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## AN EVALUATION OF FACTORS AFFECTING THE CO<sub>2</sub>- C SINK STRENGTH OF AG-LIME ADDED TO TWO TRINIDAD ACID SOILS

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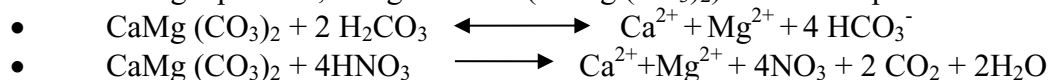
**Abstract:** The most recent Intergovernmental Panel on Climate Change (IPCC) greenhouse gas (GHG) inventory guidelines recognizes that CO<sub>2</sub> is not always the end product of ag-lime dissolution in soils and now allows countries to report on their own emission factors once it is supported by sound research findings. This study was therefore established to assess the effects of additions of organic amendments (biochar and poultry litter) and ammonium N on the magnitude of the CO<sub>2</sub> flux and the carbon sequestration potential of ag-lime when added to two diverse soils (a peaty clay and a sand). The soil treatments with the equivalent of 80g oven dry soil (ODS) were incubated in modified 500 mL mason jars. At each measurement, the alkali-trap attached to the cover was installed ensuring proper sealing of the jar opening and left for 24 hrs to absorb the CO<sub>2</sub> emitted from the soil. Fluxes were measured at days 1, 3, 6, 9, 10, 15, 18, 21, 24, 28 and, 31, and all soil treatments were initially brought to 100% field capacity and rewetted three times thereafter. Analysis of the data showed that soil type, organic matter and ag-lime additions had a significant effect (P<0.05) on CO<sub>2</sub> emissions. The effect of time was significant on the rates of CO<sub>2</sub> emissions, showing a decline in the emission rate from an overall mean of 33.8 mg CO<sub>2</sub>/kgODS/hr at day 1 down to 1.98 mg CO<sub>2</sub>/kgODS/hr. The peaty clay fluxes were consistently higher than those from the sand, and soils treated with poultry litter were also statistically (P<0.05) consistently higher than those with biochar and no organic matter additions. Given that ag-lime addition to soil is known to have a priming effect on organic matter decomposition, evidence for carbon sequestration was seen with both soils; whereby the increase in CO<sub>2</sub> emissions following the addition of ag-lime was much lower in the presence of poultry litter compared to soils with biochar and no organic matter addition.

**Keywords:** carbon dioxide (CO<sub>2</sub>), carbon sequestration, ag-lime, biochar, poultry litter, climate change, acid soils.

### INTRODUCTION

Liming agents such as agricultural lime (calcite and dolomite), are commonly applied in humid regions to raise the pH of the naturally acidic soils which are too acidic to facilitate the optimum growth of most crops (Brady and Weil, 2010; Dumale et al., 2011; West and Mc Bride, 2005). Periodic liming is also necessary to counteract soil acidification, which is commonly caused by the over use of nitrogenous and sulphur fertilizers (Fisher et al., 2003). The use of agricultural lime (ag-lime) has been identified as a contributor of carbon dioxide (CO<sub>2</sub>) emissions (Dumale et al., 2011; West and Mc Bride, 2005; IPCC, 2004). However, data on the magnitude to which ag-lime dissolution affects the flux of CO<sub>2</sub> from acid soils is limited, and it has also been noted that the flux of CO<sub>2</sub> from ag-lime is quite diverse (Dumale et al., 2011).

The revised 1996 Intergovernmental Panel on Climate Change (IPCC) on greenhouse gas inventories assumed that 100% of the carbon (C) stored in ag-lime is ultimately emitted as CO<sub>2</sub>. The most recently published 2006 guidelines on greenhouse gas inventories, however, recognizes that this is not the case and allows countries to report on their own emission factors once it is supported by sound research findings. This revision of the IPCC guidelines was as a consequence of findings by West and Mc Bride (2005), who estimated that only about 49% of the C in ag-lime is emitted as CO<sub>2</sub>. Contrary to these findings, results from a more recent study by Hamilton et al. (2007) suggest that ag-lime may actually serve both as a sequester or source of CO<sub>2</sub> depending on if its dissolution is influenced by weak acids, such as carbonic acid (H<sub>2</sub>CO<sub>3</sub>) that are released as result of root and microbial respiration, or strong acids such as nitric acid (HNO<sub>3</sub>) liberated from nitrification, respectively. These two biochemical pathways are summarized in the following equations, using dolomite (CaMg (CO<sub>3</sub>)<sub>2</sub>) as an example:



Based on results obtained from the analysis of leachate from limed agricultural plots on the Michigan State University Biological Station, Hamilton et al. (2007) proposed that ag-lime may sequester CO<sub>2</sub> equivalent to 25 percent to 50 percent of its C content in the case of H<sub>2</sub>CO<sub>3</sub> dissolution and emit CO<sub>2</sub> equivalent to as much as 60% of its C content when its dissolution is influenced by strong acids. As the estimates on the carbon sequestration potential of ag-lime made by Hamilton et al. (2007) were not based on measurement of the actual flux of CO<sub>2</sub>, this study was established to assess the effects of additions of organic amendments (biochar and poultry litter) and ammonium N on the magnitude of the CO<sub>2</sub> flux and the carbon sequestration potential of ag-lime when added to two diverse acids soils in Trinidad.

## MATERIALS AND METHODOLOGY

Two diverse acid soils (Nariva peaty clay and Piarco fine sand) of Trinidad were used in this experiment. Soil samples for both soil types were taken from farms that had a long history of vegetable production. Soils were prepared first by grounding with a metal pistol then sieving through a 2mm sieve. This procedure was repeated for the preparation of the poultry litter used in the experiment.

### Soil and organic amendment and analyses pre-incubation

Soil samples and organic amendments were characterized based on various physical and chemical properties using standard operating procedures (Sparks et al., 1996; Gee and Bauder, 1986). The results of these analyses are summarized in table 1. The potential of hydrogen (pH) was measured utilizing both calcium chloride (CaCl<sub>2</sub>) and water in a 1:1 soil: water/ CaCl<sub>2</sub> ratio. The electrical conductivity of the two soils was determined by means of the saturated paste method and dilution method, using the recommended 1:2 sample: water ratio in the case of dilution method (Sparks et al., 1996). Other analyses carried out on the two soil types included particle size distribution, using the hydrometer method; available P; and the lime requirement (Ca(OH)<sub>2</sub>) to raise the soil pH 6.5. The organic amendments were analyzed for pH in CaCl<sub>2</sub> and water using a 1:2.5 ratio; they were also analyzed based on the other parameters mentioned above for the characterisation of the two soils. The average percentage moisture and dry matter

(DM) content of the soils and organic amendments were also determined; however, these results are not presented in this paper.

### **Soil incubation and gas measurement**

A 3×2×2×2 factorial design with three levels of material (poultry litter and biochar at a rate of 5% of soil on an oven dried basis and no organic material); two levels of ag-lime (2000ppm and 0ppm of laboratory grade CaCO<sub>3</sub>); two soil types (80g ODS); and two levels of ammonium N (200ppm and 0ppm) was employed for this experiment. The treatments used in this experiment were the result of combination of these four factors and their levels. Soil treatments were incubated in modified 500mL mason jars in a laboratory at 22.3± 0.58°C for 33days. All soil treatments were initially brought up to 100% field capacity (FC) and rewetted at days 9, 19, and 26. Before each measurement, the alkali traps attached to the cover of the mason jars were filled with 5mL of 1M NaOH using a 5mL pipette. The traps were then carefully installed and properly sealed to avoid spillage and the escape of CO<sub>2</sub> from the jars and fluxes were measured 24hrs after by titrating the unreacted NaOH to a phenolphthalein end point with 1M HCL (Anderson, 1982). Fluxes were measured day 1, 3, 6, 9, 10, 15, 18, 21, 24, 28, and 31 of incubation.

### **Post-incubation analyses**

Analyses were carried out on the soil treatments at the end of the incubation period. pH was determined in water using a 1:1 ratio, while EC was determined using a 1:2 dilution. Available P was also determined.

### **Calculation of lime derived carbon (C)**

The total percentage lime derived C was calculated by first subtracting the total cumulative C of the un-limed treatments from their corresponding lime treatment. The difference was divided by the rate at which C was added in the ag-lime and then multiplied by a 100.

### **Statistical analysis**

Data were analysed using a factorial analysis of variance (ANOVA) by Gen Stat Discovery Edition statistical package. Where there were significant (P<0.05) effects of a particular treatment or their interaction, least significant differences (LSD) were used to discriminate among means.

## **RESULTS AND DISCUSSION**

The effect of soil type on the rate of CO<sub>2</sub> emissions was significant (P<0.05) at all eleven sampling times (table 2). The rate of emissions was consistently higher from the Nariva peaty clay than from the Piarco fine sand soil series. On average, the emission rates were 11.9 mg CO<sub>2</sub> kg/hr and 3.65 mg CO<sub>2</sub> kg/hr for the peaty clay and fine sand respectively. The significantly higher mean emission rate from the peaty clay as compared to the fine sand is expected. It is well understood that the rate of decomposition of indigenous carbon by soil microorganisms, which leads to the production of CO<sub>2</sub>, is higher in soils with high initial soil organic carbon (SOC)

levels than those with initially low levels (Dumale et al., 2011; Mann, 1986). Therefore, the difference in the mean emission rate is as a consequence of the higher organic carbon content in the peaty clay.

Table 1. Characterisation of soil and material pre-incubation.

EC- Electrical conductivity by dilution method							
Sample	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	EC (mS)	ECe (mS)	Av. P (ppm)	Lime Requirement (tons/ha)	Textural class
Piarco fine sand	4.43	4.05	0.2167	0.7933	51.164	1.716	Sandy loam
Nariva peaty clay	4.52	4.33	0.8000	2.085	30.167	6.543	Clay
Biochar	7.35	6.95	0.2353	NA	NA	NA	NA
Poultry litter	8.58	8.43	14.31	NA	NA	NA	NA

ECe- Saturated paste electrical conductivity

NA- Analysis not applicable

Av. P- Available phosphorus

Table 2. F probabilities as affected by individual factor treatments and their two-way interactions for CO<sub>2</sub> emission rates at various sampling times.

Source of variation	Df	n	Sampling Time (days)										
			1	3	6	9	10	15	18	21	24	28	31
Soil	1	12	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx
Mat	2	8		xxx	xxx	xxx	x	xxx	xxx	xxx	xxx	xxx	xxx
Lime	1	12	xxx	xx	x								
Amm	1	12										x	
Soil.Mat	2	4		xxx				x					xx
Soil.Lime	1	6	x		x								
Soil.Amm	1	6		x									
Mat.Lime	2	4	xx									x	
Mat.Amm	2	4											
Lime.Amm	1	6				x							
Residual	9												
Total	23												

x, xx and xxx represent statistical significance at P < 0.05, 0.01 and 0.001 respectively

Empty boxes represent no statistical significance with P > 0.05

The effect of time on the rates of emissions was very significant (P=0.001). The highest rates of emissions occurred in the early stages of incubation particularly within the first 24 hours,



decreasing progressively thereafter from 33.8 mg CO<sub>2</sub> kg/hr to 1.98 mg CO<sub>2</sub> kg/hr for the means of both soils combined (fig 1).

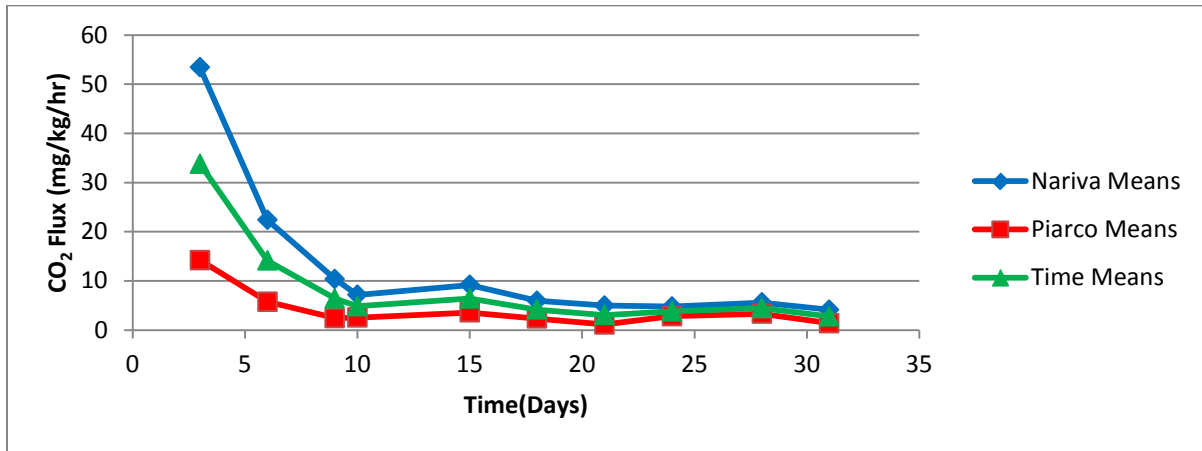


Figure 1. Temporal variation in rates of CO<sub>2</sub> emissions as affected by individual soils and their combined means.

Analysis of emissions data at the end of the experiment showed that the effect of lime was significant ( $P < 0.05$ ) on the rates of emissions. Higher mean rates of emissions were recorded from the lime treatments than the no-lime treatments. Notwithstanding this, analysis of the emissions data by days however indicated a significant ( $P < 0.05$ ) effect of ag-lime only in the first 6 days of incubation. This effect was seen to be most statistically significant ( $P < 0.001$ ) after the first day of incubation (table 2; fig 2). A similar experiment by Dumale et al. (2011) recorded a significant quantity of lime-CO<sub>2</sub> evolving within the first 24 hours of incubation.

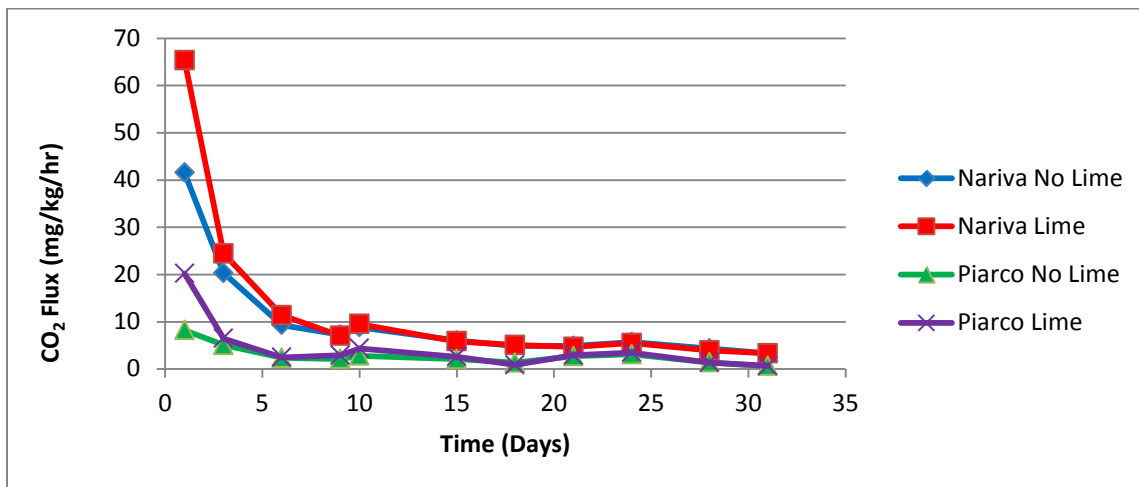


Figure 2. Interaction effect of time, soil and lime on the rates of CO<sub>2</sub> emissions

Organic material (OM) type had a significant ( $P < 0.05$ ) effect on the rates of emissions at all sampling times except day one (table 2). At day one, rates of 35.105, 31.855 and 34.565 mg CO<sub>2</sub>

Kg/ODS/hr were recorded for soils with no organic amendment and soils that were amended with biochar and poultry litter respectively. The higher fluxes from soils treated with poultry litter is expected, as the addition of readily decomposable organic material such as poultry litter, is known to significantly increase the rate of CO<sub>2</sub> emissions from soils (Hossain and Puteh, 2013). The lack of a statistically significant difference between the three organic matter treatments after the first day incubation in this study, however, may actually be an indication that the primary source of emissions from treatments without poultry litter, at least at this stage, may have been the ag-lime.

There was significant ( $P < 0.05$ ) interaction between organic material and lime—where in contrast to the no organic material amendment and biochar treatments, little difference was observed between the lime and un-limed treatments in the case of poultry litter addition (fig 3). Based on the assumption that the difference in emissions between the lime and un-lime treatments was as a result of ag-lime addition, these results suggest an enhancement of the carbon sequestration potential of ag-lime in the presence of poultry litter. Poultry litter, because of its high labile carbon content, greatly enhances microbial respiration through rapid decomposition of this labile carbon by these microorganisms (Hossain and Puteh, 2013). The addition of this amendment may have therefore led to the production of carbonic acid, which has been suggested by Hamilton et al. (2007) to enhance the carbon sequestration potential of ag-lime (equation 1 in introduction)

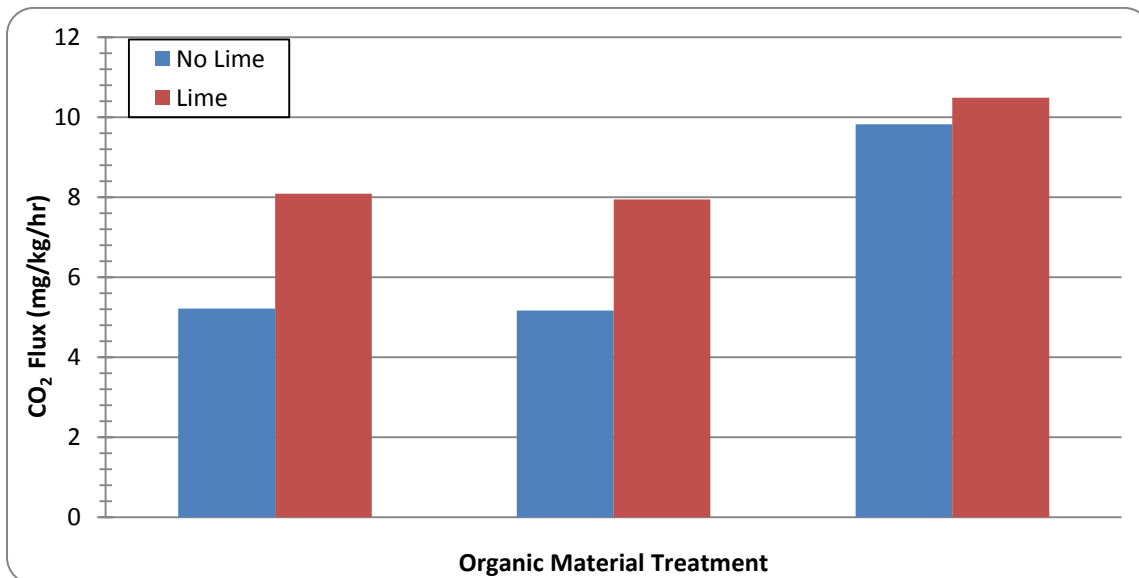


Figure 3. Interaction effect of organic material and lime on the rates of CO<sub>2</sub> emissions

$$LSD_{(0.05)} = 1.147$$

Calculations of the lime derived C showed average values as high 202% and 198% ,to as low 18% for treatments with no organic matter amendment, and biochar and poultry litter amendment respectively (fig 4a). It is important to note that the lime derived C may actually be lower than what was calculated in this experiment by the difference method, given that ag-lime addition is

known to have a positive priming effect on organic matter decomposition. The priming effect is described as a rapid turnover of soil organic matter subsequent to liming, and it results in an increase in CO<sub>2</sub> evolution from microbial respiration (Dumale et al., 2011). Lime derived C values of more than 100% in our experiment is an indication that there was some priming of SOC. With the limitations of this method of calculating lime emissions in mind, these results point to some evidence of a reduction in lime emissions when poultry litter is present. Moreover, results of the lime derived C from a second experiment, which investigated the effects of ag-lime and poultry litter rate on the CO<sub>2</sub> flux and the carbon sequestration potential of the Nariva peaty clay soil series corroborates the findings of this experiment. The results of this second experiment, presented in figure 4b, show a significant reduction in the recovery of C in the presence of poultry litter. This effect was especially prominent at the 1% poultry litter and 0.1% ag-lime combination.

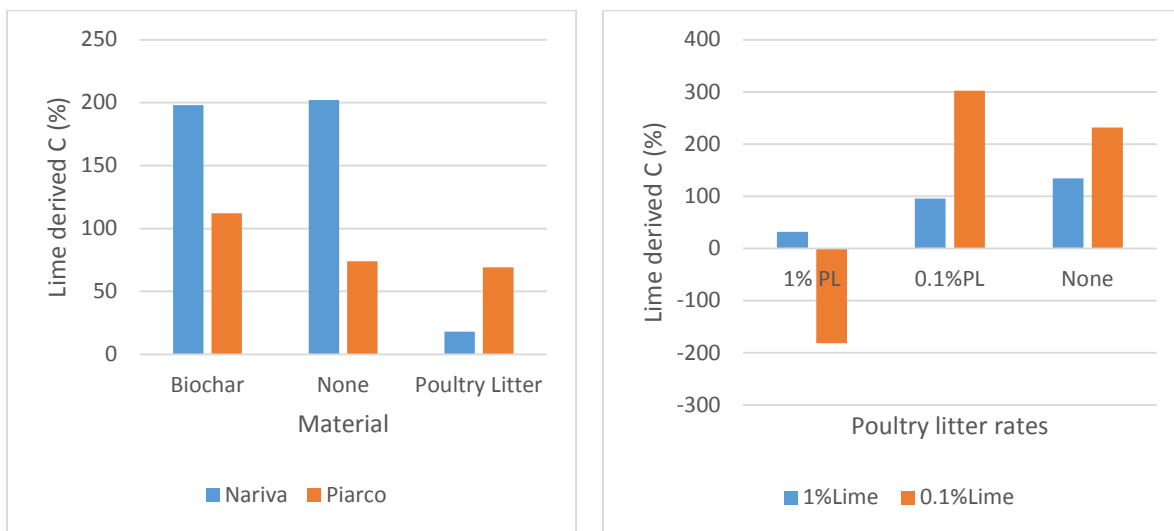


Figure 4a. Effect of OM and soil type on lime-C and Figure 4b. Effect poultry litter rates on lime-C.

Although a post incubation analysis of the soil treatments for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub> was not carried out at the time of writing this paper to assess the extent to which the added ammonium- nitrogen (N) was nitrified, the significantly ( $P < 0.05$ ) lower pH observed for soils that were treated with ammonium- N compared to soils that were not (fig 5) may serve as an indication that a significant amount of the added N had been nitrified. Hamilton et al. (2007) observed that lime switched from a net sink to a source of CO<sub>2</sub> as the concentration of NO<sub>3</sub><sup>-</sup> in infiltration waters. This phenomenon is explained by the dissolution of HCO<sub>3</sub><sup>-</sup> by H<sup>+</sup> from HNO<sub>3</sub> that is liberated during nitrification. In this current study, however, there was a generally a lack of a statistically significant effect of ammonium addition on the flux from the lime treated soil. This may have been due to the low rate at which ammonium -N was added in comparison to ag-lime. From equation 2 in the introduction of this paper, it is seen that two moles of HNO<sub>3</sub> is required to dissolve one mole of ag-lime by strong acid dissolution.

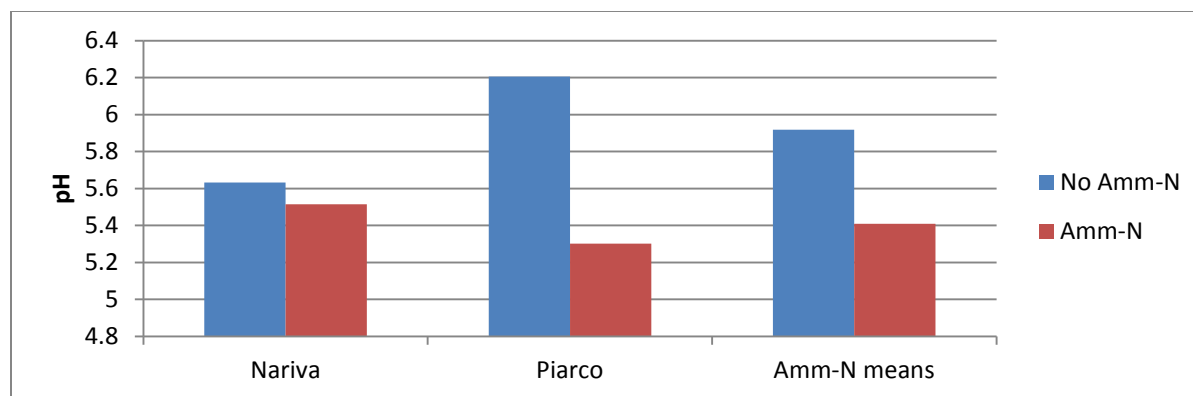


Figure 5. Interaction effect of soil and ammonium N on pH at the end of experiment one.

## CONCLUSIONS

In these studies, the addition of poultry litter in combination with ag-lime reduced lime emissions, especially for the Nariva peaty clay. This therefore suggests the need to further explore the climate change mitigation potential of ag-lime under a wider range of soils and management conditions. The use of more accurate techniques to estimate lime derived emissions is also recommended to better elucidate the mechanisms that control this phenomenon.

The application of ammonium-N and ag-lime at similar or equal rates should be considered in future experiments investigating the effect of addition of N fertilizers on the magnitude and flux of CO<sub>2</sub> from limed soils. Doing such may yield a more significant effect of ammonium N addition flux of CO<sub>2</sub> from these soils.

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