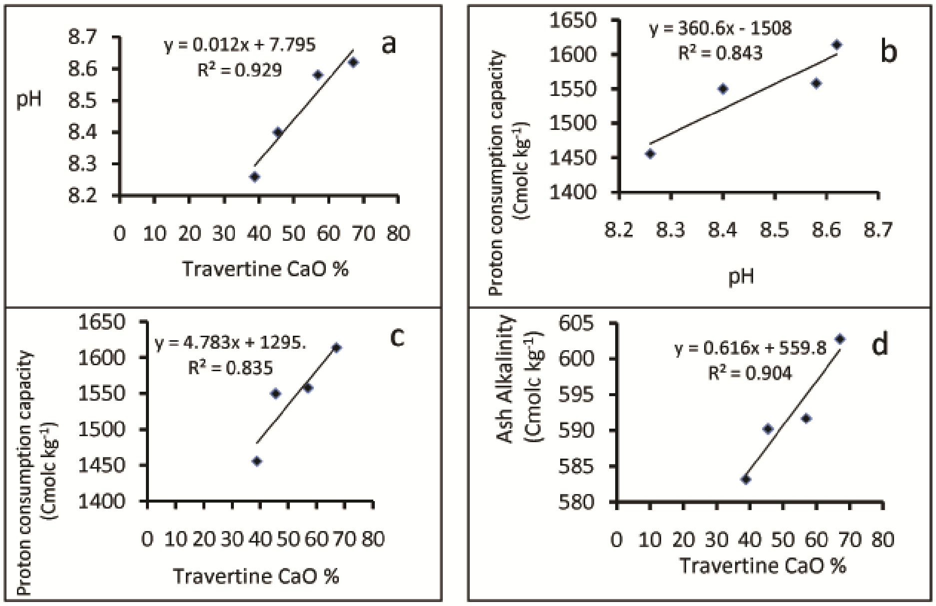


Figure 4. Linear correlation between a)travertine CaO concentration and pH, b)pH and proton consumption capacity, C) CaO travertine concentration and d) proton consumption capacity, travertine concentration of CaO and ash alkalinity.

essential when aiming for better yields according to Rashid and Ryan (2004), Welch and Graham (2004), Gupta (2005) and He et al. (2005). In addition, various studies suggest that better micronutrient provision to crops might result in more vigorous seedlings, lower vulnerability to plant diseases, and possibly also improved drought resistance (Frossard et al., 2000; Welch and Graham, 2002; Bouis, 2003; Welch and Graham, 2004). Micronutrients deficiency for crop has been reported in most part of the world, specifically Zinc (Alloway, 2009). Hence the presence of micronutrients such as Zn, Cu, Mo, Co and Cl in the travertine may offset the deficiency of some micronutrients that may be encountered in highly weathered Rwandan soils and increase yields (Fageria *et al*., 1997).

pH levels

Rwaza and Mashyuza travertine pH were found highly significant ($P \leq 0.05$) different to Gishyita and Mpenge travertine pH (Figure 1). The observed differences of pH among the travertine deposits were likely associated to the level of calcium carbonate. These ions are responsible for acid neutralization, pH increase and alkalinity increase (Brady *et al*., 1994 and Charles *et al*., 1999).

Ash alkalinity levels

Rwaza travertine was found with the highest ash alkalinity with no significant ($P \leq 0.05$) differences when compare to Mashyuza, Gishyita and Mpenge travertines ash alkalinity (Figure 2). However, the ash alkalinity values of travertine from these different deposits was the highest when compared with other values of animal and plant products already recommended as soil acidity ameliorants (Slattery *et al*., 1991; Mokolobate and Haynes, 2002; Naramabuye and Haynes, 2006).

Protons Consumption Capacity

Travertine contains carbonates functional group that are able to consume protons at their natural pH values. Their capacity to consume protons should, therefore, control their buffer characteristics and their ability to neutralize soil acidity. The proton consumption capacity as proposed by Wong *et al*. (1998), Mokolobate and Haynes (2002) and Naramabuye and Haynes (2006)**,** estimates this property and it was found that travertine from Rwaza site had proton consumption capacity level (1614 $cmol_ckg^{-1}$) highly significantly ($P \leq 0.05$) to proton consumption capacity levels of travertine from Mashyuza Gishyita while travertine from Mpenge had the lowest level of proton consumption capacity (1456 $cmol_ckg^{-1}$) (Figure 3).

The proton consumption capacity recorded from Rwanda travertine was high when compared to the other values of proton consumption capacity obtained from other kinds of liming materials such as compost, manures (Wong *et al*., 1998, Mokolobate and Haynes, 2002; Naramabuye and Haynes 2006).

There was a positive linear correlation between travertine CaO mean concentration and pH (r^2 = 0.929), pH and proton consumption capacity (r^2=0.843), CaO travertine concentration and proton consumption capacity (r^2 = 0.835) and travertine concentration of CaO and ash alkalinity, (r^2 = 0.904) (Figure 4). This positive linear correlation shows how these parameters are related as CaO content increases the pH also increase , the same behavior was observed for proton consumption capacity as well as the ash alkalinity. This positive linear correlation was likely associated to the calcium carbonates content in travertines. The calcium carbonates are known to be responsible of proton consumption by forming hydrogen carbonate and calcium ions which raise the pH and the alkalinity (Brady *et al*., 1994 and Charles *et al*., 1999).

CONCLUSION

This study revealed that travertine from Rwaza and Mashyuza have the highest Calcium Oxide weight percentage content seconded by Gishyita and Mpenge. Magnesium Oxide contents were found in order Gishyita > Mashyza > Mpenge> Rwaza though there was no significant differences recorded from these different deposits. Micronutrients (Cl, Zn, Cu, Mo and Co) were also present for all sites in levels that can balance the micronutrients deficiency that may be encountered in highly weathered Rwandan acidic soils. Proton consumption capacity and ash alkalinity recorded from Rwanda travertine were high when compared to other liming materials such as compost, manures, animal and plant product. There was also a positive linear correlation between calcium oxide content versus pH, pH versus proton consumption capacity, calcium oxide versus proton consumption capacity and calcium oxide versus ash alkalinity. This linear correlation can serve as a model to predict proton consumption capacity and ash alkalinity of any liming material when its pH and CaO content are known. The data presented in this paper should contribute to further investigations to tackle the major soil acidity problem encountered in Rwanda.

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