

SOIL CHEMICAL PROPERTIES AND WHEAT
PRODUCTION IN LIME AMENDED
ACID SOILS

By

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1999

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PRODUCTION IN LIME AMENDED and the Department

ACID SOILS

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ACNOWLEDGMENTS

I wish to express my gratitude to Oklahoma State University and the Department of Plant and Soil Sciences for allowing me the opportunity to pursue this degree. I would like to extend my sincere appreciation to my advisor, Dr. Hailin Zhang, for his wisdom, guidance, and friendship. Sincere thanks to Dr. William Raun for his guidance, encouragement and understanding. I would like to acknowledge my other committee member, Dr. Eugene Krenzer. I would also like to express my heartfelt appreciation to Michael Kress for his help in running the LACHAT. I would like to extend my gratitude to all the individuals who helped me in this work: including Doug Cossey, Joanne LaRuffa, Wade Thomason, Erna Lukina and Curt Woolfolk.

Finally, I would like to thank my husband Anatoly for his continuous help and support, and my sons Alexander and Michael for their patience and understanding.

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FOREWORD

This thesis is organized in two chapters. Each chapter is formatted as a stand-alone article following the format specification of the journal *Communications in Soil Science and Plant Analyses* and other journals of the Soil Science Society of America. This approach facilitates a more streamlined method of preparing manuscripts for publication without necessity of rewriting the thesis.

CHAPTER I

SIMULTANEOUS DETERMINATION OF SOIL Al, NH₄-N AND NO₃-N USING 1 M KCl EXTRACTION

ABSTRACT

Determination of soil Al, NH₄-N and NO₃-N is often needed from soil samples for lime and fertilizer recommendations, but Al has to be extracted and quantified separately from NH₄-N and NO₃-N according to present methods. The objective of this study was to develop a reliable method for simultaneous analyses of soil Al, NH₄-N and NO₃-N using a Flow Injection Autoanalyzer. Thirty-five soil samples from different locations with wide ranges of extractable Al, NH₄-N and NO₃-N were selected. Aluminum, NH₄-N and NO₃-N were extracted using 1 M and 2 M KCl, and quantified using a LACHAT Flow Injection Autoanalyzer simultaneously and separately. One molar KCl was found to be a suitable extractant for all three compounds when compared to 2 M KCl. The 1 M KCl extract proposed could aid in decreasing the costs associated with simultaneous NH₄-N, NO₃-N and Al analyses. Results of those three compounds analyzed simultaneously were not statistically different from those analyzed separately in 1 M KCl solution. This new procedure of simultaneous determination of NH₄-N, NO₃-N and Al increases efficiency and reduces cost for soil test laboratories and laboratory users.

Soil acidity in the southern Great Plains of the US and many other agricultural production regions of the world has become a serious problem in crop production. Both forage and grain yields have been reduced in many areas (Boman et al., 1993). Soil acidity is harmful for crops due to nutritional disorders (deficiency of Ca, Mg and Mo, decreased availability of P) as well as immediate toxicity of Al, Mn and H^+ (Carver and Ownby, 1995). In general, increased solubility of Al with soil acidification is considered to be directly related to the enhancement of its toxicity (Carver and Ownby, 1995).

High levels of soluble aluminum limit root branching and rooting depths, severely inhibiting plant growth (Alam and Adams, 1979; Foy, 1984). Soluble forms of aluminum bind inorganic P, thus reducing P plant availability (Ohki, 1985). Labile forms of soluble aluminum [Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$] can also be harmful for wheat germination (Wright et al., 1989; Alva et al., 1986).

Determination of labile Al in soils implies extraction with salt solutions and subsequent instrumental analysis of Al in the extractant. The determination of exchangeable Al is complicated by the coexistence of complex multiphase Al components in soils, sediments and minerals. Kotze et al. (1984) demonstrated that soils release some exchangeable Al in 1 M salt extract, the degree of which was soil specific. Because of the operational nature of such determination, aluminum extracted is commonly referred to as exchangeable Al (Bertsch and Bloom, 1996). The most commonly employed extractant for exchangeable Al is 1 M KCl (Bertsch and Bloom, 1996).

Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) Optical

Emission spectrometers are commonly used in Al determination both for solids and extracts (Bertsch and Bloom, 1996). However, spectrophotometric methods adjusted for specific colored complexes of aluminum seem to be more promising due to their low cost and versatility. These assays can be automated and coupled with colorimetric determination of NH_4^+ and NO_3^- thus making the procedure practical for soil monitoring. However, no simultaneous method exists for analyzing Al and other ions using a colorimetric technique.

Among varieties of colored organic complexes of Al, the 8-hydroxyquinoline complex offers minimal interference, good sensitivity, and high precision (Bloom et al., 1979). Also, Al-pyrocatechol violet complex in the presence of 1,10-phenantroline as well as Al-tiron (4,5-dihydroxy-m-benzene disulfonic acid) complex has been successfully used for Al determination in solutions, including chromatography experiments (Willet, 1989).

Colorimetric methods for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ determination have already been established using flow injection methods, but the extraction solution for soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ is different from that for Al. Two molar KCl is used as an extracting solution for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ determination while 1 M KCl is generally employed for Al. Vaughan et al., (1995) showed that there is no difference in using 1 M KCl instead of 2 M KCl as an extracting solution for $\text{NO}_3\text{-N}$. McElreath et al. (1992) found that the concentration of KCl had a significant effect on the amounts of extractable Al among the range of concentration from 0.125-1 M, the highest extractable Al values were obtained with 1 M

KCl but the effect of the concentration of KCl on soil $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ is not well documented.

Developing a method for determination of soil Al, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ from the same solution simultaneously will make soil tests more convenient and less expensive. The objectives of the present work were (i) to develop a reliable method for simultaneous determination of soil Al, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ using a colorimetric method, (ii) to evaluate the Method Detection Limits (MDL) and Limits of Quantitation (LOQ) for the method developed.

MATERIALS AND METHODS

Thirty-five soil samples from different locations in Oklahoma with a wide range of exchangeable Al, NH₄-N and NO₃-N concentrations were selected and prepared for this study. Soil samples were extracted with 2 M KCl and then with 1 M KCl, and analyzed for Al, NH₄-N and NO₃-N. Concentrations of Al, NH₄-N and NO₃-N in the extraction solution were analyzed using a LACHAT Quickchem 8000 Flow Injection Autoanalyzer (LACHAT, 1994, Milwaukee, WI.).

The instrument is equipped with NH₄⁺, NO₃⁻ and Al channels. It is capable of analyzing three compounds simultaneously from the same extractant with one computer system. Two grams of soil that had passed a 2 mm sieve were placed into a 50 mL Erlenmeyer flask. Twenty mL of KCl solution was added to the flask. Samples were shaken on a horizontal shaker for 1 hour and filtered through Watman No. 2 filter paper or equivalent. Filtrates were analyzed for Al, NH₄-N and NO₃-N. Extractions of all soils were repeated 3 times. Ammonia analysis was based on the Berthelot reaction (Weatherburn, 1967). Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitropruside is added to enhance sensitivity. The absorbency of the reaction product is measured at 630 nm, and is directly proportional to the ammonia concentration in solution. Nitrate in the extraction solution is quantitatively reduced to nitrite by passing the sample through a copperized cadmium column. The nitrite (reduced nitrate and original nitrite) is then determined by diazotising with sulfanilamide followed by coupling with N-1-naphthyl ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color, which is read at 520 nm (Mulvaney, 1996). Aluminum in the extract reacts with pyrocatechol violet in

the presence of 1,10-phenontralin at pH 6.2 to form a blue-gray color of uncertain composition. Aluminum polymers and strongly complexed aluminum molecules do not react with the pyrocatechol violet. The color formed is measured at 580 nm (Bloom and Erich, 1989).

The reliability of the method developed was evaluated using Method Detection Limit (MDL) and the Limits of Quantitation (LOQ). MDL indicates the ability of the method to determine the concentration of the analyte in a sample matrix (Klesta and Bartz, 1996). It was calculated as three times the standard deviation (S_0) from seven replications of blank samples. LOQs are the lowest level at which analytical measurements become meaningful in quantifying a result and are defined as ten times the standard deviation. Analytical results below LOQ are reported as "less than values".

Effect of KCl concentration on soil NH₄-N, NO₃-N and Al

The relationship of soil Al, NH₄-N and NO₃-N (average of three replications) extracted by 1 M KCl and 2 M KCl was examined. The regression coefficients (slope and intercept) and correlation coefficient (r^2) were obtained from Fig. 1 and reported in Table 1. The slopes of the linear curve for NH₄-N (0.94-1.2) and NO₃-N (0.98-1.13) extracted with 2 M KCl and 1 M KCl were not significantly different from 1 (Table 1). This suggests that soil NH₄-N and NO₃-N extracted with 2 M KCl is not statistically different when extracted with 1 M KCl. Therefore, 1 M KCl can be used to extract NH₄-N and NO₃-N without changing the final concentration. Vaughan (1995) obtained similar results for NO₃-N extracted with 1 M and 2 M KCl, similar comparison was not made for NH₄-N in the literature. The coefficient of correlation (r^2) is lower for NH₄-N (0.90) than for NO₃-N (0.97). This is because of the higher values of standard deviation, MDL and LOQ for soil NH₄-N than for NO₃-N.

According to McElreath et al. (1992), the concentration of KCl has a significant effect on the amounts of extractable Al in the range of concentration from 0.125-1 M; the highest extractable Al values were obtained with 1 M KCl. In the present work the slope of the linear curve for Al extracted with 2 M KCl is only half of that with 1 M KCl. It is unclear why exchangeable Al increased as KCl concentration increased from 0.1 to 1.0 M (McElreath et al., 1992), but decreased from 1.0 to 2.0 M (this study). As 1 M KCl is the commonly used extractant for exchangeable Al (Bertsch and Bloom, 1996) and changing to 2 M KCl would require new interpretations, only one molar KCl can be used as an

extractant for all three compounds without developing new interpretations for all three analytes. For example, the difference may be significant when a large

MDL and LOQ for soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al in 2 M KCl and 1 M KCl are shown in Table 2, and they are not significantly different between extractants. Therefore, substitution of extraction solutions will not change detection limits and precision of the methods.

Soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al extracted using 1 M KCl, and analyzed separately and simultaneously

In order to determine if the efficiency of lab analysis could be improved, separate analyses for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al extracted with 1 M KCl were compared with simultaneous analyses for all three analytes using the LACHAT Autoanalyzer. The correlation between results determined separately and simultaneously are shown in Fig. 2. The slopes of the linear curve between $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al determined simultaneously and separately (Table 3) were not significantly different from 1 in all three cases. Therefore, the simultaneous method for determining all three compounds can be successfully used without changing interpretation. The highest coefficient of correlation (r^2) was found with $\text{NO}_3\text{-N}$ (0.99) in comparison to 0.96 for Al and 0.78 for $\text{NH}_4\text{-N}$. The low coefficient of correlation for soil $\text{NH}_4\text{-N}$ is due to its high standard deviation, MDL and LOQ. MDL and LOQ for these three components determined simultaneously are shown in Table 4. Therefore, the simultaneous method for determining all three compounds can be used instead of separate analyses. This new procedure may increase efficiency and reduce cost for soil test laboratories and laboratory users, however, it also has a drawback that $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ can be analyzed either

independently or simultaneously in about 45 seconds per sample, while AI requires about 65 seconds per sample. This 20 second difference may be significant when a large number of samples are analyzed.

Therefore, the 12M KCl extractant can be used to determine NH_4^+ -N and NO_3^- -N in soil samples in a rapid and accurate method. The ion exchange method is a rapid and accurate method for determining NH_4^+ -N and NO_3^- -N in soil samples. The ion exchange method is a rapid and accurate method for determining NH_4^+ -N and NO_3^- -N in soil samples. The ion exchange method is a rapid and accurate method for determining NH_4^+ -N and NO_3^- -N in soil samples.

CONCLUSIONS

Amounts of soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ extracted with 2 M KCl were not statistically different from those extracted with 1 M KCl. Therefore, the 1 M KCl extractant can be used for Al, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ simultaneous extraction, and because 1 M KCl is already accepted as a common method for soil exchangeable Al analyses. All three compounds can be successfully analyzed simultaneously using a LACHAT Autoanalyzer or similar instrument. Simultaneously analyzing all three compounds allow soil testing laboratories to more efficiently conduct the analyses and would reduce the cost to producers who need Al test results as well as $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$.

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TABLE 1. Regression coefficients (intercept and slope) and coefficient of correlation (r^2) for soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al extracted with 1 M KCl and 2 M KCl. Autoanalyser

	Coefficients	St. Error	t Stat	P-value	Lower 95% CI	Upper 95% CI
$\text{NH}_4\text{-N}$						
Intercept	2.0	1.8	1.1	0.31	-1.6	5.6
Slope	1.07**	0.06	17.0	2.0E-32	0.94	1.2
r^2	0.9					
$\text{NO}_3\text{-N}$						
Intercept	0.9	1.06	0.8	0.08	-1.3	3.04
Slope	1.06**	0.03	27.3	1.2E-20	0.98	1.13
r^2	0.96					
Al						
Intercept	-2.6**	0.85	-3.1	0.005	-4.34	-0.86
Slope	2.07**	0.08	23.7	1.5E-21	1.89	2.25
r^2	0.95					

** Significant at the 0.01 probability level

TABLE 2. Method Detection Limit (MDL) and the Limits of Quantitation (LOQ) for soil NH₄-N, NO₃-N, and Al in 2 M KCl and 1 M KCl using a LACHAT Autoanalyzer.

Sample No	2 M KCl			1 M KCl		
	NO ₃ -N	NH ₄ -N	Al	NO ₃ -N	NH ₄ -N	Al
	----- mg kg ⁻¹ -----			----- mg kg ⁻¹ -----		
1	-0.32	0.67	0.30	0.67	0.63	0.22
2	0.35	0.32	-0.17	0.55	1.55	0.31
3	0.03	0.90	0.02	0.33	0.32	0.41
4	0.01	0.20	-0.14	0.43	0.82	0.55
5	0.04	0.20	0.01	0.22	0.33	0.82
6	-0.43	-0.74	0.13	0.33	1.22	0.65
7	-0.46	-0.13	-0.25	-0.45	0.73	0.53
S ₀	0.29	0.54	0.19	0.22	0.50	0.20
MDL ^a	0.87	1.62	0.57	0.66	1.50	0.60
LOQ ^b	2.90	5.40	1.90	2.20	5.00	2.00

^aMDL=3S₀, ^bLOQ =10S₀

TABLE 3. Regression coefficients (intercept and slope) and coefficients of correlation (R^2) for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Al extracted with 1 M KCl, determined simultaneously and separately.

Coefficients	St. Error	t Stat	P-value	Lower 95%	Upper 95%	
$\text{NH}_4\text{-N}$						
Intercept	3.23	3.1	1.1	0.31	-1.6	9.6
Slope	0.95**	0.1	9.35	1.2E-09	0.9	1.2
r^2	0.78					
$\text{NO}_3\text{-N}$						
Intercept	1.1	0.60	1.84	0.08	-0.16	2.36
Slope	1.03**	0.02	47.6	1.6E-19	0.99	1.08
r^2	0.98					
Al						
Intercept	-1.76	1.69	-1.0	0.31	-5.23	1.7
Slope	1.01**	0.04	27.6	8.0E-21	0.93	1.08
r^2	0.96					

** Significant at the 0.01 probability level

TABLE 4. Method Detection Limit (MDL) and the Limits of Quantitation (LOQ) for soil NH₄-N, NO₃-N and Al in 1 M KCl when they are simultaneously determined by Lachat Autoanalyzer.

Replication	NO ₃ -N	NH ₄ -N	Al
	-----mgkg ⁻¹ -----		
1	0.33	0.21	0.27
2	0.55	0.04	0.12
3	0.52	0.13	0.41
4	0.34	-0.32	0.65
5	0.09	0.2	0.81
6	0.63	1.26	0.6
7	0.65	1.0	0.51
S ₀	0.20	0.56	0.23
MDL ^a	0.6	1.71	0.69
LOQ ^b	2	5.6	2.3

^aMDL=3S₀, ^bLOQ = 10S₀

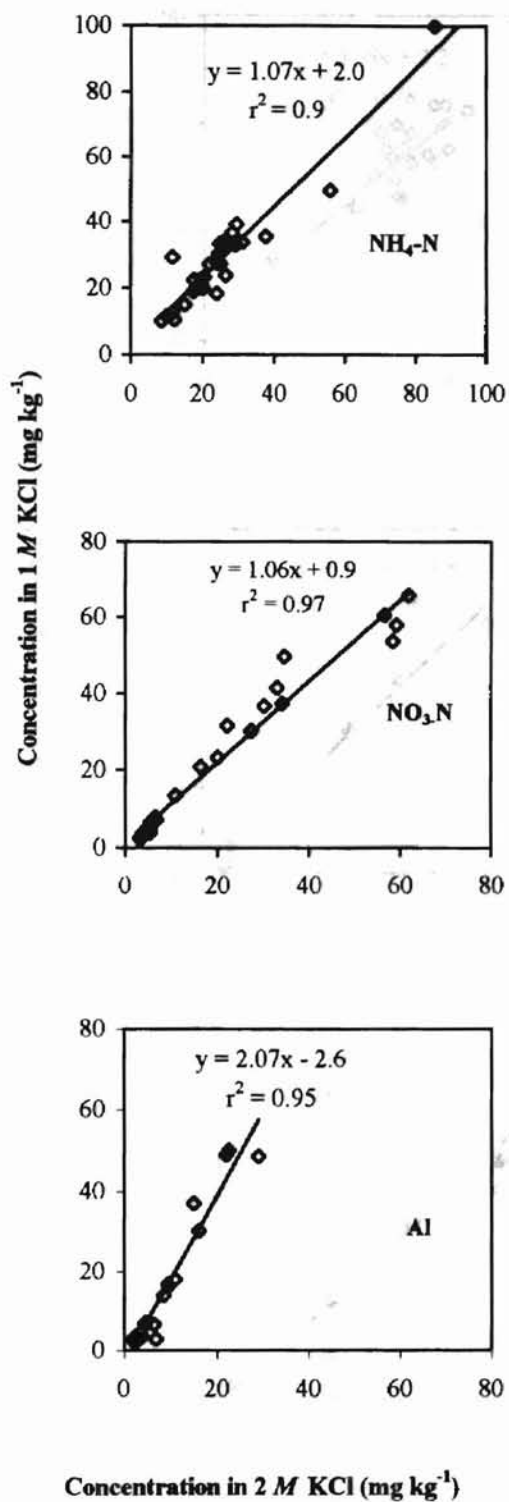


FIGURE 1. Relationship between soil NH₄-N (top), NO₃-N (middle) and Al (bottom) extracted with 1 M (Y) and 2 M KCl (X) solution.

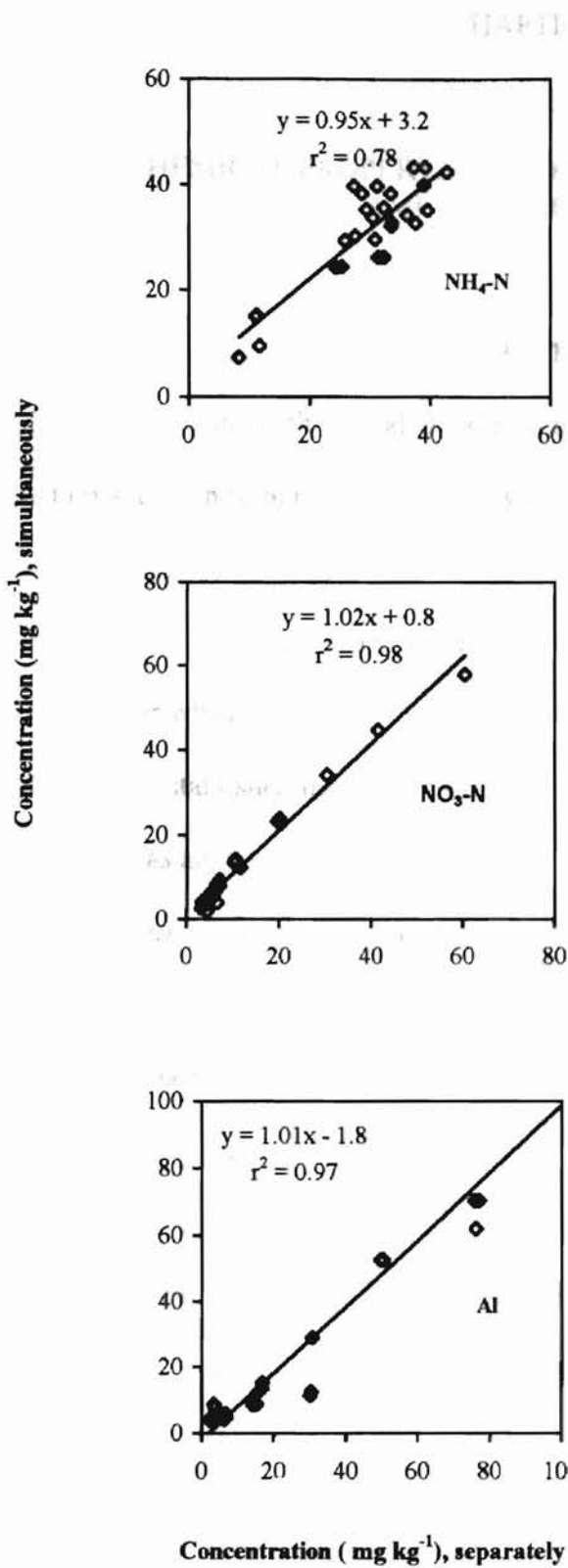


FIGURE 2. Correlations between soil NH₄-N, NO₃-N and Al extracted with 1 M KCl, determined separately (X) and simultaneously (Y) with a LCHAT Autoanalyzer.

CHAPTER 2

SOIL CHEMICAL PROPERTIES AND WHEAT PRODUCTION IN LIME AMENDED ACID SOILS

ABSTRACT

Soil acidity in north-central Oklahoma has become a serious problem to crop production and both forage and grain yields have been reduced in many areas due to low soil pH. This study investigated the effects of 7 lime rates on soil pH, soil exchangeable and extractable Al, exchangeable cations, micronutrients, as well as the forage and grain yields of winter wheat ('Tonkawa') in a field with an initial pH of 4.5. Field lime rate test plots were established in the June of 1997 under conventional tillage on a Tabler silt loam. Lime was applied on July 10, 1997. Forage was harvested in December of 1997 and 1998 and grain was harvested in July of 1998 and 1999. Lime increased soil pH, decreased both exchangeable and extractable soil Al, and increased the sum of base cations. One quarter of the normal lime rate (the rate to raise soil pH to 6.8) raised soil pH to above 5.5 (which is sufficient for wheat growth) in the first two weeks and then slowly increased to a stable level three and a half-month after lime application. The effect of liming on soil pH lasted the entire study period (740 days). The exchangeable Al or percent of Al saturation was inversely related to the sum of the base cations (K, Na, Ca, Mg) in the region of pH 4.3-5.0. Liming did not reduce extractable micronutrients (Fe, Mn, Zn and Cu) to a deficient level for wheat production. Wheat forage yields harvested in December 1997 and 1998 were linearly correlated with lime rate up to nearly one half the full rate and then leveled off with additional lime applied.

However, wheat grain yields were not significantly increased by lime rates probably due to the fact that wheat roots were able to grow out of the toxic environment and proliferate in non toxic subsoil in the later stage and support equal grain yield since only surface soil is acidified. Liming is an effective remediation to raise soil pH, reduce Al toxicity levels and increase wheat fall forage yields.

Oklahoma State University

Soil acidity and soil aluminum toxicity

Aluminum is extremely common throughout the world and often considered relatively harmless under neutral and alkaline conditions. However, in acidic environments, it can be a major limiting factor or toxicant to many plants and aquatic organisms.

Soil acidity in north-central Oklahoma has become a serious problem in crop production as both forage and grain yields have been reduced in many areas due to low soil pH (Boman et al., 1993). Soil acidity is harmful for plant growth due to nutritional disorders (deficiency of Ca, Mg and Mo, decreased availability of P) as well as immediate toxicity of soluble Al, Mn and H^+ (Carver and Ownby, 1995). In general, increased solubility of Al and soil acidification are considered to be directly related to the enhancement of its toxicity (Carver and Ownby, 1995). There are several main factors of the stepwise soil acidification (Westerman, 1981). Nitrification of ammonium-nitrogen fertilizers, such as anhydrous ammonia (widely used for wheat production), eventually results in production of hydrogen ion thus contributing soil acidity. Basic cation (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) removal in forage, grain and straw is also a contributing factor to soil acidity. Decomposition of organic residues also contributes to soil acidity via the release of carbon dioxide and its subsequent hydrolysis resulting in the formation of carbonic acid. Mineral weathering and subsequent leaching of basic cations produces acidification similar to that produced by grain-forage-straw removal.

In addition to the described acidification phenomena, the chemistry and role of Al in soil acidification and crop production is of special interest. Under acidic conditions, Al in aluminosilicates becomes soluble. The Al^{3+} ions in soil solution are then

hydrolyzed to form electrically neutral $\text{Al}(\text{OH})_3^0$ and three H^+ ions (Westerman, 1981). Therefore, Al^{3+} ions released from clay serve as a catalyst of soil acidification. Soils enriched with Al can maintain the process of accelerated acidification. As pH increases, the aluminum turns to hydroxo-Al complexes, including simple mononuclear $\text{Al}(\text{H}_2\text{O})_{6-n}(\text{OH})_n^{(3-n)+}$ and polynuclear species of various sizes and degrees of basicity (Shann and Bertsch, 1993; Bertsch and Bloom, 1996). At higher pH, lability and toxicity of Al markedly decrease. Insoluble aluminum hydroxide [$\text{Al}(\text{OH})_3$], aluminosilicates (e.g., Al_2SiO_5), aluminum phosphate (AlPO_4) are considered relatively nontoxic (Carver and Ownby, 1995). Soil acidity can be corrected by neutralizing acid present, which is normally done by adding basic materials. The most commonly used material is agricultural limestone. As lime raise soil pH, aluminum toxicity is alleviated. (Boman et al., 1991). That is why alkalization (liming) is a routine practice to cope with soil acidity and aluminum toxicity. High levels of soluble aluminum limit root branching and rooting depths, severely inhibiting plant growth (Alam and Adams, 1979; Foy, 1984). Aluminum toxicity to seeding wheat has been a major source of crop failure in extremely low pH Oklahoma soils (Newton et al., 1979).

Another option to cope with soil acidity is the selection of Al-tolerant cultivars (Carver and Ownby, 1995). Johnson et al. (1997) demonstrated that 50 – 74% enhancement of grain yield on Al rich non-limed soil for the Chisholm wheat line supplemented with a gene for Al tolerance compared to Chisholm. Since acid soils of the Great Plains are highly variable in Al toxicity, consideration of the target soil chemical environment is essential to predict the impact of Al-tolerance in grain yield (Johnson et

al., 1996). In the process of soil treatment and tillage, monitoring of aluminum should also be a matter of concern.

Determination of exchangeable and extractable aluminum in soils

Determination of labile Al in soils implies extraction with salt solutions and subsequent instrumental analysis of Al in the extractant. The determination of exchangeable Al is complicated by the coexistence of complex multiphase Al components in soils. Kotze et al. (1984) demonstrated that soils release some exchangeable Al in 1 M salt extract, and the degree of which was soil specific. Because of the operational nature of such determination, the aluminum thus extracted is commonly referred as exchangeable Al (Bertsch and Bloom, 1996). Actually, the selection of a method of extraction should be adjusted to the specificity of soil being investigated. According to an early Kansas State University liming study (Unruh and Whitney, 1986) 25 mg kg⁻¹ of exchangeable aluminum (1 M KCl) is the critical point for wheat growth (recommended lime rate in this study was 4.0 t. acre⁻¹ CCE). Besides exchangeable Al, extractable Al has also been used to determine Al toxicity in acid soils using much a less aggressive extractant, 0.01 M CaCl₂. Extractable Al can be superior for predicting pH/Al toxicity (Khalid and Silva, 1979; Webber et al., 1982; Wright et al., 1989; Shuman, 1990) due to the better correlation with free Al³⁺ (actually, hexaqua-Al³⁺) ion activity (Wright et al., 1989).

Percentage of aluminum saturation

Growth of plants is related to Al saturation of the effective cation exchange capacity (ECEC). Farina et al. (1980) examined exchangeable Al and pH as indicators of lime requirements for a range of soils including two Mollisols, six Ultisols, and one

Oxisol. Relative corn yield was more closely related to Al saturation or acid saturation of the cation exchange complex than either water or salt-pH values. Al saturation levels of ECEC that allow for maximum yields on highly weathered Oxisols and Ultisols have been shown to be <10% for wheat and soybeans crops, whereas corn yields were not restricted with Al saturation <35% (Kamprath, 1984).

Effect of exchangeable Al and percentage of Al saturation on crop growth

High levels of soluble aluminum limit root branching and rooting depths, severely inhibiting plant growth (Alam and Adams, 1979; Foy, 1984); soluble forms of aluminum bind inorganic P, thus inhibiting uptake of phosphorus nutrient (Ohki, 1985; Clarkson, 1967). Soluble forms of aluminum (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$) can also be harmful for wheat germination (Wright et al., 1989; Alva et al., 1986). Vlamis (1953) attributed reduced growth of barley at pH 4.2 in displaced soil solution mainly to soluble aluminum. Adams and Lund (1966) observed a common relationship between cotton root penetration and the molar activity of Al for three subsoil solutions. Webber (1982) reported that responses of barley, rapeseed and alfalfa to lime were correlated with soluble Al, exchangeable Al and percent base saturation for a large number of Canadian acid soils. Oklahoma soils with <16% Al saturation were referred as lower levels of Al potential phytotoxicity sites for wheat production (Johnson et al., 1997). Although considerable difference in tolerance to low pH exists among cultivars, using Al tolerant variety is not the only solution to the problem (Boman et al., 1993).

Aluminum species in soil solution

There are four dominant forms of Al in the pH region from 4 to 6 (Tisdale, 1993):

$\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3^0$. Among these, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ are considered to be toxic to plants. Relative abundance of the main forms of Al in soil has not been carefully studied. In order to separate toxic Al forms, the chemistry of Al in soil solutions should be examined. This could be done using computer speciation programs, e.g., MINTEQ (Lindsay and Ajwa., 1995).

The objectives of the present work were (i) to identify analytical method for determining toxic Al levels, (ii) to determine the effect of lime rates on the quantity of exchangeable or extractable Al and Al saturation, (iii) to determine the effect of liming on micronutrient availabilities, (iv) to examine the effect of liming on the yields of winter wheat forage and grain, (v) to examine the chemistry of Al in soil solutions using MINTEQ speciation computer model.

MATERIAL AND METHODS

Field experiment

Field lime rate test plots were established in the summer of 1997 under conventional tillage on a Tabler silt loam. The experimental design employed was a randomized complete block split-in-time with 7 lime rates and four replications. The lime rates used were:

- (1) Control (no lime applied),
- (2) 387 kg ha⁻¹ ECCE (1/16 normal rate),
- (3) 774 kg ha⁻¹ ECCE (1/8 normal rate),
- (4) 1550 kg ha⁻¹ ECCE (1/4 normal rate),
- (5) 3.1 t ha⁻¹ ECCE (1/2 normal rate),
- (6) 6.2 t ha⁻¹ ECCE (normal rate, lime required to raise pH to 6.8)
- (7) 9.3 t ha⁻¹ ECCE (1.5 normal rate).

Lime was applied on July 10, 1997 and incorporated immediately. Tonkawa winter wheat was planted in September, 1997 and 1998 at 134 kg ha⁻¹. The dimension of the individual plots were 3 x 5.5 m, seven plots in a row, with 1.2 m alleys between the rows and border patches to the left and to the right of the plots. Initial soil test results of surface sample (0 – 15 cm) were pH= 4.5; NO₃-N= 15.7 kg ha⁻¹; P= 120 kg ha⁻¹; K= 661 kg ha⁻¹. Subsurface soil sample (15-60 cm) had NO₃-N of 52 kg ha⁻¹. The soil organic matter content was 1.25%. Phosphorus and potassium were sufficient for wheat production but thirty-four kg N per ha were broadcast and incorporated preplant to satisfy N needs.

Forage was harvested by clipping two three meter row segments per plot from the soil surface in December of 1997 and 1998. Samples were air-dried to constant weight. Grain was harvested and weighed in June of 1998 and 1999, and the yield was calculated for each plot independently.

Soil sampling and laboratory procedures

Composites of twelve to fifteen cylindrical core samples were collected from the surface soil layer (0 – 15 cm). Soil samples were collected 10 times from each plot over a two-year period. Soil samples were then air-dried and ground to pass a 2mm sieve. Surface soil samples were analyzed for pH, buffer index (BI), NO₃-N, available K index, exchangeable and extractable Al, major cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) and micronutrients (Cu, Fe, Zn, Mn). Soil pH and BI were measured by glass electrode in a 1:1 soil:water suspension (or 1:2 soil to 0.01 M CaCl₂) and SMP buffer solution, respectively (Sims, 1996). Soil NO₃-N was extracted with 1 M KCl solution and quantified by the cadmium reduction method (LACHAT, 1994). Soil available K were extracted using Mehlich III solution (Tucker, 1992). Micronutrients were extracted by DTPA (Lindsay and Norvell., 1978.) and quantified with inductively coupled plasma spectroscopy (ICP).

Na, Ca, Mg, Fe, Cu, Zn and Mn in soil solution were determined by ICP. Exchangeable aluminum was extracted with 1 M KCl and determined colorimetrically using Al-pyrocatechol violet complex in the presence of 1,10-phenantroline and on the LACHAT Autoanalyzer (LACHAT, 1994). Extractable aluminum was extracted with 0.01 M CaCl₂ and quantified by using the same method as exchangeable aluminum. Al saturation was calculated as the measure of aluminum toxicity using the following equation (Johnson et al., 1996):

RESULTS AND DISCUSSION

Percentage of exchangeable Al determined by ICP [Al] LAQUAT

$$\text{Al saturation (\%)} = \frac{[\text{Al}]}{[\text{ECEC}]} \cdot 100$$

where [Al] is exchangeable Al (cmol kg⁻¹) and [ECEC] is effective cation exchange capacity (cmol kg⁻¹)

Where ECEC (effective cation exchange capacity) is the sum of exchangeable Na, K, Ca, Mg measured in 1 M NH₄OAc, pH 7.0, and Al measured in 1 M KCl; [] indicates concentration in cmol kg⁻¹.

Data analysis was performed using SAS (SAS Institute Inc., 1988). Percentage of aluminum saturation vs pH, and wheat forage yield were evaluated using two segment linear-plateau models (Anderson and Nelson, 1975). Linear-plateau programs were adapted using the NLIN procedure (SAS Institute Inc. 1988). Equations for the linear-plateau models were $y=b_0+b_1[\min(X,A)]$ such that b_0 is the Y intercept, b_1 is the slope of the line up to where $X(\text{pH})=A$ (point where the combined residuals were at minimum (Mahler and McDole, 1987). Best estimates for b_0 , b_1 and the point of intersection were evaluated (joint for linear and plateau portions, defined here as the critical pH) were obtained from the model which minimized combined residuals. Combination of possible values of b_0 , b_1 and the point of intersection were evaluated (holding the other two constant), that ultimately resulted in the highest coefficient of determination (Mahler and McDole, 1987).

Relations of exchangeable Al determined by ICP and LACHAT

The correlation of exchangeable Al in 1 M KCl extractant determined by LACHAT (flow injection analysis, which is a colorimetric method) and ICP (inductively coupled plasma optical emission spectroscopy) was examined. The slope of the linear curve is 1.27 (Fig. 1), which is significantly different from 1. This suggests that soil exchangeable Al determined by ICP is significantly higher than that obtained using LACHAT Flow Injection Autoanalyzer. The difference could be due to the difference of the chemistry used by these methods. The flow injection method is based on the formation of Al phenantrolin complexes and that covers three forms of Al [Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$], alternatively ICP quantifies all soluble forms of aluminum in the extracts and may include colloid particles since the extract is not filtered through any microfilter paper. Since Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$ are recognized to be potentially toxic to plant roots and soil organisms (Cronan and Grigal, 1995), it seems that the colorimetric method is more appropriate for the determination of toxic Al levels. Furthermore, the flow injection method is an efficient and accurate method for determining soluble Al, NH_4^+ , and NO_3^- from the same extraction solution (1 M KCl) and with the same equipment simultaneously (Chapter I).

Soil pH as affected by lime rate and time after lime application

Soil pH was monitored for 740 days from preliming in July 1997 to post harvest in June 1999. The average soil pH of four replications at seven lime rates is plotted with time in Figure 2. One quarter of the normal lime rate (1550 kg ha^{-1} ECCE)(lime required to raise pH to 6.8 and higher), which is the recommended rate in Oklahoma for

continuous wheat production, raised soil pH higher than 5.0 in the first two weeks and then slowly increased to a stable level in the following three and half months. One sixteenth ($387 \text{ kg ha}^{-1} \text{ ECCE}$) and $1/8$ ($774 \text{ kg ha}^{-1} \text{ ECCE}$) lime rates raised soil pH significantly from the control but less than the recommended pH 5.5 for wheat production. Slight pH increase in the control plot was probably due to lime contamination from lime treated plots. Soil pH remained at the raised level during the entire study period (740 days).

Effect of liming on exchangeable and extractable Al

Figure 3 shows how soil exchangeable Al (1 M KCl extraction) changed with lime rates and time after lime was applied. Exchangeable Al decreased as lime rates increased. One eighth of the recommended lime rate reduced Al to less than 20 mg kg^{-1} , which is below the critical level of 25 mg kg^{-1} identified by an early Kansas State University study as being toxic for winter wheat (Unruh and Whitney, 1986). However, exchangeable Al also dropped for the unlimed control plots. This is consistent with the slight pH increase in the control as described earlier. Besides exchangeable Al, extractable Al was also determined using less aggressive extractant 0.01 M CaCl_2 . Exchangeable Al is correlated with the extractable Al ($r^2=0.77$, Figure 4). The slope of the linear curve indicates that Al extracted with 0.01 M CaCl_2 is about 5% of that with 1 M KCl. This is consistent with Kotze et al. (1984) who found that 0.01 M CaCl_2 removed <10% of the ^{28}Al isotopically labeled exchangeable Al. Extractable Al is assumed to be efficient in predicting Al toxicity as a function of pH (Wright et al. 1989).

Effects of soil pH on extractable Al

Figure 5 presents relationships between extractable Al (0.01 M CaCl₂) and soil pH in water (pH_{H₂O}) and in 0.01 M CaCl₂ (pH_{CaCl₂}). Soil samples used to establish this relationship were collected 122 days after lime was applied. The reason for choosing that set of soil samples was because extractable Al did not change significantly with time (122 days). Extractable Al was highly correlated with pH_{CaCl₂} and pH_{H₂O} ($r^2=0.84$ and 0.76 , respectively, Fig. 4). This finding is consistent with Wright et al. (1989). It is assumed that the measurement of pH in 0.01 M CaCl₂ (pH_{CaCl₂}) is closer to field conditions than in H₂O (pH_{H₂O}). This may explain why the coefficient of correlation for the linear curve between extractable Al and pH_{CaCl₂} is higher than that for pH_{H₂O}. Therefore, pH_{CaCl₂} would be more reliable for predicting Al toxicity levels in acid soils.

Percentage of Al saturation

The relationship between pH_{H₂O} and the percentage of Al saturation is shown in Fig. 6 and Table 1 and was evaluated using linear-plateau models. The percentage of Al saturation decreased linearly as pH increased to 5 and then leveled off. Also percentage of aluminum saturation was highly correlated with pH ($r^2=0.88$) when pH was less than 5. There was an inverse relationship between exchangeable Al or percent of Al saturation and the sum of base cations (K, Na, Ca, Mg) in the region of pH 4.3-5.0 (Figure 7). This region was chosen because Al saturation did not change significantly with pH greater than 5. The inverse relationship could be explained by the competition of exchangeable Al and exchangeable K, Na, Ca, Mg. The relationships between exchangeable Al and Ca in the same pH range are also shown in Figure 7. The inverse relationships are consistent with previous studies (Delhaize and Rayn, 1995), where it

was noted that the symptoms of severe Al toxicity in the field resembled that of Ca deficiency.

Exchangeable Mn as affected by lime and time after lime application

Not only aluminum is toxic to plants in acid soils, but also Mn if its concentration is high enough. Figure 8 shows the inverse relationship ($r^2=0.93$) between exchangeable Mn (extracted by 1 N NH₄OAc at pH 7.0) and pH_{H₂O}. Exchangeable Mn appears to be strongly dependant on soil pH. Figure 9 shows that upon liming exchangeable Mn decreased with time until about 122 days after application, whereas in the case of Al it was only 40 days. Similar relationships between Mn and lime rates as for Al were found (Fig. 9), but in the case of Mn its concentration never dropped below 3 mg kg⁻¹, which is considered adequate for most crops. Manganese deficiency is seldomly observed in Oklahoma. The maximum concentration of Mn in this experiment was 12 mg kg⁻¹, which was much lower than the acknowledged toxic level of 50 mg kg⁻¹ (Johnson et al., 1997).

Effect of liming on soil micronutrients

The main relationship between micronutrients (DTPA extraction) and pH or aluminum is shown in Figure 10 and Table 2. Soil samples were collected 122 days after lime was applied and extracted for Cu, Fe, Mn and Zn. Soil Mn and Fe decreased as pH increased (Fig. 11, top). Also it was found that the concentration of exchangeable Fe and Mn increased as concentration of exchangeable Al increased (Figure 11, bottom). This is because Al, Fe and Mn concentrations depend on soil pH in a similar way, so the conditions favorable for the presence of one are favorable for the others, too. There was no significant relationship between Cu and Zn and pH in the range of pH studied.

Liming did not reduce soil micronutrients to the deficient level for wheat production at this study site. (wheat roots are deep enough (where pH is higher) so they have gotten out of the toxic

Effect of liming on wheat forage and grain yields (support equal grain yield)

Wheat forage yields harvested in December 1997 and 1998 were linearly correlated with lime rate up to nearly one half the full rate (3.4 Mg ha⁻¹ and 3.1 Mg ha⁻¹ for 1997 and 1998, respectively.) The relationship between forage yields and lime rate were evaluated using linear-plateau models (Fig. 12). After reaching a critical point wheat forage yield leveled off with additional lime applied. However, grain yields harvested in the summer, 1997 and 1998 did not respond to lime rates the same way as forage yields did. However, wheat grain yields were not significantly increased by lime rates probably because there was enough time for roots to penetrate deep enough (where pH is higher) so they have gotten out of the toxic environment and proliferate in non toxic subsoil and support equal grain yield.

Aluminum species in soil extracts

The effect of soil pH on Al species in soil solution of saturated paste extracts was evaluated using the U.S. EPA model MINTEQA2 (Lindsay and Ajwa., 1995). The major Al species at 3 pH levels are shown in Table 3. Species Al³⁺, Al(OH)²⁺, Al(OH)₂⁺ are considered toxic, while AlHPO₄⁺ and other forms are not toxic. At pH 4.7 the total percentage of toxic forms was 52% comparing to 37% at pH 5.2 and at pH 5.8 (Fig. 13). Thus, soils with higher pH have less Al phytotoxicity because toxic Al forms are reduced. This is consistent with previous findings (Tisdale et al., 1993) in the pH region from 4 to 6 which is similar to the pH region of this study. Fall wheat forage yields were well correlated with the amount of toxic Al forms. This suggests that toxic Al did affect the

growth of young wheat plants. As the root system develops there was enough time for roots to penetrate deep enough (where pH is higher) so they have gotten out of the toxic environment and proliferate in non toxic subsoil and support equal grain yield.

and on the exchange sites. The effect of liming on soil pH and on the exchange sites was observed. If decreases in pH were observed, the effect of liming was not observed.

1964

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1965

21

22

CONCLUSIONS

The flow injection method is more appropriate for the determination of toxic Al levels than inductively coupled plasma spectrometer. Liming is effective to raise soil pH and reduce toxic Al in the soil solution and on the exchange sites. The effect of liming on soil pH lasted for more than 2 years and no signs of decrease in pH were observed. One eighth of the normal lime rate was not enough to raise pH to above 5.5 but was enough to reduce exchangeable Al to a very low level. Extractable Al (0.01 M CaCl_2) was found to be efficient in predicting Al toxicity as the function of $\text{pH}_{\text{CaCl}_2}$. Liming did not reduce extractable micronutrients to deficient level for wheat production. Wheat forage yields were linearly correlated with lime rates up to nearly one half the full rate and then leveled off with additional lime applied. However, wheat grain yields were not significantly increased by lime rates probably because there was enough time for roots to penetrate deep enough (where pH is higher) so they have gotten out of the toxic environment and proliferate in non toxic subsoil and support equal grain yield. Soils with higher pH have less Al phytotoxicity because toxic Al forms are reduced. Liming is an effective remediation to raise soil pH, reduce Al toxicity levels and increase forage yields. More study is needed to investigate the direct effects of Al saturation percentage on wheat production. Since liming significantly affected fall wheat forage yields, it is important to consider liming for grazing or grazing and grain dual production system.

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TABLE 1. Selected soil properties affected by lime rates and time (average of 4 replications).

Days after liming	Lime rate kg ha ⁻¹	pH	P mg kg ⁻¹	ECEC	K	Na cmol kg ⁻¹	Ca	Mg	Al	Al sat %	BS
0	0	4.38	119	6.69	0.60	0.02	4.06	1.08	0.93	13.9	86.0
0	387	4.33	111	6.86	0.61	0.02	4.21	1.07	0.96	14.0	86.0
0	774	4.33	120	6.70	0.62	0.02	4.00	1.10	0.96	14.4	85.6
0	1540	4.33	118	7.07	0.59	0.02	4.32	1.12	1.01	14.3	85.7
0	3080	4.33	111	6.57	0.62	0.01	4.08	1.10	0.76	11.6	88.4
0	6080	4.33	115	6.64	0.60	0.02	3.94	1.08	1.00	15.2	84.8
0	9300	4.35	115	7.01	0.62	0.01	4.26	1.14	0.98	14.0	85.9
14	0	4.50	125	6.59	0.63	0.02	4.28	1.16	0.50	7.7	92.3
14	387	4.65	115	6.43	0.63	0.02	4.12	1.38	0.29	4.5	95.5
14	774	4.75	120	6.63	0.59	0.02	4.37	1.46	0.19	2.9	97.1
14	1540	4.90	126	6.96	0.65	0.02	4.57	1.64	0.08	1.2	98.8
14	3080	5.33	113	7.57	0.61	0.02	4.99	1.95	0.01	0.2	99.8
14	6080	5.60	118	6.71	0.61	0.01	3.92	2.16	0.01	0.2	99.8
14	9300	5.73	113	8.90	0.60	0.02	5.92	2.35	0.01	0.2	99.8
36	0	4.50	115	6.79	0.62	0.03	4.46	1.21	0.47	6.9	93.1
36	387	4.65	117	6.89	0.56	0.03	4.61	1.42	0.28	4.0	96.0
36	774	4.78	120	7.21	0.59	0.03	4.87	1.56	0.15	2.1	97.9
36	1540	4.98	118	7.58	0.59	0.03	5.08	1.81	0.05	0.7	99.3
36	3080	5.33	110	8.68	0.58	0.03	6.00	2.06	0.02	0.2	99.8
36	6080	5.53	117	8.96	0.61	0.03	6.13	2.18	0.01	0.1	99.8
36	9300	5.65	114	9.97	0.57	0.04	6.85	2.49	0.01	0.1	99.8
122	0	4.78	110	6.91	0.54	0.04	4.46	1.54	0.33	4.8	95.2
122	387	4.90	110	7.65	0.62	0.04	5.20	1.63	0.17	2.2	97.8
122	774	5.08	109	7.35	0.53	0.05	4.94	1.75	0.09	1.2	98.8
122	1540	5.45	113	8.14	0.60	0.04	5.33	2.14	0.02	0.2	99.8
122	3080	5.90	110	8.99	0.54	0.04	5.91	2.48	0.01	0.1	99.9
122	6080	6.23	110	9.76	0.52	0.04	6.59	2.60	0.01	0.1	99.9
122	9300	6.28	109	10.22	0.54	0.05	6.86	2.75	0.01	0.1	99.9
222	0	4.88	97	6.61	0.60	0.04	4.32	1.31	0.34	5.1	94.9
222	387	5.00	95	6.86	0.57	0.05	4.54	1.54	0.16	2.3	97.7
222	774	5.15	98	7.19	0.57	0.05	4.79	1.68	0.10	1.4	98.6
222	1540	5.40	103	7.87	0.58	0.04	5.23	1.99	0.03	0.3	99.7
222	3080	5.98	100	8.73	0.56	0.05	5.71	2.39	0.02	0.3	99.7
222	6080	6.18	99	9.85	0.58	0.04	6.62	2.59	0.02	0.2	99.8
222	9300	6.33	98	9.14	0.54	0.05	5.64	2.89	0.02	0.2	99.8
355	0	4.88	100	8.00	0.56	0.03	5.43	1.63	0.35	4.4	95.6
355	387	4.88	104	7.55	0.59	0.03	4.91	1.71	0.30	4.0	95.9
355	774	5.13	103	8.18	0.60	0.03	5.51	1.89	0.15	1.8	98.2
355	1540	5.25	99	8.45	0.63	0.03	5.57	2.14	0.08	1.0	99.0
355	3080	5.80	92	10.20	0.60	0.03	6.81	2.71	0.04	0.4	99.6
355	6080	6.05	96	10.52	0.61	0.03	6.98	2.89	0.02	0.2	99.8
355	9300	6.00	95	10.23	0.55	0.03	6.78	2.85	0.03	0.3	99.7
459	0	4.80	92	8.62	0.68	0.01	5.78	1.87	0.27	3.1	96.9
459	387	4.80	89	8.31	0.66	0.01	5.57	1.87	0.20	2.4	97.6
459	774	4.98	95	8.91	0.70	0.01	5.98	2.10	0.12	1.3	98.7
459	1540	5.25	92	9.84	0.68	0.01	6.62	2.46	0.06	0.6	99.4
459	3080	5.80	87	11.08	0.68	0.01	7.36	3.01	0.02	0.2	99.8
459	6080	6.00	92	11.35	0.66	0.01	7.59	3.07	0.02	0.2	99.8
459	9300	6.20	92	11.93	0.67	0.01	7.98	3.25	0.02	0.2	99.8
609	0	5.13	71	6.69	0.53	0.06	4.12	1.86	0.11	1.7	98.3
609	387	5.13	72	6.46	0.53	0.06	3.99	1.80	0.08	1.3	98.7
609	774	5.55	74	6.62	0.53	0.06	4.11	1.88	0.04	0.6	99.5
609	1540	5.58	72	7.39	0.53	0.08	4.52	2.24	0.03	0.4	99.6
609	3080	6.28	71	8.75	0.53	0.06	5.35	2.79	0.01	0.2	99.8
609	6080	6.50	74	8.92	0.53	0.06	5.42	2.90	0.01	0.2	99.8
609	9300	6.48	74	8.72	0.51	0.06	5.30	2.83	0.02	0.2	99.8
740	0	5.03	84	7.11	0.74	0.01	4.53	1.62	0.21	3.0	97.0
740	387	5.13	78	7.97	0.74	0.01	5.22	1.91	0.09	1.2	98.8
740	774	5.25	83	7.39	0.75	0.01	4.62	1.94	0.06	0.9	99.2
740	1540	5.65	82	8.59	0.74	0.01	5.58	2.20	0.05	0.6	99.4
740	3080	6.30	84	9.09	0.71	0.01	5.62	2.70	0.03	0.4	99.7
740	6080	6.50	84	9.40	0.72	0.01	6.04	2.59	0.03	0.4	99.7
740	9300	6.45	87	9.75	0.73	0.01	6.04	2.95	0.02	0.2	99.8

TABLE 2. Soil pH, exchangeable Al and micronutrients at seven lime rates 122 days after liming.

Lime rate kg ha ⁻¹	pH	Al	Cu	Mn	Fe	Zn
-----mg kg ⁻¹ -----						
0	5.0	2.5	0.92	79	101	2.0
0	4.6	39	0.98	93	120	1.6
0	4.6	31	1.00	83	128	1.6
0	4.5	48	1.00	96	164	1.6
387	4.8	20	0.92	74	117	1.7
387	4.9	10	0.78	78	108	1.8
387	5.1	5.7	0.90	67	106	1.6
387	4.8	25	1.00	96	151	1.8
774	4.9	13	0.96	80	120	1.9
774	5.0	9	0.84	85	101	1.9
774	5.1	6.7	0.96	83	107	1.8
774	5.5	1.8	0.80	89	110	2.8
1550	5.5	1.7	0.86	79	102	2.2
1550	5.5	1.2	0.80	75	94	2.1
1550	5.4	1.9	0.90	64	96	1.6
1550	5.4	1.7	1.00	95	117	2.0
3100	6.0	1.2	0.71	71	73	2.1
3100	5.9	1.1	0.76	76	72	1.8
3100	5.8	1.2	0.84	80	50	1.8
3100	5.9	1.2	1.00	78	83	2.3
6200	6.4	1.1	0.88	59	63	1.9
6200	6.0	1.1	0.69	69	74	1.9
6200	6.4	1.3	0.96	52	58	1.5
6200	6.1	1.2	1.00	74	91	1.9
9300	6.0	1.2	0.88	64	74	1.9
9300	6.2	1.3	0.90	61	75	1.9
9300	6.5	1.2	0.92	59	61	1.5
9300	6.4	1.3	1.10	63	81	1.6

Table 3. Chemical species of Al in soil saturated paste extract at 3 pH levels.

Species	pH 4.7		pH 5.2		pH 5.8	
	M*10 ⁻⁵	%	M*10 ⁻⁵	%	M*10 ⁻⁵	%
Al ³⁺	24.0	39.6	1.5	14.7	0.07	2.6
Al(OH) ²⁺	6.0	10.1	1.2	12.0	0.20	8.0
Al(OH) ₂ ⁺	1.6	2.7	1.0	10.1	0.80	26.4
AlHPO ₄ ⁺	9.1	15.1	5.0	50.0	1.70	55.4
Other forms	19.4	32.5	1.3	13.2	0.23	7.6

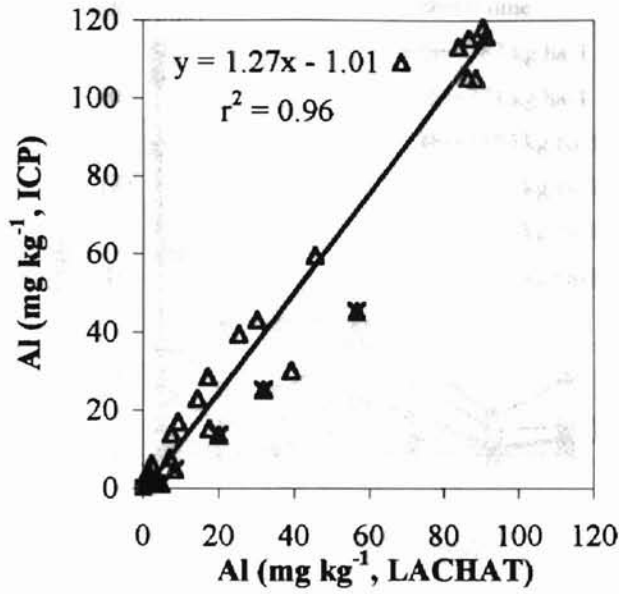


FIGURE 1. Exchangeable Al (1 M KCl) determined by Lachat Autoanalyzer and inductively coupled plasma optical emission spectroscopy (ICP).

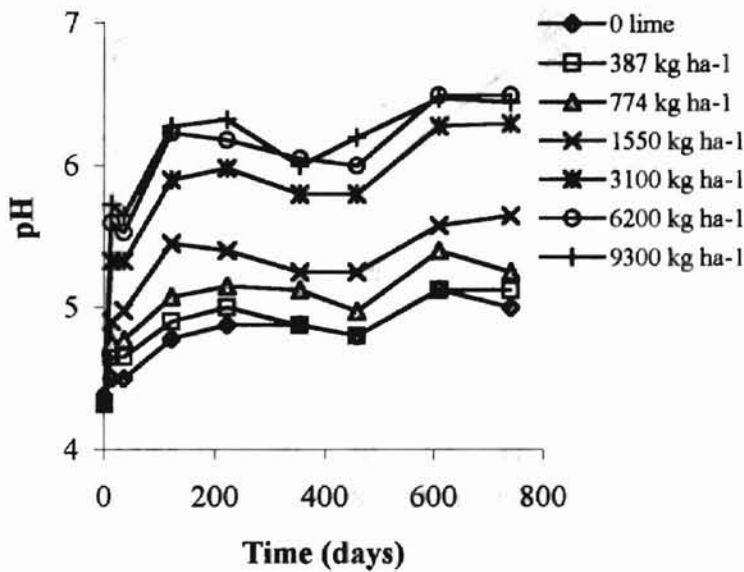


FIGURE 2. Soil pH as affected by lime rates (effective calcium carbonate equivalent) and time after lime was applied.

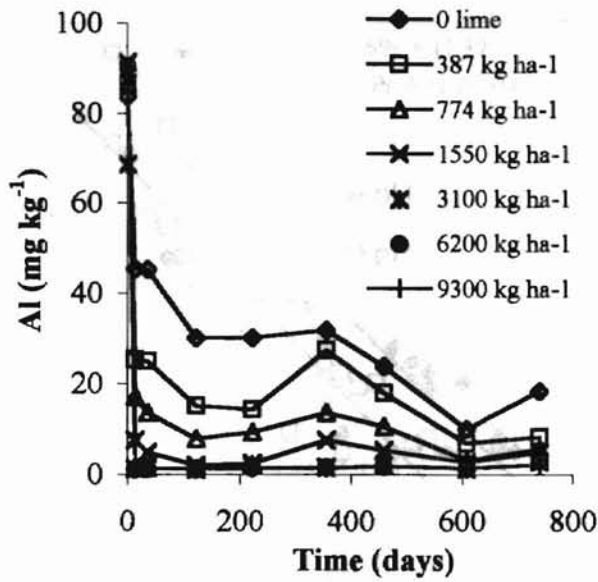


FIGURE 3. Exchangeable Al as affected by lime rates and time.

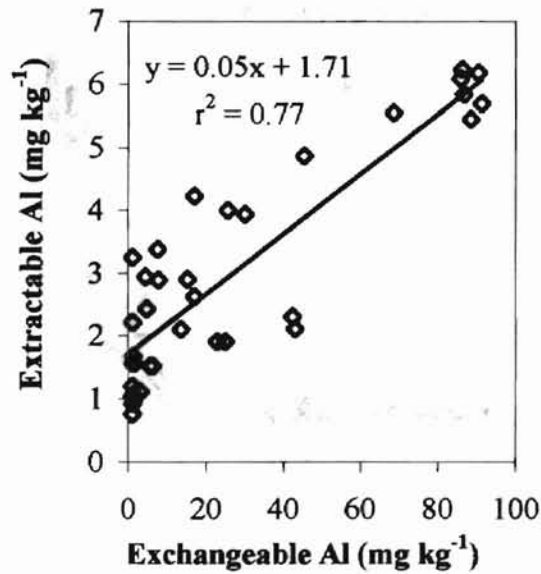


FIGURE 4. The relationship between exchangeable (1 M KCl) and extractable (0.01 M CaCl₂) Al.

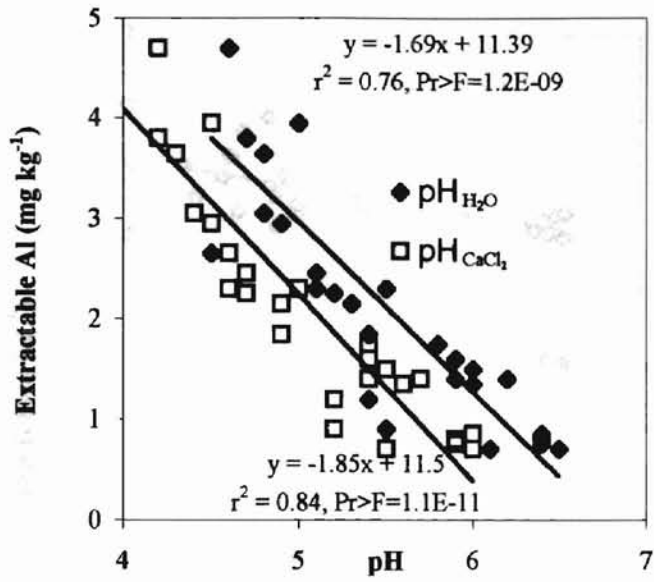


FIGURE 5. Effects of soil $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{CaCl}_2}$ on extractable Al.

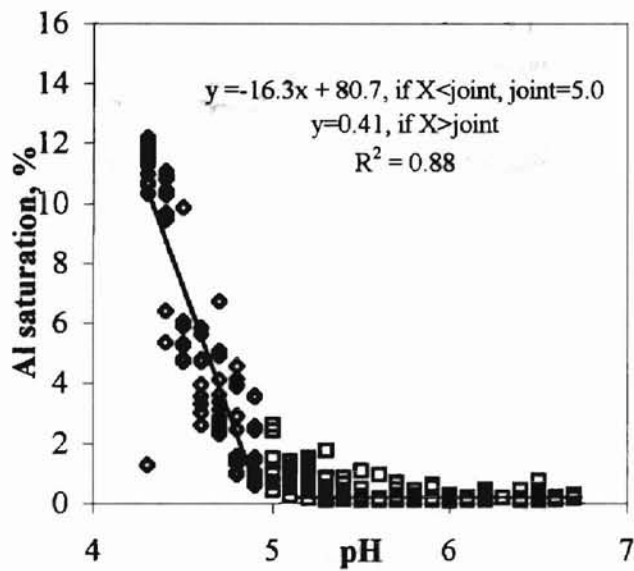


FIGURE 6. Relationship between $\text{pH}_{\text{H}_2\text{O}}$ and aluminum saturation percentage.

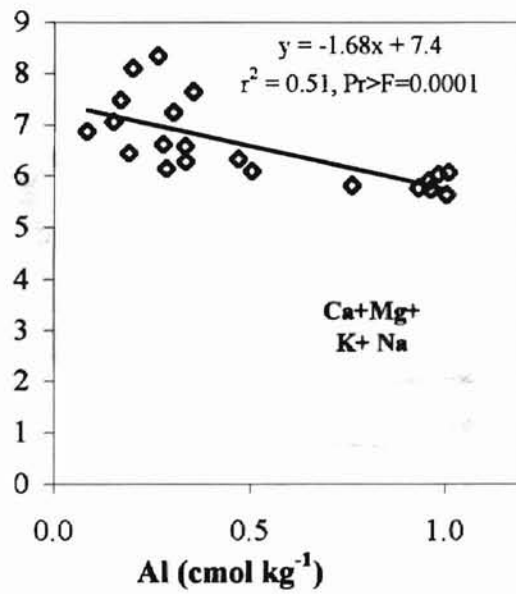
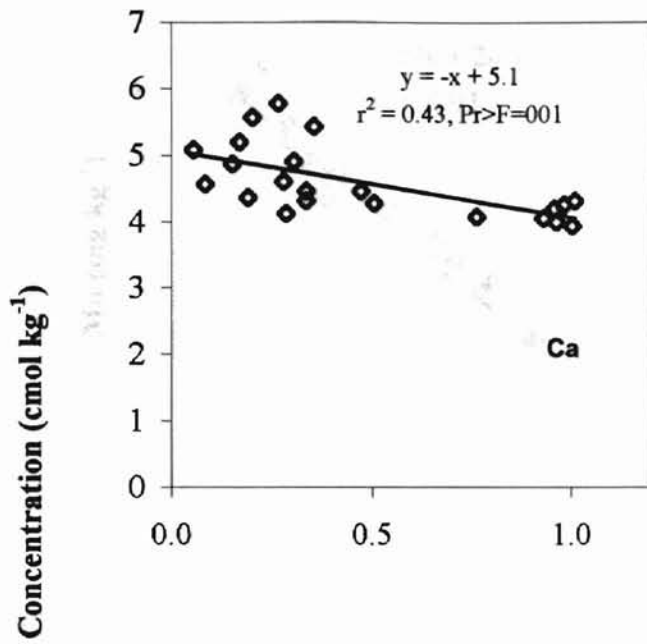


FIGURE 7. Relationship between exchangeable Al and Ca (top) and sum of base cations (bottom).

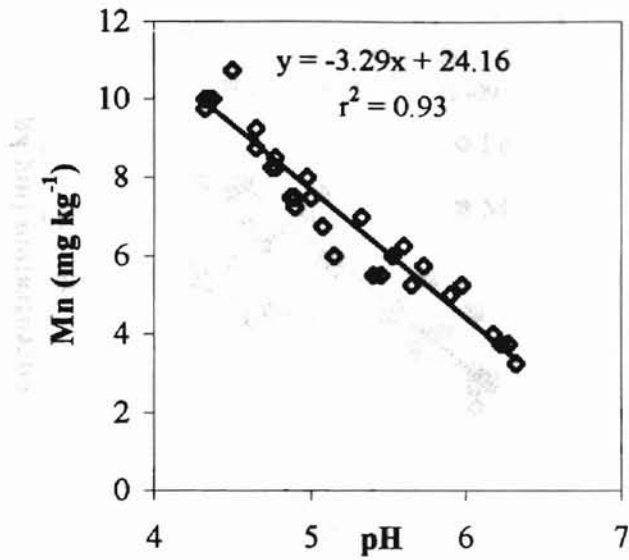


FIGURE 8. Exchangeable Mn as the function of pH_{H_2O} .

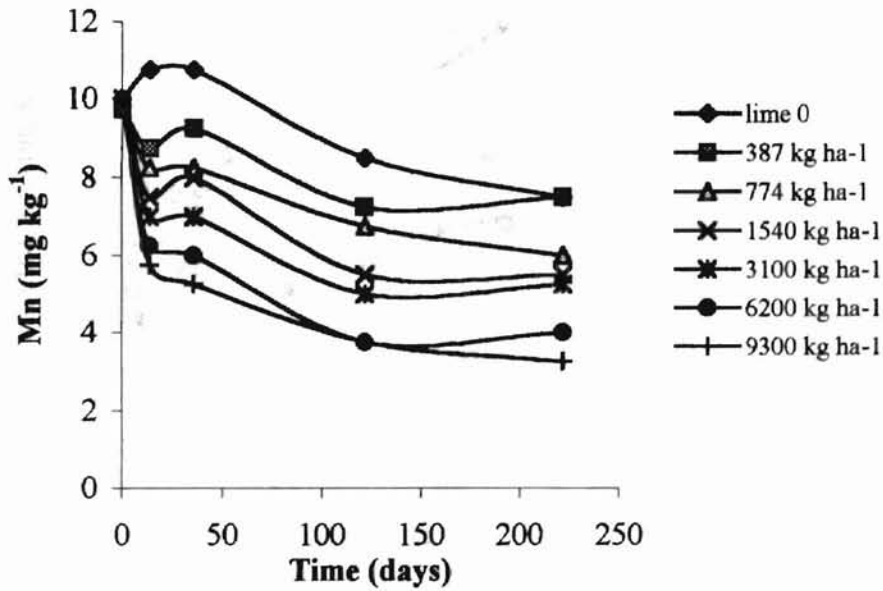


FIGURE 9. Exchangeable Mn as affected by lime rate and time.

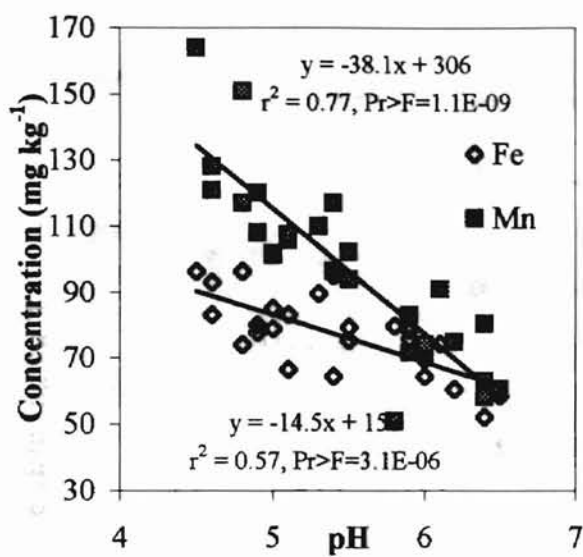


FIGURE 10. Effect of soil pH on extractable Mn and Fe .

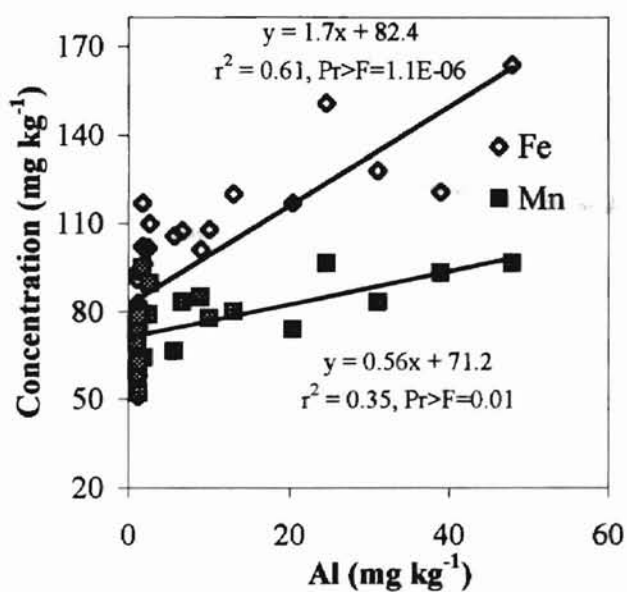


FIGURE 11. Relationship between soil Mn and Fe (extracted with DTPA) and exchangeable Al (1 M KCl).

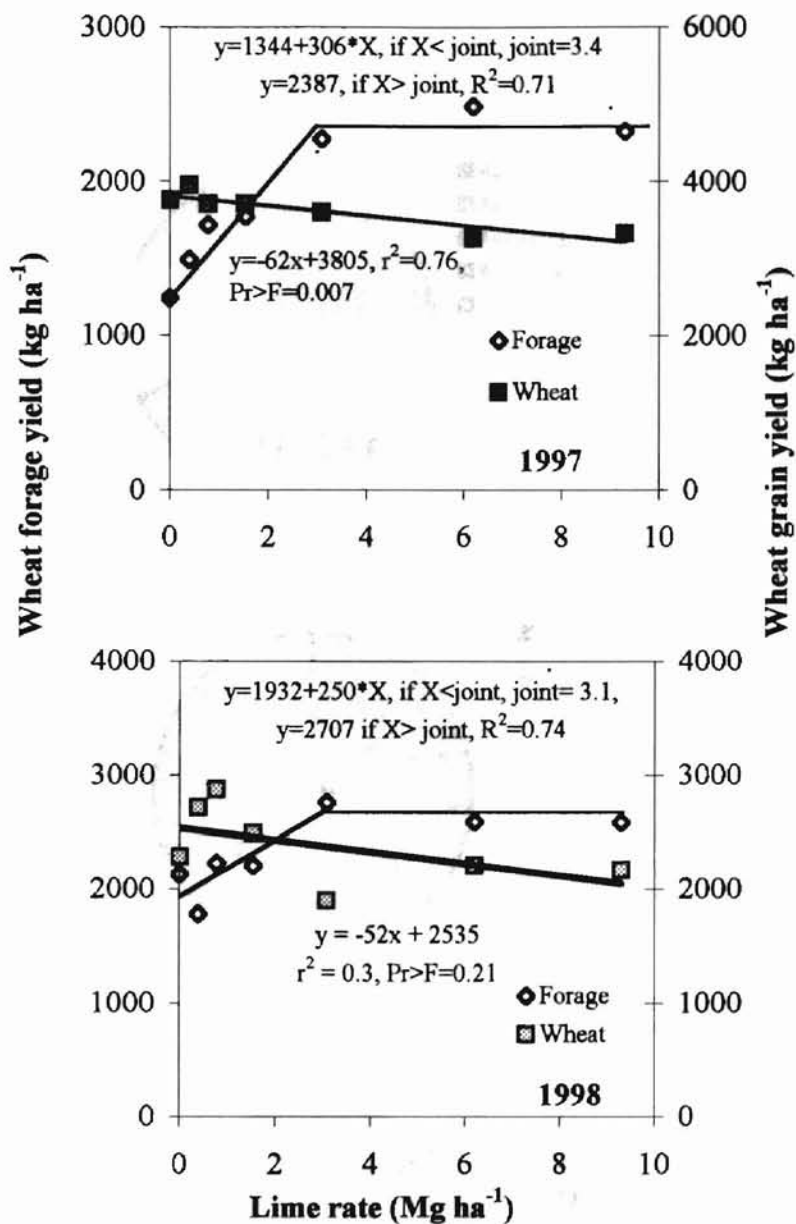


FIGURE 12. Effects of lime rates on wheat forage and grain yields during 1997-98 (top) and 1998-99 (bottom) growing seasons.

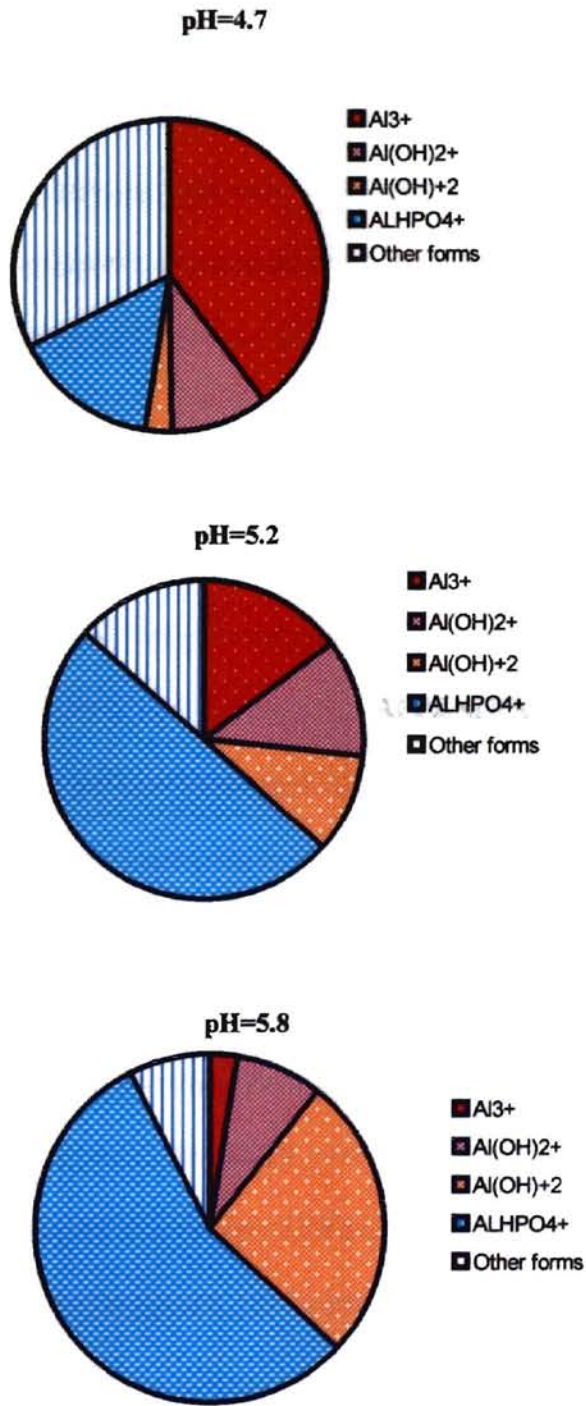


FIGURE 13. Proportions of major Al species in soil solution (saturated paste e; at three pH levels.

DETERMINATION OF NH₄-N, NO₃-N, AND AL IN SOIL
WITH AN AUTOMATIC ANALYZER

REPORT

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APPENDIX

COLORIMETRIC DETERMINATION OF NH₄-N, NO₃-N, And Al IN SOIL EXTRACTS WITH A FLOW INJECTION AUTOANALYZER

I. PRINCIPLE

Soil NH₄-N, NO₃-N, and Al are extracted with 1 M KCl and analyzed simultaneously using colorimetric method with a LACHAT Flow Injection Autoanalyzer. The LACHAT system is equipped with three analytical channels and one computer system.

II. EXTRACTION

1. Reagents

One molar KCl: In 1L volumetric flask dissolve (completely) 37.25 g KCl in approx. 800 mL distilled water. Dilute to the mark with distilled water, degas with helium or argon.

2. Procedures

- a). Weigh 2.0 g (or one scoop) of air-dried soil sample that has passed 2 mm mesh sieve in a 50 mL extraction flask.
- b). Add 20 mL of the 1 M KCl solution.
- c). Shake on a horizontal shaker for 1 hour.
- d). Filter sample through Watman No. 2 filter paper or equivalent. Collect the clear filtrate in a prelabeled 35 mL test tube.
- e). Add a drop of chloroform (CHCl₃) to each tube to prevent microbial growth and store filtrate in a refrigerator, if not analyzed immediately.

III. ANALYSIS

All three components Al, NH₄-N, NO₃-N are analyzed using LACHAT Flow Injection Autoanalyzer, using three channels simultaneously.

Colorimetric determination of $\text{NH}_4\text{-N}$ in soil extract ($\text{NH}_4\text{-N}$ channel)

Range: 6-100 mg kg^{-1} in soil.

Principle: The KCl extract is analyzed for ammonia by the phenolate method. This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitropruside is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the ammonia concentration in solution.

Reagents

1. Degassing 1 M KCl and the buffer with Helium to prevent bubble formation.
2. Potassium Chloride Carrier and Standard Diluent: In 1 L volumetric flask dissolve (completely) 37.25 g KCl in approx. 800 mL distilled water. Dilute to the mark with distilled water, degas with helium or argon.
3. Sodium phenolate: In 1 L volumetric flask dissolve 88 mL of 88% liquefied phenol or 83 g cristaline phenol in approximately 600 mL water. While stirring, slowly add 32 g sodium hydroxide.
4. Sodium hypochlorite : Dilute 250 mL or 250 g of house hold bleach (containing 5.25 % NaOCl) to 500 g with water.
5. In a 1 L volumetric flask, add 50.0 g disodium ethelendiamintetraacetate and 5.5 g sodium hydroxide in about 900 mL distilled water. Stir until the material is completely dissolved. Remove the magnetic stiring bar, dilute to the mark with distilled water, invert three times.
5. Sodium nitropruside: Dissolve 3.5 g of sodium nitropruside in 1 L of water.

Colorimetric determination of NO₃-N in soil extractions (NO₃-N, channel)

Range: 2-100 mg kg⁻¹

Principle: Nitrate is quantitatively reduced to nitrite by passing the sample through copperized cadmium column. The nitrite (reduced nitrate and original nitrite) is then determined by diasotising with sulfanilamid followed by coupling with N- (1-naphthyl) ethylendiamin dyhydrochloride. The resulting water-soluble dye has a magenta color, which is read at 520 nm.

Reagents

1. 15 M Sodium hydroxide: Add 150 g NaOH slowly to 150 mL of water.
2. Ammonium chloride buffer, pH=8.5: In 1 L volumetric flask dissolve 80 g ammonium chloride and 1 g ethelendiamin tetraacetic acid dehydrate and 988 g water. Shake or stir until dissolved. Then adjust the pH 8.5 with 15 M sodium hydroxide.
3. Sulfanilamide color reagent: To a 1 L volumetric flask add about 600 mL of water. Then add 100 mL of 85% phosphoric acid, 40 g sulfanilamide and 1 g N-1 naphthylethylenediamine dihydrochloride. Dilute to the mark and invert three times. Store in the dark bottle. This solution is stable for one month.

Colorimetric determination of Al in soil extractions (Al channel)

Range: 2-100 mg kg⁻¹ in soil.

Principle: Aluminum reacts with pyrocatechol violet in the presence of 1,10-phenontralin at pH 6.2 to form a blue-gray color of uncertain composition. Aluminum polymers and strongly complexed aluminum molecules do not react with the pyrocatechol violet. The color formed is measured at 580 nm.

Reagents EDTA Reagent: Dissolve 69 g NaOH and 5 g Na₂-EDTA in 1 L

1. **1 M Potassium Chloride Carrier Solution:** In a 1 L volumetric flask dissolve (completely) 74.5 g KCl in approx. 800 mL distilled water. Dilute to the mark with distilled water, degas with helium or argon.
2. **2 M HCL:** In a 100 mL volumetric flask add about 50-mL distilled water, slowly add 17 mL 12 M HCL. Dilute to the mark and invert three times.
3. **Acidified 1 M Potassium Chloride Diluent:** In a 1 L volumetric flask dissolve (completely) 74.5 g KCl in approx. 800 mL distilled water. Add 2 mL 2 M HCL. Dilute to the mark with distilled water and stir with a magnetic stirrer.
4. **Phenantroline Solution:** In a 1L volumetric flask, add 7.6 g hydroxylamine hydrochloride to about 800 mL distilled water. Stir until the material has completely dissolved. Add 0.56 g anhydrous 1.10-phenantroline (Aldrich Chem. 13,137-7 or equivalent) and continue stirring until material dissolves. Remove the magnetic bar, dilute to the mark with distilled water invert three times.
4. **Pyrocatechol Violet Reagent, 2.0 mM:** In a 500 mL volumetric flask, dissolve 0.386 g pyrocatechol violet in about 50 mL water. Let the solution stand for 5 min. with occasional stirring. Dilute to the mark with distilled water invert three times. Prepare this reagent fresh each day.
6. **Hexamethylenetetramine Buffer:** In a 1 L volumetric flask, add 84.0 g hexamethylenetetramine (Aldrich Chem. H1, 130-0 or equivalent) to about 900 mL distilled water. Stir until the material has completely dissolved. Remove the magnetic bar, dilute to the mark with distilled water, invert three times.

7. Sodium Hydroxide – EDTA Rinse: Dissolve 65 g NaOH and 6 g Na₄-EDTA in 1 L distilled water.

Standards for NH₄-N, NO₃-N, Al

1. 1000 mg kg⁻¹ N stock solution

Weigh out 2.86 g NH₄NO₃ in 1 L volumetric flask, dilute to the volume with 1 M KCl, and invert 3 times. Check the purity if use commercial 1000mg kg⁻¹ stock solution.

2. 200 mg kg⁻¹ N stock solution:

Take 50mL of 2000 mg kg⁻¹ N stock solution and dilute to 1 L with 1 M KCl

3. 1000ppm Al stock solution

Weigh out 8.95 g AlCl₃*6H₂O(fw=241.33) in 1 L volumetric flask, dilute to the volume with 1 M KCl, and invert 3 times.

4. 100 mg kg⁻¹ Al stock solution.

Take 100 mL of 1000 mg kg⁻¹ N stock solution and dilute to 1 L with 1 M KCl.

TABLE 1. Standard solutions for simultaneous determination of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and Al in soil extracts.

Std.	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Al,
	----- mg kg^{-1} -----		
1	10	10	10
2	5	5	5
3	2	2	2
4	1	1	1
5	0.1	0.1	0.5

VITA

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