EFFECTS OF LIGNOSULFONATE IN COMBINATION WITH UREA ON SOIL CARBON AND NITROGEN DYNAMICS

by

Jackie N. Meier

A thesis submitted to the faculty of Graduate Studies

and Research in partial fulfilment of the

requirements for the degree of the

Master of Science

Department of Renewable Resources
McGill University
Montreal, Canada

SUGGESTED SHORT TITLE

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ABSTRACT

M. Sc. J.N. Meier Renewable Resources

Lignosulfonate (LS), a by-product of the pulp and paper industry, may have the potential to increase fertilizer N availability by acting as a urease and nitrification inhibitor. Four consecutive laboratory studies were conducted to evaluate the behavior of LS in agricultural soils. The effects of various types and rates of LS on soil respiration and soil N dynamics were determined. Effects of LS in combination with fertilizers on microbial activity and N dynamics were measured. Due to the high water solubility of LS a leaching column study was conducted to determine the potential leaching of LS.

Higher rates (20% w/w) of LS initially inhibited microbial activity. Generally LS was relatively resistant to degradation by soil microorganisms and small proportions of added LS-C (<2.1%) were leached from the soil columns, but leaching was a function of soil and moisture regime. Recovery of added mineral LS-N from soil treated with LS was low (<41%). Mineral N recovered from LS plus fertilizer amended soil was higher than recovery from corresponding fertilizer treatments. Lignosulfonate reduced urea hydrolysis and the proportion of added N volatilized as NH_3-N from a LS plus urea treatment. The mineral N pool from LS plus fertilizer treated soils had significantly lower NO_3-N concentrations than corresponding fertilizer treatments. Nitrification inhibition was believed to have been due to high fertilizer concentrations. At reduced urea and LS concentrations, LS decreased NO_3-N recovery in one of four soil types. However, reduced recovery may not have been from nitrification inhibition but possibly from denitrification or chemical reactions between N and phenolics from LS.

RESUME

M. Sc. J.N. Meier Ressources Renouvelables

Le lignosulfonate (LS), un sous produit des pâtes et papiers, pourrait ameliorer la disponibilité d'azote minéral en inhibant l'action de l'uréase et des enzymes nitrificateurs. Quatres études ont été conduites afin d'évaluer le comportement du LS dans les sols agricoles. L'effet de différentes taux d'application et de différentes variétés de LS sur la respiration microbienne et la concentration d'azote dans le sol on été mesuré. L'effet de LS en combinant avec l'engrais sur l'activité microbienne et la dynamique d'azote et le potentiel de lessivage du LS dans le sols ont été mesuré.

Le taux élevés (20% m/m) du LS a inhibé l'activité microbienne. En générale, très peu de LS a été decomposé ou lessivé en dépit de sa solubilité éléve. Du montant d'azote appliqué par le LS, seulement 41% pouvait être récupéré par l'extraction (1N KCl). L'extraction d'azote provenant d'engrais minéraux a augmenté avec le traitement de LS. Le LS a réduit l'hydrolyse d'urée et la proportion d'azote volatilizé comme NH_3 du traitement combinant urée et LS. Les fractions d'azote minéral des traitements combinant le LS avec plusieurs engrais ont toutes diminué leur teneur en NO_3. Cet peut-être les taux d'engrais elevé qui est la cause de cet effet. Dans des traitements avec les taux réduit, LS on diminué la proportion de NO_3 récupéré dans un des quatre sols. Cet effet est peut-être due à la dénitrification ou la mobilisation par le LS du NO_3 plutôt qu'à l'inhibition des enzymes nitrificateurs.

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ACKNOWLEDGEMENTS

Financial support from Fonds pour la Formation de Chercheurs et l'Aide a la Recherche (FCAR) is greatly ackowledged.

I am especially grateful to my supervisor, Dr. J.W. Fyles, for his guidance, support and consistent encouragement. His continual interest and availability are greatly appreciated. I wish to thank Dr. A.F. Mackenzie for his guidance and overall supervision of this project. I would also like to express my appreciation to Dr. I.P. O'Halloran for his assistance and valuable suggestions throughout this thesis.

My great appreciation is extended to Elizabeth Russell for her critical discussions and willingness to lend a hand. My thanks to technicians Ken Gee, Khosro Mousavi and Sima Khosravi for their help with laboratory analysis. Special thanks to Dr. M. Fanous and Peter Kirby for their assistance with statistical problems. Also my appreciation for the support offered by Marie Cote and Edith Donald.

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INTRODUCTION

This thesis is part of a comprehensive program concerned with evaluating lignosulfonate (LS) as an amendment to improve phosphorus (P) and nitrogen (N) fertilizer efficiency in corn (Zea mays L.) production, and is specific to studying LS-urea interactions.

Increased areas planted to corn and requirements for higher corn yields in eastern Canada have resulted in increasing use of fertilizer N. Larger N inputs, however, have not been associated with increased fertilizer efficiency. Research has indicated that approximately 30 to 50% of applied N fertilizer is not recovered in the harvested crop. Consequently, economic returns are reduced and the potential for N pollution increased. These problems could be alleviated if efficiency of fertilizer N could be improved.

Loss of fertilizer N occurs predominantly from NH_3-N volatilization, NO_3-N leaching and denitrification. Management techniques have included the use of urease and nitrification inhibitors. Maintenance of N as urea through the action of urease inhibitors decreases the amount of NH_4-N subject to volatile loss whereas maintenance of N as NH_4-N by nitrification inhibitors reduces the NO_3-N levels subject to leaching and denitrification loss. While numerous compounds have been patented or recommended as inhibitors their use has not always proved cost effective.

Polyphenolic materials are among the vast array of compounds proposed as inhibitors. Lignosulfonate (LS), a by-product from the pulp and paper industry, is a phenyl propane derivative with similar characteristics to soil organic matter. Its availibility and low cost enhance its potential use as a urease and/or nitrification inhibitor.

This thesis is comprised of five chapters consisting of a literature review and four individual laboratory experiments.

Chapter I, the *Literature Review,* introduces the problems associated with fertilizer N applications in agricultural systems, describes some common management practices employed to improve N fertilizer efficiency and introduces LS as a product with potential to increase N efficiency. Chapter II, *Effects of Lignosulfonate (LS) on C and N Dynamics in a Clay Soil,* examines the decomposition of five types of LS at three different application rates and their effects on soil ammonium (NH_4) and nitrate (NO_3) nitrogen. Chapter III, *Effects of Lignosulfonate-Fertilizer Mixtures on Soil Respiration and N Dynamics*, evaluates the decomposition of LS in combination with urea and diammonium phosphate fertilizers as well as the effect of LS on NH_3-N volatilization and soil NH_4-N and NO_3-N. Chapter IV, *Leaching of Lignosulfonate from Soil Columns and Lignosulfonate Effects on Nitrate Leaching from Urea Fertilizer*, examines the mobility of LS within soil columns and LS effects on NO_3-N leaching from urea fertilizer. Finally Chapter V, *Evaluation of Lignosulfonate as a Nitrification Inhibitor*, compares the effectiveness of LS as an inhibitor of nitrification with urea fertilizer to a well known inhibitor in four contrasting soil types. Overall conclusions for the thesis are included in the section entitled *General Conclusions.*

CHAPTER I. LITERATURE REVIEW

FERTILIZER NITROGEN

High yielding crops of modern agriculture often demand N in excess of soil supply and sustained growth requires the input of fertilizer N on an annual basis. Most frequently used N fertilizers are applied in the NH_4^+ or NH_4^+ producing forms, such as urea (Bronson et al 1991; McCarty and Bremner 1990a; Bremner and Bundy 1974). The benefits received from these N fertilizers in increased crop yields and quality, however, are not without problems. When the natural capacity of a crop system to cycle fertilizer N is exceeded, the result may be losses of N to NH_3 volatilization, leaching or denitrification (Sahrawat 1980a).

Such losses decrease the cost-effectiveness of agricultural fertilization as well as contribute to environmental hazards. Accumulation of NO_3^- in ground or surface waters could result in contamination of drinking water (Walters and Malzer 1990a) and atmospheric losses of N_2O could contribute to depletion of the ozone layer (Firestone 1982).

Research, therefore, has been conducted to determine the factors that lead to loss of N from the soil/plant system as well as management methods to decrease loss. Particular attention has been paid to voltailization of NH_3-N, leaching of NO_3-N and denitrification.

NH_3-N Volatilization

Soil pH is a significant factor affecting NH_3-N volatilization due to the concentration of H^+ ions important in the NH_4^+ - NH_3 equilibrium in soils. Losses increase drastically when pH is above 7 (Nelson 1982) and NH_4-N containing fertilizers are particularly prone to NH_3-N volatilization when applied to calcareous soils (Ellington 1986). Urea is at greatest risk to NH_3-N volatilization because of its rapid hydrolysis to NH_4^+ and bicarbonate ions (Bayrakli 1990; Gould et al. 1986). The latter raises soil pH and consequently promotes NH_3-N volatilization. Ammonia losses increase with temperature primarily because of an

increase in the equilibrium constant (Nelson 1982), which results in a greater proportion of ammoniacal N accumulation as NH_3(aq). Moisture content of the soil is also a significant factor influencing NH_3-N volatilization mainly because NH_3-N loss is a function of soil moisture loss (Nelson 1982). Cation exchange capacity of soils plays a large role in NH_3-N volatilization (Whitehead and Raistrick 1990; Stevens et al. 1989; Reynolds and Wolf 1987) and soils with high clay and/or organic matter content adsorb the cationic NH_4-N, reducing losses to NH_3-N volatilization.

Research has indicated that 4-70% of urea-N applied to soils is lost through volatilization as NH_3 (De Datta et al. 1991; Bayrakli 1990; Whitehead and Raistrick 1990; Mulvaney and Bremner 1981). Attention, therefore, has been focused on methods to decrease NH_3-N volatilization from urea and other N fertilizers. Incorporation of fertilizer N into the soil (Fillery et al. 1984; Nelson 1982; Mikkelsen et al. 1978) increases the diffusion distance between fertilizer and air, however such modifications are not always effective (Hendrickson et al. 1987) or practical (eg. in orchards). Amendment of urea with coatings (ie. resins, waxes, silica, S) or chemical additives (ie. acidifying agents, urease inhibitors) to reduce ammoniacal N concentrations or soil microsite pH are other possible means of decreasing ammonia loss (Gould et al. 1986; Buresh 1987). Coated urea can decrease the dissolution rate of the fertilizer (Gould et al. 1986; Gullett et al. 1987; Matocha 1976) hence slowing the rate of NH_4-N released. Sulfur-coated urea has been shown to be an effective N source in rice production (Buresh 1987; Flinn et al. 1934; Katyal et al. 1975). Research on acidifying agents has included H_2SO_4 (Fenn et al. 1986), H_3BO_3 (Al-Kanani et al. 1990; Bayrakli 1990), urea-phosphates (mixtures of urea and phosphoric acid; Bremner and Douglas 1971; Stumpe et al. 1984), urea nitricphosphate (Christianson 1989), solube Ca and Mg (Fenn et al. 1986; 1981; Fenn and Miyamoto 1981) and phosphogypsum (Bayrakli 1990). While these products have been shown to reduce NH_3-N volatilization, they may not always be efficient or

practical. For instance, urea phosphates are corrosive and require special handling precautions, urea nitricphosphate is not as effective on calcareous soils and phosphogypsum may have potential gypsum disposal problems (Christianson 1989). Management techniques that reduce urease activity apply only to urea or urea containing fertilizers and are aimed at slowing the rapid urea hydrolysis process so as to decrease NH_4-N production and allow surface applied urea to migrate into the soil and hence reduce potential NH_3-N volatilization losses. A vast array of classes of compounds have been proposed as urease inhibitors (Sahrawat 1980b) and a number of reviews on research have been written (Ladd and Jackson 1982; Schmidt 1982; Sahrawat 1980b). The literature on urease inhibitors is far too voluminous to discuss in detail and is not the objective of this review. Only some of the more common inhibitors will therefore be elaborated on. Numerous sulfur (S) compounds have been studied as possible urease inhibitors. Mahli and Nyborg (1979) monitored the effects of urea in combination with thiourea (Bayrakli 1990), thioacetamide, phosphorus pentasulfide and calcium sulfide and demonstrated that all reduced urea hydrolysis by 58-29% and, that thiourea and thioacetamide were the most effective. Recent attention has been directed at ammonium thiosulfate (ATS), primarily because of its usefulness as a S source (Al-Kanani et al. 1990; Graziano 1990; McCarty et al. 1990; Bremner et al. 1986; Goos 1985). Results, however, are inconclusive. Some studies indicate that low levels of ATS (<1000 ug/g soil) reduce urea hydrolysis (Al-Kanani et al. 1990; Goos 1985) while other results suggest the contrary (Bremner et al. 1986). McCarty et al. (1990) reported delayed urea hydrolysis only when ATS was applied at rates as high as 2500 to 5000 ug/g soil, which resulted in effects on corn and wheat seed germination. Differences may involve ATS-soil interactions which will require studying. Graziano (1990) and Fox and Piekielek (1987), however, have suggested increased fertilizer efficiency with the addition of ATS to corn plots.

Hydrocarbons and phenolic compounds such as hydroquinone, a variety of benzoquinone compounds (Mulvaney and Bremner 1978), and phenylphosphorodiamidate (PPD; Watson 1990; Beyrouty et al. 1988; Hendrickson et al. 1987), 2-4 dinitrophenol (Bayrakli 1990) and naturally occuring polyphenols (Fernando and Roberts 1976) have been shown to effectively inhibit urease activity. The efficiency of these compounds, however, was a function of the compound itself and soil properties. Higher soil organic matter contents tended to decrease the effectiveness of benzoquinone and hydroquinione (Mulvaney and Bremner 1978), while the addition of organic residues with PPD increased its efficiency (Hendrickson et al. 1987). The former may have been adsorbed onto colloidal surfaces, as described by Greaves and Malcolmes (1980), whereas added organic residues (Hendrickson et al. 1987) may produce organic acids during decomposition and may have indirectly increased PPD efficiency. The investigations by Watson (1990) indicated that PPD effectiveness varied with soil type, ranging from 0 - 90% inhibition, and was primarily a function of soil pH. Calcareous soils are less responsive to PPD (Beyrouty et al. 1988; Hendrickson et al. 1987).

Although various urease inhibitors have have been shown to reduce NH_3-N volatilization there is still a lack of data with relation to crop growth.

Leaching and denitrification

Ammonium in NH_4-based fertilizers is relatively immobile in the soil, but, it is rapidly converted to NO_3-N by the biologically controlled nitrification process (Bronson et al. 1991). Nitrification is a two step process controlled by two specialized groups of bacteria: oxidation of NH_4 to NO_2 by ammonia oxidizing bacteria and the subsequent oxidation of NO_2 to NO_3 by nitrite oxidizing bacteria (Schmidt 1982). The latter portion of the process is more rapid than the former and thus, NO_3-N levels usually dominate in natural systems (Schmidt 1982). Nitrate, an anionic species, is highly mobile in the soil system and is thus, subject

to leaching. Chemical and physical factors affect the rate of NH_4-N oxidation. First among the ecological influences is acidity. Generally, nitrification is drastically reduced at a pH below 5, which may be associated with Al toxicity (Schmidt 1982; Alexander 1965). Oxygen is a requirement for all species involved in nitrification and hence soil aeration is essential (Schmidt 1982). Factors such as soil structure and moisture content determine O_2 supply. Temperatures below 5°C and above 40°C inhibit nitrifying bacteria and hence markedly decrease the nitrification process.

Denitrification is the biological reduction of NO_3-N to N_2O-N and N_2 gas (Firestone 1982). Denitrification is a function of a complex system of factors involving O_2, moisture, organic C, pH and temperature (Christiansen et al. 1990; Grundmann et al. 1988; Stevenson 1982). Enzyme activity, specific to denitrification, requires an absence of O_2 (Mahli et al. 1990; Grundmann et al. 1988; Firestone 1982). Soil moisture, therefore, is significant from the standpoint of its effects on soil aeration, and fertilizer N loss to dentirification is of great concern in flooded soils such as those used in rice production (Mahli et al. 1990). Organic materials stimulate denitrification because they act as electron donors as well as create anaerobic microsites (Parsons et al. 1991; Grundmann et al. 1988; Parkin 1987; Aulakh et al. 1984a).

Management practices to decrease leaching losses of NO_3-N might include intercropping schemes, soil erosion control and the incorporation of organic C to promote microbial immobilization (Keeney 1982). Techniques such as tilling have been shown to decrease dentrification osses (Aulakh et al. 1984b) probably due to increased soil aeration and decreased bulk density (Grundmann et al. 1988). Tilling may become increasingly important with the addition of organic residues, primarily due to higher moisture contents associated with zero-till environments (Aulakh et al. 1984a). The reduction of denitrification rates in agricultural systems may, however, contribute to increased NO_3-N

leaching (Grundmann et al. 1988). As a consequence, management techniques that reduce nitrification are advantageous relative to those that reduce denitrification.

Practices aimed at reducing nitrification primarily involve the addition of nitrification inhibitors. A wide range of compounds and materials have been proposed as nitrification inhibitors (Sahrawat 1980b). The objective of this review is not to report all compounds proposed as nitrification inhibitors, but to discuss some of the research of the more common inhibitors.

Compounds such as 2-ethynylpyridine (McCarty and Bremner 1990a), 3-methylpyrazole-1-carboxamide (McCarty and Bremner 1990b), 2-chloro-6-(trichloromethyl)pyridine (nitrapyrin; Walters and Malzer 1990a, b; Sodma et al. 1990; Magalhaes and Chalk 1987; Guthrie and Bomke 1980; Bremner and Bundy 1974) and dicyandiamide (DCD; Bronson et al. 1991; Norman et al. 1989; Yadvinder-Singh and Beauchamp 1989; Ashworth and Rodgers 1981) have been shown to block the nitrification process and consequently, reduce leaching and gaseous losses of fertilizer N. Nitrapyrin is commercially available (Hauck 1980) and has received the most attention in recent years (Bronson et al. 1991). Magalhaes and Chalk (1987) and Bremner and Bundy (1974) have, however, demonstrated that nitrapyrin can stimulate NH_3-N volatilization due to the accumulation of NH_4-N associated with inhibition of nitrification. Although many compounds effectively retard the nitrification process, the effects on crop yields and N uptake can be inconsistent. Norman et al. (1989) reported that DCD resulted in greater N uptake in rice in comparison to urea alone, while Walters and Malzer (1990a) demonstrated a reduction in corn growth with the application of nitrapyrin. The nitrapyrin, however, increased residual N concentrations in the year following inhibitor addition and consequently enhanced fertilizer N uptake (Malzer and Walters 1990a). Investigations of nitrapyrin by Sodma et al. (1990) concluded the contrary, and reported no effect after application and reduced corn growth in the second

seeding. Growth reductions may be related to toxic concentrations of NH_4-N or NO_2-N that accumulate from inhibition of nitrification (Sodma et al. 1990), and may be a function of soil type. Other studies have reported that DCD and nitrapyrin did not increase yields in wheat and corn sufficiently to warrant reduced fertilizer requirements (Bronson et al. 1991; Guthrie and Bomke 1980; Hendrickson et al. 1978).

A number of S compounds, such as methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide, hydrogen sulfide (Bremner and Bundy 1974), and thiosulfate (Janzen and Bettany 1986a) have been shown to inhibit nitrification. Carbon disulfide was the most effective S compound with the exception of thiosulfate, and was also more potent than nitrapyrin (Bremner and Bundy 1974). Maddux et al. (1985), however, found that carbon disulfide was not effective, perhaps suggesting the importance of soil type. Soils have the capacity to adsorb volatile S compounds, hence soil type may determine the degree of sorption (Guthrie and Bomke 1980). Thiosulfate was shown to inhibit the oxidation of NO_2 to NO_3, which could result in toxic accumulations of NO_2-N (Janzen and Bettany 1986a). Research on S compounds, however, receives attention because of their potential to alleviate S deficiencies in crops (Janzen and Bettany 1986b).

Phenolic materials have also been shown to inhibit nitrification in agricultural systems (Azhar et al. 1986; Sahrawat 1980b). The inhibition by polyphenols has, however, been controversial (Sivapalan 1985) and research predominantly performed in forest ecosystems. Rice and Pancholy (1972 and 1973), Baldwin et al. (1983), Olson and Reiners (1983) and Lodhi and Killingbeck (1980) suggested that phenolic materials were responsible for inhibition of nitrification in forest floors. Research conducted on a number of plant extracts by Johnson and Edwards (1979) and Montes and Christensen (1979), however, suggested no inhibition.

The mechanisms by which phenolic compounds inhibit urease activity and nitrification

are complex and are not the objective of this thesis. In agricultural systems, however, it has been suggested that phenolic materials may bind with the enzyme urease (Al-Kanani et al. 1990) and form complex structures by adsorbing nitroso and nitro groups produced during nitrification (Azhar et al. 1986).

LIGNOSULFONATE AND POTENTIAL FOR IMPROVED FERTILIZER N EFFICIENCY

The sulfite pulping process, of the pulp and paper industry, extracts lignin from wood by digestion with sulfurous acid (Browning 1963). To prevent undue degradation of cellulose a hydroxide, commonly ammonium (NH_4), calcium (Ca) or sodium (Na), is added to neutralize the acid and forms bisulfite (Glennie 1971). The lignin dissolves as lignosulfonate (LS) and, various forms of recovered LS are available depending on the neutralizing base. The exact nature of the LS molecule is unknown, but the molecule's basic building unit is a phenyl propane derivative similar to that of lignin (Reference Guide, Daishowa Chemicals). The macromolecule is thought to be made up of these units in branched, polyaromatic chains (Reference Guide, Daishowa Chemicals).

Lignosulfonate is similar to soil organic matter in its surface negative charge and colloidal properties (Hoyt and Goheen 1971), but is water soluble due to the presence of sulfonate groups (Reference Guide, Daishowa Chemicals). Lignosulfonfate is a strong chelating agent (Browning 1975) and has been used as a carrier for micronutrient fertilizers. Results have indicated that LS in combination with Fe and Zn have increased their availability to crops (Sajwan and Lindsay 1988; Cihacek 1984; Singh et al. 1986).

Lignosulfonate may also have the potential to increase the efficiency of macromolecular fertilizers because of its colloidal properties and phenolic nature. Lignosulfonate is expected

to adsorb urease and nitrification inhibitors and therefore offers potential as a urea fertilizer carrier capable of controlling these reactions in soil. If LS can significantly enhance inhibitor effects, increased inhibitor and fertilizer efficiency is anticipated. In addition, phenolic compounds, as previously discussed, have been shown to directly inhibit both urease activity and nitrification in soils.

It is expected that LS, either in combination with commercially available inhibitors or alone, might reduce gaseous (NH_3-N, N_2O and N_2) and leaching (NO_3-N) losses from fertilizer N due to inhibition effects. In comparison to other urease and nitrification inhibitors, LS is particularly attractive because of its availability and low cost.

LIGNOSULFONATE AND POTENTIAL FOR IMPROVED FERTILIZER P EFFICIENCY

Lignosulfonate is also expected to improve the effectiveness of P fertilizers. The recovery of fertilizer P by crops is often low due to soil reactions that occur following fertilization with P. Reactions involved include P precipitation by soil components such as Ca, Fe and Al hydrous oxides (Solis and Torrent 1989; Haynes 1984) and P adsorption by soil surfaces (Haynes 1984).

Organic materials have been shown to compete with phosphate ions for adsorption sites on soil colloids (Meek et al. 1979). The application of crop residues reduced phosphate adsorption by the soil (Mnkeni and MacKenzie 1985), increased P availability, and subsequently enhanced P uptake by crops (Mnkeni and MacKenzie 1988).

The similarity of LS to soil organic matter and its capacity for chelatation with cations and adsorption to soil surfaces are expected to make LS effective in reducing P retention in soils.

REFERENCES

Alexander, M. 1965. Nitrification. Pages 307-343 *in* Bartholomew, M.V. and Clark, F.E. (eds.) Soil nitrogen. Am. Soc. of Agron., Madison, Wisconsin.

Al-Kanani, T., MacKenzie, A.F. and Blenkhorn, H. 1990. Volatilization of ammonia from urea-ammonia nitrate solutions as influenced by organic and incrganic additives. Fert. Res. 23: 113-119.

Ashworth, J. and Rodgers, G.A. 1981. The compatibility of the nitrification inhibitor dicyandiamide with injected anhydrous ammonia. Can. J. Soil Sci. 61: 461-463.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1984a. The influence of plant residues in denitrification rates in conventional and zero tilled soils. Soil Sci. Soc. Am. J. 48: 790-794.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1984b. Gaseous nitrogen losses from soils under zero-till as compared to conventional till management systems. J. Environ. Qual. 13: 130-136.

Azhar, E., Verhe, R., Proot, M., Sandra, P. and Verstaete, W. 1986. Binding of nitrate-nitrogen on polyphenols during nitrification. Plant Soil 94: 369-382.

Baldwin, I.T., Olson, R.K. and Reiners, W.S. 1983. Protein binding phenolics and the inhibition of nitrification in subalpine balsam fir soils. Soil Biol. Biochem. 15: 419-423.

Bayrakli, F. 1990. Ammonia volatilization losses from different fertilizers and effect of sveral urease inhibitors, $CaCl_2$ and phosphogypsum on losses from urea. Fert. Res. 23: 147-150.

Beyrouty, C.A., Sommers, L.E. and Nelson, D.W. 1988. Ammonia volatilization from surface applied urea as affected by several phosphoroamide compounds. Soil Sci. Soc. Am. J. 52: 1173-1178.

Bremner, J.M. and Bundy, L.G. 1974. Inhibition of nitrification in soils by volatile sulfur compounds. Soil Biol. Biochem. 6: 161-165.

Bremner, J.M. and Douglas, L.A. 1971. Decomposition of urea phosphate in soils. Soil Sci. Soc. Am. Proc. 35: 575-578.

Bremner, J.M., McCarty, G.W. and Chai, H.S. 1986. Evaluation of ammonium thiosulfate as a soil nitrification and urease inhibitor. Page 175 *in* Agron. Abstracts, Am. Soc. of Agron., Madison,, Wisconsin.

Bronson, K.F., Touchton, J.T., Hauck, R.D. and Kelley, K.R. 1991. ^{15}N recovery in winter wheat as affected by application timing and dicyandiamide. Soil Sci. Soc. Am. J. 55: 130-135.

Browning, B.L. 1963. The chemistry of wood. Intersicence publishers, New York.

Browning, W. 1975. The lignosulfonate challenge. Pages 109-124 *in* Timell, T.E. (ed.). Proceedings of the 8th cellulose conference. I. wood chemicals - a future challenge. Applied Polymer Symposium No. 28.

Buresh, R.J. 1987. Relative susceptibility of conventional and experimental nitrogen sources to ammonia loss from flooded rice fields. Fert. Res. 13: 139-153.

Cihacek, L.J. 1984. Economic soil treatment of iron chlorosis in grain sorghum grown on a gypsum affected soil. J. Plant Nutr. 7(1-5): 329-340.

Christiansen, S., Simkins, S. and Tiedje, J.M. 1990. Temporal patterns of soil denitrification: their stability and causes. Soil Sci. Soc. Am. J. 54: 1614-1618.

Christianson, C.B. 1989. Ammonia volatilization from urea nitricphosphate and urea applied to the soil surface. Fert. Res. 19: 183-189.

De Datta, S.K., Buresh, R.J., Samaon, M.I., Obcemea, W.N. and Real, J.G. 1991. Direct measurement of ammonia and denitrification fluxes from urea applied to rice. Soil Sci. Soc. Am. J. 55: 543-548

Ellington, A. 1986. Ammonia volatilization losses from fertilizers applied to acid soil in the field. Fert. Res. 8: 283-296.

Fenn, P., Choi, S., Kirk, K.T. 1981. Lignolytic activity of *Phanerochaete chrysosporium*: physiology of suppression by ammonium and L-Glutamate. Arch. Microbiol. 130: 66-71.

Fenn, L.B., Matocha, J.E. and Wu, E. 1986. A comparison of calcium carbonate precipitation and pH depression on reduced ammonia loss from surface applied urea. Soil Sci. Soc. Am. J. 44: 1128-1131.

Fenn, L.B. and Miyamoto, S. 1981. Ammonia loss and associated reactions of urea in calcareous soils. Soil Sci. Soc. Am. J. 45: 537-540.

Fernando, V. and Roberts, G.R. 1976. The partial inhibition of soil urease by naturally occuring polyphenols. Plant Soil 44: 81-86.

Fillery, I.R.P., Simpson, J.R. and De Datta, S.K. 1984. Influence of field environment and fertilier management on ammonia loss from flooded rice. Soil Sci. Soc. Am. J. 48: 914-920.

Firestone, M.K. 1982. Biological denitrification. Pages 289-326 *in* Stevenson, F.J. (ed.). Nitrogen in agricultural soils. Agron. No. 22. Am. Soc. of Agron., Madison, Wisconsin.

Flinn, J.C., Mamaril, C.P., Velasco, L.E. and Kaiser, K. 1984. Efficiency of modified urea fertilizers for tropical irrigated rice. Fert Res. 5: 157-174.

Fox, R.H. and Piekielek, W.P. 1987. Comparison of surface application methods of nitrogen solution to no-till corn (Zea Mays). J. Fert. Issues 4: 7-12.

Glennie, D.W. 1971. Reactions in sulfite pulping. Pages 597-637 *in* Freudenberg, C., Sarkanen, K.V. and Ludwig, C.H. (eds.). Lignins: occurrence, formation, structure and reactions. New York, Wiley Interscience.

Goos, R.J. 1985. Identification of ammonium thiosulfate as a nitrification and urease inhibitor. Soil Sci. Soc. Am. J. 49: 232-235.

Gould, W.D., Hagedorn, C. and McCready, R.G.L. 1986. Urea transformations and fertilizer efficiency in soil. Adv. Agr. 40: 209-238.

Graziano, P.L. 1990. Improvement of nitrogen efficiency by addition of ammonium thiosulfate in the liquid fertilization of maize. Fert. Res. 24: 111-114.

Greaves, M.P. and Malcolmes, H.P. 1980. Pages 223-253 *in* Hance, R.J. Interactions between herbicides and soil. London; New York, Academic Press.

Grundmann, G.L., Rolston, D.E. and Kachanoski, R.G. 1988. Field soil properties influencing the variability of denitrification gas fluxes. Soil. Sci. Soc. Am. J. 52: 1351-1355.

Gullett, L.L. and Simmons, L. 1987. Sulfur-coated urea. U.S. Patent Document # 4,676,821.

Guthrie, T.F. and Bomke, A.A. 1980. Nitrification inhibition by N-Serve and ATC in soils of varying texture. Soil Sci. Soc. Am. J. 44:314-320.

Hauck, R.D. 1980. Mode of action of nitrification inhibitors. Pages 19-32 *in* Meisinger, J.J., Randall, G.W. and Vitosh, M.L. Nitrification inhibitors - potentials and limitations. Am. Soc. of Agron. No. 38, Madison, Wisconsin.

Haynes, R.J. 1984. Lime and Phosphate in the soil-plant system. Adv. agron. 37: 249-315.

Hendrickson, L.L., Omholt, T.E. and O'Connor, M.J. 1987. Effect of phenylphosphorodiamidate on immobilization and ammonia volatilization. Soil Sci. Soc. Am. J. 51: 1067-1071.

Hendrickson, L.L., Walsh, L.M. and Keeney, D.R. 1978. Effectiveness of nitrapyrin in

controlling nitrification of fall and spring applied anhydrous ammonia. Agron. J. 70: 704-708.

Hoyt, C.H. and Goheen, D.W. 1971. Polymeric products. Pages 833-839 *in* Freudenberg, C., Sarkanen, K.V. and Ludwig, C.H. (eds.) Lignins: occurrence, formation, structure and reactions. New York, Wiley Interscience.

Janzen, H.H. and Bettany, J.R. 1986a. Influence of thiosulfate on nitrification of ammonium in soil. Soil Sci. Soc. Am. Proc. 50: 803-806.

Janzen, H.H. and Bettany, J.R. 1986b. Release of available sulfur from fertilizers. Can. J. Soil Sci. 66: 91-103.

Katyal, J.C., Singh, B., Vlek, P.L.G. and Craswell, E.T. 1975. Fate and efficiency of nitrogen fertilizers applied to wetland rice. II. Punjab, India. Fert. Res. 6: 279-290.

Keeney, D.R. 1982. Nitrogen management for maximum efficiency and minimum pollution. Pages 605-649 *in* Stevenson, F.J. (ed.) Nitrogen in agricultural soils. Agron. No. 22., Madison, Wisconsin.

Johnson, D.W. and Edwards, N.T. 1979. The effects of stem girdling on biochemical cycles within mixed deciduous forest in eastern Tennessee. II. soil nitrogen mineralizaion rates. Oecologia 40: 259-271.

Ladd, J.M. and Jackson, R.B. 1982. Biochemistry of ammonification. Pages 209-228 *in* Stevenson, F.J. (ed). Nitrogen in agricultural soils. Agron No. 22. Am. Soc. of Agron., Madison, Wisconsin.

Lodhi, M.A.K. and Killingbeck, K.T. 1980. Allelopathic inhibition of nitrification and nitriying bacteria in a ponderosa pine (Pinus ponderosa Dougl.) community. Am. J. Bot. 67(10): 1423-1429.

Maddux, L.D., Kissel, D.E., Ball, J.D. and Raney, R.J. 1985. Nitrification inhibition by nitrapyrin and volatile sulfur compounds. Soil Sci. Soc. Am. J. 49: 239-242.

Magalhaes, A.M.T. and Chalk, P.M. 1987. Nitrogen transformations during hydrolysis and nitrification of urea. II. effects of fertilizer concentration and nitrification inhibitors. Fert. Res. 11: 173-184.

Malhi, S.S., McGill, W.B. and Nyborg, M. 1990. Nitrate losses in soils: effect of temperature, moisture and substrate concentration. Soil Biol. Biochem. 22: 733-737.

Malhi, S.S. and Nyborg, M. 1979. Rate of hydrolysis of urea influenced by thiourea and pellet size. Plant Soil 51: 177-186.

Matocha, J.E. 1976. Ammonia volatilization and nitrogen utilization from sulfur-coated ureas and conventional nitrogen fertilizers. Soil Sci. Soc. Am. J. 40: 597-601.

McCarty, G.W. and Bremner, J.M. 1990a. Evaluation of 2-Ethynylpyridine as a soil

nitrification inhibitor. Soil Sci. Soc. Am. J. 54: 1017-1021.

McCarty, G.W. and Bremner, J.M. 1990b. Evaluation of 3-Methylpyrazole-1-carboxamide as a soil nitrification inhibitor. Biol. Fertil. Soils 9: 252-256.

McCarty, G.W., Bremner, J.M. and Krogmeier, M.J. 1990. Evaluation of ammonium thiosulfate as a soil urease inhibitor. Fert. Res. 24: 135-139.

Meek, B.D., Graham, L.E., Donovan, T.J. and Mayberry, K.S. 1979. Phosphorus availability on calcareous soil after high loading rates of animal manure. Soil Sci. Soc. Am. J. 43: 741-743.

Mikkelsen, D.S., De Datta, S.K. and Obcemea, W.N. 1978. Ammonia volatilization losses from flooded rice soils. Soil Sci. Soc. Am. J. 42: 725-730.

Mnkeni, P.N.S. and MacKenzie, A.F. 1988. Ortho-polyphosphate phosphorus fertilizers as affected by added organic materials and calcium carbonate. Can. J. Soil Sci. 68: 243-250.

Mnkeni. P.N.S. and MacKenzie, A.F. 1985. Retention of ortho- and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate. Can. J. Soil Sci. 65: 575-585.

Montes, R.A. and Christensen, N.L. 1979. Nitrification and succession in the piedmont of North Carolina. Forest Sci. 25: 287-297.

Mulvaney, R.L. and Bremner, J.M. 1981. Control on urea transformations in soils. Soil Biochem. 5: 153-196.

Mulvaney, R.L. and Bremner, J.M. 1978. Use of p-benzoquinone and hydroquinone for retardation of urea hydrolysis in soils. Soil Biol. Biochem. 10: 296-302.

Nelson, D.W. 1982. Gaseous losses of nitrogen other than through denitrification. Pages 327-363 *in* Stevenson, F.J. (ed.) Nitrogen in agricultural soils. Agronomy No. 22. Am. Soc. of Agron., Madison, Wisconsin.

Norman, R.J., Wells, B.R. and Molenhauer, K.A.K. 1989. Effect of application method and dicyandiamide on urea-nitrogen-15 recovery in rice. Soil Sci. Soc. Am. J. 53: 1269-1274.

Olson, R.K. and Reiners, W.A. 1983. Nitrification in subalpine balsam fir soils: tests for inhibitory factors. Soil Biol. Biochem. 15: 413-418.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. Soil Sci. Soc. Am. J. 51: 1194-1199.

Parsons, L.L., Murray, R.E. and Smith, M.S. 1991. Soil denitrification dynamics: spatial and temporal variations of enzyme activity, populations and nitrogen gas

loss. Soil Sci. Soc. Am. J. 55: 90-95.

Reference Guide to Specialty Chemicals, Daishowa Chemicals, Que., Canada.

Reynolds, C.M. and Wolf, D.C. 1987. Influence of urease activity and soil properties on ammonia volatilization of urea. Soil Sci. 143: 418-425.

Rice, E.L. and Pancholy, S. 1972. Inhibition of nitrification by climax ecosystems. Am. J. Bot. 59(10): 1033-1040.

Rice, E.L. and Pancholy, S. 1973. Inhibition of nitrification by climax ecosystems. II. additional evidence and possible role of tannins. Am. J. Bot. 60(7): 691-702.

Sahrawat, K.L. 1980a. Urease activity in tropical rice soils and flood water. Soil Biol. Biochem. 12: 195-196.

Sahrawat, K.L. 1980b. Control of urea hydrolysis and nitrification in soil by chemicals - prospects and problems. Plant Soil 57: 335-352.

Sajwan, K.S. and Lindsay, W.L. 1988. Response of flooded rice to various sources of zinc. J. Agric. Sci., Camb. 111: 197-198.

Schmidt, E.L. 1982. Nitrification. Pages 253-288 *in* Stevenson, F.J. (ed.). Nitrogen in agricultural soils. Agron. No. 22. Am. Soc. of Agron., Madison, Wisconsin.

Singh, J.P., Karamanos, R.E , Lewis, N.G. and Stewart, J.W.B. 1986. Effectiveness of zinc fertilizer sources on nutrition of beans. Can. J. Soil Sci. 66: 183-187.

Sivapalan, K. and Fernando, V. 1985. N-mineralization in polyphenol rich plant residues and their effect on nitrification of applied ammonium sulfate. Soil Biol. Biochem. 17: 547-551.

Sodina, Z.C., Mills, H.A. and Phatak, S.C. 1990. Nitrapyrin, terrazole, atrazine and simazine influence on nitrification and corn growth. J. Plant Nutr. 13(9): 1179-1193.

Solis, P. and Torrent, J. 1989. Phosphate sorption by calcareous vertisols and inceptisols of Spain. Soil Sci. Soc. Am. J. 53: 462-466

Stevens, R.J., Laughlin, R.J. and Kilpatrick, D.J. 1989. Soil properties related to the dynamics of ammonia volatilization from urea applied to the surface of acidic soils. Fert. Res. 20: 1-9.

Stevenson, F.J. 1982. Orignin and distribution of nitrogen in soil. Pages 1-39 *in* Stevenson, F.J. Nitrogen in agricultural soils. Agronomy No. 22. Am. Soc. Agron., Madison, Wisconsin.

Stumpe, J.M., Vlek, P.L.G. and Lindsay, W.D. 1984. Ammonia volatilization from urea and urea phosphates in calcareous soils. Soil Sci. Soc. Am. J. 48: 921-927.

Walters, D.T. and Malzer, G.L. 1990a. Nitrogen management and nitrification inhibitor effects on ^{15}N urea: I. Yield and fertilizer use efficiency. Soil Sci. Soc. am. J. 54: 115-122.

Walters, E.T. and Malzer, G.L. 1990b. Nitrogen management and nitrification inhibitor effects on ^{15}N urea: II. Nitrogen leaching and balance. Soil Sci. Soc. Am. J. 54: 122-130.

Watson, C.J. 1990. The influence of soil properties on the effectiveness of phenylphosphorodiamdate (PPD) in reducing ammonia volatilization from surface applied urea. Fert. Res. 24: 1-10.

Whitehead, D.C. and Raistrick, N. 1990. Ammonia volatilization from five compounds used as fertilizers following surface application to soils. J. Soil Sci. 41: 387-394.

Yadvinder-Singh and Beauchamp, E.G. 1989. Nitrogen transformations near urea in soil: effects of nitrification inhibition, nitrifier activity and liming. Fert. Res. 18: 201-212.

CHAPTER II. EFFECTS OF LIGNOSULFONATE ON C AND N DYNAMICS IN A CLAY SOIL

ABSTRACT

Lignosulfonate (LS) may have the potential to improve fertilizer nitrogen (N) retention in soils and phosphorus (P) solubility. Potential agricultural applications of LS requires an understanding of LS behaviour in soil. A laboratory study was conducted using five types of LS (NH_4, Ca, Ca desugared, Na and K) added to a heavy clay soil (Dalhousie, Orthic Humic Gleysol) at three rates (5, 10, & 20 % w/w). Microbial activity was monitored as CO_2 evolution throughout the study and extractable N and C were measured at the end of the incubation. High application rates initially inhibited and decreased maximum CO_2 evolution. A small proportion (<17%) of the added LS-C was evolved as CO_2, indicating that LS does not decompose readily. Up to 1.8% of the LS-C retained in the soil was extractable in 1N KCl suggesting that LS, after a period of incubation, may be relatively immobile in a soil profile. Ammonium-LS treated soils had lower LS-N recovery than the other LS's suggesting chemical reactions of NO_3-N with phenolic constituents of NH_4LS.

INTRODUCTION

Lignosulfonate (LS), a macromolecular lignin derivative, is a by-product of the acid sulfite pulping process. In this process, the pulping agent is a bisulfite with an excess of free sulfurous acid. A hydroxide base, commonly calcium (Ca), sodium (Na) or ammonium (NH_4), is added to neutralize the stronger sulfonic acid, forming bisulfite, to prevent undue degradation of cellulose (Glennie 1971). Various types of LS are therefore available, depending on the neutralizing base. Lignosulfonate is similar to soil organic matter in its surface charge and colloidal properties (Hoyt and Goheen 1971) but is highly soluble in water due to the presence of sulfonate groups (Reference Guide, Daishowa Chemicals). Lignosulfonate has been used as a micronutrient carrier because of its capacity to chelate metals (Browning 1975). Lignosulfonate applied in combination with Fe and Zn increased their availability to crops, correcting Fe chlorosis in grain sorgham (Cihacek 1984) and resulting in improved Zn uptake by rice (Sajwan and Lindsay 1988) and beans (Singh et al. 1986). Chelation of metals in soil may increase the availability of fertilizer P by reducing precipitation reactions, hence LS may also have the potential to increase the efficiency of macronutrient fertilizers. There is, however, a lack of information regarding the possible interaction between LS and macronutrients.

This study was part of a research project concerned with improving N and P fertilizer efficiency in corn production. The primary goal of the program was to utilize LS as a means of controlling fertilizer reactions and transformations in the soil. Xie et al. (1991) demonstrated that LS reduced fertilizer P retention in soil through the competition for adsorption sites between LS and added P. The potential use of LS as a fertilizer component requires an understanding of its behaviour in soil.

Studies on the decomposition of LS in soil have not been reported. Since LS is a lignin

derivative it may behave like lignin and be relatively resistant to enzymatic degradation (Azam et al. 1984; Janzen and Kucey 1988). The lignin content, therefore, may be the rate regulating factor in the decomposition of LS. In contrast to lignin, however, lignosulfonate is highly water soluble and may therefore be more easily degraded. Biodegradation research has shown that the lignin in LS is bioalterable and can be substantially biodegraded in pure microbial cultures (Glanser et al. 1981; Ludquist et al. 1977).

Nitrogen supply is an important factor in crop production and therefore the effect of LS on soil N transformations is of interest. Because of its high C:N ratio, LS is expected to immobilize N after addition to soil. If, however, LS is resistant to microbial degradation the immobilization effect may be minimal.

The objectives of this study were to determine the effects of various types and rates of LS on microbial activity and on soil C in a soil microsite, in laboratory incubated soils. A second objective was to evaluate soil N changes a microsite after incubation with LS.

MATERIALS AND METHODS

A surface sample (0-20 cm) of Dalhousie clay (Orthic Humic Gleysol) was air dried and passed through a 2 mm sieve, and 100 g samples weighed into 590 ml jars. The soil had the following properties: organic C content of 38.8 g/kg, clay content of 410 g/kg, cation exchange capacity of 26 cmole/kg, and a pH of 5.7. Five types of lignosulfonate (Table 1) at three rates (5%, 10%, and 20% w/w) were uniformly mixed through the soils. The application rates were selected to represent concentrations that might be found in a microsite adjacent to a fertilizer granule or band and were based on preliminary studies (R.J. Xie, personal communication) which indicated that LS pellets (0.3 -0.4 g) diffused a limited distance into the adjacent soil producing concentrations of 5 - 15%.

Table 1. Chemical properties of lignosulfonates (LS).

		NH_4LS^z	$CaLS^y$	$Ca(ds)LS^y$	$NaLS^z$	KLS^z
lignin (%)		65.0	n.a.	n.a.	65.0	60.0
sugars (%)		17.0	20.0	4.7	10.0	10.0
sulfur (%)		6.0	5.8	5.3	6.0	6.0
nitrogen -	total (%)	4.0	0.0	0.0	2.2	2.4
	NH_4 (%)	2.64	0.0	0.0	0.15	0.52
	NO_3 (%)	0.04	0.0	0.0	0.0	0.0
carbon (%)		40.1	49.2	45.1	52.5	46.7
pH		4.5	3.6	5.7	8.0	8.0

(ds) Desugared.
^{z,y} Received from Temfibre Inc, Temiscaming, Que., Canada and Daishowa Chemicals, Que. Canada, respectively.
n.a. Not available.
note: forms of LS depend on the neutralizing base.

The treatment mixture in each jar was maintained at 80% field capacity throughout the incubation by weekly additions of deionized water. Carbon dioxide evolution was used as an indication of microbial activity. Vials containing 25 mls of 2M NaOH solution were suspended above the soil mixtures to absorb CO_2. Jars were sealed and incubated in completely randomized arrangements at 24°C for 40 days. Sodium hydroxide solutions were replaced at intervals of 2-3 days, except for the last two dates which were replaced once a week, and absorbed CO_2 measured by titrating with 1M HCl, using phenophthalein as an indicator after adding 1M $BaCl_2$ to precipitate carbonates (Anderson 1982). After the incubation soil mixtures were oven dried (75°C) and ground to pass a 2 mm sieve. Subsamples were shaken with 1M KCl for 60 minutes and suspensions filtered using #2 Whatman filter papers. Filtrates were decolorized by shaking with C black (1.33:1 C black:filtrate ratio) for 30 minutes. Filtrates were centrifuged for 20 minutes and filtered through #42 Whatman filter papers. Ammonium-N and NO_3-N concentrations were measured by using standard colorimetric autoanalyzer techniques (Keeney and Nelson 1982).

Organic C in the 1M KCl extracts was determined using a modified Walkley Black method (Nelson and Sommers 1982).

Soil conductivity was measured in 1:5 soil to water suspensions.

Statistical Analysis

The general linear models procedure was followed for the analysis of variance involving treatment combinations composed of five types of LS and three rates. The method of polynomial contrasts (Gomez and Gomez 1984) was used to determine the relationships among LS rates for total CO_2 evolved, extractable C and soil mineral N . Mineralization and nitrification data were sorted by LS and rates were compared with the control using

single degree-of-freedom contrasts. Alpha was set at 0.01 to reduce experimentwise error. All statistical analyses were done using SAS (1984).

RESULTS AND DISCUSSION

Incubation system

The major constraint of any closed incubation system is maintenance of aeration. In this study incubation containers were opened for atmospheric exchange at intervals ranging from two to three days except at the end of the study when periods were approximately seven days. This aeration regime proved insufficient to maintain an adequate O_2 supply at the unexpectedly high levels of CO_2 evolution obtained in LS treatments, and anaerobic conditions (>70% of O_2 consumed) are suspected to have developed at several dates in all treatments. The duration of anaerobic conditions, calculated from CO_2 evolution rates and headspace volume assuming standard temperature and pressure and air O_2 content of 22%, varied among LS's and among LS addition rates. Addition of 5, 10 and 20% LS resulted in anaerobic conditions during 4-8%, 3-28% and 10-47% of the incubation periods respectively. All treatments became anaerobic on the date of maximum CO_2 evolution and 10 and 20% LS treatments were anaerobic toward the end of the experiment when aeration intervals were longer.

Fluctuations in soil aeration can be expected to affect both C and N dynamics in soil. The main effect on microbial respiration would be a delay in CO_2 evolution due to the production of other C compounds by fermentation. These compounds would be easily degraded in the presence of O_2 so that the effect in our study would have been to change the pattern of CO_2 evolution. Since each incubation container would have become aerobic every few days, the overall effect is expected to have been small. The greatest effect of

anaerobic conditions on N dynamics would have been the stimulation of denitrification and concomitant loss of N from the system. A N budget calculated for NH_4LS treatments, the worst-case treatment because of the high NH_4-N concentration, at the end of the incubation indicated that 18, 14 and 12% of added N was lost from the 5, 10 and 20% treatments respectively, probably through denitrification.

CO_2 Evolution and Organic C

The pattern of CO_2 evolution was similar for all LS types, but differed among LS addition rates (Fig. 1 and 2, (a) to (d)). Patterns of evolution for the other LS types are shown in appendix figures 2.1, 2.2 and 2.3. In particular, patterns in LS types in which the duration of anaerobic periods was minor (eg. NaLS, Fig. 2) were similar to those in LS types in which anaerobic periods were significant (eg. NH_4LS, Fig. 1) suggesting that fluctuating availability of O_2 did not distort the overall trend in CO_2 evolution. The control had relatively low and constant CO_2 evolution over the 40 day incubation. The slight increase in CO_2 evolution evident in the control at the beginning of the incubation (Fig. 1 and 2 (a)) was probably a result of rewetting the soil and stimulation of microbial activity (Stevenson 1956).

Lignosulfonate application rates of 5% and 10% immediately stimulated microbial activity and produced a distinct peak in CO_2 evolution within the first eight days of the incubation (Fig. 1 and 2, (b) and (c)). Increasing the LS rate from 5 to 20% decreased maximum CO_2 evolution and delayed the period of maximum evolution (Fig. 1 and 2, (b) to (d)). This trend did not appear to be a function of an O_2 limited system as the same pattern was evident in the NaLS treatments. The 20% rate inhibited microbial activity relative to the control within the first four to eight days of the incubation.

Microbial activity, in the 5 and 10% applications, may have been stimulated initially by

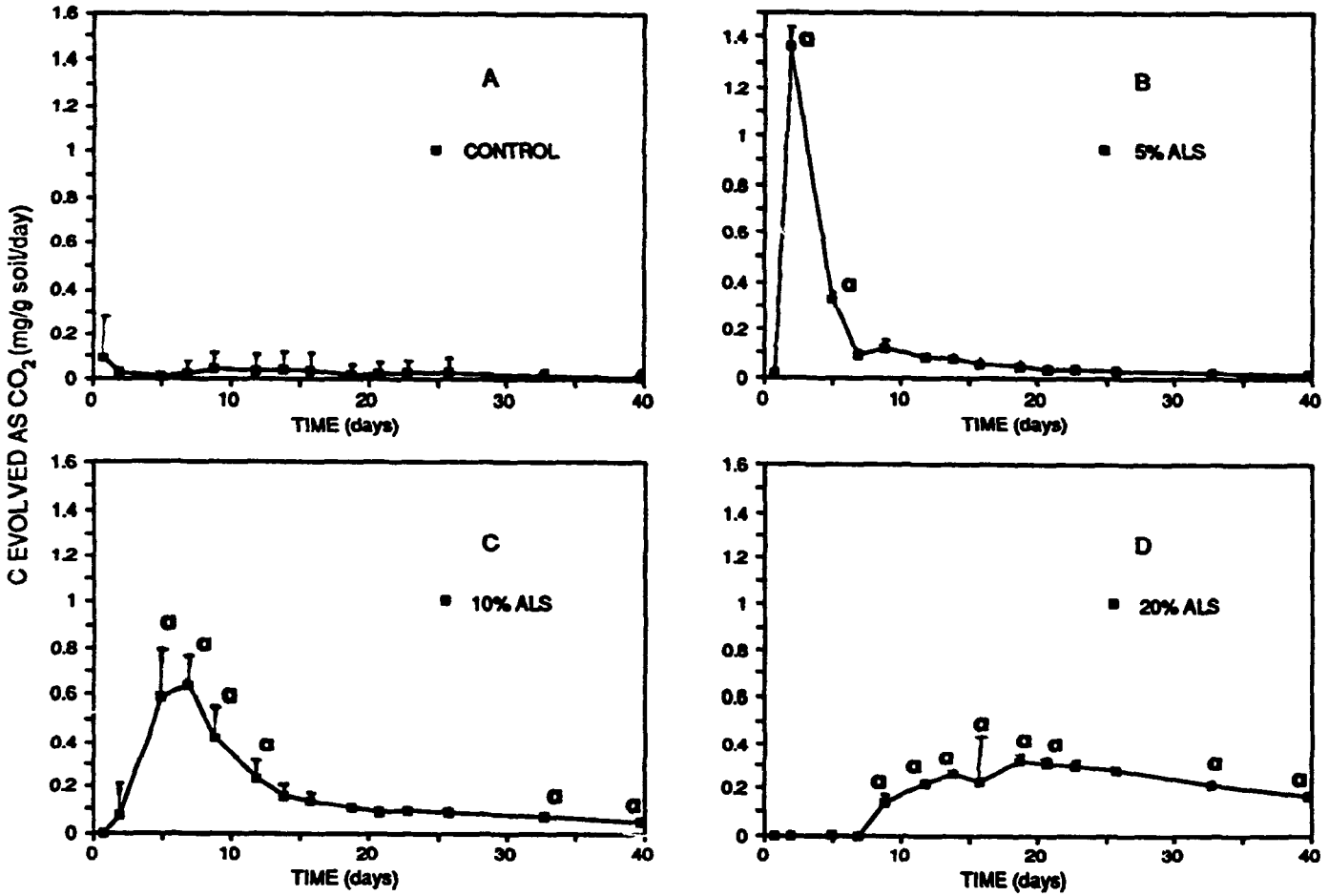


Fig. 1. C evolved as CO_2 (mg/g soil/day) in the (A) control, (B) 5% NH_4LS, (C) 10% NH_4LS, and (D) 20% NH_4LS treatments. Bars indicate upper 95% confidence limits. Dates ending periods in which >70% of O_2 in container headspace would have been consumed are indicated by "a". Note: ALS denotes NH_4LS.

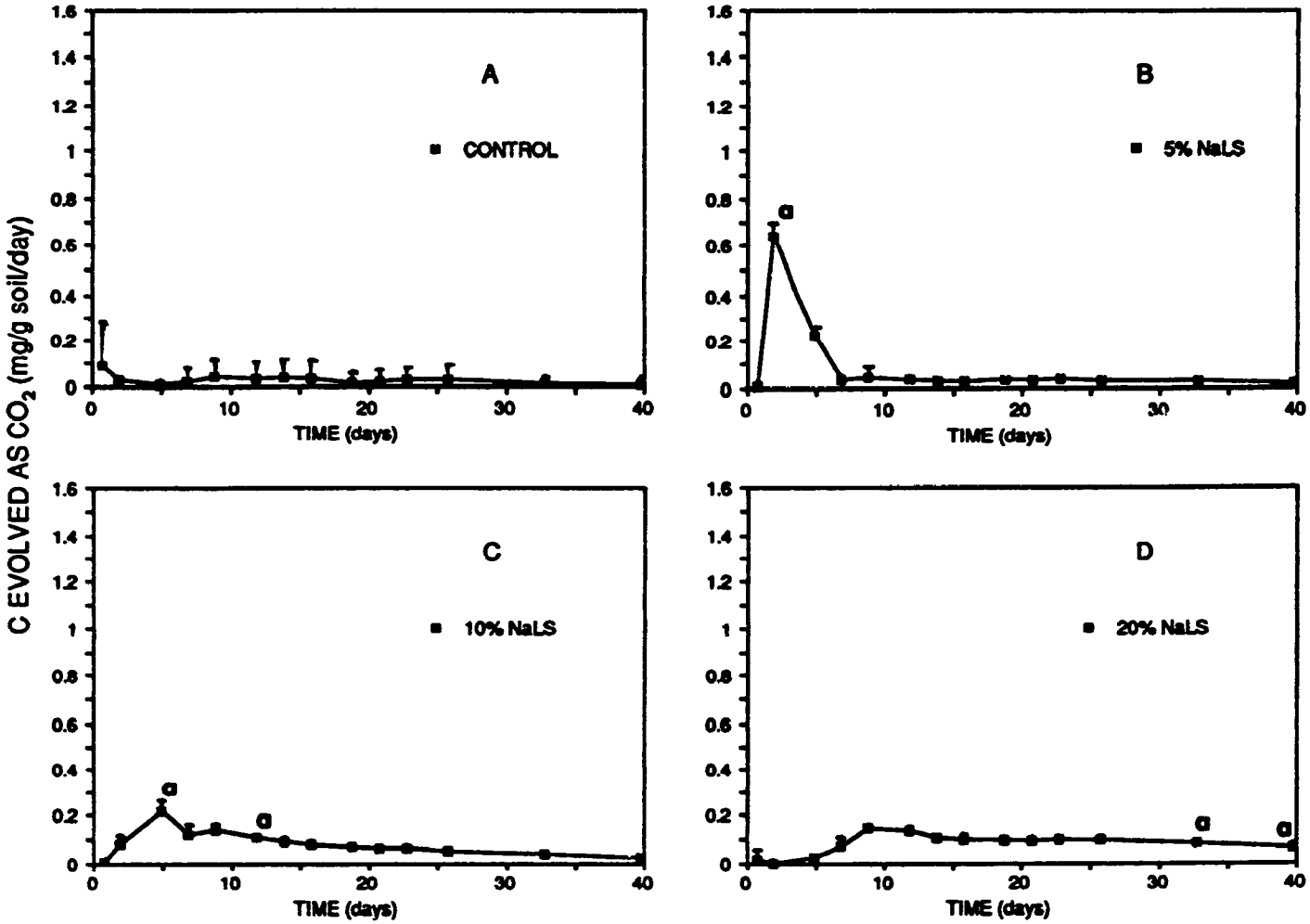


Fig. 2. C evolved as CO_2 (mg/g/day) in the (A) control, (B) 5% NaLS, (C) 10% NaLS, and (D) 20% NaLS treatments. Bars indicate upper 95% confidence limit. Dates ending periods in which >70% of O_2 in container headspace would have been consumed are indicated by "a".

the sugar content (Table 1) of the LS. Total CO_2 evolved as percent of LS added was similar to the sugar content of LS in all treatments except for Ca(ds)LS. At the high LS rates however, some inhibitory process appeared to override sugar stimulation of microbial activity. The inhibition diminished with time, perhaps as the inhibitory substance was degraded or shifts in the composition of the microflora occurred. The cause of the inhibition effect is unknown. The treatments had high electrical conductivities (8.1 to 30.9 mS/cm), suggesting that high salt contents may have inhibited microbial activity. Conductivity levels of 4 mS/cm have been shown to inhibit nitrification (Malhi and McGill 1982). The inhibition effect decreased with time, however, whereas salinity would have remained constant suggesting that salinity did not induce the inhibition effect. Phenolic compounds, derived from lignin in the LS, may have caused the inhibition because they have been shown to inhibit microbial activity (Rice and Pancholy 1972; 1973; Baldwin et al. 1983; Olsen and Reiners 1983) and are slowly degraded by microorganisms.

The diffusion of LS away from a fertilizer pellet or band would decrease its concentration as it moved into the soil at the perimeter of the microsite. Results indicate that microbial activity would be greatest in this perimeter area (low concentrations of LS) and that LS concentrations in the center of the band would inhibit biological activity. If fertilizer N were to be banded with LS, decreased N transformation rates might be expected in the center of the band whereas increased microbial immobilization might occur at the diffusion front.

Total C evolved as CO_2 from LS treatments was significantly higher ($p<0.0001$) than that evolved from the control (Table 2) indicating that LS stimulated CO_2 evolution. The proportion of added LS-C evolved as CO_2 during the incubation decreased with LS addition rate (Table 2) and CO_2 evolution was quadratically related to LS addition rate (Table 2), except for NaLS, again indicating that the high LS rate inhibited microbial activity relative

Table 2. C input and recovery after the 40 day incubation. Carbon recovered expressed as the absolute amount of C recovered as CO_2 and organic forms for each treatment and percent of added LS recovered.

Treatments		C Input	C Recovered			
			CO_2 evolved		extractable org C	
		(mg/g)	(mg/g)	(%)	(mg/g)	(%)
control		---	0.9	---	0.9	---
NH_4LS	5%	20.7	4.1_Q	15.4	1.0_Q	0.7
	10%	41.5	7.0_Q	14.6	1.6_Q	1.7
	20%	83.0	7.5_Q	8.0	2.0_Q	1.4
CaLS	5%	25.5	5.2_Q	17.0	1.1_Q	0.8
	10%	50.9	8.4_Q	14.8	1.6_Q	1.4
	20%	101.9	3.9_Q	3.0	1.9_Q	1.1
Ca(ds)LS	5%	23.3	3.4_Q	10.9	1.1_Q	1.1
	10%	46.7	4.4_Q	7.6	1.7_Q	1.8
	20%	93.4	3.1_Q	2.3	1.9_Q	1.1
NaLS	5%	27.2	2.5_{NS}	6.0	1.3_Q	1.5
	10%	54.3	3.1_{NS}	4.0	1.8_Q	1.7
	20%	108.7	3.4_{NS}	2.3	2.0_Q	1.0
KLS	5%	24.2	$2.7_{Q'}$	7.7	1.2_Q	1.2
	10%	48.3	$4.1_{Q'}$	6.7	1.7_Q	1.6
	20%	96.7	$3.8_{Q'}$	3.0	1.9_Q	1.0

(ds) Desugared.

$_{NS, Q', Q}$ Denote not related, quadratically related at $p<0.05$ and quadratically related at $p<0.01$, respectively.

to lower application rates. In all treatments, however, only a small proportion of added C was evolved as CO_2 (Table 2; (%CO_2)). This result is consistent with the expectation that LS would be resistant to decomposition, presumably because of its high lignin content.

A very small proportion of the LS retained in the soil was extractable in 1N KCL (Table 2; (C)). This suggests that after 40 days LS would be relatively immobile within the soil system, and that LS-fertilizer interactions would be limited to the band area.

Nitrogen

Small proportions (<32%) of added LS mineral N were recovered (Table 3) and mineral N levels in the Ca and Ca(ds)LS treatments were significantly lower than the control soil (Table 3).

Estimates of biomass N, calculated from total CO_2 evolution and by assuming a microbial utilization efficiency of 0.5 and a microbial C/N of 5, ranged from 500 to 1680 ug N/g soil. These calculated values are approximations because microbial utilization efficiency and C/N ratio may vary from 0.2 - 0.6 and 5 - 15 respectively (McGill et al. 1981), but suggest that the N deficit, except in the NH_4LS treatments, could have been caused by incorporation of N into microbial cells. Lowest mineral N recovery was in the NaLS treatments whereas the greatest recovery was in the KLS (5 and 10% rates, Table 3). Dominance of mineral N by NH_4 (Table 4) may suggest different remineralization rates, probably a function of the LS-C to mineral N ratios (KLS<NaLS). The addition of K^+, a strongly adsorbed cation, with N fertilizers has been shown to release clay fixed NH_4-N (Nommik and Vahtras 1982) which may have resulted in increased mineral N recovery in the KLS treatments. The cause of low mineral N recovery in the NH_4LS treatments is unknown. The dominance of mineral N by NH_4 (Table 4) suggests that periodic anaerobic conditions may have resulted in denitrification of NO_3-N from the mineral N pool. High salinity and NH_4-N concentration,

Table 3. Mineral LS-N (NH_4 + NO_3) added and mineral LS-N recovered at the end of the incubation.

Treatment		N Input	N Recovered	
		(ug/g)	(ug/g)	(%)
Control		--	81 (4)	--
NH_4LS	5%	1390	269^{NS} (78)	13
	10%	2770	511** (62)	15
	20%	5550	879** (85)	14
CaLS	5%	0	12** (3)	n.a.
	10%	0	10** (2)	n.a.
	20%	0	13** (2)	n.a.
Ca(ds)LS	5%	0	18** (3)	n.a.
	10%	0	9** (2)	n.a.
	20%	0	17** (3)	n.a.
NaLS	5%	79	60^{NS} (8)	-27
	10%	157	14** (3)	-43
	20%	314	16** (3)	-21
KLS	5%	272	168** (17)	32
	10%	544	196** (13)	21
	20%	1090	49^{NS} (10)	-3

^{NS}, ** Control not significantly different ($p>0.05$) and significantly different at $p<0.01$ from the rate, respectively.
( ) Standard errors of means (n=4).
n.a. Not applicable.

Table 4. Form of N accumulated (NH_4-N vs NO_3-N) in each treatment after the 40 day incubation. Accumulation expressed as NH_4-N minus NO_3-N.

	LS rate			
	0%	5%	10%	20%
			ug/g	
Control	-78.4 (4.0)			
NH_4LS	--	166.7^{NS} (57.2)	419.4** (57.8)	764.1** (82.4)
CaLS	--	10.4** (3.3)	9.4** (1.7)	10.9** (2.7)
CaLS (ds)	--	1.8** (3.7)	6.3** (1.4)	10.8** (2.6)
NaLS	--	-19.5** (5.2)	5.9** (1.5)	10.6** (2.7)
KLS	--	65.4** (10.6)	192.0** (13.3)	32.9** (10.3)

Positive values indicate dominance of N by mineral NH4.
^{NS} control not significantly different from the rate.
** control significantly different from the rate at $p<0.01$.
( ) standard errors of means (n=4).

however, are suspected to have inhibited nitrification (Mahli and McGill 1982; Jones and Hedlin 1970). Consequent NH_4-N accumulation may have caused chemical reactions of NH_3-N with phenolic components of LS (McClaugherty and Berg 1987). Mahli and McGill (1982), Smith and Chalk (1980) and Jones and Hedlin (1970) have reported that high NH_4-N and salt content inhibit *Nitrobacter* to a greater extent than *Nitrosomonas* and consequently an accumulation of NO_2-N may have occurred in our study. Chemical reactions between NO_2-N and phenolic constituents of soil organic matter have been shown to bring about deficits in mineral N and concomitant surpluses of non biomass organic N (Azhar et al. 1986a; 1986b; Smith and Chalk 1980). Concentrations of reactive phenolic groups would have been very high in the LS treatments and thus mineral N deficits may have occurred because of NO_2-N reactions with the lignin component of LS. Higher NH_4-N levels in the NH_4LS, relative to other LS's, may have promoted reactions with LS phenolic materials (Nelson 1982). Low pH might have also increased these reactions as well as gaseous loss of N as N_2 and N_2O (Bremner and Fuhr 1966).

CONCLUSIONS

High rates of LS initially inhibited microbial activity in soil. The small amount of C that was evolved as CO_2, indicated that LS in and around the band is resistant to decomposition and therefore remains present to participate in fertilizer-soil reactions. A small proportion of the LS-C was extractable in 1N KCl after 40 days, suggesting that most of the LS was strongly adsorbed to soil surfaces and thus supports the view that LS will coat soil surfaces and reduce P fixation. Mineral N added with NH_4LS is subject to loss, probably through chemical reaction between NO_2-N and phenolic groups of LS. The significance of such

reactions would be a build up of non biomass organic N and a decrease in NO_3-N levels subject to leaching. Whether such reactions will occur with added fertilizer N and whether chemically immobilized N can be remineralized requires further study.

REFERENCES

Anderson, J.P.E. 1982. Soil Respiration. Pages 831-866 *in* Page, A.L., Miller, R.H. and Keeney, D.R. Methods of Soil Analysis. Part 2. Agronomy No. 9, 2nd ed. Madison, Wis.

Azam, F., Haider, K. and Malik, K.A. 1984. Transformation of ^{14}C labelled plant components in soil in relation to immobilization and remineralization of ^{15}N fertilizer. Plant Soil 86: 15-25.

Azhar, E, Verhe, R., Proot, M., Sandra, P. and Verstaete, W. 1986a. Binding of nitrite-N on polyphenols during nitrification. Plant Soil 94: 369-382.

Azhar, E., Vandenabaeele, J. and Verstraete, W. 1986b. Nitrification and organic nitrogen formation in soils. Plant Soil 94: 383-399.

Baldwin, I.T., Olson, R.K. and Reiners, W.A. 1983. Protein binding phenolics and the inhibition of nitrification in subalpine balsam fir soils. Soil Biol. Biochem. 15: 419-423.

Bremner, J.M. and Fuhr, F. 1966. Tracer studies of the reaction of soil organic matter with nitrite. Pages 337-346 *in* The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting, Pergamon Press.

Browning, W. 1975. The Lignosulfonate Challenge. Pages 109-124 *in* Timell, T.E. ed. Proceedings of the 8th Cellulose Conference. 1. Wood Chemicals - A Future Challenge. Applied Polymer Symposium 28.

Cihacek, L.J. 1984. Economic soil treatment of iron chlorosis in grain sorghum grown on a gypsum affected soil. J. Plant Nutr. 7 (1-5): 329-340.

Glasner, M., Ban, S.N. and Cooney, C.L. 1981. Biodegradation of sodium sulfite liquor (NaSSL) and sodium lignosulfonate (NaLS) by a mixed culture of microorganisms. European J. Appl. Microbiol. Biotechnol. 13: 54-59.

Glennie, D.W. 1971. Reactions in sulfite pulping. Pages 597-637 *in* Freudenberg, C., Sarkanen, K.V., Ludwig, C.H. Lignins: occurrence, formation, structure and reactions. Wiley Interscience, New York.

Gomez, K.A. and Gomez, A.A. 1984. Statistical procedures for agricultural research, 2nd ed. John Wiley and Sons, Toronto, Ont.

Hoyt, C.H. and Goheen, D.W. 1971. Polymeric Products. CH. 20, Pages 833-839 *in* Freudenberg, C., Sarkanen, K.V. and Ludwig, C.H. eds. Lignins: Occurrence, Formation, Structure and Reactions. Wiley Interscience, N.Y.

Janzen, H.H. and Kucey, R.M.N. 1988. C, N and S mineralization of crop residues as influenced by crop species and nutrient regime. Plant Soil 106: 35-41.

Jones, R.W. and Hedlin, R.A. 1970. Ammonium, nitrite and nitrate accumulation in three Manitoba soils as influenced by added ammonium sulfate and urea. Can. J. Soil Sci. 50: 331-338.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen - Inorganic Forms. Pages 643-693 *in* Page, A.L., Miller, R.H. and Keeney, D.R. Methods of Soil Analysis. Part 2. Agronomy No. 9, 2nd ed. Am. Soc. Agron., Madison, Wis.

Ludquist, K., Kent, K.T. and Connors, W.J. 1977. Fungal degradation of kraft lignin and lignin sulfonates prepared from synthetic ^{14}C-lignins. Arch. Microbiol. 112: 291-296.

Malhi, S.S. and McGill, W.B. 1982. Nitrification in three Alberta soils: effect of temperature, moisture and substrate concentration. Soil Biol. Biochem. 14: 393-399.

McCarty, G.W. and Bremner, J.M. 1990. Evaluation of 3-methylpyrazole-1-carboxamide as a soil nitrification inhibitor. Biol. Fertil. Soils 9: 252-256.

McClaugherty, C. and Berg, B. 1987. Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition. Pedobiologia 30: 101-112.

McGill, W.B., Hurt, H.W., Woodmansee, R.G. and Reuss, J.O. 1981. Phoenix, a model of the dynamics of carbon and nitrogen in grassland soils. Pages 49-116 *in* Clark, F.E. and Rosswall, T. (eds). Terrestrial Nitrogen Cycles. Eco. Bull. 33: 49-116.

Nelson, D.W. 1982. Gaseous losses of nitrogen other than denitrification. Pages 327-363 *in* Stevenson, F.J. Nitrogen in Agricultural Soils. Agronomy No. 22. Am. Soc. Agron., Madison, Wisconsin.

Nelson, D.W. and Sommers, L.E. 1982. Total Carbon, organic carbon, and organic matter. Pages 539-577 *in* Methods of Soil Analysis. Part 2. Agronomy No. 9, 2nd ed. Madison, Wis.

Nommik, H. and Vahtras, K. 1982. Retention and fixation of ammonium and ammonia in soils. Pages 123-171 *in* Stevenson, F.J. Nitrogen in agricultural soils. Agronomy No. 22. Am. Soc. Agron., Madison, Wisconsin.

Olson, R.K. and Reiners, W.A. 1983. Nitrification in subalpine balsam fir soils: tests for inhibitory factors. Soil Biol. Biochem. 15: 413-418.

Reference Guide To Specialty Chemicals, Daishowa Chemicals, Quebec, Canada.

Rice, E.L. and Pancholy, S.K. 1972. Inhibition of nitrification by climax ecosystems. Amer. J. Bot. 59: 1033-1040.

Rice, E.L. and Pancholy, S.K. 1973. Inhibition of nitrification by climax ecosystems II.

Rice, E.L. and Pancholy, S.K. 1973. Inhibition of nitrification by climax ecosystems II. additional evidence and possible role of tannins. Amer. J. Bot. 60: 691-702.

Sajwan, K.S. and Lindsay, W.L. 1988. Response of flooded rice to various sources of zinc. J. Agric. Sci., Camb. 111:197-198.

SAS, 1984. SAS/EST^{TN}, User's Guide, Version 5th ed. SAS Institute Inc., Cary, North Carolina.

Singh, J.P., Karamanos, R.E., Lewis, N.G. and Stewart, J.W.B. 1986. Effectiveness of zinc fertilizer sources on nutrition of beans. Can. J. Soil Sci. 66: 183-187.

Smith, C.J. and Chalk, P.M. 1980. Fixation and loss of N during transformations of nitrite in soils. Soil Sci. Soc. Am. J. 44: 288-291.

Stevenson, F.J. 1982. Dynamics of soil nitrogen transformations. Pages 93-119 *in* Humus Chemistry: Genesis, Composition, Reactions. J. Wiley and Sons, New York.

Stevenson, I.L. 1956. Some observations of the microbial activity in remoistened air-dried soils. Plant Soil 8: 170-182.

Xie, R.J. Environmental Research and Engineering department, Alberta Research Council. P.O. Box 8330, Postal station F, Edmonton, Alberta, Canada.

Xie, R.J., Fyles, J.W., Mackenzie, A.F. and O'Halloran, I.P. 1991. Lignosulfonate effects on phosphate reactions in a clay soil: causal modelling. Soil Sci. Soc. Am. J. 55: 711-716.

Connecting Section

The first study was preliminary and addressed basic questions concerning LS behavior in a soil microsite. The study demonstrated that various forms of LS (NH_4, Ca, Ca-ds, Na and K) were not readily degraded and that higher concentrations inhibited microbial activity. The inhibitory effect of LS on biological activity at higher concentrations suggested that LS banded together with urea may decrease N transformations.

Nitrogen deficits in the NH_4LS treatment coupled with low estimates of N immobilization suggested possible chemical reactions between NH_3-N and/or NO_2-N and phenolic constituents of LS.

The following experiment was conducted to monitor the effects NH_4LS-fertilizer mixtures on microbial activity and N transformations in soil microsites.

Since the effect of all LS types on microbial activity was similar NH_4LS was chosen for future studies because of its N content.

CHAPTER III. EFFECTS OF LIGNOSULFONATE-FERTILIZER APPLICATIONS ON SOIL RESPIRATION AND N DYNAMICS

ABSTRACT

Lignosulfonate (LS) may have the potential to improve conventional nitrogen (N) fertilizer efficiency by inhibiting urease activity and nitrification as well as reducing NH_3-N volatilization by acting as an acidifying agent. On the other hand, added LS may stimulate microbial activity, hastening urea hydrolysis and nitrification.

A laboratory study was conducted using a silty clay loam incubated wth ammonium lignosulfonate (LS) (2.67 % w/w) in combination with diammoniumphosphate (DAP), urea (U) and U+DAP. The experiment monitored CO_2 evolution and NH_3-N volatilization for 69 days and extractable soil N periodically for 38 days.

Addition of LS initially increased CO_2 evolution, possibly supported by the sugar content (17%) of LS, but only a small proportion (10-22%) of the LS-C was evolved as CO_2. The proportion of added N volatilized from the LS+U treatment (25%) was lower than in the U treatment (31%). Lignosulfonate decreased urea hydrolysis slightly. A larger proportion of added inorganic N was recovered in the LS+fertilizer treatments, indicating that LS may increase fertilizer N availability. Lignosulfonate treatments accumulated N in the form of NH_4, suggesting that LS may inhibit nitrification.

INTRODUCTION

Lignosulfonate (LS), a soluble lignin derivative, is produced during the sulfite pulping process. It is a complex molecule carrying negatively charged sulfonate, hydroxyl, phenolic and carboxyl groups, which make it water soluble (Reference Guide, Daishowa Chemicals).

Research has indicated that LS may have beneficial applications in agriculture due to its capacity to chelate micronutrient fertilizers. Lignosulfonate applied in combination with micronutrients appears to enhance crop micronutrient availability and uptake (Sajwan and Lindsay 1988; Singh et al. 1986; Raese et al. 1986). Little work, however, has examined the interaction of LS with macronutrient fertilizers.

Potential NH_3-N and NO_3-N losses from N fertilizers have encouraged research on urease and nitrification inhibitors. Maintenance of added N as urea, by the activity of urease inhibitors, reduces the concentration of NH_4-N subject to volatile loss whereas maintenance of N as NH_4 reduces the concentration of NO_3-N subject to leaching. The phenolic nature of the LS suggested that it may possess some activity as a urease or nitrification inhibitor. Previous work (Chapter II) has indicated that NO_3-N concentrations in LS bands were reduced, possibly as a result of denitrification or chemical reactions between transient NO_2-N produced during nitrification and lignin constituents of LS (Azhar et al. 1986a; 1986b).

The objectives of this study were to evaluate the effects of LS on microbial activity (CO_2 evolution), NH_3-N volatilization and soil N dynamics in a fertilizer microsite containg urea and diammonium phosphate.

MATERIALS AND METHODS

A surface sample (0-15 cm) of an Ormstown silty clay loam (Orthic Humic Gleysol) was air dried, passed through a 2 mm seive and 100 g weighed into 590 ml incubation containers.

Eight treatments were applied; unamended (control), ammonium lignosulfonate (LS; Temfibre Inc., Temiscaming, Que.), urea (U), diammonium phosphate (DAP), U+DAP, LS+U, LS+DAP and, LS+U+DAP (Table 1). Formulations were based on the addition of constant LS and constant urea-N and (urea+DAP)-N, with urea being the primary N source.

Fertilizer-LS preparations were well mixed and pressed into pellets using an automatic pellet press. Magnesium stearate (0.5%) was added to facilitate pelleting.

The experiment was conducted to provide information about LS-fertilizer interactions that might occur in and around a fertilizer band. For this study pellets were placed in a band across the incubation container (7.5 cm dia.) 1 cm below the soil surface. Application rates (Table 1) were equivalent to 84 kg urea-N/ha in the field assuming 75 cm row spacing. The main limitation of this system was that diffusion into a large volume of soil was not possible. Hence, concentrations of mobile fertilizer components or derivatives (eg. NO_3-N) would probably have been higher in the incubated soil than in a field band situation. Jars were maintained at 80% (w/w) of field capactity.

Two series of containers were prepared, one (Series 1) for measurement of CO_2 evolution and NH_3-N volatilization and the other (Series 2) for destructive sampling and analysis of soil N fractions. In Series 1, treatments were replicated four times and incubation was for 69 days at 24° C. Vials containing 25 mls of 2M NaOH absorbed evolved CO_2. Excess NaOH was back titrated with 1N HCl to a phenolphthalein endpoint (Anderson 1982). Vials containing 25 mls of 4% H_3BO_3 absorbed volatilized NH_3-N. The NH_3-N was determined

Table 1. Treatment concentrations per 100 g soil.

Treatment	LS	U	DAP
		(g)	
Control	0.0	0.0	0.0
LS	2.67	0.0	0.0
U	0.0	1.01	0.0
LS+U	2.67	1.01	0.0
DAP	0.0	0.0	0.59
LS+DAP	2.67	0.0	0.59
U+DAP	0.0	0.74	0.59
LS+U+DAP	2.67	0.74	0.59

by titrating the H_3BO_3 with 0.05M H_2SO_4 using a Mettler DL-20 Automatic Titrator (Fenn and Kissel 1974). Solutions in the vials were replaced and analyzed every two to three days. In Series 2, treatments were replicated three times and incubation containers aerated every 2 days. Destructive soil samples were taken at 2, 4, 7, 11, 17, 26, 33, and 38 d. Samples were oven dried (75° C), ground to pass a 1 mm sieve and subsamples extracted in 1N KCl containing phenylmercuric acetate (5 ppm) to inhibit microbial transformations of N. Ammonium-N, NO_3-N and U-N were analyzed using standard colorimetric auto-analyzer techniques (Keeney and Nelson 1982; Bremner 1982). Soil pH was measured using a 1:1 soil to 0.01M $CaCl_2$ suspension.

Statistical Analyses

Analysis of variance and contrasts were used to compare treatments (SAS Institute Inc., 1984). Control values were subtracted from all samples. The amount of NH_4-N and NO_3-N added with the LS was subtracted from the corresponding soil NH_4-N and NO_3-N values before statistical analysis. Tukey's test was used to compare dates within treatments for inorganic N recovered ($(NH_4+NO_3+NH_3+U)$-N) because of its control of experimentwise error.

RESULTS AND DISCUSSION

CO_2 Evolution

The CO_2 evolved in the control was low and constant throughout the 69 day incubation (<0.05 mg/g soil/day, Appendix Fig. 3.1). In all treatments, CO_2 evolution reached a maximum rate within the first five days of the incubation and then decreased to a low and constant level (Fig. 1). Patterns of evolution for the other treatments are in appendix

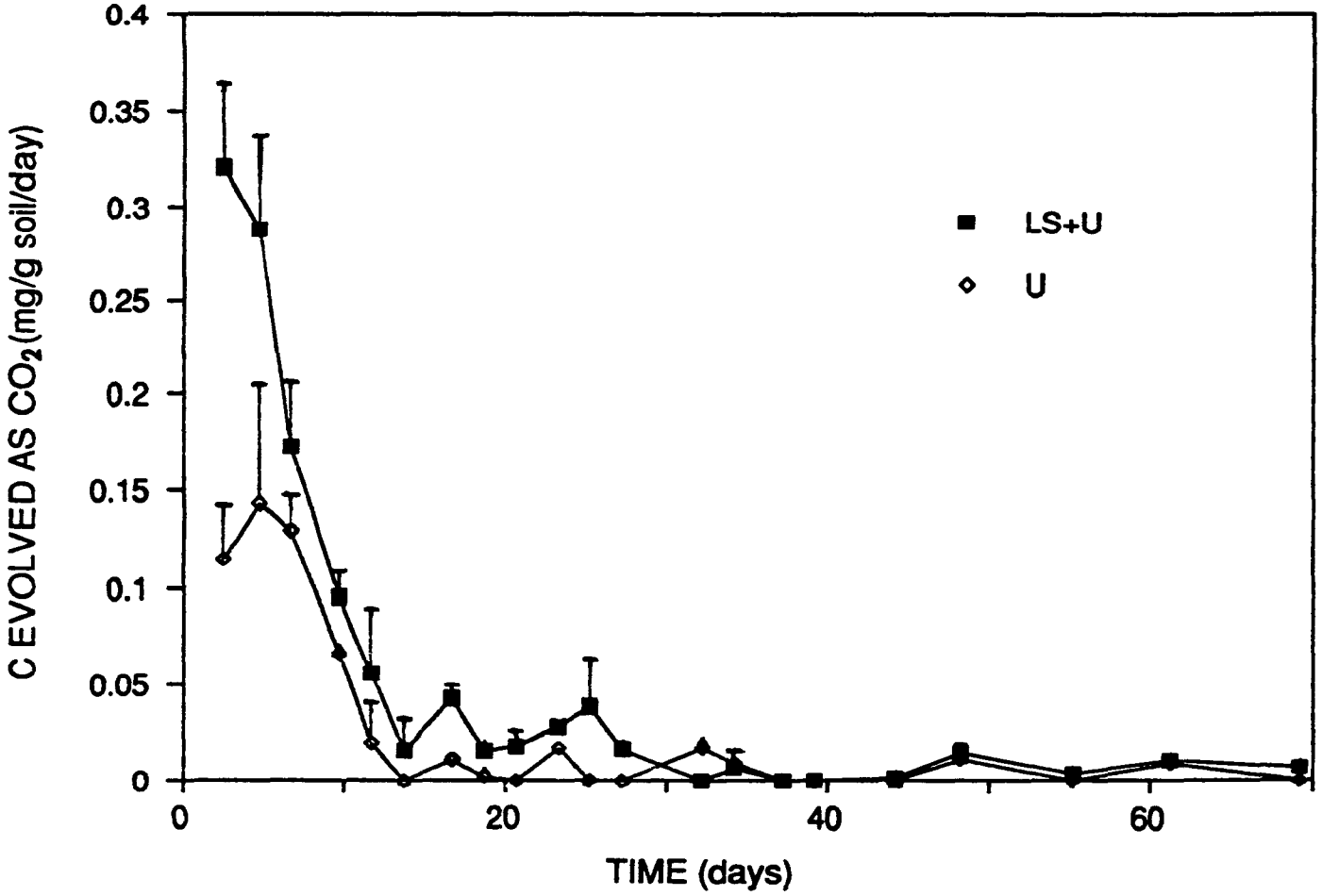


Fig. 1. C evolved as CO_2 (mg/g soil/day) during the 69 day incubation in the LS+U and U treatments. Patterns shown are typical of data from all treatments. Bars indicate upper 95% confidence limit.

figures 3.1, 3.2 and 3.3. Lignosulfonate treatments had higher levels of CO_2 evolution than treatments without LS (Fig. 1), indicating that LS within a fertilizer band would initially stimulate microbial activity. The highest CO_2 evolution occurred in the LS+U+DAP treatment (0.45 mg/g soil/day), probably because N or P were not limiting and the microorganisms were able to use LS-C more efficiently. Steady state CO_2 evolution was reached after 14 days in the LS and LS+DAP treatments but after 25 days in the LS+U and the LS+U+DAP treatments.

High initial levels of microbial activity in LS containing treatments were probably supported by the sugars (17%) contained in the LS (Reference Guide, Daishowa Chemicals). The cause of prolonged stimulation in the LS+U and LS+U+DAP treatments is unknown, but may have been the result of the larger amount of added N which may have allowed greater utilization of LS-C. Alternatively, urea has been shown to dissolve native soil organic matter (Foster et al. 1980; 1985), which may have promoted microbial activity.

Over the incubation period, only 10.4% to 22.2% of added LS-C was evolved as CO_2 (Appendix Table 3.1) in the LS treatments indicating that LS is resistant to microbial degradation and hence is retained in the soil.

Urea

Urea remained in the soil longer in the LS+U treatment than in the U treatment (Table 2), indicating a decrease in urea hydrolysis in the presence of LS. Research has indicated that humic substances, which may be similar to phenolics in LS, inhibit the urease enzyme (Al-Kanani et al. 1990; Tomar and MacKenzie 1984; Pflug and Zeichmann 1981). Lignosulfonate did not affect or increased urea hydrolysis when applied with U+DAP. Urea hydrolysis was faster with the addition of DAP (Table 2) and therefore the application of LS may not have been as effective in reducing hydrolysis. Higher microbial activity

Table 2. Urea N accumulated in the treatments (minus the control) over the 38 day incubation.

Treatment	Day							
	2	4	7	11	17	26	33	38
	(ug/g)							
U	4040^{**} (68)	2030^{NS} (87)	160^{NS} (35)	0^{*}	0^{NS}	0^{NS}	0^{NS}	0^{NS}
LS+U	4550 (135)	1880 (8)	220 (57)	130 (65)	50 (24)	0	0	0
U+DAP	2580^{NS} (20)	1200^{**} (24)	0^{NS}	0^{NS}	0^{NS}	0^{NS}	0^{NS}	0^{NS}
LS+U+DAP	2660 (99)	700 (90)	0	20 (13)	20 (13)	20 (14)	0	20 (13)

NS, *, ** Fertilizer treatment not significantly different ($p>0.05$), significantly different at $p<0.05$ and $p<0.01$, respectively, from the corresponding LS+fertilizer treatment (within date).

( ) Standard errors of means (n=3).

associated with the LS+U+DAP treatment may have stimulated urease production.

NH_3-N Volatilization

Relatively low and constant amounts (<0.17 ug/g soil/day) of NH_3-N were volatilized from the control and LS only treatment (Appendix Fig. 3.4). In all other treatments, NH_3-N volatilization reached a maximum rate during the first 7 days of the incubation (Fig. 2 A and B). Patterns of volatilization for the other treatments are in appendix figures 3.4 and 3.5. These results are consistent with other studies of NH_3-N loss following urea fertilization, that have shown maximum volatilization rates to occur up to the first 6 (Stevens et al. 1989) and 12 days (Bayrakli 1990) of incubation. Volatilization rate declined slowly following the maximum in the U, LS+U, U+DAP and the LS+U+DAP treatments (Fig. 2 A and B) but decreased rapidly in the DAP and LS+DAP treatments reaching steady state in <15 days (Appendix Fig. 3.5). During the first 7 days of the incubation the LS+U (Fig 2 A) and the LS+U+DAP (Fig. 2 B) treatments volatilized significantly more NH_3-N than U or U+DAP, respectively, suggesting that LS in the fertilizer band would initially promote NH_3-N loss. Subsequently, however, less NH_3-N was volatilized ($p<0.01$) from the LS+U (Fig. 2 (A)) treatment than the U treatment. Less NH_3-N was volatilized from the LS+U+DAP treatment than U+DAP only on the 17th day (Fig. 2 (B)). The LS+DAP treatment did not differ in NH_3-N volatilization from the DAP treatment throughout the incubation (appendix Fig. 3.5).

After 69 days, there was no significant difference in the absolute amount of N volatilized between the fertilizer and LS+fertilizer treatments (Table 3), indicating that LS did not reduce NH_3-N volatilization from urea fertilizer. But expressed on a basis of the proportion of added N volatilized, significantly less NH_3-N was volatilized from the LS+U treatment than from the U treatment (Table 3). Previous studies have demonstrated that NH_3-N loss

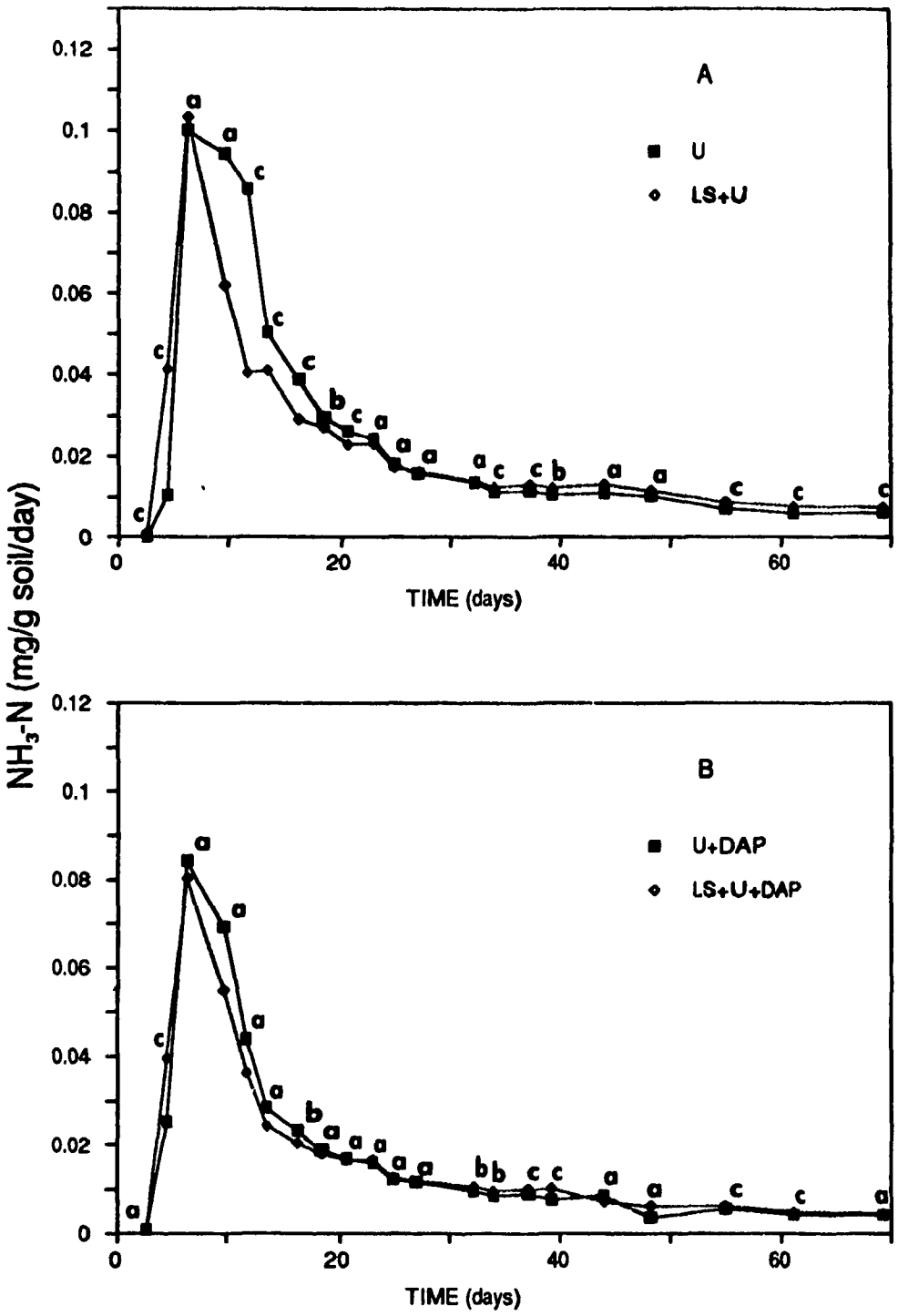


Fig. 2. NH_3-N (mg/g soil/day) volatilized during the 69 day incubation in the (A) LS+U and U treatments, (B) LS+U+DAP and U+DAP treatments. Letters, a to c, indicate no significant difference ($p>.05$), significant difference at $p<.05$ and $p<.01$, respectively, between the two treatments wthin date.

Table 3. Nitrogen input, NH_3-N volatilized (minus control) and, percent of N input volatilized during the 69 day incubation.

Treatment	N Input[z]	NH_3 Volatilized	
	(mg)	(mg)	(% of input)
LS	70	0.09 (.01)	0.13
U	475	146[NS] (11.3)	30.9*
LS+U	545	135 (5.7)	24.8
DAP	124	0.44[NS] (0.19)	0.36[NS]
LS+DAP	194	0.21 (0.05)	0.11
U+DAP	475	103[NS] (2.3)	21.8[NS]
LS+U+DAP	545	101 (2.9)	18.5

[z] Includes NH_4-N added with LS.

[NS], *, ** Fertilizer treatment not significantly different ($p>0.05$), Significantly different at $p<0.05$ and $p<0.01$, respectively, from corresponding LS+fertilizer treatment.

( ) Standard errors of means (n=4).

increases with increases in pH (Al-Kanani et al. 1990; Sullivan and Havlin 1988; Nelson 1982; Bundy and Bremner 1974; Watkins et al. 1972). Lignosulfonate significantly lowered the pH in the LS+U treatment but elevated or did not change the pH in the LS+U+DAP treatment (Table 4), suggesting that LS effects on pH may have caused the observed decrease in the proportion of N volatiled. Lignosulfonate is a colloidal material with net negative surface charges (Reference Guide, Daishowa Chemicals) and its application to soil would be expected to increase the soil cation exchange capacity and hence, may have decreased NH_3-N volatilization by adsorbing more NH_4-N (Nelson 1982). Inhibition of urease activity by LS, as previously discussed, may have contributed to reducing the proportion of N volatilized as NH_3-N.

Mineralization\Immobilization

Recovery of N as urea, NH_4, NO_3 and volatile NH_3 decreased in all treatments, except for LS+DAP, between days 2 and 7 (Table 5). This reduction in recovery coincided with the peak in CO_2 evolution, suggesting that the decrease may have been due to microbial immobilization. The subsequent increase in recovery in all treatments, except LS+U, suggests that a proportion of the immobilized N was remineralized after the 11^{th} day.

Recovery of N was low in treatments with fertilizer alone, particulary in the DAP treatment (Table 5). Estimates of microbial biomass-N in U and DAP treatments, calculated from the total CO_2 evolution and assuming microbial utilization efficiency of 0.5 and microbial C/N of 5, only ranged from 3.4 to 3.7% of added N. In these treatments a portion of this N deficit may have been a result of NH_4 fixation by clay minerals. Chen (1991) demonstrated that out of fertilizer applications of 0.84 mg urea-N/g and 0.42 mg NH_4Cl-N/g to the Ormstown soil 0.19 mg urea-N/g (23%) and 0.14 mg NH_4Cl-N/g (34%) were clay fixed. The requirement of urea hydrolysis before NH_4-N fixation may have lowered

Table 4. Soil pH, in 0.01 M $CaCl_2$, during the 38 day incubation.

Treatment	Day							
	2	4	7	11	17	26	33	38
Control	5.28** (0.01)	5.36** (0.01)	5.49** (0.01)	5.63** (0.02)	5.56** (0.01)	5.50** (0.02)	5.45NS (0.02)	5.48NS (0.02)
LS	5.40 (0.04)	5.00 (0.01)	5.26 (0.05)	5.46 (0.01)	5.50 (0.03)	5.41 (0.01)	5.41 (0.01)	5.31 (0.04)
U	7.29** (0.20)	8.00** (0.01)	7.46** (0.03)	7.51** (0.0)	7.76** (0.01)	7.60** (0.01)	7.48** (0.01)	7.55NS (0.01)
LS+U	6.89 (0.02)	7.33 (0.01)	7.08 (0.02)	7.33 (0.01)	7.67 (0.01)	7.48 (0.0)	7.30 (0.01)	7.32 (0.02)
DAP	5.89** (0.02)	5.87** (0.02)	5.92** (0.0)	6.04** (0.01)	6.07** (0.01)	5.94** (0.0)	5.77NS (0.06)	5.52NS (0.01)
LS+DAP	5.52 (0.02)	5.66 (0.01)	5.79 (0.01)	5.84 (0.03)	5.94 (0.01)	5.83 (0.0)	5.81 (0.01)	5.82 (0.46)
U+DAP	6.58NS (0.03)	7.18** (0.03)	6.63NS (0.01)	6.66** (0.02)	7.02** (0.0)	6.81** (0.02)	6.62NS (0.01)	6.74NS (0.02)
LS+U+DAP	6.59 (0.01)	6.67 (0.04)	6.63 (0.01)	6.85 (0.02)	7.33 (0.01)	7.08 (0.0)	6.69 (0.01)	6.76 (0.01)

NS, ** Fertilizer treatment not significantly different ($p>0.05$) and significantly different at $p<0.01$) from the corresponding LS+fertilizer treatment (within date),respectively.
( ) Standard errors of means (n=6).

Table 5. Nitrogen recovered (NH_4+NO_3+U+NH_3) in each treatment (minus the control) over the 38 day incubation.

Treatment	N Input[z]	Day							
		2	4	7	11	17	26	33	38
	(mg/100g)	(%)							
LS	71	40.6*a*	21.0*b*	-0.7*d*	5.7*cd*	27.3*b*	16.4*bc*	17.4*bc*	19.9*b*
U	475	**87.3*a*	**61.4*b*	**27.8*e*	**32.5*de*	**45.4*cd*	**47.5*bcd*	**48.4*bc*	**49.0*bc*
LS+U	546	113.6*a*	52.0*b*	52.9*b*	54.0*b*	62.0*b*	63.7*ab*	63.7*ab*	63.5*ab*
DAP	124	**36.6*a*	**23.3*bc*	**14.2*c*	**19.7*c*	**31.9*ab*	**40.4*a*	**40.5*a*	**40.8*a*
LS+DAP	195	86.1*a*	90.3*a*	86.2*a*	101.0*a*	107.4*a*	102.9*a*	112.9*a*	112.0*a*
U+DAP	475	NS76.3*a*	NS57.1*b*	**32.0*f*	**42.6*e*	**51.8*cd*	**51.9*cd*	**49.9*d*	**54.2*bc*
LS+U+DAP	546	96.0*a*	63.5*cd*	52.2*e*	58.6*de*	72.1*b*	71.9*b*	69.2*bc*	71.5*bc*

[z] Includes NH_4-N plus NO_3-N from LS.
Numbers in fertilizer treatments preceded by NS, ** are not significantly different ($p>0.05$) and significantly different at $p<0.01$, respectively from the corresponding LS+fertilizer treatment (within date).
Numbers followed by the same letters are not significantly different ($p>0.05$) between dates, according to Tukey's test.

NH_4-N fixation within the first few days in the U treatment in comparison to the DAP treatment.

Recovery of N was low in the LS treatment throughout the 38 days (Table 5) suggesting immobilization. Estimates of microbial N indicated that about 30% of the added LS-NH_4-N was incorporated into microbial biomass. This suggests that a large proportion of the N loss was not related to biological processes and may have been chemical in nature. Phenolic groups in lignin, similar to those in LS, have been shown to react chemically with NH_3-N (Nommik and Vahtras 1982; Stevenson 1982; Berg 1986; McClaugherty and Berg 1987) and with NO_2-N (Azhar et al. 1986a; 1986b) and such reactions may have removed inorganic N from the recovered pools. This phenomenon appeared to have been reduced with the addition of a N source. Recoveries above 100% in the LS+DAP treatment late in the incubation may indicate the mineralization of organic N added with the LS, however, dates within the LS+DAP treatment were not different suggesting that recoveries were probably not above 100%.

Larger proportions of added N were recovered in LS-fertilizer treatments throughout the incubation (Table 5). Differences in recovery appear to relate largely to the amount of mineral NH_4-N in LS treatments (Table 6). Lower total NH_3-N volatilization in LS treatments would have resulted in higher concentrations of NH_4-N but the reduction in volatilization was not sufficient to account for the substantial increase in NH_4-N concentration in LS treatments (Table 6). For instance, LS decreased NH_3-N volatilization in the LS+U treatment compared to the U treatment by approximately 50 ug/g on day 11 (Fig. 2 A) far lower than the 600 ug/g increase in NH_4-N in the LS+U treatment on that date (Table 6). The level of NH_4-N recovered within the first two days of the incubation (Table 6) is approximately 50% higher in LS treatments. The mechanisms that may have caused this effect are unknown but several mechanisms are possible. Lignosulfonate may

Table 6. Ammonium N accumulated in the treatments over the 38 day incubation. Control and NH_4-N added with the LS subtracted.

Treatment	Day							
	2	4	7	11	17	26	33	38
	(ug/g)							
U	260**	1010NS	1060**	1140**	1480**	1370**	1330**	1300**
	(4)	(30)	(43)	(21)	(4)	(31)	(14)	(8)
LS+U	1130	970	1820	1800	2140	2090	2010	1930
	(94)	(795)	(30)	(55)	(67)	(76)	(65)	(154)
DAP	520**	370**	260**	340**	490**	540**	520**	490**
	(28)	(12)	(9)	(15)	(36)	(12)	(9)	(12)
LS+DAP	1050	1160	1090	1410	1550	1480	1700	1680
	(92)	(83)	(42)	(142)	(53)	(131)	(156)	(110)
U+DAP	1170**	1620NS	1440**	1730**	2030**	1900**	1750**	1920**
	(31)	(10)	(19)	(19)	(29)	(53)	(32)	(9)
LS+U+DAP	2030	2160	2050	2200	2820	2690	2490	2550
	(30)	(51)	(22)	(43)	(60)	(97)	(28)	(63)

NS, *, ** Fertilizer treatment not significantly different ($p>0.05$), significantly different at $p<0.05$ and $p<0.01$, respectively, from the corresponding LS+fertilizer treatment (within date).

( ) Standard errors of means (n=3).

have become fixed onto soil particles and sufficiently coated clay minerals to block clay fixation of fertilizer NH_4-N and thus increased N availability, especially within the first two days of the incubation.

These data suggest that LS may enhance N recovery from a fertilizer band, thus increasing plant available N later in the growing season. As mentioned, the design of this study restricted diffusion of fertilizer materials and therefore, it is uncertain if the higher NH_4-N concentrations would remain in the band under field conditions. Lignosulfonate appears to be relatively immobile in soil (Chapter II) and therefore, it is possible that NH_4-N may become fixed onto the LS and thus be retained within the fertilizer band.

Nitrification

All treatments had lower levels of NO_3-N than the control (Table 7). High N application rates are suspected to have inhibited the nitrification process (Magalhaes and Chalk 1987) and, Malhi and McGill (1982) have demonstrated that the maximum tolerable NH_4-N concentrations for nitrification in soil is in the range of 400-800 mg/Kg, well below levels observed in some of the treatments. However, treatment effects caused by LS were apparent. In comparison to the corresponding treatments without LS, significantly less N accumulated in the form of NO_3 (Table 7). Lignosulfonate alone also decreased the production of NO_3-N in comparison to the control ($p<0.01$). The accumulation of NH_4-N and decrease in NO_3-N levels with time in LS treatments suggests that nitrification was inhibited. Phenolic compounds can also inhibit nitrification (Baldwin et al. 1983; Olson and Reiners 1983; Rice and Pancholy 1973) and such compounds derived from the LS may have added to the inhibitory effect. Inhibitory effects of phenolics or other processes (ie. salinity or NH_4-N) cannot be determined from the results of this study.

Increased NH_4-N recovery in LS+fertilizer treatments, as previously discussed, may

Table 7. Nitrate N accumulated in the treatments over the 38 day period. Control and NO_3-N added with the LS subtracted.

Treatment	Day							
	2	4	7	11	17	26	33	38
	(ug/g)							
U	-53**	-72**	-87**	-109**	-130**	-146**	-166**	-166**
	(0.5)	(0.4)	(0.5)	(0.4)	(0.3)	(0.4)	(0.1)	(0.2)
LS+U	-70	-94	-108	-107	-150	-166	-182	-182
	(0.4)	(2.3)	(0.1)	(0.3)	(0.3)	(0.0)	(0.1)	(0.6)
DAP	-56*	-74**	-84**	-95**	-84**	-33**	-8**	20**
	(0.5)	(0.1)	(0.4)	(0.5)	(8.4)	(2.0)	(1.3)	(3.4)
LS+DAP	-68	-89	-102	-124	-144	-159	-177	-175
	(0.1)	(0.4)	(0.2)	(0.2)	(0.1)	(0.3)	(0.5)	(0.9)
U+DAP	-52**	-70**	-83**	-104**	-127**	-144**	-164**	-163**
	(6.5)	(1.1)	(0.4)	(0.4)	(0.5)	(1.1)	(0.5)	(0.4)
LS+U+DAP	-68	-91	-108	-129	-150	-167	-186	-186
	(0.3)	(0.2)	(0.0)	(0.1)	(0.5)	(0.2)	(0.6)	(0.5)

*, ** Fertilizer treatment significantly different at $p<0.05$ and $p<0.01$, respectively, from the corresponding LS+fertilizer treatment (within date).
( ) Standard errors of means (n=3).
Negative values represent treatments with NO_3-N concentrations lower than the control.

therefore have been a result of nitrification inhibition.

The NH_4-N accumulation associated with nitrification inhibitors often promotes NH_3-N volatilization (Bundy and Bremner 1974), but this effect was not observed in this study, possibly due to higher amounts of NH_4-N on exchange sites. Consequently, LS may be an advantageous inhibitor when banded with urea.

CONCLUSIONS

Increased microbial activity within the fertilizer band was associated with LS treatments. Urea hydrolysis was reduced by addition of LS but the effect was probably too small to be of agronomic importance. Lignosulfonate, however, does hold promise as a fertilizer amendment as it significantly reduced the proportion of added N volatilized as NH_3-N, increased NH_4-N levels and decreased nitrification. Lignosulfonate may increase fertilizer N availibility and therefore field studies are required to determine whether LS will improve crop yields.

REFERENCES

Al-Kanani, T., MacKenzie, A.F. and Blenkorn, H. 1990. Volatilization of ammonia from urea-ammonium nitrate solutions as influenced by organic and inorganic additives. Fert. Res. 23: 113-119.

Anderson, J.P.E. 1982. Soil Respiration. Pages 831-866 *in* Page, A.L., Miller, R.H. and Keeney, D.R. (eds). Methods of Soil Analysis. Part 2. Agron. No. 9 2nd ed. Am. Soc. Agron., Madison, Wisconsin.

Azhar, E., Verhe, R. Proot, M., Sandra, P. and Verstaete, W. 1986a. Binding of nitrite-N on polyphenols during nitrification. Plant Soil 94: 369-382.

Azhar, E., Vandenabeete, J. and Verstraete, W. 1986b. Nitrification and organic nitrogen formation in soils. Plant Soil 94: 383-399.

Baldwin, I.T., Olson, R.K. and Reiners, W. A. 1983. Protein binding phenolics and the inhibition of nitrification in subalpine balsam fir soils. Soil Biol. Biochem. 15: 419-423.

Bayrakli, F. 1990. Ammonia volatilization losses from different fertilizers and the effect of several urease inhibitors, $CaCl_2$ and phosphogypsum on losses from urea. Fert. Res. 23: 147-150.

Berg, B. 1986. Nutrient release from litter and humus in coniferous forest soils - a mini review. Scand. J. For. Res. 1: 359-369.

Bremner, J.M. 1982. Nitrogen - Urea. Pages 699-890 *in* Page, A.L., Miller, R.H. and Keeney, D.R. eds. Methods of Soil Analysis. Part 2. Agronomy No. 9. Am. Soc. Agron., Madison Wisconsin.

Bundy, L.G. and Bremner, J.M. 1974. Effects of nitrification on transformations of urea nitrification in soils. Soil Biol. Biochem. 6: 369-376.

Chen, J.S. 1991. Effects of added nitrogen and potassium on selected soil properties and on yield and nutrient uptake of silage corn. M.Sc. Thesis. Department of Renewable Resources, Macdonald campus, McGill University, Montreal.

Fenn, L.B. and Kissel, D.E. 1974. Ammonium volatilization from surface applications of ammonium compounds on calcareous soils. II. Effects of temperature and rate of ammonium N application. Soil Sci. Soc. Am. Proc. 38: 606-610.

Foster, N.W., Beauchamp, E.G. and Corke, C.T. 1980. Microbial activity in a *Pinus Banksiana Lamb.* forest floor amended with N and C. Can. J. Soil Sci. 60: 199-209.

Foster, N.W., Beauchamp, E.G. and Corke, C.T. 1985. Reactions of ^{15}N-labelled urea with jack pine forest floor materials. Soil Biol. Biochem. 17(5): 699-703.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen - Inorganic Forms. Pages 643-693 *in* Page, A.L., Miller, R.H. and Keeney, D.R. eds. Methods of Soil Analysis. Part 2. Agronomy No. 9 2nd ed. Am. Soc. Agron., Madison Wisconsin.

Magalhaes, A.M T. and Chalk, P.M. 1987. Nitrogen transformations during hydrolysis and nitrification of urea. II. Effects of fertilizer concentration and nitrification inhibitors. Fert. Res. 11: 173-184.

Malhi, S.S. and McGill, W.B. 1982. Nitrification in three Alberta soils: effect of temperature, moisture and substrate concentration. Soil Biol. Biochem. 14:393-399.

McClaugherty, C. and Berg, B. 1987. Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition. Pedobiologia 30: 101-112.

Nelson, D.W. 1982. Gaseous losses of N other than through denitrification. Pages 327-363 *in* F.J. Stevenson ed. Nitrogen in Agriculatural Soils. Agron. No. 22. Am. Soc. Agron., Madison, Wisconsin.

Nommik, H. and Vahtras, K. 1982. Retention and fixation of ammonium and ammonia in soils. Pages 123-171 *in* Stevenson, F.J. ed. Nitrogen in Agricultural Soils. Agron. Monogr. No. 22. Agron. Soc., Madison, Wisconsin.

Olson, Richard K. and Reiners, William A. 1983. Nitrification in subalpine balsam fir soils: tests for inhibitory factors. Soil Biol. Biochem. 15: 413-418.

Pfulg, N.M. and Zeichmann, W. 1981. Inhibition of malate dehydrogenase by humic acids. Soil Biol. Biochem. 13: 293-299.

Rice, E.L. and Pancholy, S.K. 1973. Inhibition of nitrification by climax ecosystems. II. Additional evidence and possible role of tannins. Amer. J. Bot. 60(7): 691-702.

Raese, J.T., Parish, C.L. and Staiff, D.C. 1986. Nutrition of apple and pear trees with foliar sprays, trunk injections and soil applications of iron compounds. J. Plant Nutr. 9: 987-999.

Reference Guide to Specialty Chemicals, Daishowa Chemicals, Quebec, Canada.

Sajwan, K.S. and Lindsay, W.L. 1988. Response of flooded rice to various sources of zinc. J Agric. Sci. 111: 197-198.

SAS, 1984. SAS/EST™, User's Guide, Version 5_{th} ed. SAS Institute Inc., Cary North Carolina.

Singh, J.P., Karamanos, R.E., Lewis, N.G. and Stewart, J.W.B. 1986. Effectiveness of zinc fertilizer sources on nutrition of beans. Can. J. Soil Sci. 66: 183-187.

Stevens, R.J., Laughlin, R.J. and Kilpatrick, D.J. 1989. Soil properties related to the dynamics of ammonia volatilization from urea applied to the surface of acidic soils. Fert. Res. 20: 1-9.

Stevenson, F.J. 1982. Dynamics of soil nitrogen transformations. Pages 93-119 *in* Humus Chemistry: Genesis, Composition, Reactions. J. Wiley and Sons, New York.

Sullivan, D.M. and Havlin, J.L. 1988. Agronomic use of ammonium thiosulfate to improve nitrogen fertilizer efficiency. J. Fert. Iss. 5: 37-44.

Tomar, J.S. and MacKenzie, A.F. 1984. Effects of catechol and p-benzoquinone on the hydrolysis of urea and energy barriers of urease activity in soils. Can. J. Soil Sci. 64: 51-60.

Watkins, S.H.R.F., Strand, D.S., DeBell, D.S. and Esch (Jr.), J. 1972. Factors influencing NH_3 Losses from urea applied to northwestern forest soils. Soil Sci. Soc. Am. Proc. 36: 354-357.

Connecting Section

The previous studies demonstrated that LS either alone or in combination with fertilizer was not easily degraded, implying that a large proportion of added LS-C was retained in the soil. Initial calculations for the first experiment indicated that a large proportion of added LS-C was extractable in 1M KCl, suggesting that LS would be mobile within the soil system and may therefore pose a threat to groundwater quality. A leaching column system was set up to monitor the leaching of LS.

The calculations in the first study however, subsequently proved to be erroneous and recalculation of the extractable LS-C indicated that a very small proportion of LS-C was actually extractable in 1M KCL, suggesting that LS would not be mobile within a soil profile. The third study was therefore, implemented under an erroneous assumption.

The leaching study was, however, not fully unwarranted. Extractable C in the first study had been measured at the end of a 40 day incubation. This period would have allowed for microbial alteration of LS as well as soil-LS reactions, possibly rendering LS less mobile. Thus, the third study provided valuable information on LS leaching immediately following application.

CHAPTER IV. LEACHING OF LIGNOSULFONATE FROM SOIL COLUMNS AND LIGNOSULFONATE EFFECTS ON NITRATE LEACHING FROM UREA FERTILIZER

ABSTRACT

Lignosulfonate (LS) has shown potential as an additive to increase the efficiency of urea fertilizer but, because of its high solubility, may move with percolating water through the soil and thus pose a groundwater contamination risk. Movement of LS through columns of two contrasting soils (silty clay loam and heavy clay) under three moisture regimes (0.51, 0.90 and 1.80 cm H_2O/wk) was examined to determine the potential for LS to move through the soil. Leaching from LS treatments removed 0.15% - 2.1% of the added LS-C depending on water regime and soil. In both soils, significantly more C was leached from the high moisture regime than in the low moisture regime. Lignosulfonate-C leached through the Dalhousie soil in greater quantities than in the Ormstown soil (0.14% - 2.1% and 0.16% - 1.25%, respectively), suggesting that the mobility of LS may be dependent on soil type.

Leaching from U treatments removed 0.02% - 15.38% of the added N as NO_3 depending on soil type and moisture regime. Increasing moisture regime significantly increased NO_3-N leaching. Treatments containing LS decreased leachate NO_3-N, soil NO_3-N and increased soil NH_4-N compared to treatments without LS, suggesting that LS may decrease nitrification of native soil NH_4-N. Lignosulfonate, however, did not decrease NO_3-N leaching from urea fertilizer.

INTRODUCTION

Lignosulfonate (LS), a waste product from the sulfite pulping process, has the potential to be used in agricultural systems as a micronutrient (Sajwan and Lindsay 1988; Singh et al. 1986; Cihacek 1984) and macronutrient (Xie et al. 1991) carrier. Lignosulfonate, however, is highly soluble in water (Reference Guide, Daishowa Chemicals) and may therefore be mobile within a soil profile and pose a threat to groundwater quality.

The primary objective of the study was to determine the potential for LS to leach through a simulated plow layer in laboratory columns and to determine the effect of soil type and moisture regime on LS leaching. Previous experiments (Chapters II and III) indicated that LS may disrupt and/or inhibit nitrification, possibly by reacting with transient NO_2-N, and therefore, a secondary objective was to determine whether LS added with urea fertilizer would reduce leaching of NO_3-N through the soil column. Nitrate from agricultural sources is a major groundwater pollutant and the concern to protect groundwater quality is growing (Martinez and Guiraud 1990; Owens 1990). The purpose of the experiment was not to elucidate mechanisms, but to determine potential behavioral differences with respect to moisture regimes and soil.

MATERIALS AND METHODS

A free drainage system (system drained by gravity) was chosen because of inexpensive installation and easy maintenance. The leaching column setup consisted of a polypropylene container 12 X 9 cm in dimension, with a series of 4 mm (dia.) holes on the bottom to allow for drainage, above a polypropelene collection vessel.

Surface samples (0 - 20 cm) of two contrasting soils, an Ormstown silty clay loam (Orthic

Humic Gleysol) and a Dalhousie heavy clay (Orthic Humic Gleysol), were air dried and ground to pass a 2 mm sieve. A total of 970 g of each soil was placed into leaching columns by layers to ensure uniform bulk densities within and between columns.

Twelve treatment combinations were used; control (C), ammonium lignosulfonate (LS; Temfibre Inc., Temiscaming, Que.), urea (U) and LS+U at three moisture rates (0.51, 0.90 and 1.80 cm H_2O/week). The high moisture treatment was based on the average weekly rainfall data for the growing season (May to August inclusive) for the Ste. Anne de Bellevue area, Quebec (Canadian Climate Normals). Rainfall events were meant to simulate field conditions in a microenvironment within the plow layer after a heavy rain. Water was applied once a week for three months. The intention was to approximate uncropped field lysimeter conditions (Bergstrom 1990) as opposed to conventional laboratory leaching techniques. Laboratory leaching techniques are widely used to simulate short term reactions and transport of ions through soil columns (Phillips et al. 1988; Shaviv et al. 1986), whereas lysimeter studies are conducted under field conditions and allow for a more natural situation with more microbial interaction.

Leaching columns were sealed, preventing any evaporation losses. Lignosulfonate and urea were applied in pellets, 2 cm in diameter by 1 cm height. Lignosulfonate and urea application rates were equivalent to 2.5 g LS/container and 0.45 g N/container, respectively.

Prior to LS and U application, soil in the leaching columns was saturated with water and allowed to drain for three days to approximate field capacity. Fertilizer pellets were then placed at a 2.9 cm depth. The treatments were incubated for one week prior to the first 'rainfall' addition. The leachate was collected and the volume measured weekly for the duration of the experiment. Phenylmercuric acetate (PMA, 5 ppm) was added to each leachate container to inhibit enzyme activity in the leachate.

Leachate Organic C, NH_4-N and NO_3-N

The leachate was analyzed for organic C using a modified Walkley-Black procedure (Nelson and Sommers 1982). The leachate was analyzed for NH_4-N and NO_3-N using a Tecator steam distillation system (Bremner and Mulvaney 1982; Kjeltec Steam Distillation Manual). Values were multiplied by the corresponding volumes of drainage water to determine total fluxes.

Soil NH_4-N and NO_3-N

After 3 months, the soil columns were sampled in 5 depths (2, 2, 2, 3 cm and remainder). Soil samples were oven dried (75° C) and ground to pass through a 1 mm sieve. Soil subsamples were extracted with 1M KCl-PMA and analyzed for NH_4-N and NO_3-N using standard colorimetric auto-analyzer procedures (Keeney and Nelson 1982).

Statistical Analysis

For all variables measured, data had a non-normal distribution, with heterogeneous variances. A logarithmic transformation was applied prior to statistcal analysis. A four-way factorial model (LS, U, moisture and soil) was used to analyze for main effects and interactions. Interactions obtained were statistically significant but had low F values and were suspected to have been induced by strong main effects with high F values (M. Fanous, personal communication). Since main effects F values were high relative to interaction effect F values the interactions were considered relatively unimportant and consequently, the data was reanalyzed and interpreted as if there were no significant interactions. Thus, data was sorted by treatment (C, LS, U AND LS+U) to test for soil and moisture main effects and interactions. Moisture main effects and interactions were tested using polynomials. For discussion purposes, the original four-way ANOVA will be refered to as

the Main ANOVA whereas the data reanalyzed by sorting by treatment will be refered to as the Simplified ANOVA. Results are reported as means and 95% confidence limits calculated on the transformed data and retransformed to the linear scale. All statistical analysis was done using the SAS system (1984).

RESULTS AND DISCUSSION

Leaching Column Function

In a gravitational drainage system, the soil at the bottom of the column must become saturated before water can drain out of the column (Bergstrom 1990). This resistance arises from a surface tension at the soil-air boundary at the bottom of the column and can modify soil-water conditions throughout the soil column. This problem may have been important in this study, because of the shallow depth of the soil column, and may have resulted in imperfect drainage. At the end of the 3 month incubation, both soils were approxiamtely 6% above field capacity. Consequently, the column did not realistically simulate field conditions of saturation and drainage during and following rainfall events. The continually wet soil would have represented a 'worst case' condition in terms of leaching of LS-C through the column and the results are thus conservative. Soil saturation, and concomitant anaerobic conditions would also have increased denitrification, and thereby reduced nitrate accumulation and leaching, particularly in treatments with added C (Parsons et al. 1991; Christensen et al. 1990; Parkin 1987).

Total Leachate C

Total amounts of added C leached from the soil columns ranged from 0.15 to 2.1% of added LS-C (Table 1) depending on soil type and water regime as indicated by soil and

Table 1. Means of total leachate C (n=4), lower and upper 95% confidence limits and, percent of added LS-C leached after the three month incubation in the Ormstown and Dalhousie soils in the three moisture regimes (0.51, 0.90 and 1.80 cm H_2O/wk).

	Ormstown		Dalhousie	
Treatment	mg	%	mg	%
C 1[z]	4.3 (3.1,5.7)	n.a.	4.2 (3.7,4.6)	n.a.
C 2	6.4 (3.8,9.9)	n.a.	5.8 (5.1,6.5)	n.a.
C 3	9.2 (5.5,14.1)	n.a.	6.2 (4.2,8.6)	n.a.
LS 1	5.9 (3.4,9.3)	0.2	10.9 (5.6,18.9)	0.7
LS 2	10.2 (5.4,17.5)	0.4	23.0 (20.4,25.5)	1.7
LS 3	21.8 (10.9,38.6)	1.2	27.2 (21.6,32.9)	2.1
U 1	3.6 (1.6,6.9)	--	3.3 (1.9,5.2)	--
U 2	5.2 (2.3,10.3)	--	5.4 (1.9,12.8)	--
U 3	7.9 (5.0,11.6)	--	12.1 (6.6,21.3)	--
LS+U 1	8.4 (2.9,20.4)	0.4	10.8 (4.6,22.0)	0.7
LS+U 2	15.6 (8.6,25.7)	0.9	20.6 (17.5,23.7)	1.5
LS+U 3	19.2 (9.7,34.0)	1.0	7.7 (5.2,10.7)	0.1

n.a. Not applicable.
-- Not determined.
( ) Lower and upper 95% confidence limits, respectively.

[z] 1, 2, 3 Moisture regimes 0.51, 0.90 and, 1.80 cm H_2O/wk, respectively.

moisture effects obtained in the simplified ANOVA (Table 2). A main ANOVA (Appendix Table 4.20.) demonstrated that two 3-way interactions of LS by U by soil (F=5.34) and LS by U by moisture (F=3.80) were statistically significant at the 0.05 level, suggesting that the amount of C leached was also a function of LS and U application. The three-way interactions, however, were believed to have been induced by a strong LS main effect (F=158.53), and as a result interactions were considered not important. Lignosulfonate treatments leached more C (LS effect ($p<0.01$), Appendix Table 4.20) and behaved differently in the two soils (Table 1). Lignosulfonate applied alone leached significantly more C in the Dalhousie soil than the Ormstown (Table 1), indirectly indicating a LS by soil interaction and suggesting that the mobility of LS may be dependent on soil type. The Dalhousie is a heavy clay soil and may be more prone to developing larger, irregular pore cavities which would have facilitated C leaching. The lack of a soil by moisture interaction (Table 2) indicated that the leaching of added C with moisture regime followed the same trend in both soil types, and increased from low to high (Table 1), quadratically ($p<0.05$) in the LS+U treatment and linearly ($p<0.01$) in the remaining treatments (Table 2). This suggests that the potential for groundwater contamination with LS would be higher in regions with more humid climates or under management practices that promote water movement through soil. A very small percentage (<2.1%) of added LS-C, however, was leached from the high moisture regime.

Soil C, non transformed C data and C leached per week are presented in appendix tables 4.1 to 4.7.

Total Leachate NO_3-N and Soil NO_3-N

The percentage of added U-N leached as NO_3-N was low (Table 3). A greater proportion of NO_3-N was retained in the soil (Table 4), indicating that nitrification was active in the

Table 2. Table of probabilities from simplified ANOVA of leachate C, NH_4-N and NO_3-N and soil NH_4-N and NO_3-N.

Effect	Control	U[Y]	LS[Y]	LS+U
Leachate C				
SOIL	0.07	0.51	0.01	0.36
MOIST[Z]	0.01_{L}	0.01_{L}	0.01_{L}	$0.01_{Q'}$
SOIL*MOIST	0.26	0.49	0.20	0.68
Leachate NH_4-N				
SOIL	0.03	0.78	0.18	0.01
MOIST	0.25	0.77	0.04_{L}	0.68
SOIL*MOIST	0.78	0.44	0.12	0.17
Leachate NO_3-N				
SOIL	0.63	0.19	0.63	0.04
MOIST	0.01_{L}	0.03_{L}	0.01	$0.01_{Q'}$
SOIL*MOIST	0.32	0.86	$0.01_{Q1,L2}$	0.61
Soil NH_4-N				
SOIL	0.03	0.78	0.18	0.01
MOIST	0.25	0.77	$0.04_{Q'}$	0.68
SOIL*MOIST	0.78	0.44	0.12	0.17
Soil NO_3-N				
SOIL	0.05	0.07	0.01	0.34
MOIST	0.44	0.01_{L}	0.34	0.01_{Q}
SOIL*MOIST	0.22	0.10	0.62	$0.05_{NS1,Q2}$

n.a. Not applicable.

$_{NS, L, Q}$ Not related ($p>0.05$), linearly and quadratically related at $p<0.01$, respectively.

$_{L', Q'}$ Linearly and quadratically related at $p<0.05$, respectively.

$_{1, 2}$ Ormstown and Dalhousie soil, respectively.

[Z] MOIST denotes moisture regime.

[Y] LS, U denote lignosulfonate and urea treatments, respectively.

Table 3. Means of total leachate NO_3-N (n=4), lower and upper 95% confidence limits and percent of added N leached as NO_3-N after the three month incubation in the Ormstown and Dalhousie soils in the three moisture regimes (0.51, 0.90 and 1.80 cm H_2O/wk).

	Ormstown		Dalhousie	
Treatment	mg	%	mg	%
C 1[z]	0.5 (0.2, 1.0)	n.a.	0.2 (0.1,0.6)	n.a.
C 2	0.5 (0.3,0.8)	n.a.	0.5 (0.1,2.8)	n.a.
C 3	3.0 (1.9,4.4)	n.a.	3.9 (2.2,6.3)	n.a.
LS 1	0.4 (0.1,1.4)	0.0	0.2 (0.1,0.3)	0.0
LS 2	2.8 (0.9,7.4)	2.3	0.9 (0.3,2.0)	0.4
LS 3	0.8 (0.3,1.8)	0.0	3.7 (1.6,7.5)	0.0
U 1	5.9 (0.9,105.5)	1.2	16.5 (1.9,98.0)	3.6
U 2	9.9 (1.9,38.5)	2.1	21.1 (1.6,184.7)	4.6
U 3	51.0 (29.6,80.3)	10.7	70.8 (43.6,105.9)	15.0
LS+U 1	0.9 (0.1,9.2)	0.1	5.2 (0.1,113.3)	0.9
LS+U 2	1.1 (0.1,7.5)	0.1	1.7 (1.1,2.3)	0.2
LS+U 3	20.3 (3.2,94.4)	3.2	85.2 (54.0,124.5)	14.8

n.a. Not applicable.
( ) Lower and upper 95% confidence limits, respectively.

[z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.

Table 4. Means of soil NO_3-N (n=4), lower and upper 95% confidence limits and percent of N added recovered as NO_3-N after the three month incubation in the Ormstown and Dalhousie soils in the three moisture regimes (0.51, 0.90 and 1.80 cm H_2O/wk).

	Ormstown		Dalhousie	
Treatment	mg	%	mg	%
C 1[z]	5 (3,9)	n.a.	9 (3,24)	n.a.
C 2	11 (1,69)	n.a.	12 (3,33)	n.a.
C 3	4 (2,7)	n.a.	17 (8,31)	n.a.
LS 1	6 (5,7)	1	27 (9,65)	17
LS 2	6 (4,7)	0	15 (3,49)	3
LS 3	5 (3,8)	1	15 (6,33)	0
U 1	180 (66,418)	39	213 (151,283)	44
U 2	163 (99,246)	34	80 (62,100)	15
U 3	73 (54,93)	15	45 (18,99)	6
LS+U 1	93 (31,235)	16	190 (97,334)	33
LS+U 2	43 (9,156)	6	14 (3,49)	0
LS+U 3	61 (22,140)	10	38 (31,44)	4

n.a. Not applicable.
( ) Lower and upper 95% confidence limits, respectively.

[z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.

soils and NO_3-N leaching was ineffective. Leaching of NO_3-N varied with treatment, soil type and moisture regime (Table 2). A 3-way interaction of LS by U by moisture (F=7.14), was evident in the main ANOVA (Appendix Table 4.20.), indicating that the effect of water regime was modified by LS and U application. The interaction, however, was not believed to have been important because of a strong U main effect (F=135.54). A LS effect ($p<0.01$), Appendix Table 4.20) indicated that less NO_3-N was leached from LS containing treatments (Table 3). An interaction between LS and U (Appendix Table 4.20) had a low F value (11.65) and was believed to have been unimportant because of a strong U main effect (F value 135.54). The lack of interaction suggests that LS did not significantly reduce NO_3-N leaching from the U fertilizer. The simplified ANOVA (Table 2) indicated that the leaching of NO_3-N from the LS treatment was not dependent on soil whereas in the LS+U treatment more NO_3-N was leached from the Dalhousie soil. This may suggest that NO_3-N leaching from urea fertilizer in combination with LS is dependent on soil type. The simplified ANOVA (Table 2) indicated that NO_3-N leaching increased linearly ($p<0.01$) with moisture regime in the C, and U treatments and quadratically ($p<0.05$) in the LS+U treatment, respectively (Table 3). There was a soil by moisture interaction (Table 2) in the LS treatment indicating that the amount of NO_3-N leached increased quadratically ($p<0.01$) and linearly ($p<0.01$) in the Ormstown and Dalhousie soils, respectively (Table 3). The increased NO_3-N leaching with increased moisture rates is consistent with other studies that found that NO_3-N leaching from N fertilizers increased with high levels of irrigation (Owens 1990) and that most NO_3-N was removed during the winter and spring periods when percolate volumes were greatest (Stevenson and Neilson 1990).

The amount of NO_3-N retained in the soil varied with treatment, soil and moisture (Table 2). The main ANOVA indicated that LS interacted with moisture (F value 6.05, Appendix Table 4.21), the interaction was believed to have been important as it did not

appear to have been induced by strong LS and moisture effects (F values 4.34 and 9.42, respectively), suggesting that the amount of NO_3-N retained in LS treatments varied with moisture regime. A LS effect ($p<0.01$, Appendix Table 4.21) demonstrated that less soil NO_3-N was recovered in LS containing treatments (Table 4). Lower leachate NO_3-N and soil NO_3-N recovered in treatments containing LS may suggest that LS reduced nitrification or because of the C supply increased denitrification (Aulakh and Rennie 1987).

Significantly more soil NO_3-N was recovered in the LS treatment in the Dalhousie soil than in the Ormstown soil (Table 2 and 4), but, the leaching data for the LS treatment (Table 3), indicated that both soils leached similar amounts of NO_3-N. When LS was in combination with U, the amount of soil NO_3-N recovered was similar in both soils (Table 2) and more NO_3-N was leached from the Dalhousie soil (Table 2 and 3). This may indicate that the Dalhousie soil had a higher nitrification capacity than the Ormstown soil, but the reason for reduced NO_3-N leaching from the LS treatment in the Dalhousie soil is unknown.

Non transformed NO_3-N data and NO_3-N leached per week are presented in appendix tables 4.8 to 4.13.

Total Leachate NH_4-N and Soil NH_4-N

Only a small percentage of added N was leached out as NH_4-N, as would be expected for a cationic species (Table 5), and NH_4-N leaching was a function of treatment, soil and moisture (Table 2). The main ANOVA (appendix Table 4.21.) indicated a LS by U by moisture interaction (F=3.18), however, it was suspected to have been induced by strong U and moisture main effects (F=33.23 and 61.29, respectively), and thus considered not important. The simplified ANOVA (Table 2) demonstrated that more NH_4-N was leached from the the Dalhousie soil in the C and LS+U treatments than in the Ormstown soil (Table 4), suggesting that NH_4-N leaching was a function of soil and treatment. Moisture regime

Table 5. Means of total leachate NH_4-N (n=4), lower and upper 95% confidence limits and percent of added N leached as NH_4-N after the three month incubaion in the Ormstown and Dalhousie soils in the three moisture regimes (0.51, 0.90 and 1.80 cm H_2O /wk).

	Ormstown		Dalhousie	
Treatment	mg	%	mg	%
C 1[z]	0.2 (0.1,0.3)	n.a.	0.7 (0.5,0.9)	n.a.
C 2	0.7 (0.3,1.5)	n.a.	1.3 (0.3,4.6)	n.a.
C 3	0.6 (0.2,1.4)	n.a.	2.6 (0.9,5.9)	n.a.
LS 1	0.2 (0.1,0.6)	0.0	0.7 (0.3,1.5)	0.0
LS 2	0.6 (0.1,2.6)	0.0	1.8 (0.9,3.3)	0.6
LS 3	1.9 (0.7,4.2)	1.3	3.3 (1.6,5.9)	0.7
U 1	0.5 (0.3,0.8)	0.1	1.0 (0.7,1.3)	0.1
U 2	0.7 (0.3,1.3)	0.0	2.7 (0.9,6.9)	0.3
U 3	3.2 (1.6,5.6)	0.6	7.1 (3.8,12.0)	1.0
LS+U 1	0.9 (0.5,1.3)	0.1	1.3 (0.4,3.2)	0.1
LS+U 2	1.1 (0.6,2.1)	0.1	2.1 (1.1,3.7)	0.1
LS+U 3	2.7 (1.3,5.0)	0.4	5.0 (2.5,8.9)	0.4

n.a. Not applicable.
( ) Lower and upper 95% confidence limits, respectively.

[z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.

had an effect only in the LS treatment, (Table 2) in which NH_4-N leaching increased linearly ($p<0.01$), and may have been due to increased LS leaching.

As expected, a larger proportion of NH_4-N was retained in the soil (Table 6) than lost in leachate. A LS effect ($p<0.01$, Appendix Table 4.21) indicated that in LS containing treatments more NH4-N accumulated in the soil. This NH_4-N accumulation may suggest that LS inhibited nitrification rather than stimulated denitrification. Significantly more NH_4-N from the LS+U treatment was retained in the Ormstown compared to the Dalhousie soil (Table 2 and 6). This NH_4-N accumulation, coupled with the lower leachate NO_3-N levels, suggests that there was less nitrifying activity in the Ormstown soil than in the Dalhousie soil.

Non transformed NH_4-N data and NH_4-N leached per week are presented in appendix tables 4.14 to 4.19.

Table 6. Means of soil NH_4-N (n=4), lower and upper 95% confidence limits and percent of added N recovered as NH_4-N in the soil columns after the three month incubation in the Ormstown and Dalhousie Soils in the three moisture regimes (0.51. 0.90 and 1.80 cm H_2O/wk).

	Ormstown		Dalhousie	
Treatment	mg	%	mg	%
C 1	93 (81,105)	n.a.	59 (52,65)	n.a.
C 2	115 (57,205)	n.a.	93 (25,281)	n.a.
C 3	101 (78,126)	n.a.	64 (48,82)	n.a.
LS 1	110 (56,193)	17	129 (72,208)	70
LS 2	85 (63,109)	0	78 (64,92)	0
LS 3	181 (88,331)	80	100 (50,180)	36
U 1	163 (98,249)	16	88 (62,118)	6
U 2	208 (112,348)	21	119 (19,560)	6
U 3	154 (114,198)	11	87 (73,101)	5
LS+U 1	249 (156,499)	37	126 (49,276)	12
LS+U 2	482 (192,1039)	67	70 (55,85)	0
LS+U 3	304 (119,668)	37	89 (76,103)	5

n.a. Not applicable.
( ) Lower and upper 95% confidence limits, respectively.

[z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.

CONCLUSIONS

Small proportions of added LS-C leached indicate that LS application to soil is unlikely to pose a threat to groundwater quality. Leaching loss, however, was higher in the heavy clay than in the clay loam soil and losses were higher in wetter soils. Leaching loss of LS applied in the early spring may therefore, be greatest if heavy rains occur. An accumulation of soil NH_4-N relative to NO_3-N in LS containing treatments suggests that LS may decrease nitrification. Lignosulfonate did not, however, decrease NO_3-N leaching from the urea treatments, suggesting that LS may have little agronomic value for this use.

REFERENCES

Bergstrom, L. 1990. Use of lysimeters to estimate leaching of pesticides in agricultural soils. Envir. Polln. 67: 325-347.

Bremner, J.M. and Mulvaney, C.S. 1982. Nitrogen - total. Pages 595-622 *in* Page, A.L, Miller, R.H. and Keeney, D.R. Methods of soil analysis part 2. Agron. No. 9, 2nd ed. Am. Soc. Agron., Madison, Wisconsin.

Christensen, Soren, Simkins, Stephen and Tiedje, James M. 990. Temporal patterns of soil denitrification: their stability and causes Soil Sci. Soc. Am. J. 54· 1614-1618.

Cihacek, L.J. 1984. Economic soil treatment of iron chlorosis grain sorghum grown on a gypsum affected soil. J. Plant Nutr. 7: 329-340.

Canadian Climate Normals, Precipitation 1951-1980, Vol. 3. Environment Canada.

Fanous, M. Department of Plant Science, McGill University, Macdonald campus, Ste. Anne de Bellevue, Que.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen - inorganic forms Pages 643-693 *in* Page, A.L., Miller, R.H. and Keeney, D.R. Methods of Soil analysis part 2. Agron. No. 9, 2nd ed. Am. Soc. Agron., Madison, Wisconsin.

Kjeltec Steam Distillation Manual, distilling unit 1002. Tecator AB. Box 70, S-263 21, Hoganas, Sweden.

Martinez, J. and Guiraud, G. 1990. A lysimeter study of the effects of a ryegrass catch crop, during a winter/maize rotation, on nitrate leaching and on the following crop. J. Soil Sci. 41: 5-16.

Nelson, D.W. and Sommers, L.E. 1982. Total carbon, organic carbon and organic matter. Pages 539-577 *in* Page, A.L., Miller, R.H. and Keeney, D.R. Methods of soil analysis part 2. Agron. No. 9, 2nd ed. Am. Soc. Agron., Madison, Wisconsin.

Owens, L.B. 1990. Nitrate-nitrogen concentrations in percolate from lysimeters planted to a legume-grass mixture. J. Environ. Qual. 19: 131-135.

Parkin, T. 1987. Soil microsites as a source of denitrification variability. Soil Sci. Soc. Am. J. 51: 1194-1199.

Parsons, L.L., Murray, R.E. and Smith, M. S. 1991. Soil denitrification dynamics: spatial and temporal variations of enzyme activity, populations, and nitrogen gas loss. Soil Sci. Soc. Am. J. 55: 90-95.

Phillips, I.R., Black, A.S. and Cameron, K.C. 1988. Effect of cation exchange on the ditribution and movement of cations in soils with variable charge. II. Effect of lime or phosphate on potassium and magnesium leaching. Fert. Res. 17: 31-46.

Reference Guide to Specialty Chemicals, Daishowa Chemicals, Quebec, Canada.

Sajwan, K.S. and Lindsay, W.L. 1988. Response of flooded rice to various sources of zinc. J. Agric. Sci., Camb. 111: 197-198.

SAS, 1984. SAS/EST^N, user's guide, Version 5th ed. SAS Institute Inc., Cary North Carolina.

Shaviv, A., Jury, W.A. and Pratt, P.F. 1986. Exchange, fixation, and precipitation of cations during leaching of soils amended with manure: 1. Column experiments. Soil Sci. 141: 237-243.

Singh, J.P., Karamanos, R.E., Lewis N.G. and Stewart, J.W.B. 1986. Effectiveness of zinc fertilizer sources on nutrition of beans. Can. J. Soil Sci. 66: 183-187.

Stevenson, D.S. and Neilson, G.H. 1990. Nitrogen additions and losses to drainage in orchard-type irrigated lysimeters. Can. J. Soil Sci. 70: 11-19.

Xie, R.J., Fyles, J.W., MacKenzie, A.F. and O'Halloran, I.P. 1991. Lignosulfonate effects on phosphate reactions in a clay soil: causal modelling. Soil Sci. Soc. Am. J. 55: 711-716.

Connecting Section

The second study suggested that LS may inhibit the production of NO_3-N. That study, however, examined the effects of LS on N transformations in microsites. Salinity and high NH_4-N concentrations associated with fertilizer band applications may, therefore, have been directly responsible for inhibiting nitrification.

In the following experiment, LS and N fertilizer concentrations were significantly reduced. The effect of LS on nitrification of fertilizer NH_4-N was evaluated.

CHAPTER V. EVALUATION OF LIGNOSULFONATE AS A NITRIFICATION INHIBITOR

ABSTRACT

Lignosulfonate (LS), a phenolic by-product from the sulfite pulping process, may have the potential to inhibit nitrification. A previous study (Chapter III) has indicated that LS may decrease NO_3-N production. A laboratory incubation study was conducted to compare the effectiveness of LS and dicyandiamide (DCD) as nitrification inhibitors. Samples from four contrasting soils were incubated with six treatments: control, ammonium lignosulfonate (LS), urea (U), LS+U, U+Dicyandiamide (U+inh) and LS+U+inh. Lignosulfonate, U and DCD were applied at 3360 Kg/ha, 621 Kg N/ha and 15 Kg/ha, respectively. Fertilizer and chemicals for each treatment were mixed and applied in powder form. Dicyandiamide decreased NO_3-N recovery in the Chicot and Ormstown soils by 31 to 95%. However, degree of reduction was dependent on time. Lignosulfonate decreased NO_3-N production in the U+inh treatment by 73% in the St Rosalie soil at at week six, whereas DCD alone did not decrease nitrification in the U+inh treatment. Lignosulfonate, however, did not increase NH_4-N recovery, suggesting that LS may have enhanced denitrification or reactions with NH_3-N or NO_2-N.

INTRODUCTION

Ammonium or NH_4 producing fertilizers, such as urea, are often inefficient N sources for crops because of rapid biological oxidation of NH_4 to NO_3, which is subject to loss by leaching and dentrification (Bronson et al. 1991; McCarty and Bremner 1990a; Magalhaes and Chalk 1987) Growing concern about pollution of ground and surface waters has encouraged research on nitrification inhibitors Many inhibitors have been patented, but, most of these compounds are not effective (McCarty and Bremner 1990b). Previous incubation studies (Chapters II and III) have indicated that lignosulfonate (LS), a lignin derivative (Reference Guide, Daishowa Cemicals) and waste product from the pulp and paper industry, may have the potential to decrease nitrification of fertilizer N, possibly by binding with NH_3-N (Stevenson 1982) or NO_2-N (Azhar et al. 1986).

This study was conducted to evaluate the effectiveness of LS as a nitrification inhibitor and to compare it to a commercially available inhibitor, dicyandiamide (DCD), in four contrasting soils Dicyandiamide was chosen for its N content (67%) and because it is not strongly adsorbed onto organic matter (Ashworth and Rodgers 1981).

MATERIALS AND METHODS

Surface samples of four contrasting soils (Table 1) were air dried, passed through a 2 mm sieve and weighed in 100 g samples into 590 ml incubation containers. Soils were preincubated at 80% field capacity for four weeks to permit equilibration of chemical and microbiological processes. Six treatments were applied, unamended (control), ammonium lignosulfonate (LS, Temfibre Inc., Temiscaming, Que.), urea (U), LS+U, U+dicyandiamide (U+inh) and LS+U+inh. Nitrification inhibitor dicyandiamide (DCD) was applied at a rate

Table 1. Characteristics of the Chicot, Dalhousie, Ormstown and St. Rosalie soils.

Series	Sub Group	Texture[z]	pH	Org C	Clay
				(g/Kg)	(g/Kg)
Chicot	Dystric Brunisol	SCL	5.8	10.2	390
Dalhousie	Humic Gleysol	HC	5.7	38.8	410
Ormstown	Humic Gleysol	SiCL	5.6	18.8	320
St. Rosalie	Humic Gleysol	C	5.2	19.1	500

[z] SCL, HC, SiCL and C Denote: Sandy clay loam, heavy clay, silty clay loam and clay, respectively.

of 15 Kg/ha following McCarty and Bremner (1990a) and Ashworth and Rodgers (1981). Lignosulfonate and U were added at rates equivalent to 3360 Kg/ha and 621 Kg N/ha, respectively. The U rate was applied at three times the field rate and the LS applied at 2.6:1 LS to U, the same ratio that appeared to inhibit nitrification in a previous study (Chapter III). Treatments were mixed and added in powder form to a localized site in the soil. Incubation containers were sealed and incubated in completely randomized arrangements at 24 ° C for four and six weeks. Containers were kept at 80% field capacity and were aerated every 2 days to allow for atmospheric exchange and to reduce inhibitory effects on NO_3-N production associated with volatile NH_3 accumulation. At four and six weeks soils were dried and passed through a 2 mm sieve. Subsamples were shaken in 1M KCl for 60 minutes and suspensions filtered using #2 Whatman filter papers. Filtrates were analyzed for NH_4-N and NO_3-N concentrations by using the Kjeltec Steam Distillation Unit (Keeney and Nelson 1982; Kjeltec System 1002 Distilling Unit Manual).

Statistical Analysis

The experimental design was a three-way unbalanced factorial model consisting of treatment, soil and date. The experimental results were analyzed for each soil and date by analysis of variance with contrasts using the general linear models procedure (GLM) of SAS (SAS Institute Inc.1984).

RESULTS AND DISCUSSION

Interaction between treatment, soil and date significantly affected NO_3-N levels and a treatment by soil interaction significantly affected NH_4-N levels (Table 2). Interpretation of the three-way interaction for NO_3-N was complicated, and therefore data were analyzed

Table 2. Table of probabilities from ANOVA for NH_4-N and NO_3-N.

Source	NH_4-N	NO_3-N
TREAT[Z]	**	**
SOIL[Y]	**	**
DATE[X]	**	**
TREAT*SOIL	*	**
TREAT*DATE	NS	NS
SOIL*DATE	NS	**
TREAT*SOIL*DATE	NS	**

[Z] Treatment (C, LS, U, LS+U, U+inh, LS+U+inh).
[Y] Soil (Chicot, Dalhousie, Ormstown, St. Rosalie).
[X] Date (four and six weeks).
NS, *, ** Not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

by soil and date seperately. Variance among dates for NH_4-N was not homogeneous and therefore could not be pooled. For convenience, data were also analyzed by soil and date.

Treatment and soil interactions are inferred from the results of treatment contrasts within soils. Only contrasts directly pertaining to DCD and LS effects on nitrification were determined. An inhibitor effect of DCD was apparent in all soils except in St. Rosalie (Tables 3 - 6, contrast 6). Dicyandiamide was effective in reducing NO_3-N levels, but the degree of reduction varied among treatments, soils and sampling dates. In the Chicot soil, DCD in combination with U or LS+U decreased NO_3-N recovery by 35 and 31%, respectively, at week four (Table 3, contrasts 4 and 5), whereas in the Ormstown soil DCD reduced NO_3-N recovery by 66% with U at week six and and by 95% with LS+U at week four (Table 5, contrasts 4 and 5). Ammonium-N recovery, however, was not increased by DCD in the Ormstown soil (Table 5, contrasts 4 and 5), suggesting that DCD may not have decreased nitrification. Dicyandiamide in combination with U or LS+U had no effect on NO_3-N recovery in the Dalhousie soil (Table 4, contrasts 4 and 5). A lack of inhibitor effect with U or LS+U in the St. Rosalie and Dalhousie soils (Table 2) may be due to the higher clay and organic matter contents which might have adsorbed some of the DCD (Keeney 1980) and hence reduced its efficiency. Percent decreases in NO_3-N production by DCD in the Chicot and Ormstown soils were similar to results obtained by Rodgers (1983).

Urea hydrolysis has been shown to be complete by one and two weeks in a silty clay loam and clay soil, respectively, (Rodgers 1983) and may suggest that maximum DCD efficiency in our study may have occurred prior to the four and six week sampling dates. A LS effect was apparent in all soils except for Chicot (Tables 3 - 6, contrast 3). Effects of LS on NH_4-N and NO_3-N recovery were not consistent with respect to soil, date or treatment. The LS effect in the Ormstown soil demonstrated an increase in NH_4-N recovery at week four (Table 5, contrast 3). Although the reason for the increase is unknown, Chen (1991) has

Table 3. Recovery of added N[Z] as NH_4-N and NO_3-N after four and six weeks of incubationn in the Chicot soil and treatment contrasts.

Treatment		Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(%)		(%)	
T_1	LS[Y]	9.5 (5.5)	102.8 (8.6)	-1.2 (2.3)	100.1 (6.9)
T_2	U[X]	-0.7 (0.3)	82.2 (2.1)	1.1 (0.4)	86.0 (1.6)
T_3	LS+U	4.6 (1.8)	74.5 (4.3)	1.5 (.07)	84.0 (0.9)
T_4	U+INH[W]	13.7 (2.5)	53.1 (4.7)	6.7 (1.6)	76.4 (2.2)
T_5	LS+U+INH	18.0 (1.3)	51.6 (0.9)	8.3 (1.5)	71.1 (3.7)
Contrast					
1	T_2vsT_3	NS	NS	NS	NS
2	T_4vsT_5	NS	NS	NS	NS
3	T_2+T_4vsT_3+T_5	NS	NS	NS	NS
4	T_2vsT_4	**	**	*	NS
5	T_3vsT_5	*	*	*	NS
6	T_2+T_3vsT_4+T_5	**	**	**	*
7	T_3vsT_4	NS	*	*	NS

[Z] Includes 4.02 mg (NH_4 + NO_3)-N added with LS.
[Y] Lignosulfonate.
[X] Urea.
[W] Urea plus dicyandiamide.
( ) Standard errors of means (n=4).
NS, *, ** Not significant ($p>0.05$) and significant at $p<0.05$ and $p<0.01$, respectively.

Table 4. Recovery of added N[z] as NH_4-N and NO_3-N after four and six weeks of incubation in the Dalhousie soil and treatment contrasts.

Treatment		Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(%)		(%)	
T_1	LS[Y]	14.2 (2.6)	27.5 (4.9)	8.0 (2.8)	-2.0 (8.1)
T_2	U[X]	7.0 (0.6)	45.3 (1.5)	2.6 (0.5)	47.5 (0.5)
T_3	LS+U	12.0 (0.4)	38.6 (1.6)	7.5 (0.3)	40.2 (1.2)
T_4	U+INH[W]	14.0 (0.8)	34.9 (1.5)	6.5 (0.4)	41.4 (3.7)
T_5	LS+U+INH	16.7 (1.0)	30.1 (0.9)	10.4 (0.5)	38.9 (1.1)
Contrast					
1	T_2vsT_3	*	NS	*	NS
2	T_4vsT_5	NS	NS	NS	NS
3	T_2+T_4vsT_3+T_5	*	NS	*	NS
4	T_2vsT_4	**	NS	NS	NS
5	T_3vsT_5	NS	NS	NS	NS
6	T_2+T_3vsT_4+T_5	**	*	*	NS
7	T_3vsT_4	NS	NS	NS	NS

[z] Includes 4.02 mg (NH_4 + NO_3)-N from LS.
[Y] Lignosulfonate.
[X] Urea.
[W] Urea plus dicyandiamide.
( ) Standard errors of means (n=4).
NS, *, ** Not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

Table 5. Recovery of added N[Z] as NH_4-N and NO_3-N after four and six weeks of incubation in the Ormstown soil and treatment contrasts.

Treatment		Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(%)		(%)	
T_1	LS[Y]	6.4	-11.6	10.7	2.7
		(1.7)	(3.0)	(8.9)	(5.0)
T_2	U[X]	13.9	8.6	12.2	18.6
		(0.5)	(0.8)	(0.6)	(1.4)
T_3	LS+U	16.0	9.6	14.5	11.8
		(0.2)	(0.8)	(0.4)	(1.4)
T_4	U+INH[W]	16.1	4.0	14.0	6.3
		(0.5)	(1.2)	(1.0)	(0.5)
T_5	LS+U+INH	19.8	0.49	18.2	6.2
		(1.7)	(0.9)	(0.6)	(0.6)
Contrast					
1	T_2vsT_3	NS	NS	NS	NS
2	T_4vsT_5	NS	NS	NS	NS
3	T_2+T_4vsT_3+T_5	*	NS	NS	NS
4	T_2vsT_4	NS	NS	NS	**
5	T_3vsT_5	NS	**	NS	NS
6	T_2+T_3vsT_4+T_5	*	**	NS	**
7	T_3vsT_4	NS	NS	NS	NS

[Z] Includes 4.02 mg (NH_4 + NO_3)-N from LS.
[Y] Lignosulfonate.
[X] Urea.
[W] Urea plus dicyandiamide.
( ) Standard errors of means (n=4).
NS, *, ** Not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

Table 6. Recovery of added N[Z] as NH_4-N and NO_3-N after four and six weeks of incubation in the St. Rosalie soil and treatment contrasts.

Treatment		Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(%)		(%)	
T_1	LS[Y]	40.6 (9.4)	-40.4 (6.9)	35.2 (7.0)	25.1 (3.9)
T_2	U[X]	49.6 (3.5)	2.5 (0.8)	42.8 (2.6)	19.0 (1.5)
T_3	LS+U	56.7 (2.3)	-2.3 (0.9)	48.4 (1.7)	11.7 (0.9)
T_4	U+INH[W]	44.2 (1.5)	-2.11 (1.5)	52.0 (2.2)	16.6 (4.0)
T_5	LS+U+INH	49.7 (2.5)	-4.3 (0.7)	52.1 (1.1)	4.5 (0.6)
Contrast					
1	T_2vsT_3	NS	NS	NS	NS
2	T_4vsT_5	NS	NS	NS	*
3	T_2+T_4vsT_3+T_5	NS	NS	NS	**
4	T_2vsT_4	NS	NS	NS	NS
5	T_3vsT_5	NS	NS	NS	NS
6	T_2+T_3vsT_4+T_5	NS	NS	NS	NS
7	T_3vsT_4	NS	NS	NS	NS

[Z] Includes 4.02 mg (NH_4 + NO_3)-N from LS.
[Y] Lignosulfonate.
[X] Urea.
[W] Urea plus dicyandiamide.
( ) Standard errors of means (n=4).
NS, *, ** Not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

demonstrated that out of a fertilizer application of 0.84 mg urea-N/g soil to Ormstown soil 0.19 mg urea-N/g soil (23%) was clay fixed. Lignosulfonate applied to the Ormstown soil may have become adsorbed onto soil particles and as a result blocked some clay fixation sites.

In the Dalhousie soil, LS in combination with U significantly increased NH_4-N recovery on both dates, but it had no effect on NO_3-N recovery (Table 4, contrast 1). Urea additions to the Dalhousie soil may have had similar effects as in the Ormstown soil. Lignosulfonate may have become adsorbed onto soil particles and thus may have reduced clay fixation of urea NH_4-N. A significant increase in NH_4-N recovery did not occur when LS was applied with DCD (Table 4, contrast 2). Although the reason for this is unknown, DCD may have become adsorbed onto the LS (Keeney 1980) reducing the amount of LS that may have become adsorbed onto soil particles. Consequently, LS may not have blocked clay fixation sites.

The St. Rosalie clay soil has also been shown to fix 0.25 mg urea-N/g soil from a 0.84 mg urea-N/g soil application (30% of added N clay fixed) (Chen 1991), however, LS did not increase NH_4-N recovery. The type of clay mineral and its fixing capacity may have an influence on the effects of LS increasing NH_4-N recovery. Greater concentrations of LS may therefore be necessary in the St. Rosalie soil to achieve similar results. Whatever the mechanism, this data suggests that LS may have the potential to increase urea NH_4-N availability in certain soil types. Lignosulfonate in combination with DCD in the St. Rosalie soil decreased NO_3-N recovery by 73% at week six (Table 6, contrast 2), suggesting that it may enhance DCD efficiency in a certain soils. Recovery of NH_4-N was not increased and therefore LS may not have reduced nitrification. Lignosulfonate may have increased denitrification because of its C content (Aulakh and Rennie 1987) or increased chemical fixation of NH_3-N (Stevenson 1982) and/or NO_2-N (Azhar et al. 1986) with its phenolic

constituents.

CONCLUSIONS

Dicyandiamide reduced NO_3-N recovery in the Chicot and Ormstown soils. The addition of LS with DCD decreased NO_3-N recovery in the St. Rosalie soil. However, reduced recovery may not have been a result of nitrification inhibition. Lignosulfonate probably has little effect as a nitrification inhibitor. Lignosulfonate did increase NH_4-N recovery in two soils and therefore may enhance NH_4-N availability of urea fertilizers.

REFERENCES

Ashworth, J. and Rodgers, G.A. 1981. The compatibility of the nitrification inhibitor dicyandiamide with injected anhydrous ammonia. Can. J. Soil Sci. 61: 461-463.

Aulakh, M.S. and Rennie, D.A. 1987. Effect of wheat straw incorporatin on dentirification of nitrogen under anaerobic and aerobic conditions. Can. J. Soil. Sci. 67: 825-834.

Azhar, E., Vandenabeete, J. and Verstraete, W. 1986. Nitrification and organic nitrogen formation in soils. Plant Soil 94: 383-399.

Bronson, K.F., Touchton, J.T., Hauck, R.D. and Kelley, K.R. 1991. ^{15}N recovery in winter wheat as affected by application timing and dicyandiamide. Soil Sci. Soc. Am. J. 55: 130-135.

Chen, J. 1991. Effects of added nitrogen and potassium on selected soil properties and on yield and nutrient uptake of silage corn. M.Sc. Thesis. Renewable Resources Department, McGill University, Macdonald Campus. Ste. Anne de Bellevue, Que.

Keeney, D.R. 1980. Factors affecting the persistence and bioactivity of nitrification inhibitors. Pages 33-46 *in* Meisinger, J.J., Randall, G.W. and Vitosh, M.L. (eds.). Nitrification Inhibitors - Potentials and Limitations. Am. Soc. Agron., Madison, Wisconsin.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen - inorganic forms. Pages 643-693 *in* Page, A.L., Miller, R.H. and Keeney, D.R. Methods of Soil Analysis. Agron. No. 9, 2nd ed. Am Soc. Agron., Madison Wisconsin.

Kjeltec System 1002 distilling Unit Manual, Tecator, AB. Box 70 S-263 21 hoganas, Sweden.

Magalhaes, A.M.T. and Chalk, P.M. 1987. Nitrogen transformations during hydrolysis and nitrification of urea. I. Effect of soil properties and fertilizer placement. Fert. Res. 11: 161-172.

McCarty, G.W. and Bremner, J.M. 1990a. Evaluation of 2-Ethynylpyridine as a soil nitrification inhibitor. Soil Sci. Soc Am. J. 54: 1017-1021.

McCarty, G.W. and Bremner, J.M. 1990b. Evaluation of 3-methylpyrazole-1-carboxamide as a soil nitrification inhibitor. Biol. Fertil. Soils 9: 252-256.

Reference Guide to Specialty Chemicals, Daishowa Chemicals, Que., Canada.

Rodgers, G. A. 1983. Effect of dicyandiamide on ammonia volatilization from urea in soil. Fert. Res. 4: 361-367.

SAS, 1984. SAS/ESTTN, User's Guide, 5th edn. SAS Institute Inc., Cary, North Carolina.

Stevenson, F.J. 1982. Dynamics of soil nitrogen transformations. Pages 93-119 *in* Humus Chemistry: Genesis, Composition, Reactions. J. Wiley and Sons, New York.

GENERAL CONCLUSIONS

Results demonstrated that LS did not decompose readily and that LS would remain in the soil to react with fertilizer-soil components. Small quantities of LS were extractable in 1M KCl suggesting that LS was relatively immobile within the soil system and therefore its effects on nutrient reactions or transformations would be limited to the band area. Small proportions of LS leached from soil columns supporting the findings that LS is relatively immobile within a soil system and suggests that LS application to soil is unlikely to pose a threat to groundwater quality.

Higher rates of LS inhibited microbial activity and suggested that LS when banded with urea might decrease N transformations.

Incubation of LS in combination with urea fertilizer reduced urea hydrolysis in a band, however, probably not sufficently for agronomic value. Within a fertilizer band LS increased mineral N recovery, reduced nitrification and the proportion of added N volatilized as NH_3-N from LS plus urea fertilizer. Nitrification inhibition was believed to have been caused by high fertilizer concentrations.

Under reduced fertilizer concentrations, LS decreased nitrification in one of four soils and increased recovery of NH_4-N in two of four soils used. Lignosulfonate had reduced NO_3-N levels when added in combination with DCD in the St. Rosalie soil but a lack of NH_4-N accumulation indicates that reduced NO_3-N recovery may not have been a result of nitrification inhibition. This suggests that the strong nitrification inhibition apparent in the second experiment (Chapter III) most likely occurred because of high NH_4^+ and salt contents associated with fertilizer band concentrations. Lignosulfonate increased recovery

of fertilizer N and may, therefore, have the potential to enhance fertilizer N efficiency. Field studies are necessary to determine if LS has agricultural importance as a fertilizer additive to improve N fertilizer availability.

APPENDIX I

Table 2.1. Soil NH_4-N after 40 day incubation in the Dalhousie soil.

Treatment		Replicates			
		1	2	3	4
		(mg/g soil)			
Control		0.001	0.001	0.002	0.001
NH_4LS^{Z}	5%	0.375	0.133	--	0.144
	10%	0.412	0.392	0.388	0.669
	20%	0.923	0.933	0.897	0.532
$CaLS^{Y}$	5%	0.007	0.017	0.019	0.002
	10%	0.007	0.009	0.007	0.016
	20%	0.008	0.006	0.020	0.014
$Ca(ds)LS^{X}$	5%	0.008	0.010	0.010	0.011
	10%	0.009	0.007	0.006	-0.005
	20%	0.012	0.010	0.009	0.024
$NaLS^{W}$	5%	0.017	0.024	0.017	0.024
	10%	0.008	0.011	--	0.009
	20%	0.011	0.011	--	0.017
KLS^{V}	5%	0.160	0.096	0.101	0.109
	10%	0.230	0.182	0.158	0.205
	20%	0.051	0.039	0.050	-0.005

[Z] Ammonium lignosulfonate.
[Y] Calcium lignosulfonate.
[X] Desugared calcium lignosulfonate.
[W] Sodium lignosulfonate.
[V] Potassium lignosulfonate.

Table 2.2. Soil NO_3-N after 40 day incubation in the Dalhousie soil.

Treatment		Replicates			
		1	2	3	4
		(mg/g soil)			
Control		0.0673	0.0782	0.0852	0.0887
NH_4LS^Z	5%	0.0635	0.0394	-0.0014	0.0501
	10%	0.0010	0.0551	0.0683	0.0581
	20%	0.0626	0.0560	0.0581	0.0527
$CaLS^Y$	5%	0.0007	0.0012	0.0010	0.0004
	10%	0.0005	0.0004	0.0002	0.0004
	20%	0.0014	0.0011	0.0008	0.0005
$Ca(ds)LS^X$	5%	0.0156	0.0014	0.0012	0.0138
	10%	0.0013	0.0015	0.0007	-0.0015
	20%	0.0023	0.0023	0.0037	0.0044
$NaLS^W$	5%	0.0194	0.0538	0.0356	0.0510
	10%	0.0051	0.0035	-0.0015	0.0029
	20%	0.0034	0.0026	-0.0016	0.0023
KLS^V	5%	0.0614	0.0286	0.0584	0.0561
	10%	0.0021	0.0007	0.0023	0.0021
	20%	0.0025	0.0017	0.0023	0.0020

[Z] Ammonium lignosulfonate.
[Y] Calcium lignosulfonate.
[X] Desugared calcium lignosulfonate.
[W] Sodium lignosulfonate.
[V] Potassium lignosulfonate.

Table 2.3. Soil pH, in 0.01 M $CaCl_2$, after 40 day incubation in the Dalhousie soil. Control (0% LS) was 5.06 (.01).

	LS rate		
	5%	10%	20%
NH_4LS^Z	5.34 (.02)	5.21 (.06)	4.76 (.005)
$CaLS^Y$	5.56 (.01)	4.28 (.01)	4.24 (.01)
$CaLS(ds)^X$	6.61 (.01)	7.01 (.03)	6.94 (.04)
$NaLS^W$	6.35 (.22)	7.02 (.01)	7.39 (.02)
KLS^V	6.04 (.04)	6.31 (.01)	6.31 (.02)

[Z] Ammonium lignosulfonate.
[Y] Calcium lignosulfonate.
[X] Desugared calcium lignosulfonate.
[W] Sodium lignosulfonate.
[V] Potassium lignosulfonate.
( ) Standard errors of means (n=4).

Appendix I: Figures

Fig.2.1. Carbon evolved as CO_2 (mg/g soil/day) in (A) control, (B) 5% CaLS, (C) 10% CaLS and (D) 20% CaLS treatments. Bars indicate upper 95% confidence limits.

Fig.2.2. Carbon evolved as CO_2 (mg/g soil/day) in (A) control, (B) 5% Ca(ds)LS, (C) 10% Ca(ds)LS and (D) 20% Ca(ds)LS treatments. Bars indicate upper 95% confidence limits.

Fig.2.3. Carbon evolved as CO_2 (mg/g soil/day) in (A) control, (B) 5% KLS, (C) 10% KLS and (D) 20% KLS treatments. Bars indicate upper 95% confidence limits.

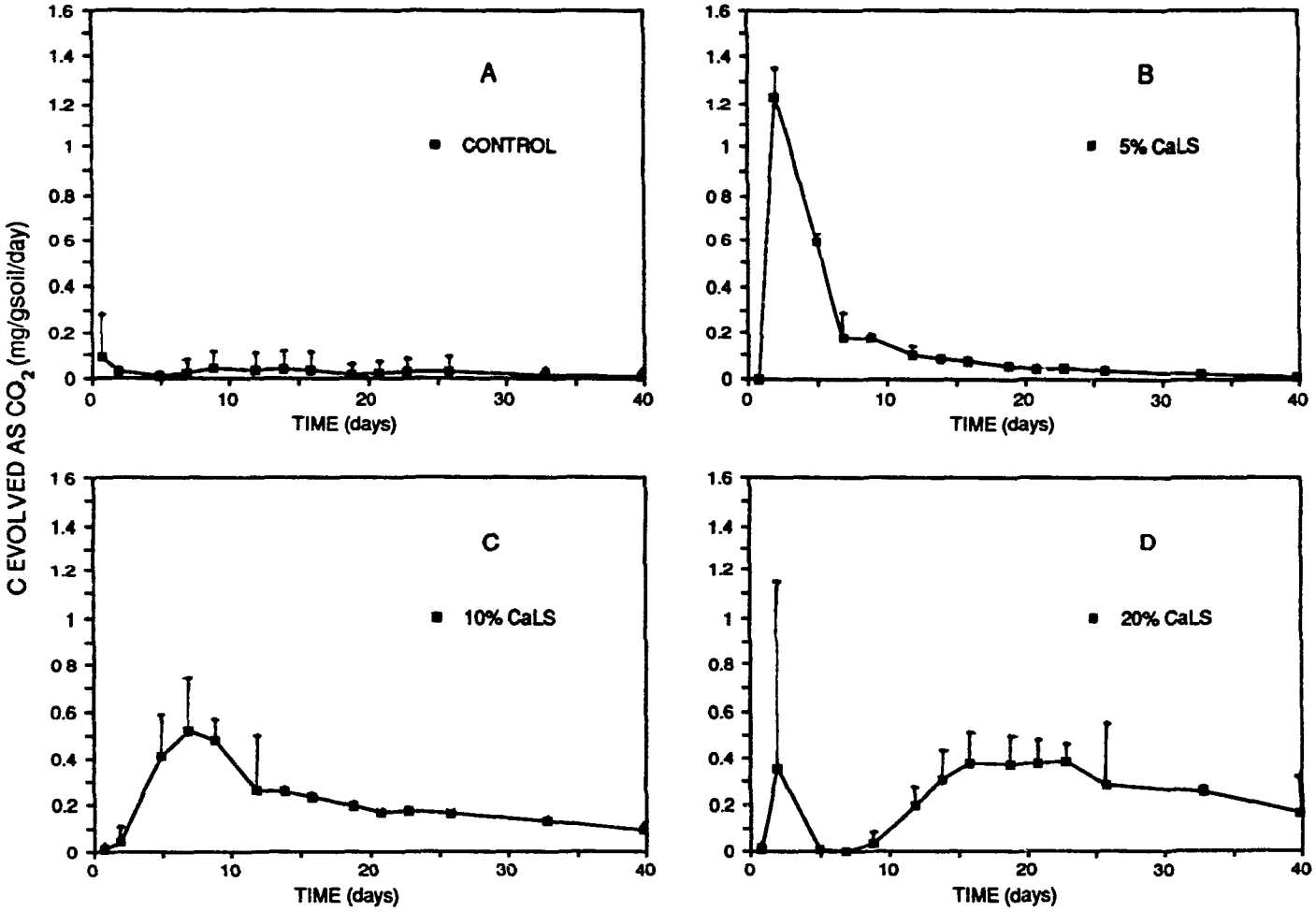

A
CONTROL
B
5% CaLS
C
10% CaLS
D
20% CaLS
C EVOLVED AS CO_2 (mg/gsoil/day)
TIME (days)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
10
20
30
40

Fig. 2.1.

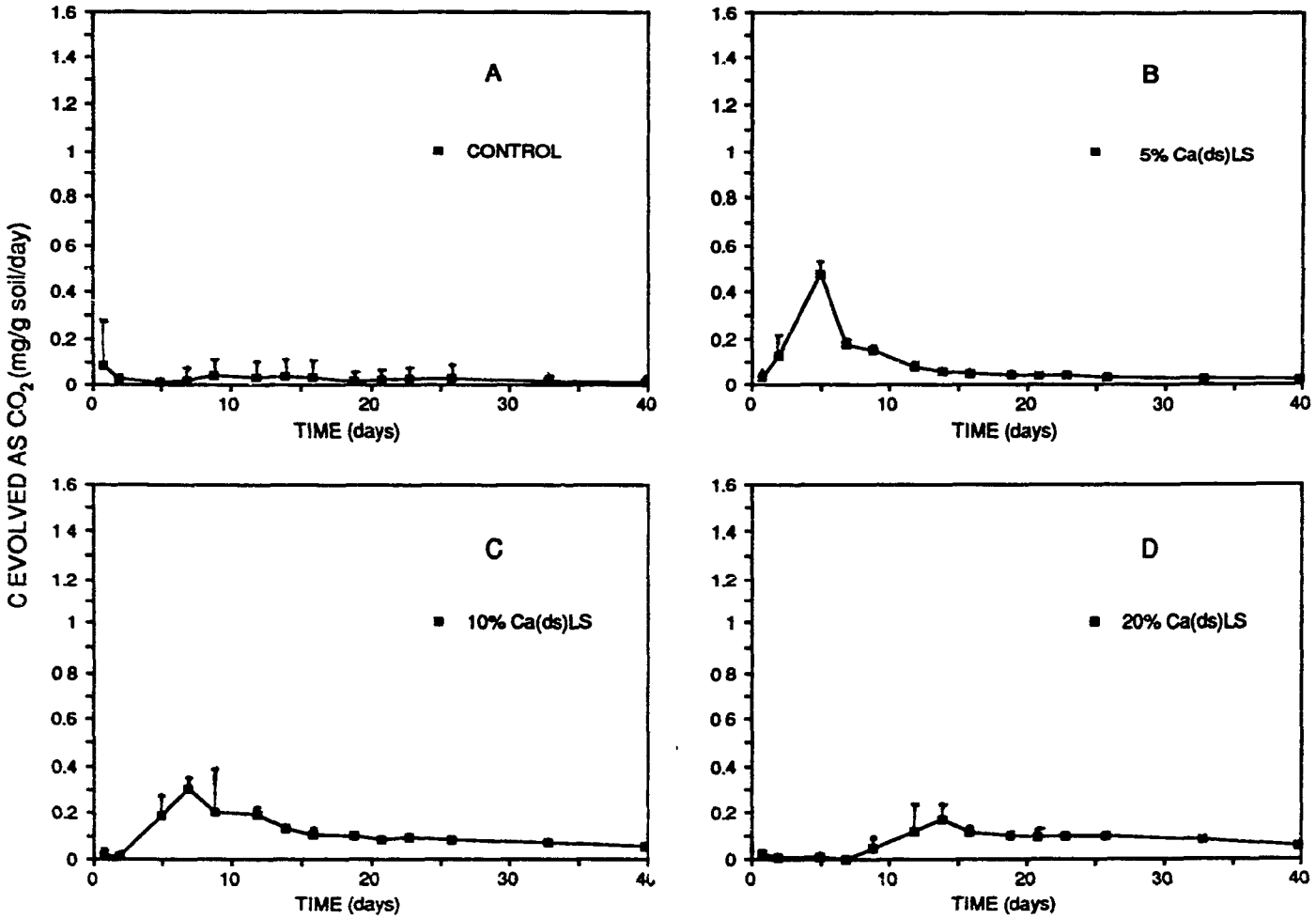

A
CONTROL
B
5% Ca(ds)LS
C
10% Ca(ds)LS
D
20% Ca(ds)LS
C EVOLVED AS CO_2 (mg/g soil/day)
TIME (days)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
10
20
30
40

Fig. 2.2.

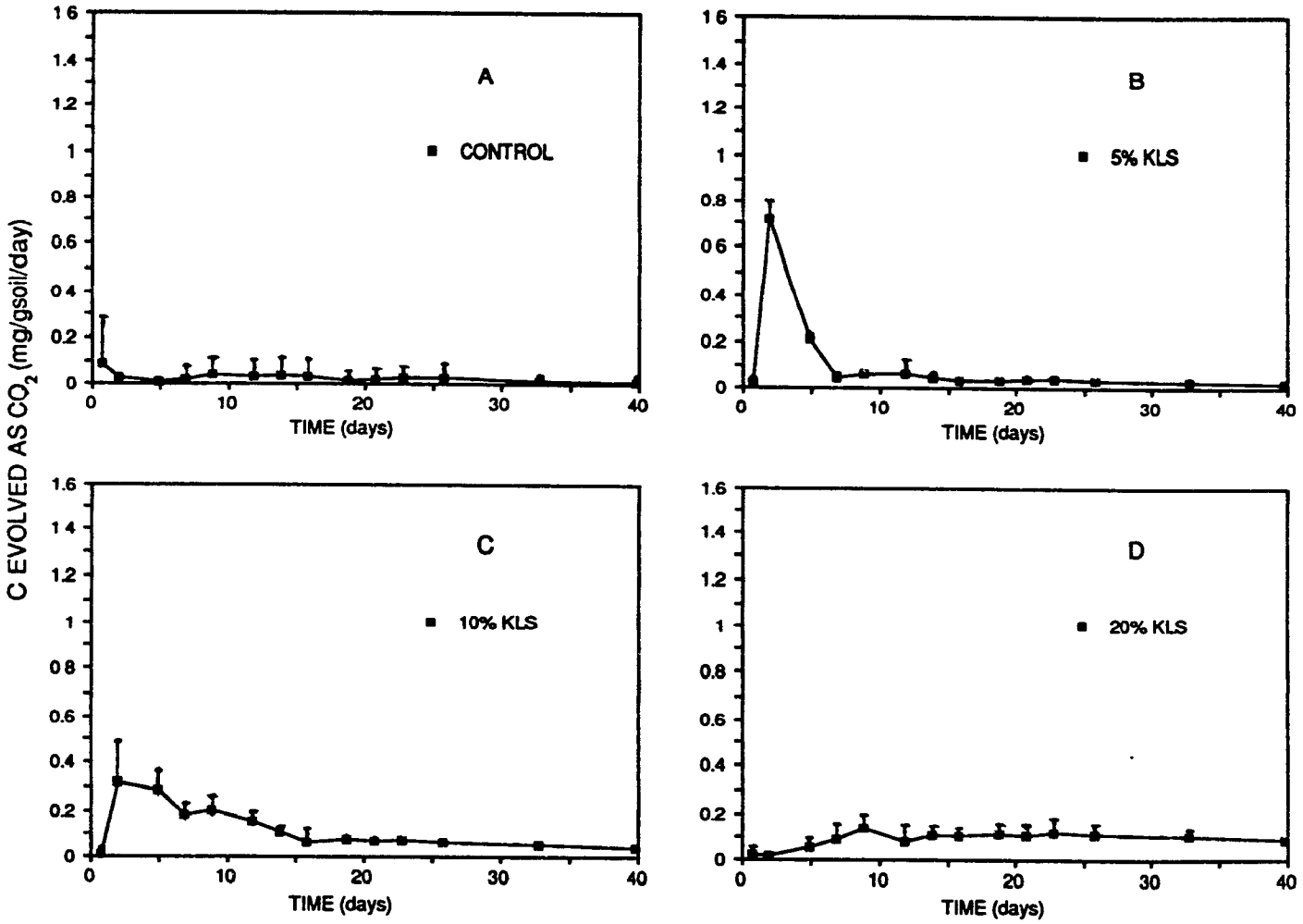

A
CONTROL
B
5% KLS
C
10% KLS
D
20% KLS
C EVOLVED AS CO_2 (mg/gsoil/day)
TIME (days)
TIME (days)
TIME (days)
TIME (days)

Fig. 2.3.

APPENDIX II

Table 3.1. Carbon input, total C evolved as CO_2 (minus control) and percent of added C[Z] evolved as CO_2 during the 69 day incubation.

Treatment	C Input (mg)	CO_2 Evolved (mg)	Added C[Z] Evolved (%)
LS[Y]	1070.7	140.6 (6.3)	13.1
U[X]	202.0	123.9** (8.7)	61.3**
LS+U	1070.7	263.6 (10.2)	13.0
DAP[W]	---	4.9** (3.2)	---
LS+DAP	1070.7	116.6 (4.7)	10.4
U+DAP	202.0	101.5** (2.9)	50.2**
LS+U+DAP	1070.7	339.7 (53.3)	22.2

[Z] In LS treatments, CO_2 evolved from corresponding fertilizer treatments was subtracted.
[Y] Ammonium lignosulfonate.
[X] Urea.
[W] Diammonium phosphate.
** Significant difference at $p<0.01$ between ferilizer treatment and corresponding LS+fertilizer treatment (within date).
( ) Standard errors of means (n=4).

Table 3.2. Soil NH_4-N during 38 day incubation in the Ormstown soil.

Treatment	Rep	Day							
		2	4	7	11	17	26	33	38
		(mg/g soil)							
Control	1	0 09	0.24	0.36	0.49	0.15	0 19	0.17	0 16
	2	0.11	0.25	0.39	0.33	0.16	0.17	0.15	0.19
	3	0.15	0 25	0.47	0.28	0.21	0.26	0.22	0.20
LS[z]	1	0.42	0.51	0 47	0 50	0.52	0.47	0.48	0.48
	2	0.48	0.47	0.55	0.52	0 53	0 49	0 46	0.48
	3	0.50	0.44	0.45	0 53	0.45	0.46	0.46	0 49
U[y]	1	0.36	1.33	1 37	1.48	1 66	1.52	1.54	1.48
	2	0.38	1.22	1 48	1.48	1.65	1.65	1.52	1.51
	3	0.38	1.22	1.55	1.55	1.65	1.56	1 48	1.48
LS+U	1	1.83	2.76	2.90	2.97	3.14	2.90	2 90	3.20
	2	2.20	3.05	3 02	2.93	2.87	2.96	3.05	2.72
	3	1.87	--	2.93	2.75	3.08	3.20	2.78	2 58
DAP[x]	1	0.68	0.59	0.65	0.70	0.59	0.74	0.72	0 66
	2	0.57	0.62	0 69	0.74	0.64	0 78	0.68	0.66
	3	0.66	0.64	0.67	0.68	0.74	0.74	0.69	0.71
LS+DAP	1	1.79	2.31	2.11	2.37	2.44	2 22	2.26	2.77
	2	1.76	1.96	2.28	2.27	2.56	2.28	2 61	2.32
	3	2.12	2.11	2.26	2.84	2.34	2.73	2.92	2.65
U+DAP	1	1.22	1 85	1.81	2.05	2.26	1 98	1.87	2.11
	2	1.35	1 85	1.84	2.11	2.21	2.14	1 93	2 08
	3	1.29	1 89	1.89	2.12	2.13	2.20	2.00	2.11
LS+U+DAP	1	2.85	3.00	3.21	3.21	3 64	3.38	3.39	3.54
	2	2.94	3.15	3.12	3.27	3 87	3.77	3.45	3.52
	3	2.82	3.21	3.18	3.39	3 65	3.70	3.33	3.30

[z] Ammonium lignosulfonate.
[y] Urea.
[x] Diammonium phosphate.

Table 3 3 Soil NO_3-N during 38 day incubation in the Ormstown soil.

Treatment	Rep	Day							
		2	4	7	11	17	26	33	38
		(mg/g soil)							
Control	1	0.065	0.092	0.102	0.134	0.146	0.176	0.190	0.186
	2	0 069	0.081	0 099	0.118	0 152	0 154	0.175	0.167
	3	0.070	0.094	0 108	0.123	0.140	0.158	0.184	0.192
LS[z]	1	0.010	0.013	0.014	0.015	0.018	0.021	0.022	0.023
	2	0 010	0.012	0.013	0.015	0.018	0.020	0.021	0.025
	3	0.011	0.013	0.013	0.016	0.018	0.020	0.025	0.026
U[y]	1	0.014	0.017	0 015	0 016	0.017	0.016	0.017	0.015
	2	0.015	0 016	0.015	0.015	0.016	0.017	0.017	0.016
	3	0.016	0 017	0.017	0.016	0.016	0.016	0.017	0.016
LS+U	1	0.010	0.009	0.007	0.007	0.009	0.008	0.012	0.009
	2	0.009	0 008	0.007	0.007	0.008	0.008	0.012	0.011
	3	0.008	--	0.006	0.008	0.007	0.008	0.012	0.012
DAP[x]	1	0.013	0.015	0.019	0.029	0.042	0.130	0.172	0.208
	2	0 011	0 015	0.020	0.031	0.077	0.134	0.176	0.194
	3	0.013	0 015	0.020	0.029	0.067	0.126	0.177	0.202
LS+DAP	1	0.011	0.012	0.012	0.012	0.013	0.016	0.016	0.020
	2	0.011	0 011	0.013	0.012	0.013	0.016	0.018	0.017
	3	0.011	0.011	0.012	0.011	0.014	0.015	0.017	0.017
U+DAP	1	0.000	0.022	0 019	0.020	0.020	0.016	0.020	0.017
	2	0.025	0.017	0.020	0.020	0.019	0.020	0.018	0.019
	3	0.022	0.019	0.020	0.022	0.018	0.020	0.021	0.019
LS+U+DAP	1	0.012	0 009	0.007	0.007	0.009	0.006	0.007	0.008
	2	0 010	0.009	0 007	0.007	0.008	0.007	0.009	0.007
	3	0.011	0.008	0.007	0.007	0.007	0.007	0.009	0.006

[z] Ammoinium lignosulfonate.
[y] Urea.
[x] Diammonium phosphate.

Appendix II: Figures

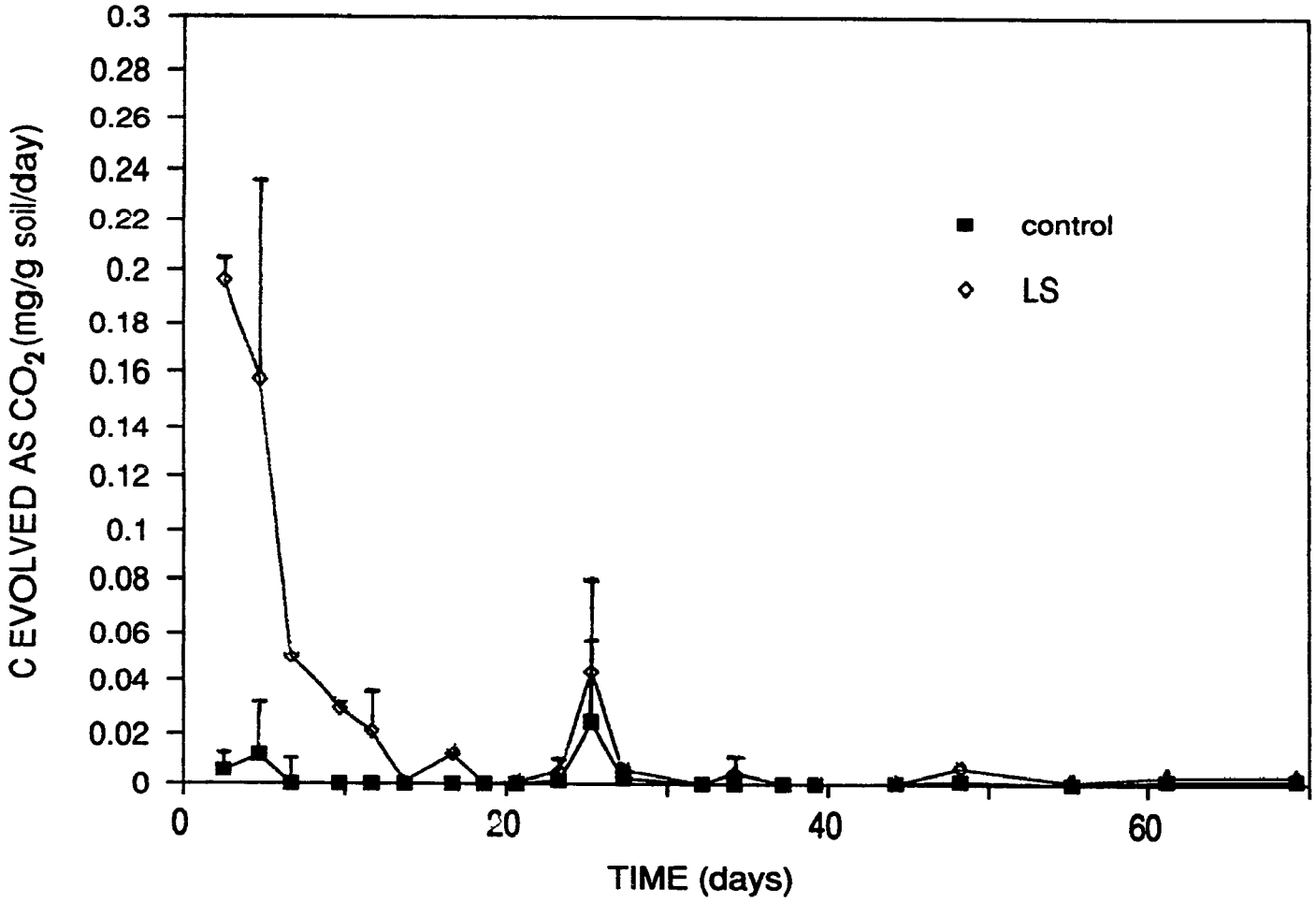
Fig.3.1. Carbon evolved as CO_2 (mg/g soil/day) during the 69 day incubation in the C and LS treatments. Bars indicate upper 95% confidence limits.

Fig.3.2. Carbon evolved as CO_2 (mg/g soil/day) during the 69 day incubation in the LS+DAP and DAP treatments. Bars indicate upper 95% confidence limits.

Fig.3.3. Carbon evolved as CO_2 (mg/g soil/day) during the 69 day incubation in the LS+U+DAP and U+DAP treatments. Bars indicate upper 95% confidence limits.

Fig.3.4. Ammonia-N (mg/g soil/day) volatilized during the 69 day incubation in the C and LS treatments. Letters a to c indicate no significant difference ($p>.05$), significant difference at $p<.05$ and $p<.01$, respectively, between the two treatments within date.

Fig.3.5. Ammonia-N (mg/g soil/day) volatilized during the 69 day incubation in the LS+DAP and DAP treatments. Letters a to c indicate no significant difference ($p>.05$), significant difference at $p<.05$ and $p<.01$, respectively, between the two treatments within date.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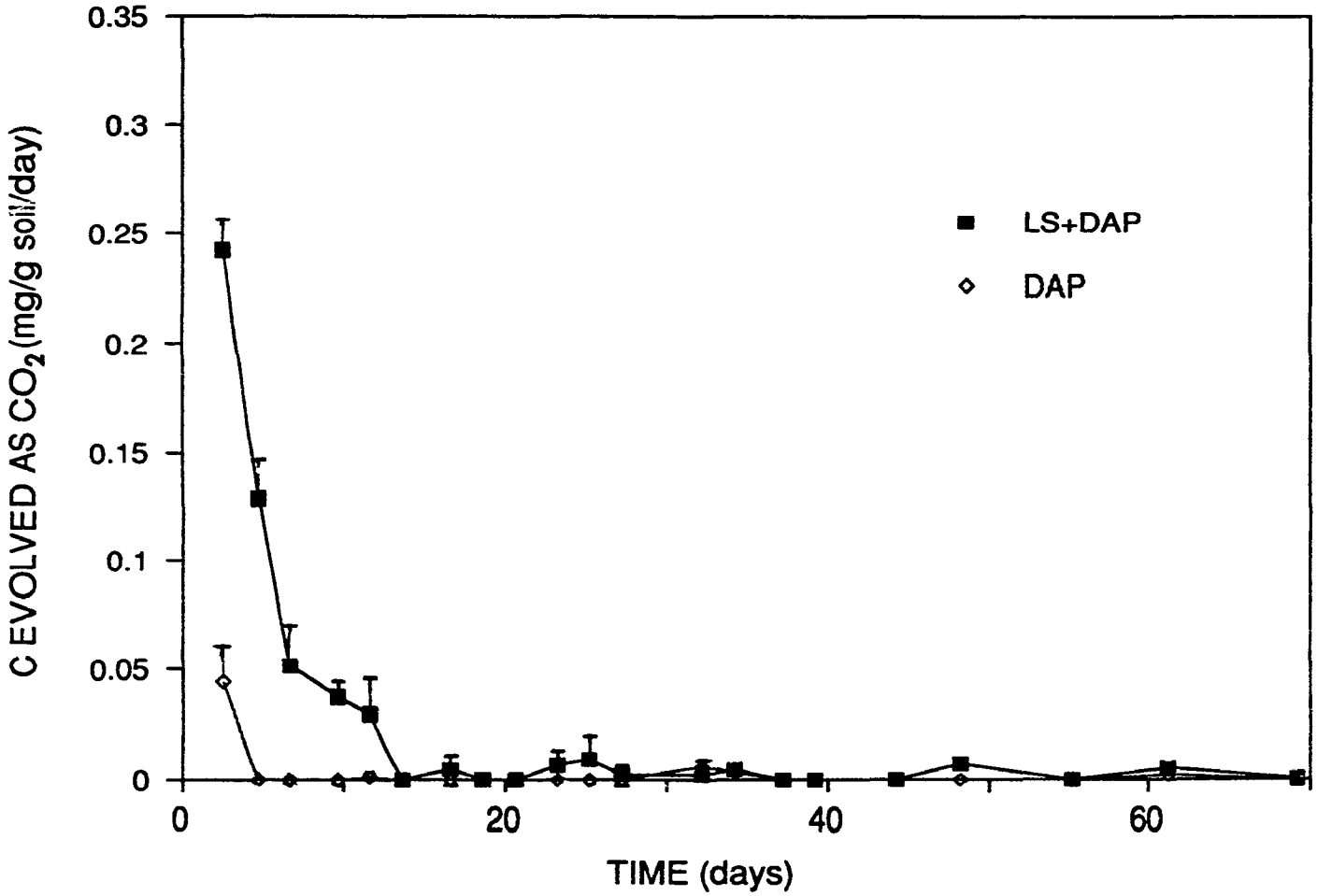
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
C EVOLVED AS CO_2 (mg/g soil/day)
0
20
40
60
TIME (days)
control
LS

Fig. 3.1.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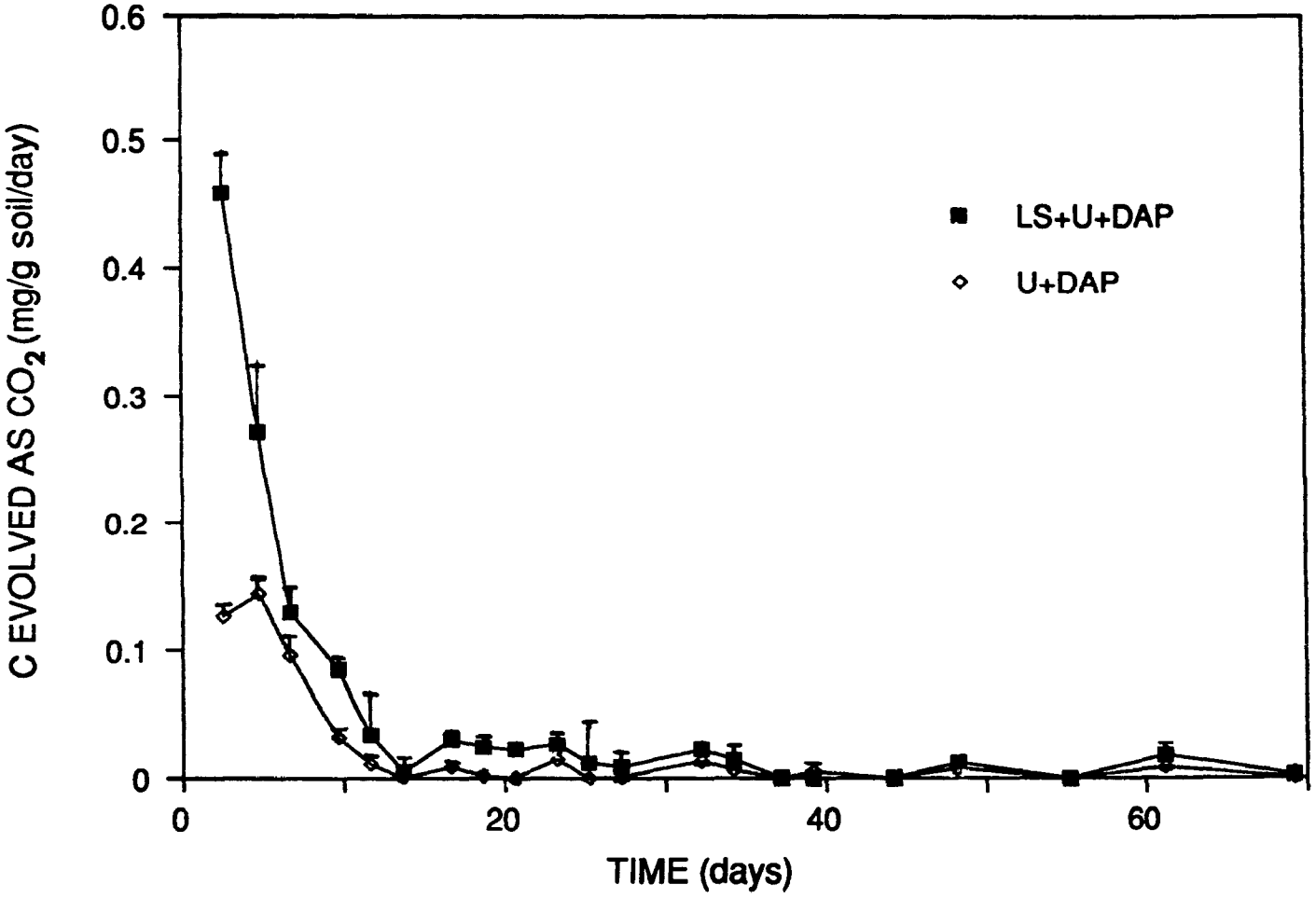
0.2
0.15
0.1
0.05
0
0
20
40
60
C EVOLVED AS CO_2 (mg/g soil/day)
TIME (days)
LS+DAP
DAP

Fig. 3.2.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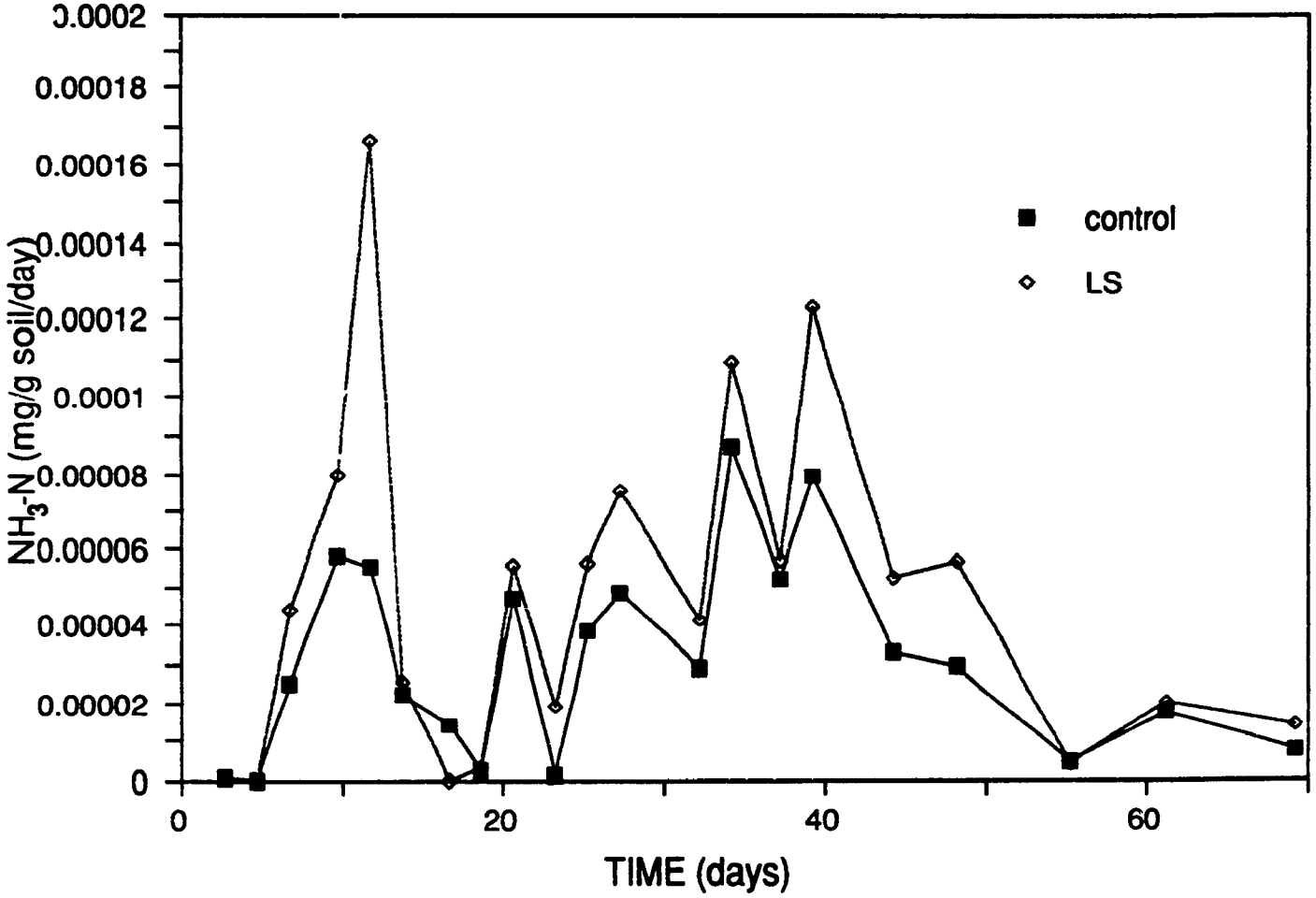
0.3
0.2
0.1
0
C EVOLVED AS CO_2 (mg/g soil/day)
0
20
40
60
TIME (days)
LS+U+DAP
U+DAP

Fig. 3.3.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0.00018
0.00016
0.00014
0.00012
0.0001
0.00008
0.00006
0.00004
0.00002
0
NH_3-N (mg/g soil/day)
control
LS
0
20
40
60
TIME (days)

Fig. 3.4.

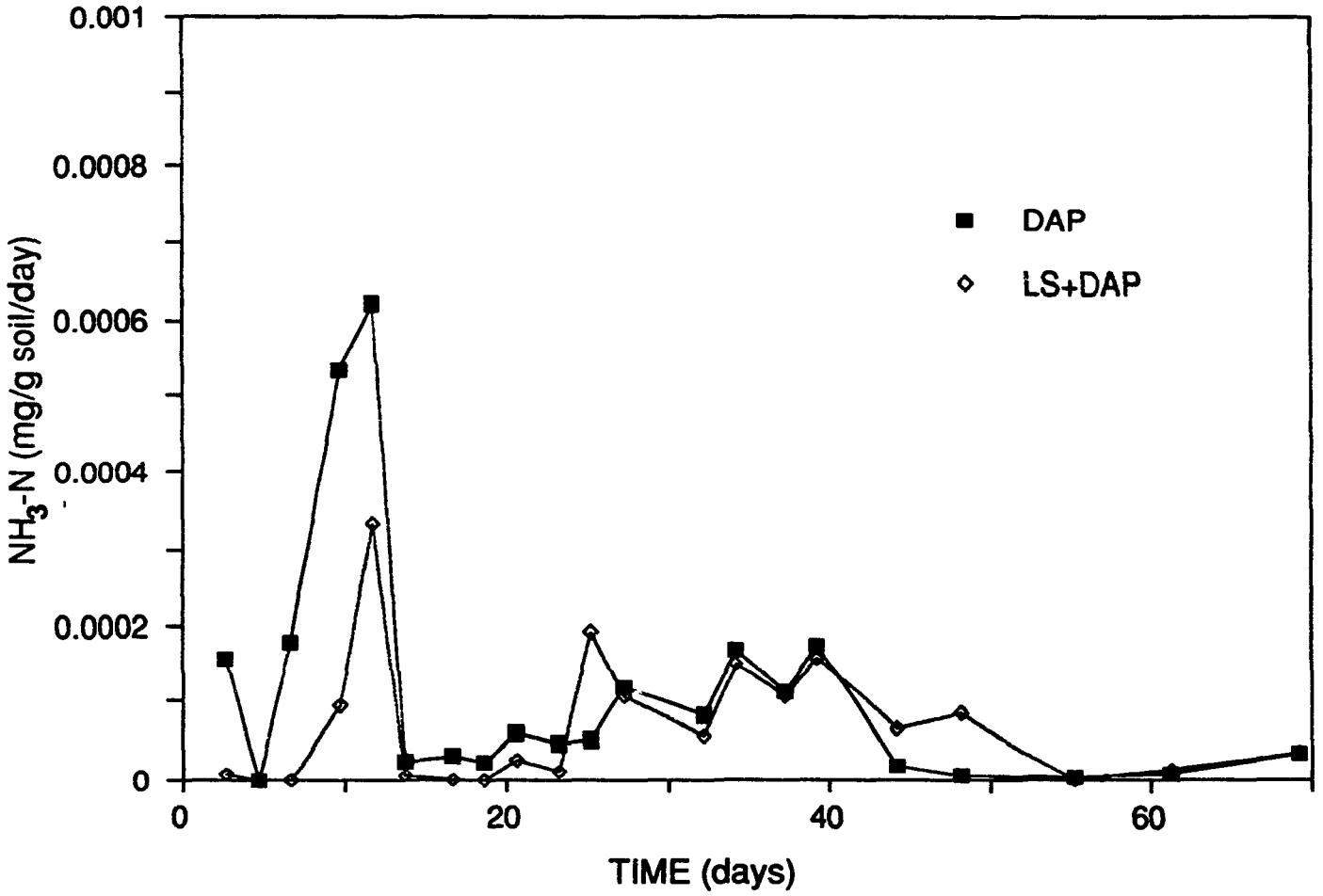
0.001
0.0008
0.0006
0.0004
0.0002
0
NH_3-N (mg/g soil/day)
DAP
LS+DAP
0
20
40
60
TIME (days)

Fig. 3.5.

APPENDIX III

Table 4.1. Soil C (means (n=4) of antilog data), lower and upper 95% confidence limits and percent of added LS-C retained in the soil columns after the three month incubation.

Treatment[Y]	Ormstown	Dalhousie
	(g)	(g)
C 1[Z]	17.7 (15.3,20.0)	25.4 (23.8,26.7)
C 2	16.6 (13.5,19.7)	27.4 (25.0,29.6)
C 3	16.9 (14.4,19.2)	32.4 (30.7,33.8)
LS 1	18.3 (16.9,19.5)	27.1 (22.6,31.7)
LS 2	17.2 (16.2,18.0)	32.5 (29.9,34.9)
LS 3	17.0 (15.1,18.8)	33.6 (31.0,35.8)
U 1	17.5 (17.2,17.8)	26.0 (23.5,28.4)
U 2	17.9 (14.0,22.0)	31.9 (31.0,32.6)
U 3	17.4 (15.8,18.8)	30.8 (25.5,36.1)
LS+U 1	18.4 (17.6,19.2)	25.5 (20.7,30.3)
LS+U 2	16.6 (16.4,16.8)	33.6 (29.1,37.9)
LS+U 3	17.7 (17.0,18.2)	31.9 (29.7,33.8)

( ) Lower and upper 95% confidence limits, respectively.

[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2)/wk, respectively.

Table 4.2. Total C leached (non transformed data) from the Ormstown soil during the twelve week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	4.21	3.42	4.45	5.59
	LS	6.39	8.53	5.88	3.83
	U	6.95	2.29	3.50	3.00
	LS+U	8.31	3.53	10.04	16.7
2	C	5.66	4.42	7.45	9.04
	LS	6.35	13.52	8.79	14.58
	U	7.01	3.86	8.87	3.10
	LS+U	19.10	21.23	15.64	9.39
3	C	6.58	7.69	12.91	11.00
	LS	26.98	13.13	18.71	33.87
	U	10.22	9.59	7.09	5.66
	LS+U	14.75	23.01	12.75	31.49

[Z] 1,2,3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2)/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.3. Total C leached (non transformed data) from the Dalhousie soil during the twelve week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	4.42	3.84	4.46	4.07
	LS	10.45	14.97	6.25	14.25
	U	3.24	2.37	2.92	5.23
	LS+U	21.77	6.35	9.48	10.45
2	C	5.39	5.91	5.57	6.43
	LS	22.40	25.42	23.23	21.32
	U	4.08	7.52	10.64	2.58
	LS+U	20.76	22.57	17.89	21.58
3	C	6.90	4.54	7.96	5.97
	LS	25.21	23.89	27.56	32.85
	U	14.13	18.96	8.27	9.73
	LS+U	20.55	13.89	23.78	16.06

[Z] 1,2,3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.4.A. Carbon leached per week from the Ormstown soil during the first six weeks of the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	1.56 (0.68)	0.00	0.20 (0.02)	0.11 (0.06)	0.09 (0.16)	0.43 (0.31)
	LS	0.90 (0.25)	0.02 (0.03)	0.22 (0.13)	0.13 (0.07)	0.14 (0.14)	0.46 (0.21)
	U	0.58 (0.13)	0.00	0.42 (0.12)	0.42 (0.52)	0.25 (0.24)	0.29 (0.13)
	LS+U	0.84 (0.14)	0.00	0.27 (0.12)	0.33 (0.17)	0.31 (0.22)	1.05 (0.43)
2	C	2.71 (3.67)	0.00	0.50 (0.49)	0.23 (0.18)	1.14 (1.26)	0.67 (0.25)
	LS	1.36 (0.77)	0.03 (0.04)	0.19 (0.13)	0.12 (0.08)	1.05 (1.01)	1.39 (0.87)
	U	0.49 (0.21)	0.05 (0.05)	0.52 (0.27)	0.47 (0.44)	0.88 (0.86)	2.07 (1.30)
	LS+U	0.86 (0.53)	0.00	0.66 (0.90)	0.69 (0.19)	0.39 (0.31)	1.91 (0.48)
3	C	0.55 (0.54)	0.39 (0.41)	2.21 (1.10)	1.66 (1.16)	1.01 (1.29)	3.96 (1.39)
	LS	0.49 (0.19)	0.11 (0.15)	1.79 (1.34)	2.78 (1.44)	1.11 (1.21)	4.49 (1.26)
	U	0.56 (0.26)	0.40 (0.69)	1.45 (1.10)	1.67 (1.48)	0.54 (0.93)	2.86 (0.94)
	LS+U	0.52 (0.26)	0.84 (0.65)	1.23 (1.12)	1.69 (1.71)	1.35 (2.11)	3.63 (3.08)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosufonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.4.B. Carbon leached per week from the Ormstown soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.25 (0.41)	0.68 (0.26)	0.88 (0.13)	0.87 (0.83)	0.99 (0.52)	0.18 (0.16)
	LS	0.23 (0.31)	0.83 (0.92)	0.49 (0.13)	0.53 (0.31)	0.75 (0.37)	0.02 (0.04)
	U	0.36 (0.63)	0.16 (0.14)	0.67 (0.56)	0.57 (0.39)	0.61 (0.63)	0.24 (0.24)
	LS+U	0.33 (0.39)	1.07 (1.03)	1.14 (0.60)	1.45 (1.09)	1.84 (0.97)	0.67 (0.70)
2	C	0.00	0.29 (0.22)	0.68 (0.47)	1.23 (0.40)	1.38 (0.73)	0.25 (0.28)
	LS	0.09 (0.13)	1.08 (1.72)	0.74 (0.37)	0.70 (0.74)	1.60 (0.77)	0.19 (0.20)
	U	1.07 (1.12)	1.48 (1.48)	1.76 (0.78)	1.40 (0.94)	2.44 (1.27)	0.42 (0.42)
	LS+U	0.36 (0.39)	0.90 (0.92)	1.47 (0.22)	1.25 (1.29)	1.14 (1.18)	0.36 (0.41)
3	C	1.17 (1.04)	1.20 (0.83)	1.93 (0.56)	1.80 (1.69)	0.03 (0.03)	0.08 (0.14)
	LS	2.08 (2.81)	1.10 (1.14)	1.81 (0.82)	2.00 (0.98)	0.00	0.32 (0.34)
	U	0.85 (0.63)	0.98 (0.96)	1.52 (0.48)	1.39 (0.95)	0.35 (0.36)	0.05 (0.06)
	LS+U	0.22 (0.21)	1.42 (1.63)	1.36 (0.73)	0.73 (0.42)	0.07 (0.13)	0.07 (0.07)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.5.A. Carbon leached per week from the Dalhousie soil during the first six weeks of the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	0.27 (0.09)	0.38 (0.30)	0.73 (0.76)	0.99 (0.59)	0.46 (0.40)	1.46 (0.45)
	LS	0.26 (0.15)	0.19 (0.04)	0.32 (0.18)	0.23 (0.18)	0.29 (0.50)	1.06 (0.66)
	U	0.18 (0.04)	0.76 (0.27)	0.56 (0.34)	1.06 (0.91)	0.84 (1.13)	1.19 (1.07)
	LS+U	0.30 (0.05)	1.15 (0.52)	0.92 (0.42)	0.66 (0.32)	0.90 (0.43)	0.87 (1.04)
2	C	0.99 (0.35)	2.32 (1.28)	2.23 (1.39)	1.90 (1.18)	1.32 (0.80)	0.59 (0.67)
	LS	1.32 (0.68)	2.31 (1.44)	2.24 (1.78)	1.98 (0.85)	1.22 (1.16)	1.24 (1.26)
	U	1.5 (0.61)	1.95 (1.11)	1.80 (1.28)	1.74 (0.87)	0.99 (0.78)	0.83 (0.53)
	LS+U	1.20 (0.68)	1.08 (0.75)	1.86 (1.07)	1.18 (1.25)	0.97 (0.97)	2.14 (1.43)
3	C	1.70 (0.18)	0.25 (0.04)	2.89 (1.87)	1.54 (1.16)	1.37 (1.58)	3.39 (3.40)
	LS	2.77 (0.62)	3.11 (2.69)	3.05 (2.03)	2.59 (1.87)	1.84 (1.33)	1.04 (0.82)
	U	0.76 (0.19)	1.97 (1.18)	2.14 (1.45)	1.52 (0.97)	1.75 (0.35)	1.79 (1.72)
	LS+U	0.75 (0.34)	3.40 (0.24)	3.92 (0.52)	2.21 (0.65)	5.09 (1.81)	1.68 (1.17)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/week, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.5.B. Carbon leached per week from the Dalhousie soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.73 (0.55)	0.70 (0.45)	0.70 (0.18)	1.06 (0.68)	0.59 (0.46)	0.40 (0.28)
	LS	0.66 (0.80)	0.81 (0.29)	0.59 (0.39)	1.13 (0.72)	0.58 (0.94)	0.39 (0.50)
	U	0.68 (0.70)	0.60 (0.41)	0.66 (0.86)	1.57 (1.43)	0.68 (0.68)	0.29 (0.29)
	LS+U	1.12 (0.73)	0.71 (0.20)	0.27 (0.29)	0.44 (0.31)	0.21 (0.22)	0.25 (0.41)
2	C	1.25 (0.68)	0.98 (0.46)	0.63 (0.70)	1.22 (1.05)	1.19 (1.80)	0.31 (0.54)
	LS	0.99 (0.59)	0.52 (0.53)	0.59 (0.61)	0.70 (0.64)	0.80 (0.86)	0.02 (0.03)
	U	1.08 (0.91)	1.77 (1.28)	0.87 (0.66)	0.98 (0.81)	0.40 (0.40)	0.23 (0.40)
	LS+U	0.96 (1.07)	0.70 (0.76)	0.67 (0.66)	1.08 (0.78)	0.10 (0.17)	1.06 (1.06)
3	C	1.95 (1.54)	0.81 (1.31)	0.46 (0.46)	0.78 (0.49)	0.46 (0.64)	0.66 (1.15)
	LS	2.09 (0.97)	4.82 (2.42)	0.51 (0.53)	0.86 (0.84)	1.35 (2.11)	0.01 (0.03)
	U	1.40 (0.83)	0.74 (0.76)	0.39 (0.40)	0.74 (0.44)	0.16 (0.28)	0.13 (0.14)
	LS+U	0.64 (0.13)	0.53 (0.53)	0.36 (0.08)	0.32 (0.15)	0.70 (0.70)	0.30 (0.30)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.6. Soil C (non transformed data) in the Ormstown soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	4.21	3.42	4.45	5.59
	LS	6.39	8.53	5.88	3.83
	U	6.95	2.29	3.50	3.00
	LS+U	8.31	3.53	10.04	16.73
2	C	5.66	4.42	7.45	9.04
	LS	6.35	13.52	8.79	14.58
	U	7.01	3.86	8.87	3.10
	LS+U	19.10	21.23	15.64	9.39
3	C	6.58	7.69	12.91	11.00
	LS	26.98	13.13	18.71	33.87
	U	10.22	9.59	7.09	5.66
	LS+U	14.75	23.01	12.75	31.49

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.7. Soil C (non-transformed data) in the Dalhousie soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	4.42	3.84	4.46	4.07
	LS	10.45	14.97	6.25	14.25
	U	3.24	2.37	2.92	5.23
	LS+U	21.77	6.35	9.48	10.45
2	C	5.39	5.91	5.57	6.43
	LS	22.40	25.42	23.23	21.32
	U	4.08	7.52	10.64	2.58
	LS+U	20.76	22.57	17.89	21.58
3	C	6.90	4.54	7.96	5.97
	LS	25.21	23.89	27.56	32.85
	U	14.13	18.96	8.27	9.73
	LS+U	20.55	13.39	23.78	16.06

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.8. Total NO_3-N leached (non-transformed data) form the Ormstown soil during the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	0.96	0.62	0.31	0.37
	LS	1.18	0.11	0.35	0.41
	U	0.37	13.76	4.61	51.73
	LS+U	0.57	10.81	0.44	0.27
2	C	0.59	0.40	0.68	0.30
	LS	2.11	1.24	5.99	4.05
	U	3.95	31.08	16.25	4.78
	LS+U	0.41	0.52	0.82	8.45
3	C	3.80	2.69	3.77	2.15
	LS	0.92	1.52	0.75	0.36
	U	43.66	56.03	76.98	35.87
	LS+U	49.08	34.34	25.26	4.02

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.9. Total NO_3-N leached (non-transformed data) from the Dalhousie soil during the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	0.13	0.38	0.47	0.17
	LS	0.29	0.17	0.13	0.12
	U	36.34	25.51	33.15	2.40
	LS+U	0.21	15.79	33.43	6.57
2	C	0.63	2.62	0.17	0.21
	LS	0.52	1.39	0.55	1.54
	U	60.25	29.62	2.09	53.56
	LS+U	1.28	2.27	1.57	1.79
3	C	3.89	2.48	4.40	5.68
	LS	4.60	1.69	4.96	4.70
	U	76.23	90.35	78.68	46.26
	LS+U	114.19	78.32	97.22	60.48

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.10.A. Nitrate-N leached per week from the Ormstown soil during the first six weeks of the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	0.05 (0.04)	0.08 (0.04)	0.03 (0.02)	0.03 (0.03)	0.18 (0.12)	0.03 (0.06)
	LS	0.01 (0.02)	0.05 (0.02)	0.06 (0.07)	0.05 (0.07)	0.14 (0.13)	0.05 (0.04)
	U	0.04 (0.04)	0.10 (0.09)	0.46 (0.48)	0.69 (1.13)	1.18 (1.81)	0.19 (0.17)
	LS+U	0.10 (0.02)	0.02 (0.02)	0.03 (0.06)	0.06 (0.10)	0.04 (0.02)	0.08 (0.10)
2	C	0.11 (0.01)	0.10 (0.08)	0 06 (0.06)	0.07 (0.06)	0.03 (0.02)	0.01 (0.01)
	LS	0.47 (0.32)	0.07 (0.09)	0.50 (0.51)	0.62 (0.44)	0.53 (0.40)	0.47 (0.35)
	U	0.23 (0.09)	0.05 (0.02)	0.32 (0.32)	0.38 (0.30)	0.76 (0.60)	0.95 (0.97)
	LS+U	0.15 (0.06)	0.03 (0.01)	0.11 (0.14)	0.04 (0.03)	0.04 (0.05)	0.05 (0.05)
3	C	0.19 (0.02)	0.52 (0.46)	0.67 (0.60)	0.47 (0.35)	0.27 (0.20)	0.29 (0.17)
	LS	0.18 (0.01)	0.06 (0.04)	0.07 (0.09)	0.13 (0.16)	0.03 (0.04)	0.08 (0.08)
	U	0.50 (0.17)	1.83 (1.06)	2.66 (2.43)	4.59 (4.61)	4.83 (4.10)	5.15 (2.71)
	LS+U	0.12 (0.19)	0.41 (0.42)	2.72 (3.06)	3.20 (3.75)	2.67 (2.73)	3.38 (2.67)

[Z] 1, 2, 3 Moisture regime 0.51, 0.90 and 1.80 cm H_2)/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.10.B. Nitrate-N leached per week from the Ormstown soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.02 (0.02)	0.02 (0.02)	0.00	0.07 (0.05)	0.01 (0.01)	0.04 (0.02)
	LS	0.02 (0.04)	0.02 (0.03)	0.00	0.06 (0.03)	0.02 (0.02)	0.00
	U	2.65 (3.99)	1.53 (1.62)	3.38 (3.58)	2.86 (2.95)	1.91 (1.65)	2.61 (4.50)
	LS+U	0.09 (0.13)	0.34 (0.57)	0.51 (0.89)	0.67 (1.04)	0.71 (1.05)	0.35 (0.55)
2	C	0.00	0.00	0.00	0.05 (0.01)	0.05 (0.02)	0.01 (0.01)
	LS	0.27 (0.21)	0.19 (0.13)	0.00	0.06 (0.03)	0.11 (0.04)	0.04 (0.03)
	U	1.52 (1.75)	1.51 (1.61)	1.66 (1.60)	1.88 (1.65)	2.51 (1.87)	2.24 (1.32)
	LS+U	0.09 (0.15)	0.21 (0.36)	0.28 (0.48)	0.29 (0.50)	0.70 (0.95)	0.54 (0.92)
3	C	0.18 (0.07)	0.14 (0.06)	0.07 (0.04)	0.06 (0.03)	0.15 (0.01)	0.08 (0.04)
	LS	0.05 (0.06)	0.02 (0.03)	0.02 (0.01)	0.01 (0.02)	0.21 (0.20)	0.02 (0.02)
	U	5.92 (2.83)	7.09 (3.17)	3.18 (1.42)	6.45 (2.26)	6.32 (1.69)	4.60 (1.67)
	LS+U	3.17 (2.20)	2.54 (1.64)	2.50 (1.42)	2.62 (1.45)	2.71 (1.86)	2.11 (1.98)

[Z] 1, 2, 3 Moisture regime 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.11.A. Nitrate-N leached per week from the Dalhousie soil during the first six weeks fo the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	0.02 (0.04)	0.03 (0.01)	0.04 (0.02)	0.03 (0.01)	0.02 (0.02)	0.02 (0.02)
	LS	0.03 (0.05)	0.02 (0.01)	0.02 (0.02)	0.02 (0.01)	0.01 (0.01)	0.03 (0.02)
	U	0.20 (0.13)	0.12 (0.03)	0.37 (0.30)	1.15 (0.71)	1.72 (1.17)	2.93 (2.18)
	LS+U	0.12 (0.05)	0.12 (0.18)	0.27 (0.32)	0.40 (0.42)	0.74 (1.12)	1.10 (1.40)
2	C	0.38 (0.43)	0.17 (0.27)	0.13 (0.17)	0.05 (0.04)	0.01 (0.01)	0.01 (0.01)
	LS	0.15 (0.16)	0.10 (0.08)	0.09 (0.06)	0.04 (0.03)	0.05 (0.02)	0.08 (0.06)
	U	0.37 (0.44)	1.23 (0.84)	3.84 (2.63)	3.03 (2.47)	2.57 (2.08)	1.26 (1.01)
	LS+U	0.68 (0.32)	0.19 (0.14)	0.09 (0.05)	0.17 (0.05)	0.06 (0.03)	0.04 (0.01)
3	C	2.17 (0.40)	0.96 (0.43)	0.16 (0.17)	0.21 (0.07)	0.02 (0.03)	0.04 (0.05)
	LS	1.51 (0.50)	0.69 (0.35)	0.42 (0.10)	0.20 (0.07)	0.10 (0.08)	0.06 (0.07)
	U	2.45 (1.03)	6.58 (3.67)	3.03 (2.06)	10.62 9.52)	4.52 (2.70)	5.62 (2.99)
	LS+U	1.85 (0.91)	6.86 (1.60)	8.25 (3.01)	9.74 (3.31)	12.63 (3.98)	8.80 (1.89)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.11.B. Nitrate-N leached per week from the Dalhousie soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.00	0.00	0.00	0.01 (0.01)	0.12 (0.11)	0.00
	LS	0.00	0.01 (0.01)	0.00	0.01 (0.00)	0.05 (0.02)	0.00
	U	2.01 (1.23)	3.71 (3.01)	0.98 (1.10)	3.57 (2.55)	5.83 (3.17)	1.76 (1.31)
	LS+U	1.72 (1.99)	2.09 (2.08)	2.13 (1.34)	2.29 (2.71)	1.87 (1.62)	1.13 (0.79)
2	C	0.02 (0.01)	0.00	0.04 (0.03)	0.02 (0.03)	0.06 (0.02)	0.01 (0.01)
	LS	0.02 (0.01)	0.01 (0.01)	0.38 (0.20)	0.02 (0.01)	0.05 (0.07)	0.01 (0.01)
	U	5.41 (4.59)	4.73 (3.86)	4.23 (4.08)	2.57 (1.56)	4.72 (3.16)	2.40 (1.73)
	LS+U	0.03 (0.01)	0.02 (0.02)	0.13 (0.09)	0.02 (0.04)	0.21 (0.05)	0.08 (0.04)
3	C	0.07 (0.07)	0.00 (0.01)	0.10 (0.10)	0.11 (0.10)	0.19 (0.15)	0.07 (0.07)
	LS	0.08 (0.13)	0.00 (0.01)	0.18 (0.05)	0.12 (0.17)	0.33 (0.20)	0.27 (0.19)
	U	9.35 (4.97)	8.19 (2.77)	9.16 (0.98)	4.80 (2.11)	4.46 (2.37)	4.10 (2.81)
	LS+U	11.23 (3.87)	6.90 (0.86)	10.06 (2.89)	5.49 (3.60)	3.67 (2.04)	2.05 (0.52)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.12. Soil NO_3-N (non-transformed data) in the Ormstown soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	3.66	4.80	4.51	8.92
	LS	--	5.59	6.54	5.79
	U	130.19	164.91	112.67	436.55
	LS+U	44.45	215.11	11.36	71.49
2	C	5.21	9.05	76.064	4.15
	LS	5.20	4.71	6.30	6.76
	U	183.25	207.68	114.30	--
	LS+U	26.69	30.07	25.01	175.60
3	C	--	6.17	3.15	2.83
	LS	3.17	7.73	4.04	5.68
	U	71.05	86.09	57.48	80.69
	LS+U	88.47	112.15	46.36	29.65

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.13. Soil NO_3-N (non-transformed data) in the Dalhousie soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	4.99	17.54	16.09	5.57
	LS	42.41	10.37	35.35	32.87
	U	278.69	209.32	209.15	167.67
	LS+U	174.80	143.65	347.31	150.96
2	C	4.23	11.18	17.76	22.63
	LS	7.61	51.35	13.40	8.68
	U	79.37	64.58	92.42	87.23
	LS+U	17.70	6.84	6.65	45.27
3	C	26.23	14.96	20.63	9.46
	LS	28.25	17.07	7.23	16.25
	U	25.77	51.12	34.18	94.92
	LS+U	37.98	33.29	--	42.79

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.14. Total NH_4-N leached (non-transformed data) from the Ormstown soil during the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	0.25	0.29	--	0.15
	LS	0.18	0.58	0.11	0.24
	U	0.63	0.43	0.41	0.72
	LS+U	0.89	0.57	0.97	1.21
2	C	0.64	0.60	0.46	1.55
	LS	0.47	0.48	2.54	0.17
	U	1.21	0.43	0.88	0.51
	LS+U	1.07	1.95	1.24	0.68
3	C	0.36	1.14	0.38	0.99
	LS	2.46	0.83	2.14	3.00
	U	5.09	3.28	1.89	3.31
	LS+U	3.90	1.68	1.97	3.98

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.15. Total NH_4-N leached (non-transformed data) from the Dalhousie soil during the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	0.92	0.56	0.72	0.63
	LS	0.57	1.04	0.32	1.08
	U	0.75	1.07	1.01	1.17
	LS+U	2.29	0.71	0.71	2.25
2	C	1.58	0.34	2.67	1.92
	LS	2.12	1.63	3.00	1.11
	U	2.32	1.78	7.29	1.67
	LS+U	3.68	1.33	1.98	2.05
3	C	3.22	4.14	3.06	1.05
	LS	1.98	3.55	2.96	5.57
	U	5.56	6.55	5.64	12.41
	LS+U	4.41	5.67	3.05	8.24

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.16.A. Ammonium-N leached per week from the Ormstown soil during the first six weeks of the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	0.07 (0.04)	0.02 (0.03)	0.03 (0.01)	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)
	LS	0.04 (0.02)	0.02 (0.02)	0.01 (0.02)	0.00	0.02 (0.01)	0.00 (0.01)
	U	0.06 (0.03)	0.14 (0.14)	0.03 (0.02)	0.00	0.04 (0.02)	0.00
	LS+U	0.01 (0.01)	0.04 (0.02)	0.02 (0.01)	0.01 (0.01)	0.03 (0.02)	0.03 (0.02)
2	C	0.02 (0.02)	0.05 (0.04)	0.05 (0.03)	0.01 (0.01)	0.01 (0.02)	0.03 (0.03)
	LS	0.08 (0.04)	0.75 (0.97)	0.00	0.00 (0.01)	0.00	0.00
	U	0.03 (0.04)	0.15 (0.19)	0.04 (0.02)	0.01 (0.01)	0.02 (0.01)	0.04 (0.02)
	LS+U	0.04 (0.00)	0.07 (0.05)	0.03 (0.02)	0.05 (0.03)	0.07 (0.06)	0.10 (0.02)
3	C	0.07 (0.03)	0.05 (0.03)	0.07 (0.05)	0.05 (0.05)	0.05 (0.05)	0.09 (0.04)
	LS	0.03 (0.02)	0.13 (0.06)	0.17 (0.10)	0.19 (0.10)	0.17 (0.09)	0.23 (0.09)
	U	0.69 (0.45)	0.19 (0.10)	0.26 (0.05)	0.22 (0.03)	0.21 (0.06)	0.33 (0.11)
	LS+U	0.47 (0.58)	0.17 (0.03)	0.24 (0.13)	0.25 (0.04)	0.21 (0.03)	0.32 (0.16)

[Z] 1, 2, 3 Moisture regime 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.16.B. Ammonium-N leached from the Ormstown soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.00	0.00	0.03 (0.01)	0.06 (0.01)	0.00	0.00
	LS	0.02 (0.03)	0.00	0.04 (0.03)	0.05 (0.03)	0.02 (0.02)	0.03 (0.06)
	U	0.02 (0.02)	0.02 (0.04)	0.11 (0.03)	0.09 (0.04)	0.01 (0.01)	0.00
	LS+U	0.03 (0.03)	0.05 (0.04)	0.16 (0.05)	0.16 (0.07)	0.18 (0.09)	0.18 (0.04)
2	C	0.05 (0.03)	0.05 (0.04)	0.13 (0.08)	0.14 (0.09)	0.09 (0.07)	0.18 (0.05)
	LS	0.02 (0.02)	0.01 (0.01)	0.02 (0.02)	0.00	0.00	0.01 (0.02)
	U	0.04 (0.04)	0.05 (0.03)	0.11 (0.04)	0.09 (0.07)	0.01 (0.02)	0.16 (0.18)
	LS+U	0.10 (0.03)	0.11 (0.05)	0.14 (0.06)	0.14 (0.08)	0.20 (0.12)	0.20 (0.11)
3	C	0.05 (0.03)	0.05 (0.05)	0.07 (0.05)	0.03 (0.04)	0.03 (0.04)	0.08 (0.05)
	LS	0.18 (0.11)	0.21 (0.11)	0.22 (0.11)	0.22 (0.14)	0.12 (0.13)	0.22 (0.15)
	U	0.29 (0.09)	0.28 (0.11)	0.31 (0.12)	0.23 (0.12)	0.19 (0.13)	0.17 (0.13)
	LS+U	0.17 (0.04)	0.17 (0.03)	0.18 (0.07)	0.19 (0.13)	0.20 (0.22)	0.29 (0.35)

[Z] 1, 2, 3 Moisture regime 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.17.A. Ammonium-N leached per week from the Dalhousie soil during the first six weeks of the incubation.

Treatment[Y]		Week					
		1	2	3	4	5	6
		(mg)					
1[Z]	C	0.03 (0.02)	0.04 (0.03)	0.06 (0.03)	0.04 (0.01)	0.08 (0.02)	0.10 (0.01)
	LS	0.06 (0.01)	0.03 (0.01)	0.04 (0.05)	0.07 (0.03)	0.05 (0.04)	0.07 (0.04)
	U	0.03 (0.01)	0.04 (0.01)	0.03 (0.01)	0.04 (0.03)	0.03 (0.02)	0.03 (0.04)
	LS+U	0.07 (0.05)	0.05 (0.01)	0.08 (0.04)	0.10 (0.03)	0.08 (0.04)	0.13 (0.10)
2	C	0.06 (0.02)	0.06 (0.04)	0.08 (0.07)	0.08 (0.03)	0.08 (0.05)	0.09 (0.06)
	LS	0.11 (0.03)	0.20 (0.06)	0.20 (0.07)	0.16 (0.08)	0.19 (0.07)	0.18 (0.09)
	U	0.13 (0.05)	0.13 (0.03)	0.21 (0.03)	0.30 (0.12)	0.29 (0.09)	0.24 (0.12)
	LS+U	0.13 (0.07)	0.19 (0.05)	0.16 (0.10)	0.17 (0.06)	0.21 (0.12)	0.18 (0.06)
3	C	0.19 (0.05)	0.27 (0.10)	0.23 (0.27)	0.18 (0.07)	0.11 (0.09)	0.21 (0.08)
	LS	0.26 (0.11)	0.30 (0.17)	0.28 (0.15)	0.32 (0.13)	0.28 (0.08)	0.35 (0.08)
	U	0.19 (0.05)	0.67 (0.13)	0.56 (0.21)	1.03 (0.41)	1.14 (0.50)	1.16 (1.25)
	LS+U	0.32 (0.06)	0.56 (0.13)	0.60 (0.12)	0.63 (0.12)	0.54 (0.16)	0.60 (0.25)

[Z] 1, 2, 3 Moisture regime 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.17.B. Ammonium-N leached per week from the Dalhousie soil during the last six weeks of the incubation.

Treatment[Y]		Week					
		7	8	9	10	11	12
		(mg)					
1[Z]	C	0.03 (0.02)	0.07 (0.04)	0.07 (0.02)	0.05 (0.02)	0.05 (0.04)	0.08 (0.02)
	LS	0.06 (0.03)	0.07 (0.01)	0.06 (0.05)	0.07 (0.04)	0.08 (0.05)	0.09 (0.03)
	U	0.11 (0.06)	0.15 (0.04)	0.13 (0.07)	0.11 (0.05)	0.20 (0.06)	0.08 (0.07)
	LS+U	0.11 (0.09)	0.15 (0.16)	0.35 (0.27)	0.07 (0.05)	0.17 (0.09)	0.11 (0.06)
2	C	0.12 (0.07)	0.13 (0.08)	0.38 (0.15)	0.11 (0.09)	0.18 (0.09)	0.25 (0.12)
	LS	0.15 (0.09)	0.13 (0.06)	0.15 (0.02)	0.14 (0.06)	0.14 (0.10)	0.19 (0.13)
	U	0.25 (0.17)	0.20 (0.13)	0.43 (0.34)	0.24 (0.25)	0.39 (0.49)	0.45 (0.58)
	LS+U	0.16 (0.06)	0.14 (0.03)	0.40 (0.15)	0.19 (0.08)	0.06 (0.09)	0.27 (0.09)
3	C	0.22 (0.09)	0.17 (0.09)	0.60 (0.31)	0.20 (0.08)	0.20 (0.12)	0.29 (0.14)
	LS	0.32 (0.11)	0.22 (0.15)	0.57 (0.13)	0.22 (0.15)	0.11 (0.13)	0.28 (0.24)
	U	1.09 (1.18)	0.37 (0.24)	0.64 (0.23)	0.25 (0.12)	0.13 (0.11)	0.29 (0.13)
	LS+U	0.56 (0.37)	0.49 (0.27)	0.70 (0.37)	0.16 (0.18)	0.02 (0.04)	0.24 (0.11)

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90, and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.
( ) Standard deviations of means (n=4).

Table 4.18. Soil NH_4-N (non-transformed data) in the Ormstown soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	83.26	94.84	101.81	95.09
	LS	76.08	193.86	111.47	89.74
	U	205.53	128.04	220.18	122.69
	LS+U	316.09	205.38	235.71	488.89
2	C	110.87	108.87	72.00	199.75
	LS	78.98	105.45	73.03	--
	U	314.61	142.59	200.80	--
	LS+U	877.07	429.66	606.06	236.23
3	C	--	102.85	85.09	119.17
	LS	260.77	101.20	167.88	245.43
	U	174.92	117.35	163.15	168.12
	LS+U	218.76	207.70	268.54	704.84

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.19. Soil NH_4-N (non-transformed data) in the Dalhousie soil after the 12 week incubation.

Treatment[Y]		Replicates			
		1	2	3	4
		(mg)			
1[Z]	C	60.46	54.95	56.73	64.48
	LS	121.21	98.94	107.29	213.71
	U	78.06	81.50	77.65	121.37
	LS+U	291.46	89.37	86.23	111.69
2	C	77.01	43.26	78.18	287.76
	LS	83.90	79.04	85.43	65.58
	U	69.31	68.44	641.86	65.87
	LS+U	73.91	79.04	72.22	56.43
3	C	61.44	83.51	58.77	56.94
	LS	92.23	70.26	83.77	185.24
	U	79.56	91.58	79.18	98.36
	LS+U	79.80	91.85	--	98.11

[Z] 1, 2, 3 Moisture regimes 0.51, 0.90 and 1.80 cm H_2O/wk, respectively.
[Y] C, LS, U denote control, ammonium lignosulfonate and urea, respectively.

Table 4.20. Table of probabilities for total leachate C, NO_3-N and NH_4-N (from Main ANOVA).

Source	C	NO_3-N	NH_4-N
LS[Z]	**	**	NS
U[Y]	NS	**	**
SOIL[X]	**	NS	**
MOIST[W]	**	**	**
LS*U	NS	**	NS
LS*SOIL	*	NS	NS
LS*MOIST	NS	NS	NS
U*SOIL	NS	*	NS
U*MOIST	NS	*	NS
SOIL*MOIST	NS	NS	NS
LS*U*SOIL	*	NS	NS
LS*U*MOIST	*	**	*
U*SOIL*MOIST	NS	NS	NS
LS*SOIL*MOIST	NS	NS	NS
LS*U*SOIL*MOIST	NS	NS	NS

[Z] Ammonium lignosulfonate.
[Y] Urea.
[X] Soil (Dalhousie and Ormstown).
[W] Moisture (0.51, 0.90 and 1.80 cm H_2O/wk).
NS, *, ** Not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

Table 4.21. Table of probabilities for soil C, NO_3-N and NH_4-N in the leaching columns after the three month incubation (from Main ANOVA).

Source	C	NO_3-N	NH_4-N
LS[z]	**	*	**
U[y]	NS	**	**
SOIL[x]	**	*	**
MOIST[w]	**	**	NS
LS*U	NS	**	NS
LS*SOIL	NS	NS	NS
LS*MOIST	NS	**	NS
U*SOIL	NS	**	**
U*MOIST	NS	**	NS
SOIL*MOIST	**	*	NS
LS*U*SOIL	NS	NS	*
LS*U*MOIST	NS	NS	NS
U*SOIL*MOIST	NS	NS	NS
LS*SOIL*MOIST	NS	NS	NS
LS*U*SOIL*MOIST	NS	NS	NS

[z] Ammonium lignosulfonate.
[y] Urea.
[x] Soil (Dalhousie and Ormstown).
[w] Moisture (0.51, 0.90 and 1.80 cm H_2O/wk).
NS, *, ** not significant ($p>0.05$), significant at $p<0.05$ and $p<0.01$, respectively.

APPENDIX IV

Table 5.1. Ammonium and nitrate nitrogen at four and six weeks in the Chicot soil.

Treatment[a]	Rep	Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(ug/g)		(ug/g)	
Control	1	1.81	49.38	3.27	53.74
	2	6.24	49.67	3.73	52.57
	3	8.23	41.63	3.43	53.37
	4	3.93	53.60	--	--
LS	1	4.85	88.71	5.08	93.40
	2	10.86	82.24	4.62	94.79
	3	15.25	101.42	1.37	101.18
	4	4.62	88.25	0.91	85.47
U	1	5.77	267.75	3.03	281.94
	2	1.85	261.29	7.23	296.17
	3	2.77	292.47	7.00	278.44
	4	2.31	274.22	8.32	299.71
LS+U	1	13.50	294.41	3.70	324.42
	2	7.85	305.87	4.90	311.80
	3	38.58	236.10	15.40	322.07
	4	18.02	295.25	9.33	312.04
U+INH	1	24.95	206.53	14.70	270.74
	2	37.42	222.24	16.80	261.87
	3	63.76	152.01	19.13	274.94
	4	43.89	195.91	37.10	243.67
LS+U+INH	1	61.0	203.30	15.55	290.20
	2	55.44	210.00	40.83	251.60
	3	55.44	210.69	26.37	308.54
	4	74.85	219.47	35.23	256.97

[a] LS, U, inh denote ammonium lignosulfonate, urea and dicyandiamide, respectively.
Note: treatments incubated in 99.43 g oven dry soil.

Table 5.2. Ammonium and nitrate nitrogen at four and six weeks in the Dalhousie soil.

Treatment[z]	Rep	Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(ug/g)		(ug/g)	
Control	1	3.89	118.04	8.38	164.69
	2	4.35	139.08	5.08	136.53
	3	4.16	139.07	0.46	130.07
	4	1.83	131.76	4.62	152.01
LS	1	6.24	142.54	11.20	143.27
	2	12.12	139.77	4.62	135.15
	3	9.15	141.11	7.39	153.86
	4	10.40	150.40	8.78	147.62
U	1	25.87	246.96	10.87	277.51
	2	18.94	248.81	13.27	284.11
	3	21.48	254.36	15.71	277.69
	4	26.80	268.68	8.61	281.58
LS+U	1	43.66	250.43	28.54	267.09
	2	46.44	255.75	32.11	287.62
	3	39.57	248.89	28.65	272.38
	4	41.12	274.45	27.30	278.60
U+INH	1	45.74	223.63	24.73	252.70
	2	43.20	231.02	24.02	251.40
	3	48.28	223.63	23.79	248.81
	4	35.81	244.88	19.21	299.67
LS+U+INH	1	59.37	228.02	42.47	266.93
	2	54.52	227.79	39.73	270.76
	3	67.46	223.17	33.63	267.42
	4	49.44	239.80	38.35	283.93

[z] LS, U, inh denote ammonium lignosulfonate, urea and dicyandiamide, respectively.
Note: treatments incubated in 96.31 g of oven dry soil.

Table 5.3. Ammonium and nitrate nitrogen at four and six weeks in the Ormstown soil.

Treatment[z]	Rep	Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(ug/g)		(ug/g)	
Control	1	23.10	80.16	11.67	80.27
	2	14.09	67.69	3.73	84.23
	3	16.10	69.53	11.32	80.86
	4	11.32	70.00	7.23	79.80
LS	1	17.27	64.40	10.73	80.97
	2	17.50	64.40	25.43	79.10
	3	20.33	69.54	10.19	79.97
	4	20.33	69.54	5.60	89.60
U	1	55.53	102.43	41.07	135.80
	2	59.93	99.28	39.35	122.61
	3	52.50	91.23	45.52	145.95
	4	55.36	92.65	47.60	132.77
LS+U	1	68.38	94.95	53.67	124.37
	2	67.23	104.19	58.45	122.21
	3	67.92	104.19	52.67	104.42
	4	71.17	109.9	59.60	128.68
U+INH	1	65.15	78.55	55.36	99.51
	2	65.15	84.32	42.63	98.72
	3	59.97	93.80	52.27	95.90
	4	58.45	76.70	43.04	103.53
LS+U+INH	1	98.45	71.17	70.47	100.57
	2	83.40	82.01	70.00	96.13
	3	68.61	64.92	61.45	102.57
	4	73.20	75.72	69.77	106.87

[z] LS, U, inh denote ammonium lignosulfonate, urea and dicyandiamide, respectively.
Note: treatments incubated in 95.63 g oven dry soil.

Table 5.4. Ammonium and nitrate nitrogen at four and six weeks in the St. Rosalie soil.

Treatment[z]	Rep	Week 4		Week 6	
		NH_4-N	NO_3-N	NH_4-N	NO_3-N
		(ug/g)		(ug/g)	
Control	1	55.91	101.42	59.27	109.27
	2	60.76	108.81	42.74	120.20
	3	63.07	121.98	47.37	106.24
	4	50.13	88.48	45.50	113.00
LS	1	69.54	77.85	63.47	119.30
	2	64.92	88.48	58.67	128.51
	3	84.70	94.27	59.73	122.57
	4	81.32	89.87	74.16	122.05
U	1	17.41	107.97	175.47	158.97
	2	19.57	114.36	167.07	179.97
	3	22.78	119.21	157.50	174.37
	4	21.66	108.89	199.03	159.67
LS+U	1	27.38	107.06	210.00	144.74
	2	24.76	94.03	213.27	159.20
	3	24.36	97.34	197.09	155.47
	4	23.12	91.37	228.71	147.00
U+INH	1	19.53	105.34	195.53	198.64
	2	18.27	84.21	222.47	134.06
	3	19.76	106.98	186.43	162.02
	4	17.53	99.22	203.47	149.64
LS+U+INH	1	21.05	96.72	220.50	131.83
	2	20.88	93.45	224.32	129.14
	3	24.87	85.90	237.41	121.42
	4	23.47	86.36	217.23	126.93

[z] LS, U, inh denote ammonium lignosulfonate, urea anf dicyandiamide, respectively.
Note: treatments incubated in 92.52 g oven dried soil.