Liming Requirement for Nitrogen Fertilizer-Induced Soil Acidity: A New Examination of AOAC Guidelines

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Liming is a routine crop management practice on many agricultural soils and is partly a consequence of soil acidification by nitrification of N fertilizers. The Association of Official Analytical Chemists (AOAC) in 1934 adopted soil acidification values that suggest ammonium sulfate (AS) requires three times more lime to neutralize resultant soil acidity compared to ammonium nitrate (AN) or urea. This article reports on a critical examination of the value and discusses results of laboratory and 3-year greenhouse experiments with wheat-corn-wheat-corn-wheat grown to maturity in which the liming requirement for AS compared to urea and AN was approximately 25 to 47% less than the AOAC value. This report also discusses results from field trials where soils treated with AS, urea, or AN for tall fescue growth did not significantly decrease soil pH compared to the control over a 2- to 3-year period.

It is well-known that N fertilizers containing NH_4 can induce soil acidification by nitrification of NH_4 to NO_3, which produces hydrogen (H^+) ions. The degree of soil acidification, however, depends partly on N source. The following reactions represent three commonly used N fertilizers – AS, urea, and AN – in nitrification process (Adams, 1984):

$$(NH_4)_2SO_4 + 4\ O_2 \rightarrow 4\ H^+ + 2\ NO_3^- + 2\ H_2O \quad (1)$$

$$(NH_2)_2CO + 4\ O_2 \rightarrow 2\ H^+ + 2\ NO_3^- + CO_2 + H_2O \quad (2)$$

$$NH_4NO_3 + 2\ O_2 \rightarrow 2\ H^+ + 2\ NO_3^- + H_2O \quad (3)$$

Since all three N sources contain 2 moles of N, theoretically the acidity produced by AS should be *twice* that produced by urea or AN based on the same amount of N applied. However, Pierre (1928a,b) reported that the actual acidity that would develop from urea and AN would be only 50% of the theoretical prediction for urea and AN and 75% for AS. Therefore, the predicted acidity from AS would be *three times* (3X) that from AN or urea. In 1934, the AOAC adopted Pierre's prediction and stated that the lime requirement to neutralize soil acidity induced by AS is 3X higher than the lime requirement for AN or urea. This statement has been cited extensively over the years, but until recently was not critically examined and validated in literature.

This article presents results from 1) a long-term greenhouse experiment conducted from 2001 to 2003 with a consecutive cropping system of wheat-corn-wheat-corn-wheat grown to maturity on three soils with about the same soil pH, but varying widely in soil texture, and 2) a field study (2005-2007) examining different N sources for tall fescue pastures at two sites. The main objective was to re-examine the recommended AOAC values for Relative Lime Requirement (RLR) for AS, with respect to urea and AN.

In the greenhouse study, three topsoils (0 to 6 in.) were compared: Sharkey (Chromic Epiaquerts) with pH = 6.0 and clay = 64%; Decatur (Rhodic Paledults) with pH = 7.3 and clay = 33%; and Greenville (Rhodic Kandiults), pH 6.6 and clay = 17%. Prior to planting, Sharkey, Decatur, and Greenville were incubated with KOH, HCl, and water, respectively, to narrow the range of soil pH to the range of 6.4 to 6.6. The AS, urea, and AN were incorporated below a 20-in. depth in 35 or 48 lb pots to eliminate possible NH_3 volatilization losses from urea. The N rates applied were 90 lb N/A for the first two wheat crops and 180 lb N/A for the corn crop and the last wheat crop because of depletion of soil N. All other nutrients were applied at adequate levels for plant growth. Three replicates for each treatment including the check were made within a randomized block design. Total dry-matter yield of corn (because of erratic grain yield under greenhouse conditions) and wheat grain yield and soil pH were measured after each harvest. Soil samples were collected after the fourth or last crops and analyzed for RLR by two methods: 1) extraction with a weak buffer 1 *M* Ca-acetate solution (pH 8.0) and back titration with 0.01 *M* NaOH to pH 8.0, and 2) incubation at various rates of $CaCO_3$, as described by Chien et al. (2008). Equation [1] was used to calculate RLR in the first method:

$$RLR = [(V_{AS} - V_{Check}) / (V_{AN\ or\ urea} - V_{Check})] \quad [eq.\ 1]$$

where V is the volume of NaOH used in back titration to pH 8.0.

Equation [2] was used to calculate RLR in the second method:

$$RLR = (Q_{AS}) / (Q_{AN\ or\ urea}) \quad [eq.\ 2]$$

where Q is the quantity of $CaCO_3$ required to reach pH 6.2 (Sharkey soil) or pH 6.34 (Greenville soil) by AS, AN, and urea, based on the regression equations.

In the field study, established tall fescue was fertilized with 75 lb N/A from AS, urea, and AN in mid-March at the Southwest Research and Education Center near Mt. Vernon, Missouri, and at Bradford Research and Extension Center near Columbia. The soil series is a Dapue silt loam (pH 5.8) (Fluventic Hapludolls) at Mt. Vernon and a Leonard silt loam (pH 7.1) (Vertic Epiaqualfs) at Columbia. The clay contents of these two soils were estimated to be 20 to 30% based on the soil texture chart of the Soil Survey Staff (1960). Fourteen different N sources were tested in 2005, 2006, and 2007 at Mt. Vernon and in 2006 and 2007 at Columbia. Soil P and K levels were maintained at adequate levels for plant growth. Each treatment, including the check, was replicated five times. For the purpose of this report, only the data of AS, urea, and AN were extracted from the results.

Because all N sources were incorporated into the soils in the greenhouse study, there were no significant yield differences among AS, urea, and AN after each crop, indicating N availability of AS, urea, and AN was about the same to corn and wheat (data not shown). Soil pH after each crop followed the order of AS < urea = AN < check, according to the reactions (1), (2), and (3). Soil pH also kept decreasing compared to the check as higher N rates were applied. One example of the changes in soil pH (Δ pH) after each crop is shown in **Table 1** for Greenville soil.

Abbreviations and notes: N = nitrogen; P = phosphorus; K = potassium; NH_4 = ammonium; NH_3 = ammonia; NO_3 = nitrate; $CaCO_3$ = calcium carbonate; HCl = hydrochloric acid; KOH = potassium hydroxide.

Table 1. Changes in soil pH (ΔpH) as related to total accumulated N rate applied from three N sources to Greenville soil.

Total N rate, lb N/A	Crop	ΔpH[1] AS	Urea	AN
90	Wheat	0.22	0.05	0.05
270	Corn	0.49	0.14	0.11
360	Wheat	0.62	0.15	0.16
540	Corn	0.89	0.25	0.31
720	Wheat	1.03	0.28	0.26

[1]ΔpH = (pH of check) – (pH of N source) measured at soil to water ratio = 1:1.

Table 2. RLR values of AS with respect to urea and AN for soil samples as determined by two methods.

Soil	Soil titration method after corn (2000)		Soil incubation method after wheat (2001)		Over-all average	Clay content, %
	AS/Urea	AS/AN	AS/Urea	AS/AN		
Sharkey	1.55	1.54	1.60	1.64	1.58	64
Decatur	2.08	2.14	2.16	1.92	2.07	33
Greenville	2.22	1.93	2.39	2.45	2.25	17

The results of the RLR values obtained by the titration and soil incubation methods for the soil samples treated with AS, urea, and AN are shown in **Table 2**. The over-all average RLR values are 1.58, 2.07, and 2.25 times higher for AS with respect to urea and AN for Sharkey, Decatur, and Greenville soils, respectively. These values are below the AOAC value (3.00) and represent 47%, 31%, and 25% less than the AOAC value, respectively. The Sharkey value is also less than the theoretical value (2.00) as predicted from reactions (1), (2) and (3), while the RLR values of Decatur and Greenville soils are close to the theoretical value. Thus, the results do not support liming guideline adopted by the AOAC that states AS requires 3.0 times more lime than urea and AN to neutralize soil acidity induced by nitrification of N fertilizers. In this study, Sharkey soil had very high clay content (64%), and therefore, its ΔpH value was less than that of Decatur and Greenville (data not shown). Data in **Table 2** show that the liming requirement to neutralize soil acidity induced by nitrification does not depend only on N source, but also on the soil clay content (soil texture) or pH-buffering capacity. **Table 2** shows that the over-all RLR value of AS with respect to urea and AN increased with decreasing soil clay content. This is a factor that is not considered in the AOAC recommendation for liming the acidified soils that are induced by N fertilizers containing NH_4^+-N.

The field data of forage show only the initial harvest responded to N applied. Between 60 and 80% of the annual dry matter was harvested at the initial sampling date in May and few treatment differences were measured in the two subsequent harvests. Thus, the yields shown are only for the initial harvest each year **(Table 3)**. Ammonium sulfate ranked at the top for nearly all harvests and locations. At Mt. Vernon, AS produced over 1,000 lb/A more forage than that fertilized with urea in the spring of 2005 and 2007 and produced more forage than AN in 2007. Urea and AN produced equal amounts of forage in every case except one: yields from plots fertilized with urea produced about 500 lb/A less than AN in Mt. Vernon in 2007. In each case, precipitation was not recorded for 3 to 6 days after fertilizers were applied in mid-March.

Table 3. Late May forage yield of tall fescue fertilized with different N sources.

N source	Mt. Vernon 2005	Mt. Vernon 2006	Mt. Vernon 2007	Columbia 2006	Columbia 2007
	lb/A				
AN	8,080	3,972	3,674	4,601	4,826
Urea	7,779	3,680	3,139	4,037	4,716
AS	8,832	3,987	4,183	4,407	4,915
Check (No N)	4,231	1,653	1,565	1,688	2,166
LSD (p = 0.05)	1,023	626	420	790	553

Table 4. Final soil pH of plots treated with different sources of N fertilizers for three (Mt. Vernon) or two (Columbia) successive springs. Each N source was applied in mid-March at 75 lb N/A to the same plots each year.

N source	Mt. Vernon	Columbia
	Soil pH	
AN	5.92	6.92
Urea	5.86	6.92
AS	5.62	6.76
Check (No N)	5.84	6.96
LSD (p = 0.05)	NS	NS

The final soil pH for each location is shown in **Table 4**. Although AS tended to lower soil pH more than other treatments did at both locations, there were no significant differences based on LSD (p = 0.05). Neither urea nor AN lowered soil pH as compared to the check. Thus, there appeared to be no need for liming in Mt. Vernon soil treated with a total accumulated N rate of 215 lb N/A for tall fescue growth after 3 years from AS, urea, or AN.

These results suggest that the AOAC standard that states AS requires 3X more lime than urea and AN to neutralize soil acidification induced by nitrification of N sources should not be universally accepted. Other than N source, factors such as initial soil pH, soil texture, soil pH buffering capacity, soil moisture, accumulated total N rate applied, method of N placement, climate, or even crop species, should also be considered. Further work, especially field trials, is needed to delineate all these factors and make a better recommendation of liming requirements for soils treated with N fertilizers. BC

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