COMPARING THE EFFECTIVENESS OF CALCIUM PRODUCTS IN NEUTRALIZING SOIL ACIDITY

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ABSTRACT

Proper pH management is the foundation of a good soil fertility program. Soil pH influences nutrient availability, root growth and function. Acid soils are neutralized by the addition of carbonates, oxides, and hydroxides present in limestone products. However, there is a common perception among some producers that calcium is responsible for the neutralization of acid soils rather than the carbonates associated with calcium in the limestone. The effectiveness of three calcium products in raising soil pH were compared to an untreated check in acid soils. A field study was conducted at 16 locations across Kentucky. A laboratory incubation study was conducted at the University of Kentucky Research and Education Center using the same application rates as the field trial. Treatments included an untreated check, liquid calcium chloride (5 gallon acre-1), pelletized lime (RNV 83), and ag lime (RNV 79). Pelletized lime and ag lime were applied at a rate of 2 ton acre-1 of 100% effective lime after adjusting for product RNV. The field study resulted in significantly higher soil pH at the 3 month, 12 month and 24 month sample dates with ag lime and pelletized lime compared to the untreated check and liquid calcium. The lab study resulted in higher soil pH values with ag lime and pelletized lime than the check and liquid calcium at each sample date (1, 3, 6 and 12 month). The untreated check and liquid calcium products did not change soil pH. This was expected due to the inability of liquid calcium ($CaCl_2$) to consume acidity. To effectively neutralize soil acidity and increase soil pH, the addition of products that contain carbonates, oxides, or hydroxides must be utilized. The results of this study support the chemical foundations associated with soil acidity neutralization reactions - calcium chloride doesn't neutralize acidity and calcium carbonates do.

INTRODUCTION

Proper soil pH management is the foundation of a good forage soil fertility program. Soil pH indicates the amount of active acidity present in the soil and influences nutrient availability, plant root growth and function, the rate of many biological processes and herbicide activity (Miller and Kissel, 2010). Lime application rate is based on the amount of active acidity and the soil buffer pH (Sikora, 2006). Application of acid neutralizing products are added to the soil to neutralize acid soil pH. The primary products used for pH management in field agricultural settings are some form of calcitic or dolomitic limestone. Some producers and ag retailers believe or claim that calcium is responsible for the neutralization rather than the carbonates associated with calcium in the limestone, but this is not true. Limestone application rates are adjusted according to their relative neutralizing value (RNV). The RNV is influenced by the purity and the fineness of the limestone. Some companies offer products that claim to neutralize acidity by adjusting the amount of base cations (Ca, Mg, K, or Na) present on the exchange complex by adding minute amounts of Ca in the form of calcium chloride ($CaCl_2$). To neutralize acidity, the proton (H^+) must be consumed. The neutralization reaction of calcitic limestone is demonstrated in equation 1.

Equation 1. $CaCO_3 + 2H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 + Ca^{2+}$

The acidity or proton in equation remains after the addition of $CaCl_2$ and has no liming ability according to equation 2.

Equation 2. $CaCl_2 + 2H^+ \rightarrow Ca^{2+} + 2H^+ + 2Cl^-$

Based on numerous questions and concerns from Kentucky producers, agribusiness, and agricultural producers we designed a field and laboratory experiment to test the effectiveness of liquid calcium chloride compared to traditional liming materials utilized in forage production.

MATERIALS AND METHODS

Field and laboratory incubation studies were established concurrently in the summer of 2021. The same treatments were used for both studies: a non-treated check (nothing applied), liquid calcium at 5 gallon acre^{-1}, pelletized lime (RNV = 83), and agricultural lime (RNV 79). Both pelletized lime and ag lime were applied at 2 ton acre^{-1} 100% effective lime, after adjusting the rate for the RNV of the product. Data was analyzed using SAS version 9.4 (Cary, NC).

The field study was conducted at 16 locations across Kentucky on private farms with assistance from agriculture agents and on two University of Kentucky Agricultural Experiment Stations (UKAES) located at Lexington, KY and 200 miles away at Princeton, KY. The field study utilized a randomized and replicated small plot treatment arrangement with 25 ft^2 plots and three replications. Soil samples for the field study were collected prior to treatment application, approximately 3 months later and approximately one year after initial treatment application. The two sites on the UKAES had samples collected again two years after treatment applications. Results for the field study were reported as the average soil water pH across locations. Forage data was collected approximately 3 months after treatment application immediately prior to hay harvest and analyzed by near infrared spectroscopy to include: dry matter (DM), crude protein (CP), acid detergent fiber (ADF), neutral detergent fiber (NDF), and total digestible nutrients (TDN).

The incubation study utilized the surface 6 inches of a Crider silt loam (Typic Paleudalf) soil with an initial soil water pH of 5.2. This soil was removed of large clods, roots and plant material prior to screening to pass a 2-mm sieve. We placed 1.8 oz (50 g) of air-dried soil in 4 oz specimen cups with small holes in the cap to allow for gas exchange. Treatments were replicated 4 times. Cups were maintained at 80% water filled pore space by weight until shortly before the 6-month sample date. Shortly before the 6-month samples were to be analyzed the building was destroyed by an EF-4 tornado. Most samples were recovered after the tornado but cup moisture wasn't maintained for the 12-month samples. Destructive sampling occurred at 1, 3, 6 and 12 months. Results for the incubation study were reported as soil water pH.

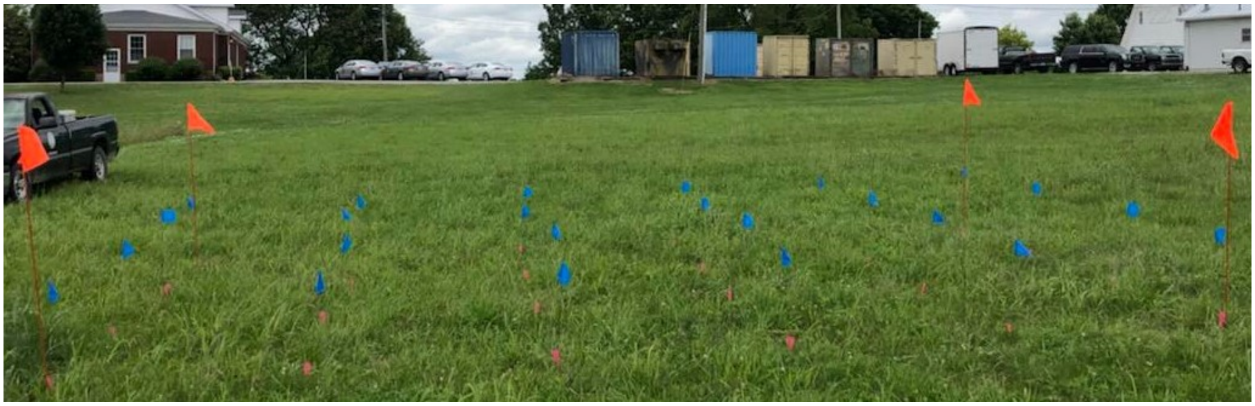

Figure 1. Generalized plot layout for field study. Plot whiskers were used to mark plot location when flags had to be removed for general plot management operations.

RESULTS AND DISCUSSION

Field Trial pH Change

Soil pH values in the field trials reacted as expected according to equation 1 and equation 2. The soil pH values were similar (pH = 5.8) at the beginning of the experiment prior to any treatment being applied. Treatments that received products containing carbonates (i.e. ag lime and pelletized lime) resulted in an increase in soil pH and treatments that did not contain carbonates (check and liquid calcium) did not change within a given period (Table 1). The addition of limestone to agricultural fields is not considered an immediate reaction, like an application of urea fertilizer. A noticeable pH change isn't expected to occur immediately rather it will occur over several months or up to a few years (Ritchey and McGrath, 2022). A slight increase in soil pH (0.3 to 0.4 units) was noticed with ag lime and pelletized lime at the 3-month sample collection time where soil pH showed a slight decrease at the 3-month sample collection time with the check and liquid calcium. Soil pH 1 year after application was 0.7 units higher for the ag lime and pelletized lime compared and significantly greater than the check and liquid calcium product. Soil pH for the two locations sampled at 24 months were statistically greater with the ag lime and pelletilzed lime than the check and liquid calcium chloride product. There was no statistical difference in pH between the Ag lime and pelletized lime for the field experiment (Figure 1).

Table 1. Soil pH values for the field trial, prior to treatment application and 3, 12, and 24 months following treatment application. Results for 3 and 12 months are averaged across 16 locations. Results for 24 months are averaged over 2 locations.

	------------------------------------ Soil pH -------------------------------------			
Treatment	Initial pH Pr>F (0.854)	pH 3 month Pr>F (<0.001)	pH 12 month Pr>F (<0.001)	24 month Pr>F (0.003)
Check	5.8 a[1]	5.6 a	5.9 a	5.4 a
Liquid Calcium	5.8 a	5.7 a	5.8 a	5.4 a
Pelletized Lime	5.8 a	6.1 b	6.5 b	6.0 b
Ag Lime	5.8 a	6.2 b	6.5 b	5.8 b

[1] Letters in the same column that are different indicate significant treatment differences at the 0.1 level of significance.

Lab Incubation pH Change

Soil pH values responded to the applied treatments in the lab incubation as expected according to equation 1 and equation 2. The initial soil pH value was 5.2 at the onset of the experiment prior to treatment application. One month after treatment application the pelletized lime and ag lime had significantly increased soil pH by 0.7 and 0.9 units from the initial soil pH (Table 1). Soil pH increased 1.1 and 1.0 units at the 3-month sample date for the pelletized and ag lime treatments. However, during the same time period the untreated check and the liquid calcium treatments were 0.1 to 0.2 units less than the initial soil pH (i.e. soil pH decreased with time). The short-term results of the incubation were very promising for the limestone products. Ideal soil and environmental conditions led to a rapid neutralization reaction of soil acidity in this incubation time.

Results up to the 6-month sampling date were very promising and illustrate how ideal, controlled laboratory conditions will improve the speed of a neutralization reaction compared to those that occur in the field in ambient soil conditions. Conditions were maintained in the laboratory where we expected the neutralization reaction to proceed as fast as possible. For example, soil moisture was maintained at 80 pore filled volume, temperature was near room temperature, and gas exchange between the cups and atmosphere were allowed to occur. A one unit change is soil pH would not be expected to occur in field settings in 1 to 3 months due to less than ideal environmental conditions being constantly present where they occurred in the laboratory setting.

An F-4 tornado destroyed the storage room where the samples were stored for this experiment on Dec 10, 2021. The samples that were recovered were collected and moved to another location but soil moisture and temperature was not maintained moving forward. The specimen cups dried and were exposed to greater fluctuations in ambient temperatures. This might have slightly influenced the results of the 6-month incubation time and particularly the 12-month incubation duration. The soil pH was still increasing at the 6-month sample time and resulted in an increase of 1.5 and 1.4 units with the pelletized and ag lime over that of the untreated check (Table 1). This was a slight increase in soil pH over the 3-month sample date, but not as much as expected based on the previous results. The soil pH for the untreated check and liquid calcium were 5.0, which is slightly lower than the original pH values at the initiation of the incubation and statistically lower than the soil pH values resulting from the calcium carbonate products. This is a clear indication that the liquid calcium product ($CaCl_2$) has no liming ability.

Soil pH values resulting from the 12-month sample date had increased over the initial samples but were not as high as the 6-month sample date, they had decreased slightly. The soil pH for the pelletized lime was 6.3 and was 6.2 for the ag lime at the 12-month sample date (Table 1). The untreated check and liquid lime had also remained around 5.0 - 5.1. These results could potentially be due to the soil drying and fluctuating soil temperature after the tornado event. These results would be more typical of what would be expected in field settings.

Table 2. Soil pH values for the laboratory incubation trial for soil pH 1-month, 3-month, 6-month, and 12-month after treatment application. Initial soil pH was 5.2 for all treatments prior to treatment application.

	-------------------- Soil Laboratory Incubation Time --------------------------			
Treatment	1 month	3 month	6 month	12 month
Pr>F	(<0.001)	(<0.001)	(<0.001)	(<0.001)
Check	5.2 a[1]	5.1 b	5.0 a	5.1 a
Liquid Calcium	5.3 a	5.0 a	5.0 a	5.0 a
Pelletized Lime	5.9 b	6.3 d	6.5 b	6.3 b
Ag Lime	6.1 b	6.2 c	6.4 b	6.2 b

[1] Letters in the same column that are different indicate significant treatment differences at the 0.1 level of significance.

Forage Yield and Feed Nutritive Value

Although no positive results for a change is soil pH were observed from the liquid calcium, we wanted to test the influence of the treatments on the yield and feed value of the different forages in this experiment. No significant results were seen for yield or any of the feed nutritive components 3 months after treatments were applied (Table 3). Although soil pH is an important component to a good soil fertility, significant improvement in pH, thus yield or feed nutritive factors were not expected in the time frame of this study (i.e. between the first and second cutting). The random variation of the results is indicative of variable stand densities within given hayfield or pasture situations. We maintained the small plot size to reduce soil pH variation within individual fields. The small plot size used for yield determination was good to limit soil pH differences within the study site, but better estimates of forage yield may have benefited from a larger sampling size.

Table 3. Forage yield and feed nutritive results from the field study approximately 3 months after treatment application. The results are averaged across 16 field locations.

Treatment	DM[1] (lb $acre^{-1}$)	CP[2] (%)	ADF[3] (%)	NDF[4] (%)	TDN[5] (%)
Pr>F[6]	0.620	0.865	0.793	0.693	0.575
Check	1,874	11.6	37.1	60.3	58.8
Liquid Calcium	1,968	11.5	36.7	60.8	59.2
Pelletized Lime	2,119	11.0	37.6	61.5	58.3
Ag Lime	1,832	11.1	37.4	60.2	58.5

[1] DM = forage dry matter reported in kg ha^{-1}
[2] CP = crude protein reported as a percent
[3] ADF = acid digestible fiber reported as a percent
[4] NDF = neutral digestible fiber reported as a percent
[5] TDN = total digestible nutrients
[6] No statistical differences observed at the 0.1 level of significance

CONCLUSIONS

Results of the field trials indicate that proven practices to neutralize soil acidity still hold true. The results of the field trials support the results of the laboratory incubation study, which agree with sound chemistry foundations. The products that were expected to neutralize soil pH (i.e. those containing carbonates) did neutralize soil pH and increased soil pH within a given incubation period. However, there was no consistent difference between liming products. Products not containing carbonates – liquid calcium ($CaCl_2$) have no mechanism to change soil pH and did not change soil pH in this experiment. In short, to effectively neutralize soil acidity and increase soil pH the addition of products that contain carbonates, oxides, or hydroxides must be utilized – not products that just contain calcium or chloride. Forage yield and feed nutritive values were similar regardless of treatment. Economics of liming material, coupled with the effectiveness, should be considered when determining liming materials.

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