National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UREA AND ACIDIC PHOSPHATE INTERACTIONS IN FERTILIZER MICROSITES AND THEIR EFFECT ON CORN (Zea mays L.) YIELD AND NUTRIENT USE EFFICIENCY

by

MINGXIAN FAN

Department of Renewable Resources
McGill University, Montreal
April, 1993

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

National Library of Canada
Acquisitions and Bibliographic Services Branch
395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada
Direction des acquisitions et des services bibliographiques
395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-91899-3

Canada

Suggested short title

UREA AND PHOSPHATE IN MICROSITES AND THEIR EFFECTS ON CORN

ABSTRACT

Ph.D. Mingxian Fan Renewable Resources

Fertilizer applications of urea and triple superphosphate (TSP) suffer from low efficiency for corn production. Band or broadcast application of urea with acidic-P fertilizers may increase fertilizer efficiency. Urea and acidic-P fertilizer interactions in soil-fertilizer microsites were investigated using two Quebec soils. Adding acidic phosphates such as TSP and monoammonium phosphate (MAP) to urea reduced pH in microsites, urea hydrolysis, NH_3 volatilization, and increased soil NH_4- and NO_3-N contents. Ammonia loss decreased as P_2O_5 : urea-N ratios increased. Adding urea to P fertilizer increased soil pH and P sorption when using $CaCl_2$ as the electrolyte. Urea application increased 0.5 *M* $NaHCO_3$ extractable P. Banding urea with TSP caused dissolution of organic matter in soils, and increased P diffusion and P concentration in soil solution sampled with filter paper or in 1 *M* KCl extraction. Two years of field experiments demonstrated that banding urea with TSP or MAP increased soil extractable P (Mehlich-3), N and P nutrient uptake, plant growth and development of corn. Greater P fertilizer efficiencies and higher yields were achieved by banding urea-acidic P fertilizers.

RESUME

Ph D

Mingxian Fan

Ressources renouvelable

L'efficacité des engrais d'urée et de super triple phosphate (STP) pour le maïs n'est pas élevée. Les applications en bande ou à la volée d'urée avec les phosphates acidiques pourraient augmenter leur efficacité. Les interactions d'urée et de phosphates acidiques dans les microsites d'engrais furent examinées dans deux sols Québecois. L'addition de phosphates acidiques comme le STP et le phosphate monoammoniacal (PMA) à l'urée a réduit le pH dans les microsites, l'hydrolyse d'urée, la volatilisation de NH_3 et a augmenté la quantité de NH_4- et NO_3-N dans le sol. Les pertes de NH_3 furent réduites quant aux augmentations du rapport P_2O_5 : urée. L'addition d'urée à l'engrais phosphaté a augmenté le pH et l'adsorption de P dans un système utilisant une solution de $CaCl_2$ comme électrolyte. L'addition d'urée a augmenté le niveau de P extrait avec 0.5 M $NaHCO_3$. L'application d'urée en bande avec le STP a dissout la matière organique dans le sol, augmenté la diffusion de P et augmenté la quantité de P dissout dans le sol, en utilisant des papiers filtres ou des extraits de M KCl comme méthode d'analyse. Deux années d'expériences a démontré que l'application d'urée en bande avec le STP ou PMA a fait accroître le P extrait avec la solution Mehlich-3, l'absorption de N et P et la croissance et le développement du maïs. L'efficacité plus élevée de P comme engrais et l'augmentation en rendements furent atteintes en utilisant des mélanges d'urée et d'engrais phosphatés acidiques en bande.

PREFACE

Urea, triple superphosphate (TSP) and monoammonium phosphate (MAP) are important N and P fertilizers and their use is growing in the world. However, several problems have been encountered in the use of urea and P fertilizers which reduce their efficiency as fertilizers. The purpose of this research was 1) to investigate the interactions between urea and acidic phosphate fertilizer in soil-fertilizer microsites using two acid Quebec soils, and 2) to evaluate the agronomic benefits and fertilizer efficiency from band applications of urea with acidic phosphate fertilizers in the field.

This thesis comprises seven chapters, preceded by a general introduction. Chapter I is a review of current literature, which discusses the reactions limiting fertilizer efficiency when urea and acidic P fertilizer are applied to soil and the potential benefits from interactions between urea and acidic P fertilizers. Hypotheses to be tested were generated from this review. Chapter II presents a rapid method of measuring pH changes in soil-fertilizer microsites. Chapter III examines the effect of P fertilizers on pH changes, urea hydrolysis and NH_3 volatilization. Chapter IV presents the results of the interaction between urea and acidic P fertilizers on P sorption in soils, and Chapter V examines P diffusion and P availability in soil. Chapter VI evaluates the effect of banding of urea with acidic P fertilizer in acid soils on fertilizer efficiency and corn yield under field conditions. Chapter VII provides some general conclusions and suggestions for future work. Finally, the Appendices contains detailed results related to this thesis.

Chapter II through VI are presented in paper format, and conform to the requirements set by the Faculty of Graduate Studies and Research. The following statement is excerpted from the Guidelines Concerning Thesis Preparation (1991):

> The candidate has the option, subject to the approval the Department, of including as part of the thesis the text, or duplicated published text (see below), of an original paper, or papers. In this case the thesis must still conform to all other requirements explained in Guidelines Concerning Thesis Preparation. Additional material (procedural and design data as well as descriptions of equipment) must be provided in sufficient detail (e.g. in appendices) to allow a clear and precise judgement to be made of the importance and originality of the research reported. The thesis should be more than a mere collection of manuscripts published or to be published. It must include a general abstract, a full introduction and literature review and a final overall conclusion. Connecting texts which provide logical bridges between different manuscripts are usually desirable in the interests of cohesion.
>
> It is acceptable for theses to include as chapters authentic copies of papers already published, provided these are duplicated clearly on regulation thesis stationary and bound as an integral part of the thesis. Photographs or other materials which do not duplicate well must be included in their original form. In such instances, connecting texts are mandatory and supplementary explanatory material is almost always necessary.
>
> The inclusion of manuscripts co-authored by the candidate and others is acceptable but, the candidate is required to make an explicit statement on who contributed to such work and to what extent, and supervisors must attest to the accuracy of the claims before the Oral Committee. Since the task of the Examiners is made more difficult in these cases, it is in the candidate's interest to make the responsibilities of authors perfectly clear. Candidates following this option must inform the Department before submitting the thesis for review.

Chapter II has been published in the Canadian Journal of Soil Science, 73: 129-132, 1993. Chapters III, IV, and VI are prepared as three papers and have been submitted to the Soil Science Society of America Journal. All of these three papers have been accepted for publication. Chapters III and IV will be published in May-Jun. issue, 1993 and Sept.-Oct. issue, 1993, respectively. Chapter V has been submitted to the Fertilizer Research and has been accepted for publication. Chapter IV was co-authored by the candidate, his supervisor Professor A.F. MacKenzie, and Professor I.P.O'Halloran. The other four papers were co-authored by the candidate and his supervisor Professor A.F. MacKenzie. The candidate was responsible for conducting all original research and for preparing the five manuscripts. Supervisory assistance was provided by Professor A.F. MacKenzie through general guidance and editorial correction and comments during the preparation of the manuscripts. Additional editorial comments for Chapter IV were supplied by Professor I.P. O'Halloran.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Professor A.F. MacKenzie, for his dedicated support, guidance, and "open-door policy". Special thanks also to Professor I.P.O'Halloran for his critical discussion and helpful suggestions throughout the study.

I am also grateful to Dr. G. Mehuys, Professor and Chairman, to Dr. W. Marshall, Professor of Agricultural Chemistry and Food Science, to Dr. T. Moore, Professor of Geography, McGill, and Dr. T. Ross, Agriculture Canada for their encouragement and critical review of my proposal and the thesis.

I also wish to express my appreciation to the support staff who helped out in various ways: Peter Kirby, Khosro Mousavi, Mary Côté, Edith Donald, Gabriel Perras, and Helene Lalonde.

I also wish to extend a special thanks to Baochang Liang for his valuable help in my study, to the community of the Department of Renewable Resources for creating a warm climate in which the study was carried out.

Financial support from the Natural Sciences and Engineering Research Council of Canada for this research, through Operating Grand OGP0002957, is gratefully acknowledged.

I dedicate this work to my wife, Wang Li, and my son, Xiaozhu Fan for their understanding, support and love over the years.

CONTRIBUTIONS TO KNOWLEDGE

Interactions of urea with phosphates in soil-fertilizer microsites and their effects on corn (Zea mays L.) yield and fertilizer efficiency in acid soils were investigated. Several contributions to knowledge are presented.

1) A rapid method for measuring pH in fertilizer microsites was developed using a combination microelectrode and an agar-pH indicator-soil medium. This method allows precise monitoring and visualization of dynamic changes in pH near microsites around fertilizer granules or bands.

2) Adding TSP and MAP to urea significantly reduced total NH_3 volatilization, maximum daily rates of NH_3 loss and delayed the time of maximum NH_3 loss rate on both soils. Ammonia loss decreased as P : urea ratios increased. Ammonia loss from urea was increased with added DAP. The effects of phosphates were related to their effects on pH in soil-fertilizer microsites and subsequently urea hydrolysis. This new finding has major implications for the application of urea-P mixtures or fertilizer granules for no-till fertilization or for crops where fertilizer applications are restricted to soil surfaces.

3) Increase in P sorption and decrease in solution P with added urea was found when using $CaCl_2$ as the electrolyte, which was related to precipitation of Ca-P compounds at higher pH values.

4) Banding urea with TSP increased 1 *M* KCl extractable P, soil solution

P sampled with filter paper, sorbed P concentration and total P diffusing from the band. Urea hydrolysis caused dissolution of soil organic matter, which might inhibit precipitation of insoluble phosphates. These results indicate that banding urea with TSP could benefit P diffusion to plant roots and increase fertilizer P availability.

5) Banding urea with TSP or MAP (N:P_2O_5 ratio of about 1:1.5 to 3) increased soil extractable P (Mehlich-3), improved plant growth and N and P uptake of corn, and increased corn yield. Greater fertilizer use efficiencies and residual effects of P fertilizer were found when acidic P fertilizer was banded with a small amount of urea in acid soils. These results suggest banding application of the mixture of urea with acidic P fertilizers such as TSP or MAP (with the ratio of about N:P_2O_5 1:1.5 to 3, and the banded urea-N is limited to under 60 kg ha^{-1}) can be considered as a technique for increasing both crop yield and fertilizer efficiency in acid Quebec soils, and the potential advantage of producing fertilizer granules of urea-acidic P fertilizer mixtures.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Page

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

INTRODUCTION

Modern agricultural technology based on continuing research has contributed greatly to the success of present agricultural strategies. One of the important tools of improved agricultural technology is fertilizer use, particularly nitrogen (N) and phosphorous (P) fertilizers. Nitrogen is one of the most important factors limiting crop production, especially in regions where soils are low in organic matter. Phosphorous deficiency is a major yield limiting factor in acid soils (Clark, 1982). According to Sanchez and Salinas (1981), nearly all acid soils of tropical America are P deficient. Applying N and P fertilizers to these soils has been vital in increasing food production in these areas.

Fertilizers have become more expensive, warranting their efficient use to get maximum output from each input of nutrient. Efficiency in the use of N from ammonium based fertilizers is estimated at 28 to 59 % under Quebec conditions (Miller and MacKenzie, 1978), while that for P is only about 10 to 20% (Barber, 1980; Barrow 1980).

Improving fertilizer N and P efficiency will help not only in food production but in minimizing pollution of our environment through excess fertilizer applications. The most effective way to improve N and P utilization is by minimizing N losses at the farm level and by increasing P availability in soils (Engelstad and Terman, 1985).

Urea, triple superphosphate (TSP) and monoammonium phosphate (MAP) are concentrated and cheap solid fertilizers and their use in world agriculture is growing more rapidly than that of any other fertilizer (Boswell et al., 1985;

Newbould, 1989). World use of urea in agriculture is expected to increase from 90 million tonnes (Mt) in 1990 to a projected 111-134 Mt by the year 2000 (Newbould, 1989). In Canada, 50% of total N sold in 1991 was urea-N, and MAP and TSP accounted for 80% of the total P sold in 1991 (Korol and Rodrigues, 1993). Yet these fertilizers have some inherent disadvantages. With the use of urea, agronomists have long recognized two disadvantages: damage to seedlings and loss of NH_3 (Court, 1964; Fenn and Miyamoto, 1981; Ellington, 1986). These problems result largely from the rapid hydrolysis of urea. With P fertilizer, microsite acidification from acidic fertilizers could dissolve reactive cations such as Fe^{3+}, Al^{3+}, Ca^{2+} and Mn^{2+}. These ions could precipitate phosphate, consequently reducing P availability in soil.

To avoid or reduce these disadvantages, band application of urea and acidic phosphate blends or compacted mixtures are suggested as ways to increase efficiency through synergistic interactions in soils and in crop response. The acidic environment produced by phosphate might neutralize the pH increase from urea hydrolysis and reduce urea damage to growing plants or/and inhibit NH_3 loss (Stumpe, 1984; Lu et al., 1987). Meanwhile, urea hydrolysis in soil could increase the concentration of HCO_3^- and OH^-, which might enhance the solubility of P fertilizer reaction products and inhibit P adsorption on soil (Kissel et al., 1988). However, interactions of urea and acidic phosphate in soils and their effects on crop yield have not been studied extensively. Therefore, research for this thesis was designed to determine the mechanisms of the interactions of urea and acidic phosphates in soils and investigate advantages of band applications of urea and acidic phosphate fertilizers in improving crop yields and fertilizer economics under field conditions.

CHAPTER I

LITERATURE REVIEW

1. GENERAL PRINCIPLES

In most arable soils urea is rapidly converted to unstable ammonium carbamate by soil urease activity (Sahrawat, 1980). Ammonium carbamate readily decomposes to produce NH_4^+, OH^- and HCO_3^- according to the following reaction:

$$CO(NH_2)_2 + H_2O \xrightarrow{\text{urease}} H_2NCOONH_4$$

$$H_2NCOONH_4 + 2H_2O \longrightarrow 2NH_4^+ + OH^- + HCO_3^-$$

Ammonium carbamate produces a marked rise in pH and NH_4^+ concentration around fertilizer particles. This increase of pH results in NH_3 loss as represented by the following reaction:

$$NH_4^+ + OH^- \Longleftrightarrow NH_3 + H_2O$$

These changes in soil solution properties with urea hydrolysis influence N transformations in soil, root environment, and crop development (Tisdale et al., 1985; Yadvinder-Singh and Beauchamp, 1989).

Agronomists have encountered several problems in the use of urea as a fertilizer, including abrupt increases in soil pH, NH_3 and nitrite toxicity to seedlings, and gaseous losses of NH_3 (Bremner, 1978; Creamer and Fox, 1980; Keller and Mengel, 1986). The NH_3 loss from surface placed urea can reach 60 to 80% of the applied N (Fenn and Richards, 1986; Gould et al., 1986). These gaseous losses depend on many soil characteristics and environmental factors, such as the initial pH of the soil and its buffer capacity, and wind turbulence at the soil surface. Losses are also affected by the activity of urease, and the diffusion of urea and its products into the soil (Rachhpal-Singh and Nye, 1984).

Researchers have attempted to avoid conditions favourable to extensive NH_3 losses by adding materials to urea that inhibit dissolution and hydrolysis of urea, or retard the increase in pH associated with hydrolysis. Coating materials that slow the dissolution of urea have been found to reduce NH_3 volatilization (Matocha, 1976), but high costs have reduced their use by farmers (Parr, 1976). A number of urease inhibitors have been tested in recent years, but the rates of application required to inhibit the urease activity are often economically prohibitive (Sahrawat, 1980).

Phosphoric acid, TSP, MAP, ordinary superphosphate (OSP) and polyphosphate hydrolyse to phosphoric acid and are termed acidic P fertilizers. Their effectiveness is determined by the properties of both the P fertilizers and soil being fertilized and by the reactions which occur between the P fertilizers and various soil constituents. Dissolution of granules of water soluble P fertilizers is fairly rapid, even under conditions of low soil moisture. A nearly saturated solution of the P fertilizer material is formed in and around fertilizer granules, droplets and bands. It has been shown that saturated solutions of TSP and MAP have pH values of 1.0 and 3.5 (Table 1).

When the concentrated P solution moves into the surrounding soil, it will dissolve some soil minerals resulting in the release of large quantities of soil cations such as Fe^{3+}, Al^{3+}, Mn^{2+} Ca^{2+} and Mg^{2+}. Phosphorus in the concentrated solution reacts with these cations to form precipitates with various solubilities.

Table 1. Composition of saturated solutions of P fertilizers (Sample et al., 1980).

Compound	Formula	pH	P (mol L^{-1})	Accompaning cation (mol L^{-1})	
Monocalcium Phosphate	$Ca(H_2PO_4)_2.H_2O$	1.0	4.5	Ca	1.3
Monoammonium Phosphate	$NH_4H_2PO_4$	3.5	2.9	NH_4	2.9
Monopotassium Phosphate	KH_2PO_4	4.0	1.7	K	1.7
Diammonium Phosphate	$(NH_4)_2HPO_4$	8.0	3.8	NH_4	7.6

In addition, P can be adsorbed on soil constituents at the periphery of the soil-fertilizer reaction zone, where P concentrations are much lower. Both precipitation and adsorption occurring at the application site would reduce P availability in soils. This process is termed P fixation. However, rates of change and availabilities of the soil-fertilizer reaction products to crops are influenced by soil properties and environmental conditions. For example, soil pH has a profound influence on the amount and manner in which soluble P becomes fixed. It was reported that P forms low solubility compounds with Fe^{3+} and Al^{3+} at low pH, more soluble compounds with Ca^{2+} and Mg^{2+} at pH value near neutrality, and low solubility compounds with Ca^{2+} at higher pH values (Sample et al., 1980). There is a wide range in solubility of these precipitated phosphate compounds and their availability to crops is usually greatest within the pH range of about 6 to 7 for most agricultural soils. The adsorption of P in acid soil by iron and aluminum oxides also declines with increasing pH (Naidu and Syers, 1990).

2. POTENTIAL BENEFITS FROM INTERACTIONS OF UREA AND ACIDIC PHOSPHATES

Interactions of P and N are economically important because of the dominant role of N and P as fertilizer nutrients in most cropping systems (Malcolm and Farina, 1986). Extensive research has been conducted in the past on agronomic effectiveness of combinations of N and P fertilizers. Some of the studies included urea and acidic phosphates (Engelstad and Terman, 1980), but mostly involved urea-phosphoric acid compounds (Frank, 1986; Urban et al., 1987). Potential benefits from the interaction of urea and acidic P fertilizers should be explored.

1) Improvement of N and P use efficiency by crops

The addition of N fertilizers in combination with P often enhances plant uptake of P. There is evidence that N promotes P uptake by 1) increasing top and root growth; 2) altering plant metabolism; and 3) increasing solubility and availability of P.

A number of researchers have reported a synergistic effect on root growth of supplying N and P together (Sahrawat, 1988). A greater root mass with added N is believed to be responsible for increasing crop uptake of P. Another mechanism for NH_4-N effect on P uptake is P absorption enhancement by the root (Leonce and Mill, 1966; Miller et al., 1970). Leonce and Miller (1966) considered that increased absorption of P by plants receiving NH_4-N was attributed to: a) the rapid assimilation of NH_4-N which increased P uptake; b) the lowering of the pH in the rhizosphere due to NH_4^+ absorption, the resulting increased proportion of $H_2PO_4^-$ to HPO_4^{-2} in solution and enhanced P uptake; c) the applied N resulted in a larger amounts of plant N compounds, some of which either contained P (nucleoproteins), or required P for their formation, and d) increased NH_4^+ ion which increased the activity of P carrier complexes.

2) Reduction of damage to seedling roots or inhibition of NH_3 volatilization

The Tennessee Valley Authority (TVA, 1978) has evaluated low-pH fertilizers such as urea•phosphoric acid (UP). Urea•phosphoric acid was equivalent to conventional higher analysis fertilizers as a P source and had reduced NH_3 losses compared with urea. Such material was superior when fertilizer was topdressed for pastures (Frank, 1986). The acidic environment produced by acidic phosphates might delay or completely inhibit NH_3 volatilization (Stumpe et al., 1984). Bremner and Dougles (1971) found that phosphoric acid reduced gaseous losses of NH_3 by retarding hydrolysis and by reducing the increase in pH from hydrolysis of urea. Urban et al. (1987) showed that UP application decreased NH_3 losses as compared to urea alone due to a reduction in pH. Chien et al. (1987) measured NH_3 volatilization losses from urea on the surface of two soils (Windthorst pH 7.6 and Savannah pH 7.0) and found almost no NH_3 loss for $Mn(Urea_4)Cl_2$ compacted with TSP at a mole ratio of $Ca(HPO_4)_2$:urea of 1:1 or 1:2. However, N losses of 11% to 24% for

$Mn(Urea_4)Cl_2$ alone, and 25% to 39% for prilled urea were found. They concluded that additional acidity produced from hydrolysis of TSP reduced NH_3 losses when materials were applied as multicomponent granules of the metal salt plus urea plus TSP.

Acidic phosphate fertilizers such as MAP and TSP may influence the performance of urea in soil by curtailing the rise in soil pH and resultant loss of NH_3. Inclusion of MAP with urea in fertilizer blends placed with seed of small grain has improved the effectiveness of urea in several research trials in the Prairie provinces of Canada (Beaton, 1976). The contribution of these acidic phosphate materials to the buffering capacity of the soil was believed to be mainly responsible for the reported beneficial interaction with urea (Nyborg, 1979; Ferguson et al., 1984).

The reduction of NH_3 losses from MAP and ammonium polyphosphate (APP), however, was thought to be through the formation of metastable reaction products such as $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$ and $Ca(NH_4)_2P_2O_7 \cdot H_2O$ in soil (Terman, 1979), and calcium ammonium phosphate. Formation of these compounds would tend to inhibit volatilization (Frank, 1985). Furthermore, the H_3PO_4 component in P fertilizers has been found to retard the enzymatic hydrolysis of urea by soil urease, thereby, reducing NH_3 losses for urea (Fenn and Miyamoto, 1981).

The use of acidic phosphate or phosphoric acid as an inhibitor of NH_3 volatilization is made more attractive by the fact that the inhibitor has value as a fertilizer material and can interact with N to increase N and P availability to crops.

3) Increasing of P availability

Reducing P precipitation and increasing solubility of soil-fertilizer P reaction products was suggested as the primary effect of a pH increase on P availability of acidic P fertilizers when applied in acid soils (Hanson and Westfall, 1985; Kamprath, 1987).

Urea hydrolysis could neutralize acidity released from the solution of acidic phosphates. Such a pH increase would reduce the activity of Fe^{3+}, Al^{3+} and Ca^{2+}, reducing P precipitation that might occur during the diffusion process (Olsen, et al., 1954). With the increase of pH, P adsorption could be reduced due to greater competition of HCO_3^-, and OH^- with phosphate ions for sorption and the increase of negative charges on soil particles (Naidu and Syers, 1990). However, it was also reported (Eze and Loganathan, 1990), that P adsorption can be increased with pH increases due to the precipitation of amorphous Fe and Al oxides, which form new P adsorption sites. This pH rise, moreover, increased HPO_4^{-2} over $H_2PO_4^{-1}$ concentration in soil solution, which was more easily sorbed by Fe and Al oxides (Bowden, 1980; Haynes and Swift, 1989).

Hanson and Westfall (1985) found dual application of NH_4OH plus ammonium pyrophosphate (APP) resulted in the increase of $NaHCO_3$- or Bray-extractable P in three soils. Uptake of P from urea + OSP was higher than that from DAP when fertilizers were either incorporated or placed into soil (Lu et al., 1987). Lu et al. (1987) suggested that reaction products of OSP in calcareous soils would be more soluble than reaction products of DAP. Dicalcium phosphate dihydrate (DCPD; $CaHPO_4 \cdot 2H_2O$) has been identified as the major initial reaction product of MCP, which is the P component in OSP, whereas octacalcium phosphate (OCP; $Ca_8H_2(PO_4)_6 \cdot 3H_2O$) and hydroxyapatite (HAP; $Ca_{10}(OH)_2(PO_4)_6$) are the principal reaction products from DAP application to soil.

The availability and efficiency of applied P depend on not only the content of available P but also the rate and extent of P movement into soil from fertilizer granules (Benbi, 1987). Applied P fertilizer in the soil typically moves only a short distance (Sharpley, 1987; Eghball and Sander, 1989; Eghball et al., 1990). This movement is primarily by diffusion processes (Barber et al., 1963; Barber, 1984). Diffusion of P through soil is much slower than in pure water for three reasons: (i) soil water occupies only part of the soil so that the cross-sectional area for diffusion is less; (ii) the diffusion path is tortuous because the water is present as films around soil particles; and (iii) most of the diffusible P is adsorbed on soil surfaces which equilibrate with and buffer the small amount of P in soil solution (Barber, 1980).

Assuming that P diffused mainly through solution, Nye and Tinker (1977) proposed a method (Eq.[1]) for calculating the effective diffusion coefficient, De, in soil

$$De = D\theta f \, dC_l/dC, \qquad [1]$$

where D is the diffusion coefficient in water (for $H_2PO_4^-$, D=0.89 X 10^{-5} cm^2 sec^{-1} at 25 °C), θ is the volumetric moisture content of the soil, *f* is a tortuosity factor and dC_l/dC is the inverse of the buffer capacity of the soil.

For P that is strongly adsorbed on the surface of soil particles, buffering capacity is one of the most important soil factors influencing diffusion of applied P into the soil. Increasing the buffering capacity of P reduces De, and consequently also reduces the distance of diffusion. The buffering capacity of P is measured by P adsorption or desorption isotherms. Increasing added P or reducing soil sorption would reduce the buffering capacity of a soil, because a higher proportion of the added P would subsequently remain in solution (Bhadoria, et al., 1991). Therefore, if band application of acidic phosphate fertilizers with urea could reduce P precipitation and adsorption in soil, it would be beneficial to the movement of P into soil by reducing the P buffering capacity of soil.

However, research has also demonstrated negative results from application of urea and urea-phosphoric acid mixtures. Stumpe et al. (1984) revealed that rapid precipitation of calcium phosphates near the placement site and diffusion of urea away from the fertilizer placement was responsible for the poor performance of granular urea-phosphoric acid in highly calcareous soils. He concluded that urea-urea phosphate mixtures should not be recommended as a means of reducing NH_3 volatilization on highly calcareous soils. However use on noncalcareous soils and soils low in $CaCO_3$ merits further testing.

When certain N and P fertilizers are applied to soil, they could enhance dissolution of soil organic matter, which would play a vital role in P precipitation and P availability. Application of either aqueous or anhydrous NH_3 (Tomasiewiz and Henry, 1985), MAP (Bell and Black, 1970) and the combinations of NH_4OH and MAP or APP (Myers and Thien, 1988) solubilized organic matter in soil. High pH levels produced by NH_3 or NH_4OH could disperse organic matter (Schnitzer, 1978). Chien et al. (1987) found that urea hydrolysis enhanced P dissolution and availability from compacted phosphate rock (PR) in soils having medium to high soil organic matter contents, compared to that from compacted PR plus NH_4Cl or PR plus $(NH_4)_2SO_4$. It appears unlikely that N presence or availability from urea and NH_4Cl or $(NH_4)_2SO_4$ would be a limiting factor for plant growth. It is more likely that the better performance of urea than NH_4Cl in increasing P availability to maize from the compacted PR was due to the interaction of urea hydrolysis and soil organic matter that resulted in a greater dissolution of PR in the soil. During the incubation period with urea, soil pH ranged from 8.5 to 9.7, which would solubilize soil organic matter. Dissolved organic matter could chelate Ca^{2+} ions, and remove them from solution, providing a driving force for the dissolution of PR at high soil pH values. Such a mechanism has been demonstrated by Chien (1979) by using a specific Ca-electrode to monitor the reduced Ca-ion activity in the soil solution.

Organic matter and its decomposition products such as organic anions, could markedly reduce P sorption by soil (Earl et al., 1979; Hue, 1991). Reduced P sorption was believed to be due to the complex formation between organic acids and Fe or Al compounds of the soil and competition of organic anions with phosphate for adsorption sites.

Organic acids also affect P precipitation. Hydroxyapatite (Inskeep and Silvertooth, 1988), OCP and DCPD (Grossl and Inskeep, 1991) precipitation was inhibited by organic acids common to soil environments such as humic, fulvic, tannic and citric acids. These organic acids inhibited the rate of precipitation by adsorbing onto crystal seeds that act as nuclei for new crystal growth. Organic constituents may inhibit formation of thermodynamically stable Ca phosphates, thereby maintaining higher solution P levels in soils.

Regardless of the mechanisms involved, the role of organic matter in increasing P availability would have important implications for many regions of the world. Thus, the interaction between urea and P fertilizers on soil organic matter solubility might increase the agronomic effectiveness of P fertilizers for the regions where most soils are acid and P deficient.

Research has been mainly on the effect of urea and phosphoric acid on fertilizer availability and efficiency to crops. There are very few reports on band applications of urea and TSP/MAP blends or compacted mixtures, and the interaction between them in soil-fertilizer microsites. However, urea, TSP and MAP have now become the major solid N and P fertilizers, and most acid soils require P as well as N fertilizer for crop production. These fertilizers have a relatively high degree of acidity and could produce microsite acidification in soil. Therefore, there is a need to study the possible interaction between urea and acidic P fertilizers such as TSP and MAP on improved fertilizer availability and efficiency in soils. A new technique should be developed to promote efficient fertilizer management that can get both maximum yield and best return from application of urea and acidic phosphate fertilizers.

3. HYPOTHESES

From the review of literature several hypotheses arise.

It is hypothesized that band applications in acid soils of urea combined with acidic P fertilizers as blends or compacted mixtures would avoid or reduce urea damage to seedlings and losses of NH_3 from urea hydrolysis, yet increase P availability in the crop-soil system, and consequently improve N and P use efficiency by the crop.

A general model of the interaction of urea with acidic P fertilizer is shown (Figure 1). Potential effectiveness related to the interaction of these fertilizers is described as follows:

a) Acidification with acidic phosphates will inhibit urease activity and retard or delay urea hydrolysis. A rapid rise in NH_3 concentration and pH in the microsite near urea fertilizer granules will be reduced with added P fertilizers;

b) Potential N losses and damage to seedling growth from urea hydrolysis will be reduced by neutralization with acidic phosphates;

c) Hydrolysis of urea will reduce soil acidification by acidic phosphate fertilizer and will depress the activity of cations such as Fe^{3+}, Al^{3+} and Ca^{2+} in soil solution, reducing the precipitation of P and increasing solubility of P reaction products in soil.

d) The HCO^{-}_{3}, and OH^{-} produced from urea hydrolysis can inhibit competitively phosphate adsorption or replace P ions from the surface of soil particles, reducing soil buffering capacity. Therefore, the availability of phosphate in the soil around the fertilizer microsite can be increased, and diffusion of P in soil enhanced with added urea.

e) Application of urea banded with acidic P fertilizers might solubilize organic matter in soil. Dissolved organic matter could reduce P sorption and precipitation, and increase P movement in soil.

f) A positive interaction of urea and acidic phosphate fertilizers on nutrient availability in soil will result in the improvement of N and P uptake and utilization, plant growth and yield. Both economic and agronomic efficiency of N-P fertilizers will be promoted.

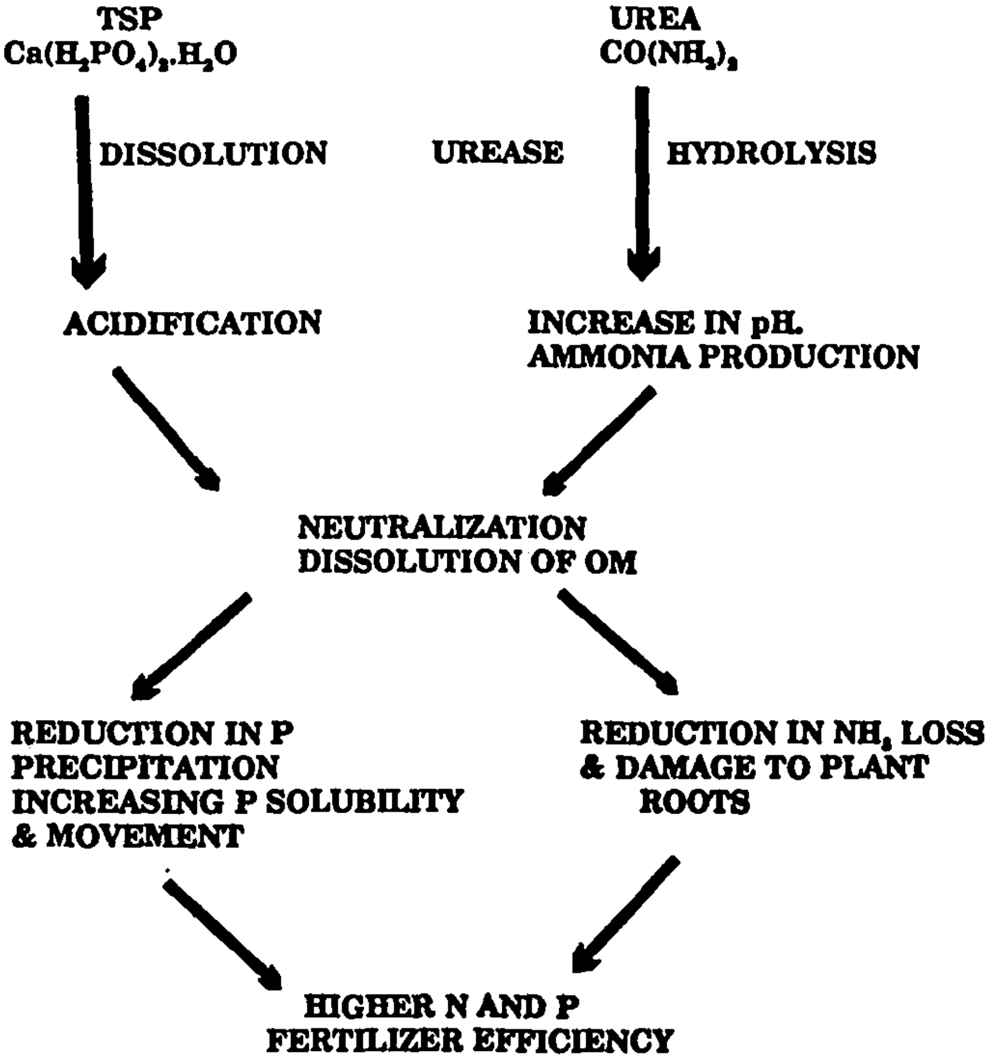


Figure 1. Model of interactions of added urea and TSP in soil

4. OBJECTIVES

The objectives of this research were to determine the mechanisms of interactions between urea and acidic phosphate fertilizers in different soils and to model their reactions in soils. Experiments were designed to study dynamic changes in pH, urea hydrolysis, NH_3 volatilization and the availability and movement of P in soils. Agronomic benefits from band applications of urea with acidic phosphate fertilizers were evaluated in the field to identify a "best" technique for increasing both crop yield and fertilizer efficiency.

5. REFERENCES

Barber, S.A., J.M. Walter, and E.H. Vasey. 1963. Mechanisms for the improvement of plant nutrients from the soil and fertilizer to the plant root. J. Agric. Food Chem. 11:204-207.

Barber, S.A. 1984. Soil nutrient bioavailability: a mechanistic approach. John Wiley & Sons, New York.

Barber, S.A. 1980. Soil-plant interaction in phosphorous nutrition, p.336-360. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.). The role of phosphorus in agriculture. American Society of Agronnmy. Madison. WS., USA.

Barrow, N.J. 1979. The description of desorption of phosphate from soil. J. Soil Sci. 30: 259-270.

Beaton, J.D. 1976. Fertilizer nitrogen. p.47-54. *In* Proc. Western Canada Nitrogen Symp., Alberta Soil Sci. Alberta Agriculture.

Bell, L.C., and C.A. Black. 1970. Comparison of methods for identifying crystalline phosphates produced by interaction of orthophosphate fertilizers with soils. Soil Sci. Soc. Am. Proc. 34:579-582.

Benbi, D.K. 1987. The movement into soil of P from superphosphate grains and its availability to plants. Fert. Res. 12:21-36.

Bhadoria, P.B.S., J. Kaselowsky, N. Claassen, and A. Jungk. 1991. Soil phosphate diffusion coefficients: their dependence on phosphorus concentration and buffer power. Soil Sci. Soc. Am. J. 55:56-60.

Boswell, F.C., J.J. Meisinger and N.L. Case. 1985. Production, marketing and use of nitrogen fertilizers, p.229-286 *In* Engelstad, O.P.(eds) Fertilizer technology and use, 3rd Edition. Soil Sci.Soc.Am.Inc. Madison WS., USA.

Bowden, N.J. 1980. Describing the adsorption of phosphate, citrate and selenite on a variable-charge minerals surface. Aust. J. Soil. Res. 18:49-60.

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

Bremner, J.M. 1978. Urease activity in soils. p.149-191. *In* Soil enzymes. Academic press, New York.

Chien, S.H. 1979. Dissolution of phosphate rock in acid soils as influenced by nitrogen and potassium fertilizers. Soil Sci. 127:371-376.

Chien, S.H., D. Sompongse, J. Henao and D.T. Hellums. 1987. Greenhouse evaluation of phosphorus availability from compacted phosphate rocks with urea or urea and triple superphosphates. Fert. Res. 14:245-256.

Chien, S.H., C,B. Christianson, M.S. Lupin and G.E. Peters. 1987. Compaction of metal salt-urea complexes with triple superphosphate. Fert. Res. 16:181-191.

Clark, R.B. 1982. Plant response to mineral element toxicity and deficiency, p. 71-142. *In* M.N. Christensen and C.F. Lewis (eds.). Breeding plants for less favourable environments. John Wiley and Sons, New York.

Court, M.N. 1964. Toxicity as a cause of inefficiency of urea as a fertilizer. J.

Soil. Sci. 15:42-48; 15:49-65.

Creamer and R.H. Fox. 1980. The toxicity of banded urea or DAP to corn as influenced by soil temperature, moisture and pH. Soil Sci. Soc. Am. J. 44:296-300.

Earl, K.D., J.K. Syers, and J.R. McLaughlin. 1979. Origin of the effects of citrate, tartrate, and acetate on phosphate sorption by soils and synthetic gels. Soil Sci. Soc. Am. J. 43:674-678.

Eghball, B. and D.H. Sander. 1989. Distance and distribution effects of phosphorous fertilizer on corn. Soil Sci. Soc. Am. J. 53:282-287.

Eghball, B., D,H. Sander and J. SKopp. 1990. Diffusion, adsorption, and predicted longevity of banded P fertilizer in three soils. Soil Sci. Soc. Am. J. 54:1161-1165

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

Engelstad, O.P. and G.L. Terman. 1980. Agronomic effectiveness of phosphate fertilizers, p.311-332. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath, (eds.). The role of phosphorus in agriculture. American Society of Agronnmy. Madison. WS., USA.

Eze, O.C. and P. Loganathan. 1990. Effect of pH on phosphate sorption of some Paleudults of southern Nigeria. Soil Sci. 150:613-621.

Fenn, L.B., and J. Richards. 1986. Ammonia loss from surface applied urea-acid products. Fert. Res. 9:265-275.

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

Ferguson, R.B., D.E. Kissel, J.K. Koelliker, and W. Basel. 1984. Ammonia volatilization from surface applied urea: effect of hydrogen ion buffering capacity. Soil Sci. Soc. Am. J. 48:578-582.

Frank, P. 1985. Latest developments in acid phosphate fertilizers, International Fertilizer Development Centre, Muscle Shoals, AL. USA. (unpublished presentation).

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

Grossl, P.R. and W.P. Inskeep. 1991. Precipitation of dicalcium phosphate in the presence of organic acids. Soil Sci. Soc. Am. J. 55:670-675.

Hanson, R.L. and D.G. Westfall. 1985. Orthophosphate solubility transformation and availability from dual applied nitrogen and phosphorus. Soil Sci. Soc. Am. J. 49:1283-1289.

Haynes, R.J. and R.S. Swift. 1989. The effects of pH and drying on adsorption of phosphate by aluminium-organic matter associations. J. Soil Sci. 40:773-781.

Hue, N.V. 1991. Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. Soil Sci. 152:463-471.

Inskeep, W.P., and J.C. Silvertooth. 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. Soil Sci. Soc. Am. J. 52:941-946.

Kamprath, E.J. 1987. Enhanced phosphorus status of maize resulting from nitrogen fertilization of high phosphorus soil. Soil. Sci. Soc. Am. J. 51:1522-1526.

Keller, G.D. and D.B. Mengel. 1986. Ammonia volatilization from N fertilizer surface applied to no-till corn. Soil Sci. Soc. Am. J. 50:1060-1063.

Kissel D.E., M.L. Cabrera, and R.B. Ferguson. 1988. Reactions of ammonia and urea hydrolysis products with soil. Soil Sci. Soc. Am. J. 52: 1793-1796.

Korol M. and C. Rodrigues. 1993. Canadian fertilizer consumption, shipments ans trade, 1991/1992. Agriculture Canada

Leikam, D.R., L.S. Murpy, D.E. Kissel, D.A. Whitney and H.C. Moser, 1983. Effects of nitrogen and phosphorus application method and nitrogen source on winter wheat grain yield and leaf tissue phosphorus. Soil Sci. Soc. Am. J. 47:530-535.

Leonce, F.S. and M.H. Miller. 1966. A physiological effect of nitrogen on phosphorus absorption by corn. Agron. J. 58:245-249.

Lindsay, W.L. and H.F. Stephenson. 1959. Nature of the reactions of monocalcium phosphate in soils. I. The solution that reacts with soil. Soil Sci. Soc. Am. Proc. 23:12-18.

Lindsay, W.L., A.W. Frazier and H.F. Stephenson. 1962. Identification of reaction products from phosphate fertilizers in soils. Soil Sci. Soc. Am. Proc. 26:446-452.

Lu, D.Q., S.H. Chien, J. Henao, and D. Somponges. 1987. Evaluation of short-term efficiency of diammonium phosphate versus urea plus single superphosphate on a calcareous soil. Agron. J. 79:896-900.

Malcolm, E.S. and M.P. Farina. 1986. Phosphorus interaction with other nutrients and lime in field cropping system. Adv. Soil Sci. 5:201-251.

Miller, M.H., C.P. Mamaril, and G.J. Blair. 1970. Ammonium effects on P absorption through pH changes and phosphorus precipitation at the soil-root interface. Agron. J. 62:524-527.

Miller, P.L. and A.F. MacKenzie. 1978. Effects of manures, ammonium nitrate and S-coated urea on yield and N uptake of N by corn and on subsequent inorganic N levels in soils in southern Quebec. Can. J. Soil Sci. 58:153-158.

Motocha, J.E. 1976. Ammonia volatilization and nitrogen utilization from sulphur-coated urea and conventional nitrogen fertilizers. Soil Sci. Soc. Am. J. 40:597-601.

Myers R.G. and S.J. Thien. 1988. Organic matter solubility and soil reaction in an ammonium and phosphorous application zone. Soil Sci. Soc. Am. J. 52:516-522.

Naidu, R. and J.K. Syers. 1990. Effect of liming on phosphate sorption by acid soil. J. Soil Sci. 41:163-175.

Newbould, P. 1989. The use of nitrogen fertilizer in agriculture. Plant Soil. 115:297-311.

Nyborg, M. 1979. Losses of soil and fertilizer nitrogen in northern Alberta, p.56-84. *In* Effective use of nutrient resources in crop production. Proc. Alberta Soil Sci. Workshop. Edmonton, AL.

Nye, P.H. and P.B. Tinker. 1977. Solute movement in the soil-root system. Blackwell Sci. Publ., Oxford. England.

Olsen, S.R., C.V. Cole, F.S. Watanable, and L.A. Dean. 1954. Estimation of available P in soils by extracting with $NaHCO_3$ in soil nutrient availability. USDA Circ. 939.

Rachhpal-Singh and P.H. Nye. 1984. Diffusion of urea, ammonium and soil alkalinity from surface applied urea. J. Soil Sci. 35:529-538.

Rachhpal-Singh and P.H. Nye. 1984. The effect of soil pH and high urea concentration on urease activity in soil. J. Soil Sci. 35:519-527.

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

Sahrawat, K.L. 1988. Effect of nitrogen on growth, and nitrogen and phosphorus uptake in tops and roots of sorghum grown in an Alfisol and a Vertisol. Fert. Res. 17: 119-137.

Sample, E.C., R.J. Soper and G.J. Racz. 1980. Reactions of phosphate fertilizers in soils, p.263-304. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath, (eds.). The role of phosphorus in agriculture. American Society of Agronnmy. Madison. WS., USA.

Sanchez, P.A., and J.G. Salinas. 1981. Low input technologies for managing oxisols and ultisols in tropical America. Adv. Agron. 34:279-406.

Schnitzer, M. 1978. Some observations on the chemistry of humic substances. Agrochimica. 22:216-225.

Sharpley, A.N. 1987. Relative availability of native, residual, and fertilizer P to winter wheat. Soil Sci. Soc. Am. J. 51: 1531-1535.

Stumpe, J.M., P.L.G. Vlek and W.L. Lindsay. 1984. Ammonia volatilization from urea and urea phosphates in calcareous soils. Soil Sci. Soc. Am. J. 48:921-926.

Terman, G.L. 1979. Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments and crop residues. Adv. Agron. 31:189-223.

Tomasiewicz, D.J. and J.L. Henry. 1985. The effect of anhydrous ammonium applications on the solubility of soil organic carbon. Can. J. Soil Sci. 65:737-747.

Tennessee Valley Authority. 1978. Reduction of NH_3 losses from urea applied to soil surfaces, pp.39-41. *In* 12th Demonstration of new developments in fertilizer technology, TVA. Muscle Shoals, AL.

Tisdale, S.L., W.L.Nelson and J.D.Beaton. 1985. Soil fertility and fertilizers. Macmillan Pub. Co. New York.

Urban, W.J., W.L. Hargrove, B.R. Bock and R.A. Raunikar. 1987. Evaluation of urea - urea phosphate as a nitrogen source for no-tillage production. Soil Sci. Soc. Am. J. 51:242-246.

Williams, C.H. 1971. Reactions of surface applied superphosphate with soil. Aust. J. Soil Res. 9:95-106.

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

Young, R.D., D.G. Westfall and G.W. Colliver. 1985. Production, marketing and use of phosphorous fertilizers, p.342-376. *In* Engelstad, O.P.(eds). Fertilizer technology and use, 3rd Edition. Soil Sci.Soc.Am., Madison. WS., USA.

CHAPTER II

A RAPID METHOD FOR MEASURING DYNAMIC CHANGES IN pH OF SOIL MICROSITES AROUND FERTILIZERS

1. ABSTRACT

Nutrient availability from banded fertilizers will depend on properties of the fertilizer band or microsite. Increased pH from urea hydrolysis may change P fertilizer reactions with the soil. A rapid method is described which allows precise measurement and visualization of dynamic changes in pH near microsites around fertilizer granules or bands. One day after application of urea and triple superphosphate fertilizers into the soil, a 0.75% agar solution containing 0.06% bromocresol purple was poured onto the soil surface. The pH was measured using a combination microelectrode placed on the agar and the pH range was estimated from agar colour 2, 4, 6 and 8 days after placement of the fertilizer mixture. Triple superphosphate reduced and retarded pH increases from urea hydrolysis. The results demonstrate the ability of the agar method to monitor pH changes around fertilizer granules or bands.

Key words: pH, agar, triple superphosphate, fertilizer, microsite, urea

2. INTRODUCTION

Fertilizer availability and utilization by crops is modified by fertilizer and soil properties and by microsite reactions which occur near the fertilizer granules, droplets or bands. Changes in soil pH with added fertilizer may influence fertilizer reactions. Chemical processes such as ammonia volatilization, P fixation and precipitation of micronutrients are known to be pH dependent (Lindsay 1962; Myers and Thien 1988).

To characterize pH changes around fertilizer granules, some studies have used mechanical separation of soil around fertilizer granules or bands (Lindsay and Stephenson 1959; Creamer and Fox 1980; Ferguson et al. 1984) or have used soil leachates (Myers and Thien 1988). These methods, however, either destructively sample fertilizer - soil environments or take average values from soil leachates, and they cannot be used to evaluate continuing soil pH changes around such microsites.

Weisenseel et al. (1979) demonstrated distinct pH changes along roots by using an agar medium containing bromocresol purple. With this method, Marschner et al. (1982) measured pH changes and reducing processes at root surfaces of intact plants. Thus far, the technique has not been applied to fertilizer microsites.

The objectives of this study were to evaluate the agar-dye technique for measuring soil pH changes in fertilizer microsites without damaging the sites. The reactions of urea and triple superphosphate (TSP) in soil were used to assess the sensitivity of the agar method to measure pH changes.

2. MATERIALS AND METHODS

Agar solution was prepared by adding 7.50 g agar powder to 1 L of water, followed by autoclaving at 70 °C for 30 minutes. Bromocresol purple was mixed into the resulting solution. Final indicator concentration was 0.06 %. The pH of the solution was adjusted to the pH of the soil under study (pH=5.0) with dilute NaOH or H_2SO_4 solutions. The solution was kept fluid at 40 °C in a water bath until used.

A surface soil sample was obtained from a Ste. Rosalie clay (Humic Gleysol) at pH 5.0, Mehlich No.3 extractable P at 17.6 kg P/ha. 80 g (<2 mm) was spread evenly into a petri dish (15X100 mm). The sample was moistened to 80% field capacity and incubated at a temperature of 25 ± 0.5 °C. After one day's incubation, urea and TSP were mixed and placed into a soil depression in the centre of the dish. One day later, 50 ml of the agar-bromocresol purple solution was poured onto the soil surface and the dish covered. The pH was measured by inserting the sensitive point of a combination microelectrode (Flat surface Ag/AgCl model No.13-620-83, Fisher Scientific. 8505 ch. Devonshire Rd., Montreal) into the agar medium (Fig. 1). Further, the dimension of pH change was estimated from changes in colour of the agar. Measurements were made at 2, 4, 6 and 8 days after fertilizer applications.

Completely cross-classified combinations of two urea rates (Urea1, 20 mg N/dish; Urea2, 40 mg N/dish) and two TSP rates (TSP1, 20 mg P_2O_5/dish; TSP2, 40 mg P_2O_5/dish) were examined using three replications.

3. RESULTS AND DISCUSSION

The results confirmed that acidic phosphate fertilizers such as TSP could retard and reduce pH increases from urea hydrolysis when both are applied to soil (Table 1). After two days, the agar pH of Urea1 and Urea2 treatments reached 7.5 to 7.8, about 15 to 20 mm away from fertilizer microsites (Table 1). Agar pH values above that of the control persisted up to 8 days at distance of up to 30 mm from the fertilizer microsite. Treatments with TSP alone showed marked reduction in agar pH values, which persisted up to 6 days after fertilizer addition for TSP1 and 8 days for TSP2. Effects were noted up to 20 mm from the microsites. With urea+TSP mixtures, pH values after two days were 4.0 to 5.0 at 10 to 15 mm. After four days, agar pH values for the urea+TSP treatments ranged from pH 4.0 to 5.0, depending on the combinations of urea and TSP rates, from 10 to 25 mm away from fertilizer microsites. At high urea rates, or low TSP rates, pH values of 6.5 to 7.0 were found beyond the acidified regions, indicating diffusion of urea or urea reaction products beyond the TSP reaction sites. At six days, all urea+TSP treatments exhibited two pH zones, a low pH zone at 5 to 20 mm and a higher pH beyond, indicating continued diffusion of urea beyond the TSP reaction zone (Fig. 2). After eight days, the two pH zones had merged. Agar pH approached normal values, but the effect of TSP on agar pH was still observed as noted by lower pH values for urea+TSP2 treatments, compared with urea or urea+TSP1 treatments.

The agar colour changes indicated that different rates of diffusion of TSP and urea reaction products occurred. The purple colour of the indicator (pH>6.5) developed outside the yellow circle (pH<5.0) with urea+TSP treatments. Then slowly the purple zone merged with the yellow zone. Urea or urea reaction products diffused faster than TSP into the surrounding soil, and increased pH. Subsequently, urea reaction products reduced the acidic environment created by TSP.

In general, agar techniques facilitate pH measurements with microelectrodes, due to a better electrode contact with the agar layer than with the soil. Agar layers should not be too thick because this reduces the sensitivity of the method.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, through Operating Grant OGP0002957.

5. REFERENCES

Creamer, F.L. and Fox, R.H. 1980. The toxicity of banded urea or diammonium phosphate to corn as influenced by soil temperature, moisture and pH. Soil Sci. Soc. Am. J. 44:296-300.

Ferguson, R.B., Kissel, D.E., Koelliker, J.K., and Basel, W. 1984. Ammonia volatilization from surface applied urea: Effect of hydrogen ion buffering capacity. Soil Sci. Soc. Am. J. 48:578-582.

Lindsay, W.L. and Stephenson, F.H. 1959. Nature of the monocalcium phosphate monohydrate in soils: I. The solution that reacts with the soil. Soil Sci. Soc. Am. Proc. 23:12-18.

Lindsay, W.L. 1962. Identification of reaction products from phosphate fertilizers in soils. Soil Sci. Soc. Am. Proc. 26:446-452.

Marschner, H., Römheld, V., and Ossenberg-Neuhaus, H. 1982. Rapid method for measuring changes in pH and reducing processes along roots of intact plants. Z. Pflanzenphysiol. Bd. 105:407-416.

Myers, R.G. and Thien, S.J. 1988. Organic matter solubility and soil reaction in an ammonium and phosphorous application zone. Soil Sci. Soc. Am. J. 52:516-522.

Weisenseel, M.H., Dorn, A., and Jaffe, L.F. 1979. Natural H^+ currents traverse growing roots and root hairs of barley (Hordeum vulgare L.). Plant Physiol. 64:512-518.

Table 1. Effect of urea and triple superphosphate (TSP) on microelectrode pH values of agar placed on soil fertilizer granule microsites

Urea	TSP	Days after fertilizer application			
		2	4	6	8
N	P_2O_5				
mg/dish		pH (mm)			
0	0	5.0	5.0	5.0	5.0
20	0	7.5(15)[z]	8.0(15)	6.5(20)	5.5(30)
40	0	7.8(20)	8.0(30)	7.0(30)	6.0(30)
0	20	4.5(10)	4.5(20)	4.5(20)	4.8(10)
0	40	4.0(15)	4.2(25)	4.5(30)	4.5(20)
20	20	4.5(10)	4.5(10); 7.0(10-20)[y]	4.5(5); 6.5(5-20)	5.5(30)
20	40	4.0(10)	4.0(25)	4.5(20); 6.0(20-25)	5.0(30)
40	20	5.0(15)	5.0(10); 7.0(10-20)	5.5(10); 7.0(10-25)	6.0(30)
40	40	4.5(15)	4.5(15); 6.5(15-25)	4.5(10); 6.5(10-25)	5.5(30)
$LSD_{0.05}$[x]		0.4	0.3	0.4	0.4

[z] the numbers in parentheses indicate the distance in mm from fertilizer site estimated using agar colour.

[y] the second set of pH values were found at distances in mm (in parentheses) from fertilizer site.

[x] Least significant differences critical values at 0.05 level of T test.

Figure 1. Apparatus for a rapid method to measure and visualize dynamic changes in pH near microsites around fertilizer granules.

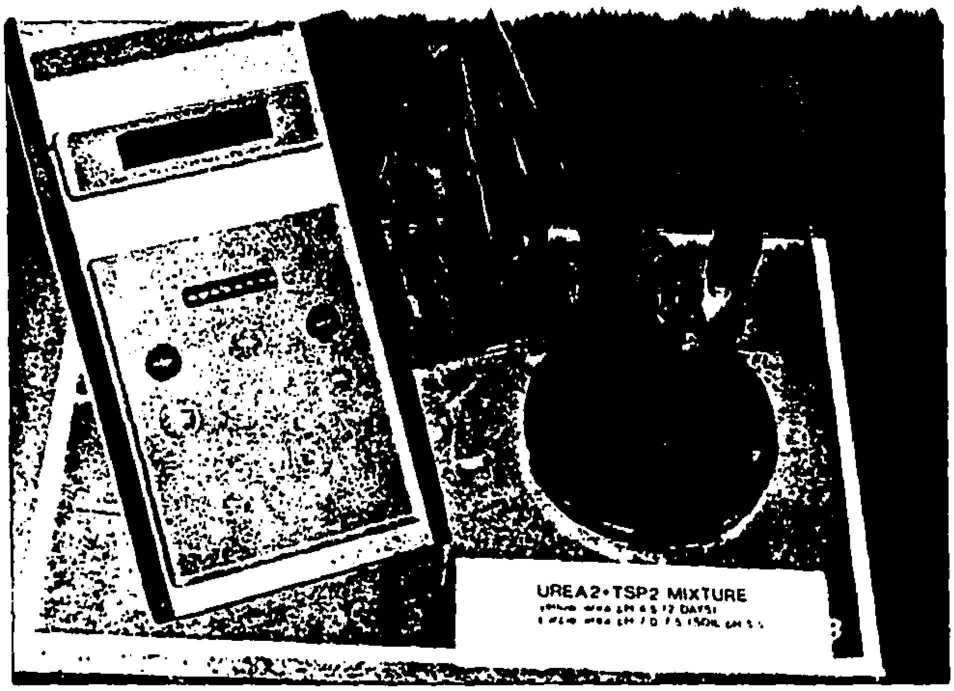
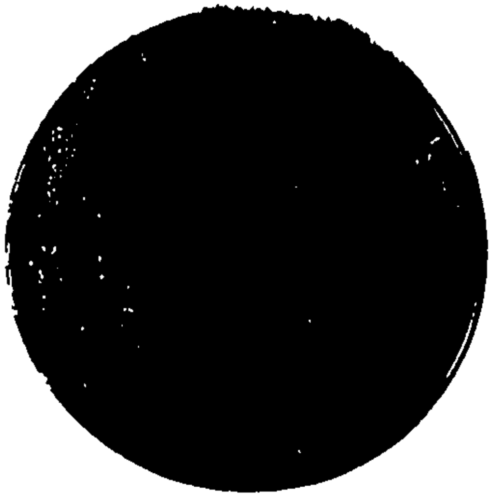
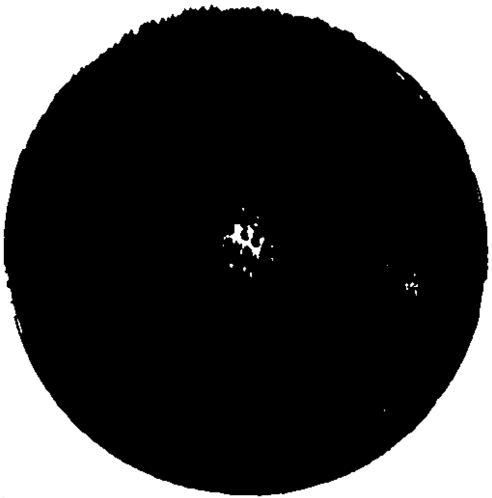

UREA2•TSP2 MIXTURE

Figure 2. Agar pH after six days. Left; urea only treatment, purple colour or dark area (pH 7.0) up to 30 mm from point of fertilizer addition. Right; urea+triple superphosphate (TSP) treatment with two pH zones, a low pH zone (yellow colour) at 0 to 10 mm and a higher pH zone (purple colour or dark area) 10 to 30 mm, indicating diffusion of urea beyond the TSP reaction zone. Dish is 100 mm in diameter.



UREA 40 g.dish^{-1}
SIX DAYS
Red area pH:5.0-5.5; purple area pH: 6.5-7.0)



UREA 40 g.dish^{-1} TSP 40 g.dish^{-1}
SIX DAYS
(Yellow area pH:4.5; red area pH:5.0-5.5
purple area pH: 6.5-7.0)

CONNECTING PARAGRAPH

In Chapter II, a rapid method was described which allows precise measurement and visualization of dynamic changes in pH around fertilizer granules or bands. The results not only demonstrated the ability of the agar method to monitor pH changes around fertilizer granules, but also showed that TSP could reduce and delay pH increases from urea hydrolysis. The effect of TSP on pH increases from urea hydrolysis could have an important impact on NH_3 volatilization.

Ammonia volatilization is a major disadvantage in urea application to soil, resulting in low fertilizer N efficiency. Rates and amounts of NH_3 volatilization are affected by soil properties such as initial pH, urease activity, clay content, organic matter content, and water content. Different phosphates would produce different pH environments in the microsite around fertilizer granules, based on their composition. In the following Chapter, the effect of different phosphate fertilizer carriers (TSP, MAP and DAP) with urea on soil pH, urea hydrolysis and NH_3 volatilization is studied on two eastern Canadian soils, a Ste. Rosalie clay and a Ormstown silty clay loam.

CHAPTER III

UREA AND PHOSPHATE INTERACTIONS IN FERTILIZER MICROSITES: AMMONIA VOLATILIZATION AND pH CHANGES

1. ABSTRACT

Ammonia (NH_3) volatilization from urea fertilizer reduces the efficiency of N fertilizer use by crops. Reduction of NH_3 loss may be possible through addition of acidic materials. The objectives of this study were to compare the effects of three phosphate fertilizers on NH_3 volatilization, urea hydrolysis and pH changes with surface applied urea. Surface soil samples from two Typic Humaquepts, a Ste. Rosalie clay (very fine silty, mixed, acid, frigid) and an Ormstown silty clay loam (fine silty, mixed, non-acid, frigid) were used. Mixtures of two rates of urea, four rates of P, and three P fertilizers (triple superphosphate, TSP; monoammonium phosphate, MAP; diammonium phosphate, DAP) were compared. Ammonia volatilization increased on both soils, as application rates increased from 0.5 g N kg^{-1} soil to 2.0 g N kg^{-1} soil. Adding TSP and MAP to urea reduced NH_3 loss from 30% to 90% on both soils compared with urea alone. Ammonia loss decreased as P : urea ratios increased. No significant difference was found in NH_3 loss between TSP and MAP. Ammonia loss from urea was increased with added DAP, because of a resulting high pH. Adding TSP or MAP to urea reduced maximum daily rates of NH_3 loss and delayed the time of maximum NH_3 loss rate by 5 to 10 d. The effect of acidic phosphates on NH_3 loss was related to their effect in reducing pH in the fertilizer microsite and retarding urea hydrolysis. Mixtures of acidic P fertilizers with urea increased soil NH_4- and NO_3-N contents. Surface-applied urea fertilizer efficiency could be increased if applied together with TSP or MAP.

Fertilizer granules of urea-P mixtures would be beneficial for hay and pasture application, no-till fertilization or for crops where applications are restricted to soil surfaces.

2. INTRODUCTION

Urea, triple superphosphate (TSP) and monoammonium phosphate (MAP) are important fertilizers in world agriculture. However, these fertilizers have inherent disadvantages which reduce their efficiency. Ammonia (NH_3) volatilization is a major avenue for N loss from surface-applied urea (Fenn and Miyamoto, 1981). Volatilization losses can occur from acid as well as alkaline soils due to high pH and NH_4 concentrations in the microsite where urea granules dissolve and hydrolyse (Fenn and Richards, 1986). The reactions can be summarized as follows:

$$CO(NH_2)_2 + 3H_2O \text{ -------> } 2NH_4^+ + OH^- + HCO_3^-$$

$$NH_4^+ + OH^- \text{ <======> } NH_3 + H_2O$$

The NH_3 volatilization from surface-placed urea has been reported to vary from 1 to 80 % of the applied N in agricultural soil (Gould et al., 1986; Christianson, 1989) and from 8.5 to 45% in forest soils (Marshall and Debell, 1980). Reduction of NH_3 losses can be achieved by i) coating the urea granule with materials that slow the dissolution of urea (Matocha, 1976), ii) reducing hydrolysis with urease inhibitors (Bremner and Douglas, 1971), iii) additions of neutral salts containing Ca or K (Fenn and Miyamoto, 1981), or iv) reducing microsite pH with acidic materials (Stumpe et al., 1984). High costs of amendments, however, reduced their use by farmers (Sahrawat, 1980). Therefore, low cost, readily available materials could be used to advantage.

Acidification of the fertilizer microsite is a mechanism for reducing NH_3

volatilization, which could be achieved through the addition of certain P fertilizer materials. Such treatments would have the added benefit of supplying P, while reducing N loss from urea. An example is urea-phosphate, a mixture of urea and phosphoric acid. This product has been shown to reduce NH_3 volatilization from urea and reduce seedling damage (Bremner and Douglas, 1971; Fenn and Richards, 1986; Fenn et al., 1990). However, such mixtures are corrosive and require special precautions in handling and storage. Like phosphoric acid, TSP and MAP are acidic upon solution as P fertilizers, but they have good chemical and physical properties suitable for handling and storage. When applied to soil, TSP dissociates into dicalcium phosphate dihydrate (DCPD) plus phosphoric acid (Lindsay and Stephson, 1959) as follows;

$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \text{ ----> } CaHPO_4 \cdot 2H_2O + H_3PO_4$$

MAP can be considered to hydrolyse to a solution of a strong acid and weak base;

$$NH_4H_2PO_4 + H_2O \text{ -----> } NH_4OH + H_3PO_4.$$

Saturated solutions of TSP and MAP have pH values of 1.0 and 3.5 respectively (Sample and Soper, 1980). In contrast, diammonium phosphate (DAP) in saturated solution has a pH of 8.0, and should have little effect on NH_3 volatilization, or may increase NH_3 loss as the result of the following reaction in soil;

$$(NH_4)_2HPO_4 + 2H_2O \text{ -----> } 2NH_4OH + H_3PO_4.$$

Urea which hydrolyses in environments with lower soluble and desorbable

Ca levels is susceptible to higher NH_3 losses (Fenn et al., 1981). Monocalcium phosphate alone with urea, in a calcareous soil, did not reduce NH_3 loss; however, NH_3 loss was reduced in an acid soil (Fenn and Hossner, 1985; Fenn et al., 1990). Since TSP contains large amounts of Ca (120-140 g kg-1), the presence of Ca may serve to reduce NH_3 volatilization from mixtures of urea and TSP.

It is hypothesized that urea combined with TSP and MAP will reduce NH_3 loss from urea hydrolysis in neutral or acidic soils. Acidification with acidic phosphates would tend to retard urea hydrolysis, decrease the high pH from urea hydrolysis and increase NH_4/NH_3 ratios.

The objectives of this research were to determine the effect of commercial phosphate fertilizers (TSP, MAP and DAP) mixed with urea on urea hydrolysis, NH_3 volatilization, and soil pH in two acid soils.

3. MATERIALS AND METHODS

1). Soils

Surface soil samples (0-15 cm) from two Typic Humaquepts, a Ste. Rosalie clay (very fine silty, mixed, acid, frigid) and an Ormstown silty clay loam (fine silty, mixed, non-acid, frigid), differing in pH, texture and Ca content (Table 1) were used to compare the effect of added P on NH_3 volatilization from urea. Samples were taken from cultivated fields which had received little fertilization. Soil samples were air-dried and ground to pass a 2-mm sieve.

2). Ammonia volatilization and urea hydrolysis

Two laboratory experiments were conducted to compare N loss via NH_3 volatilization from urea and P fertilizer mixtures. In the first experiment, treatments consisted of urea (0.5 and 2.0 g N kg^{-1} soil), and three sources of P (TSP, MAP and DAP) with variable rates of P (0, 0.22 and 0.43 g P kg^{-1} soil with 0.5 g urea-N, 0, 0.43, 0.86 and 1.72 g P kg^{-1} soil with 2.0 g urea-N kg^{-1} soil; Table 2 in Chapter III and Table 2 in Appendices). Mixtures were applied to 100 g air dried soil and for this system, 1 g kg^{-1} was equivalent to 263 kg ha^{-1} on an area basis. Soils alone were included in the treatments as controls. To determine the net effect of ammonium containing P fertilizers (MAP and DAP) on NH_3 volatilization from urea, in the second experiment, P fertilizer was applied either alone (0.22 or 0.43 g P kg^{-1}) or with a constant rate of urea (0.5 g N kg^{-1}; Table 3). Fertilizer mixtures were applied as finely ground materials (fertilizer grade; < 1 mm) on the center of the soil surface in each treatment. Soils, or soils treated with equivalent amounts of TSP, MAP or DAP were included in the treatments for comparison. Three replicates of each treatment were used in a completely randomized design.

Ammonia volatilization was measured in a forced-draft system using covered jars swept with air (Al-Kanani and MacKenzie, 1990). In this method, 100 g air-dried soil to provide a depth of 2 cm was placed in a 7 cm (inside diameter) by 12.5 cm long screw top jar. The soil was moistened to field capacity. The jars with soil were incubated at 25 °C for four d to initiate urease activity before applying fertilizers. Following the application of fertilizers, jars were covered immediately and connected to the air train. Incoming air passed through 2 L of 1 *M* H_2SO_4 to remove ambient NH_3, then through 4 L distilled water to humidify the air before entering the jar. Distilled water was added to the soil twice a week to replenish evaporated water. Jars were designed to allow passage of air across the top of soil sample and out of the jar. Air flow was maintained at 6 L min^{-1} per jar throughout the incubation period, corresponding to about 15 air volume exchanges per minute. A Gilmont flow meter (Gilmont Instrument, Inc., Great Neck, NY) was used to measure and adjust air flow through individual jars. Air coming from sample jars passed into 100 ml of 20 g L^{-1} boric acid solution contained in Erlenmyer flasks. The boric acid solution was removed daily and titrated with 0.05 *M* H_2SO_4 to determine NH_3 for the first week after application, and every other day for two additional weeks. All incubations were at 25 °C.

After 24 d, soils were extracted by shaking for 1 hour with 1 *M* KCl+ 5 mg L^{-1} phenylmercuric acetate (PMA). Filtrates were analyzed for urea (Mulvaney and Bremner, 1979), NH_4 by the sodium salicylate/sodium nitroprusside method, and NO_2+NO_3 by the copperized Cd method (Keeney and Nelson, 1984), using a Technicon Autoanalyzer (Technicon Instruments Corporation, USA). Recovery of added N was calculated from the summation of volatilized NH_3, urea, NH_4, NO_3 and NO_2 content in soil, after subtracting amounts present in control samples.

Urea hydrolysis rates (0.5 g N kg^{-1} soil) were compared using three rates of added TSP (0, 0.22, and 0.43 g P kg^{-1} soil). Soil samples (10.0 g air-dried) were incubated for four d in Erlenmyer flasks at water content of field capacity at 25 °C. Fertilizer treatments were applied on the soil surface. After 1, 2, and 4 d, the moist soil was extracted with 1 *M* KCl+5 mg L^{-1} PMA solution (1:10) and the filtered solution was analyzed for urea, NH_4, and NO_2+NO_3 as mentioned above.

Analysis of variance and regression were conducted using the GLM and REG procedures of the Statistical Analysis System (SAS Institute, 1985). Total NH_3 loss, maximum NH_3 loss rate and the time of maximum NH_3 loss rate were calculated and used to compare the effect of fertilizer sources and rates on NH_3 losses. Total NH_3 losses were calculated based on differences of NH_3 loss between treatments and controls without N in the first experiment. In the second experiment, urea treatment NH_3 losses were corrected for NH_3 losses from control soils, or soils treated with equivalent amounts of TSP, MAP or DAP. The effect of P rates and sources on NH_3 loss were tested with contrasts.

3). Microsite pH changes

Fertilizer microsite pH in both soils was studied. The fertilizer treatments were the same as those used in the NH_3 volatilization study at constant N (Table 2). Soil (80 g) was placed into a petri dish (1.5X15 cm) to a depth of 0.5 cm and moistened to the same water content as in the NH_3 volatilization experiments. After one d incubation, mixtures of finely ground commercial fertilizer were placed in the center of the dish in an area of 1 cm diameter or less. After one d of reaction, 50 ml of agar solution was spread on the soil surface and the dish covered. The agar solution (7.5 mg g^{-1}) contained 0.6 mg g^{-1} bromocresol purple and was adjusted to the pH of the soil (Marschner et al., 1982). Measurement of pH along the fertilizer-soil gradient was made using a glass microelectrode (Flat surface Ag/AgCl model, Fisher Scientific. P.Q., Canada) at 2, 4, and 6 d after fertilizer application. Estimates of the extent of pH change were made based on the range of colors produced in the agar. The processes of pH change from the site of mixtures of urea and phosphates were recorded in terms of pH, distance from fertilizer microsite and time.

4. RESULTS

1). Ammonia volatilization at constant rates of total N application

The total cumulative volatilization losses ranged from 1.6 to 20.9% of the N applied, depending on soil and the rate and source of P applied (Table 2).

At 2.0 g N kg^{-1} soil rates, NH_3 losses were similar on the two soils. On both soils, a reduction in NH_3 volatilization was observed when either TSP or MAP were added with urea. Reduction in NH_3 loss ranged from 30% to 95% of the urea alone treatments. A linear correlation was found between NH_3 loss and the ratio of P : N in the fertilizer mixture (r=0.99**). When the P : N ratio was about 0.43:1, NH_3 losses were reduced to about 50% of the urea alone treatments.

No differences were found between TSP and MAP for reducing NH_3 loss.

Diammonium phosphate did not affect the percentage of applied N volatilized as NH_3. Because MAP and DAP contained 12% and 21% NH_4-N respectively, added urea was reduced as MAP and DAP rates were increased. Thus, with higher MAP or DAP, NH_3 losses could have been reduced due to reduced urea addition.

2). Ammonia volatilization at constant rates of urea

When urea-N was applied at 0.5 g kg^{-1} soil, added TSP and MAP reduced NH_3 losses (Table 3). Reductions in NH_3 loss were quadratic with increasing TSP and MAP for the Ste. Rosalie soil, and for MAP with the Ormstown soil, and linear for TSP in the Ormstown soil. Quadratic decreases were a result of a marked decrease in NH_3 loss at the first level of added P, followed by a smaller subsequent decrease at the second level of added P. Addition of TSP reduced NH_3 volatilization more than addition of MAP on Ste. Rosalie soil (Table 3). However, there was no difference between TSP and MAP on the Ormstown soil. Increased NH_3 loss compared to urea alone was found when DAP was added with urea on both soils, and losses were more pronounced at higher DAP rates. Ammonia losses from urea alone were lower on the Ste. Rosalie soil than with the Ormstown soil. However, the difference between soils was minimum at the high urea rate (Table 2).

3). Rate of NH_3 volatilization

Addition of TSP and MAP reduced the maximum daily rate of NH_3 loss and delayed the time of maximum NH_3 volatilization rate from urea-treated soil

(Figure 1). Without P fertilizer, the maximum rate of NH_3 loss from urea was 0.59 mg N jar^{-1} day^{-1} for Ormstown soil and 0.32 mg N jar^{-1} day^{-1} for the Ste. Rosalie soil at 0.5 g N kg^{-1} soil rate. With urea alone treatments, the time of peak NH_3 loss was about six to seven days after application of urea. The maximum rates of NH_3 loss increased to near 4.5 mg N jar^{-1} day^{-1} on both soils when N rate was increased to 2.0 g N kg^{-1} soil.

Adding TSP or MAP with urea significantly reduced the maximum rate of NH_3 loss to about 10 to 50% of that of the urea alone treatment. Added TSP or MAP also delayed the time of peak NH_3 loss by about 1 to 5 d at 0.5 g N kg^{-1} soil application rate, and 6 to 10 d at 2.0 g N kg^{-1} soil application rate, varying with the amount of TSP or MAP applied and with soil. On both soils, maximum rate of NH_3 loss decreased as acidic P fertilizer increased ($r = 0.96^{**}$).

Two NH_3 loss peaks were observed when DAP was added with urea in the first experiment (Figure 1). The first peak occurred on the first day after fertilizer application to soil. This peak corresponded to NH_3 loss from DAP itself, as it was observed in the second experiment in DAP only treatments (Figure 2). The second peak occurred three or four days after application, about two days earlier than in the urea only treatment. This indicated that DAP, in spite of reduced addition of urea, hastened the NH_3 volatilization from urea hydrolysis. At a constant rate of urea-N in the second experiment, DAP increased maximum daily rates of NH_3 loss from urea (Figure 2).

4). Recovery of added N at constant N rates

The reduction of total NH_3 volatilization losses due to added TSP or MAP resulted in an increase in NH_4 and NO_3 remaining in both soils (Table 4). At the end of the incubation experiment, soil NH_4 and NO_3 in the urea+TSP and urea+MAP treatments was found to be 40% higher than that of urea and urea+DAP treatments in the Ormstown soil. In the Ste. Rosalie soil, soil NH_4 and NO_3 in urea+TSP and urea+MAP treatments was 15 to 20% higher than that of urea and 40 to 60 % higher than that of the urea+DAP treatment. However the sum of inorganic N recovered ranged from 63 to 77% of the applied N in Ormstown soil and 82 to 97% in Ste. Rosalie soil, except for the urea+DAP treatment which was only 64%.

5). Microsite pH changes

Microsite pH studies showed a strong effect of TSP application on soil pH in both soils (Figures 3, 4). In the Ste. Rosalie soil, addition of urea increased soil pH to 7.0 at the site of placement on the second day of incubation (Figure 3). The effect of urea hydrolysis on soil pH reached to 15 mm from the site of fertilizer placement. Soil pH increased to 7.8 at a distance of 10 mm from the fertilizer site on day four. The increased pH values decreased with time, though an elevated pH was found at day eight extending to a distance of 35 mm from the fertilizer site.

Upon application of urea+TSP mixtures, soil pH at the site of placement was reduced to 4.0 or 4.5, the decrease being related to the application rates of

TSP. Acidification by TSP extended from 10 to 15 mm from the fertilizer site after four days, depending on the TSP application rate. For two days, the pH stayed below or at the normal level, indicating little urea hydrolysed. On day four, urea movement and hydrolysis at the low rate of TSP was noted by the increase in soil pH to 6.8 outside the acidified region. At the higher TSP application rate, no increase in pH was noted. On day six, a pH increase to 6.5 in the region outside the acidified area was noted at 15 mm from fertilizer site for the low TSP application rate, and to pH 6.2 at a distance of 25 mm from the fertilizer site at the high TSP application rate. On day eight, at the low application rate of TSP, pH values were higher with the urea treatments than the control soil up to 20 cm from fertilizers. For the high rate of TSP, the pH was lower at 0 to 5 cm, but higher at 15 to 20 cm than the control soil. Urea alone had uniformly higher pH values.

In the Ormstown soil, addition of urea increased soil pH to 7.5 at 0 to 10 mm from the fertilizer site on the second day of incubation, and the pH increase from urea hydrolysis decreased gradually to the soil initial value at 30 mm (Figure 4).

Addition of TSP and MAP to urea reduced soil pH to 5.0 and 5.2, respectively, at the site of placement. But the pH in the treatments of urea+TSP increased to 6.5 in the region outside the acidified area from 15 to 20 mm from fertilizer site for the treatments of urea+TSP, and from 15 to 25 mm for the urea+MAP treatment. This indicates the acidification by low rate of TSP or MAP in Ormstown soil extended only to 10 mm from the fertilizer site after two days. Beyond this acidified area, the alkalinity from urea hydrolysis masked the acidification by TSP or MAP.

Addition of DAP to urea increased soil pH to 8.0 at the distance of 0 to 10 mm from the fertilizer site, even higher than urea alone. The pH decreased with distance, and the initial soil pH value was observed 35 mm from the fertilizer site.

Total NH_3 loss expressed as a percentage of added N was linearly related to the pH in the fertilizer microsite (Figure 5). As the pH decreased, the total NH_3 loss from urea decreased.

It was also observed that the maximum rate of NH_3 loss generally corresponded to the maximum soil pH around fertilizer sites. This can be seen by comparing the treatments with or without TSP at the 0.5 g kg^{-1} soil urea rate. Without TSP, the maximum rate of NH_3 loss occurred at six days after application on the Ste. Rosalie soil, the time when soil pH reached its highest value of around 7.8. On the treatment with TSP, the maximum rate of NH_3 loss occurred later, at about eight days after application. The maximum soil pH of 6.8 occurred near the beginning of the maximum rate of that treatment.

6). Urea recoveries

In the Ormstown soil, urea concentration in soil was lower than that for the Ste. Rosalie soil at all times (Table 5), indicating higher hydrolysis rates in the Ormstown soil. The higher pH of Ormstown soil, compared to the Ste.

Rosalie soil may have contributed to the higher hydrolysis rate. On both soils, adding TSP to urea increased urea recovery. Added TSP inhibited urea hydrolysis in the fertilizer microsite, probably due to reduced activity of urease with decreased pH (Bremner and Douglas, 1971).

5. DISCUSSION

Ammonia volatilization was affected by rates of urea application to acid soils. With urea only, NH_3 losses increased as the N rate increased on both soils. As the applied urea rates increased, the difference in NH_3 loss between soils decreased. The lower volatilization from Ste. Rosalie soil than from the Ormstown soil might be due to the lower soil pH and higher clay content of the Ste. Rosalie soil. The increased alkalinity from urea hydrolysis may have exceeded the buffer capacity or the retaining ability of soil near the microsite. Thus even in acid, clay soils, the loss of N from urea can be significant at high rates of urea.

From the results of these experiments, both acidic P fertilizers (TSP and MAP) reduced NH_3 volatilization from urea. This was considered to be from three effects: firstly, the H_3PO_4 produced from hydrolysis of acidic phosphates in soil would acidify the soil surrounding the urea-phosphate mixture. When pH is less than 5.5, urea would be hydrolysed more slowly (Delanue and Patrick, 1970). Then urea could diffuse out of the acidified soil and hydrolyse. This would effectively increase the volume of soil with which the urea was mixed, and also increase the time required for complete hydrolysis. Secondly, after urea hydrolysis, the lower pH would benefit the formation of NH_4^+ over NH_3. A third effect might be due to the formation of metastable reaction products such as $Ca(NH_4)_2(HPO_4)_2$ (Terman, 1979). Comparing TSP with MAP, the more acidic nature and Ca present in TSP may have been responsible in part for its greater effect on NH_3 volatilization on the Ste. Rosalie soil. Effects of acidic P fertilizers were probably more pronounced than they would be in the field due to restricted diffusion of urea away from P sources in the jar.

Conversely, the effect of DAP in increasing total NH_3 loss and shortening the time of peak NH_3 loss may have been due to either enhanced urea hydrolysis at higher pH, or the higher pH effect on NH_3 volatilization, or both. The optimum pH for soil urease activity was found to be pH 7.0 - 9.0 (Bremner and Douglas, 1971; Rachhpal-Singh and Nye, 1984), which was within the pH range produced by our urea+DAP mixtures. The reason for decreased recovery of added N with urea + DAP mixture compared with TSP or MAP is unknown, but could be due to a substantial amount of N being converted in the soil to fixed NH_4, or organic N, or denitrified.

Ammonia volatilization is still a significant mechanism of N loss when urea and urea plus DAP mixtures are surface applied to acid soils. It is suggested that applying mixtures of acidic phosphate fertilizer with urea has potential to increase the efficiency of surface-applied urea fertilizer due to reduced NH_3 losses. The most benefit of such a system would be in surface application of N and P to hay and pasture field, or no-till practices. For these advantages to occur, combination of the two materials in a fertilizer granule would have to be developed. Difficulties with making granules of urea and TSP have been noted (Chien, et al., 1987), but not with urea + MAP.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, through operating grant OGP0002957.

6. REFERENCES

Al-Kanani, T. and A. F. Mackenzie. 1990. The influence of formula modifications and additives on ammonia losses from surface-applied urea-ammonium nitrate solution. Fert. Res. 22:49-59.

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

Chien, S.H., C.B. Christianson, M.S. Lupin and G.E. Peters. 1987. Compaction of metal salt-urea complexes with triple superphosphate. Fert. Res. 14:181-191.

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

Delanue R. D. and W.H. Patric. 1970. Urea conversion to ammonia in water-logged soil. Soil Sci. Soc. Am. Proc. 34:603-607.

Fenn, L. B., J.E. Matocha, and E. Wu. 1981. A comparison of pH depression and carbonate precipitation as pathways for calcium reduction of ammonia from surface-applied urea. Soil Sci. Soc. Am. J. 45:1128-1131.

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

Fenn, L. B. and L.R. Hossner. 1985. Ammonia volatilization from ammonium or ammonium forming nitrogen fertilizers. Adv. Soil Sci. 1:123-169.

Fenn, L. B. and J. Richards. 1986. Ammonia loss from surface applied urea-acid products. Fert. Res. 9:265-275.

Fenn, L. B., G. Tatum, and G. Horst. 1990. Ammonia loss from surface-placed mixtures of urea-calcium-potassium salts in the presence of phosphorus. Fert. Res. 21:125-131.

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

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen- inorganic forms. p.643-693. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Lindsay, W.L. and H.F. Stephenson. 1959. Nature of the reactions of monocalcium phosphate monohydrate in soils: I. The solution that reacts with the soil. Soil Sci. Soc. Proc. 23:12-18.

Marshall, V.G. and Debell, D.S. 1980. Comparison of four methods of measuring volatilization losses of nitrogen following urea fertilization of forest soil. Can. J. Soil Sci. 60:549-563.

Marschner, H., Romheld, V., and Ossenberg-Neuhaus, H. 1982. Rapid method for measuring changes in pH and reducing processes along roots of intact plants. Z. Pflanzenphysiol. Bd. 106:407-416.

McLean, E.O. 1982. Soil pH and lime requirement. p.199-244. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Mulvaney, R.L. and Bremner, J. M. 1979. A modified diacetyl monoxime method for colorimetric determination of urea in soil extracts. Commun. Soil Sci. Plant Anal. 10: 1163-1140.

Nelson, D.W. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. p.539-577. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Rachhpal-Singh and P. H. Nye. 1984. The effect of soil pH and high urea concentration on urease activity in soil. J. Soil Sci. 35:519-527.

Rhoades, J.D. 1982. Cation exchange capacity. p.149-157. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

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

Sample, E. C. and R. J. Soper. 1980. Reactions of phosphate fertilizers in soils. p.263-304. *In* F. E. Khasanch, E. C. Sample and E. J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy. Madison. WS., USA.

SAS Institute. 1985. SAS user's guide: statistics. 5th ed. SAS Inst., Cary, NC.

Stumpe, J. M. P.L.G. Vlek, and W.L. Lindsay. 1984. Ammonia volatilization from urea and urea phosphates in calcareous soils. Soil Sci. Soc. Am. J. 48:921-926.

Terman G. L. 1979. Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments and crop residues. Adv. Agron. 31:189-223.

Figure 1. Effect of added triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) on the rate of daily NH_3 loss from Ste. Rosalie and Ormstown soils at two rates of total urea plus phosphate N (T-N) in the first experiment. Vertical bars represent LSD at 0.01 probability level.

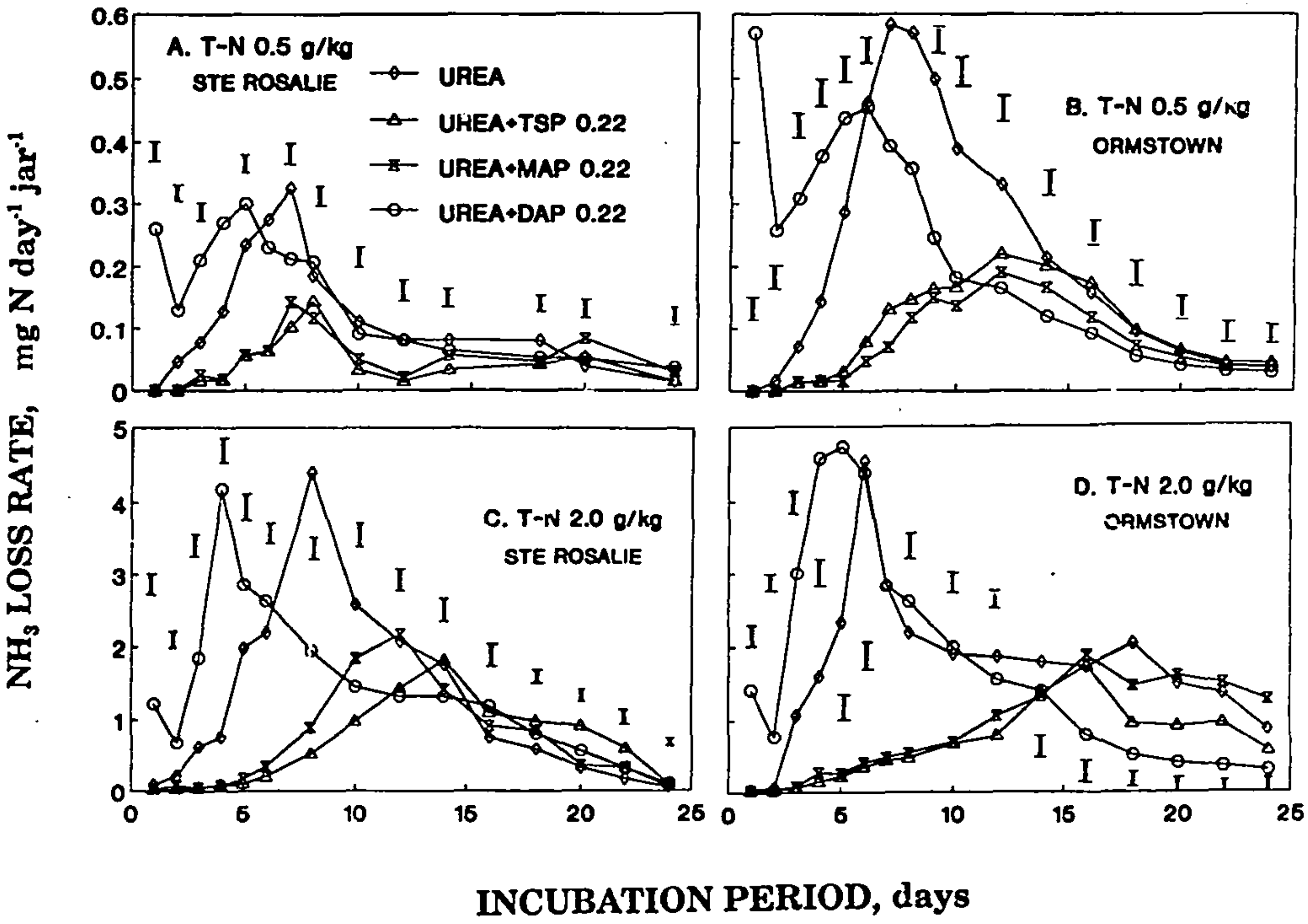

A. T-N 0.5 g/kg
STE ROSALIE
B. T-N 0.5 g/kg
ORMSTOWN
C. T-N 2.0 g/kg
STE ROSALIE
D. T-N 2.0 g/kg
ORMSTOWN
UREA
UREA+TSP 0.22
UREA+MAP 0.22
UREA+DAP 0.22
NH$_3$ LOSS RATE, mg N day^{-1} jar^{-1}
INCUBATION PERIOD, days
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
4
5
0
5
10
15
20
25

Figure 2. Effect of added diammonium phosphate (DAP) and urea on the rate of NH_3 daily loss from the Ormstown soil in the second experiment at the application rate of 0.5 g urea-N kg^{-1}. Vertical bars represent LSD at 0.01 probability level.

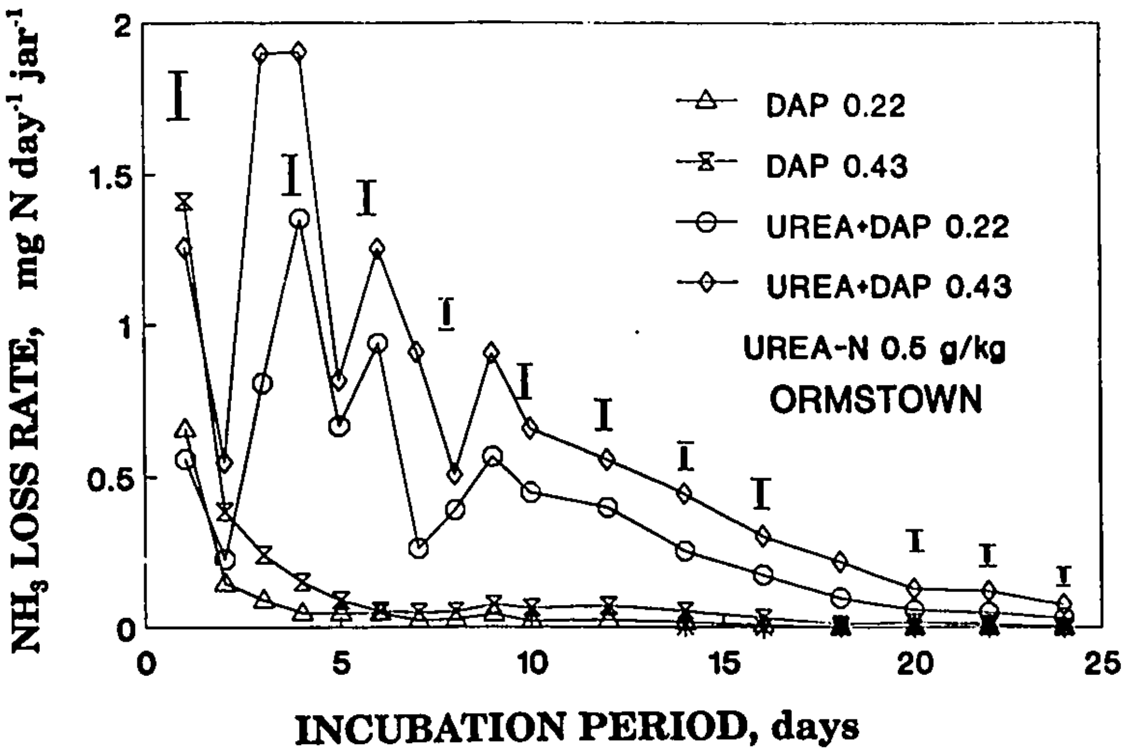

NH$_3$ LOSS RATE, mg N day^{-1} jar^{-1}
INCUBATION PERIOD, days
0
0.5
1
1.5
2
0
5
10
15
20
25
DAP 0.22
DAP 0.43
UREA+DAP 0.22
UREA+DAP 0.43
UREA-N 0.5 g/kg
ORMSTOWN

Figure 3. Soil pH changes with time from fertilizer microsite after application of urea and triple superphosphate (TSP) on the Ste. Rosalie soil. Vertical bars represent LSD at 0.01 probability level.

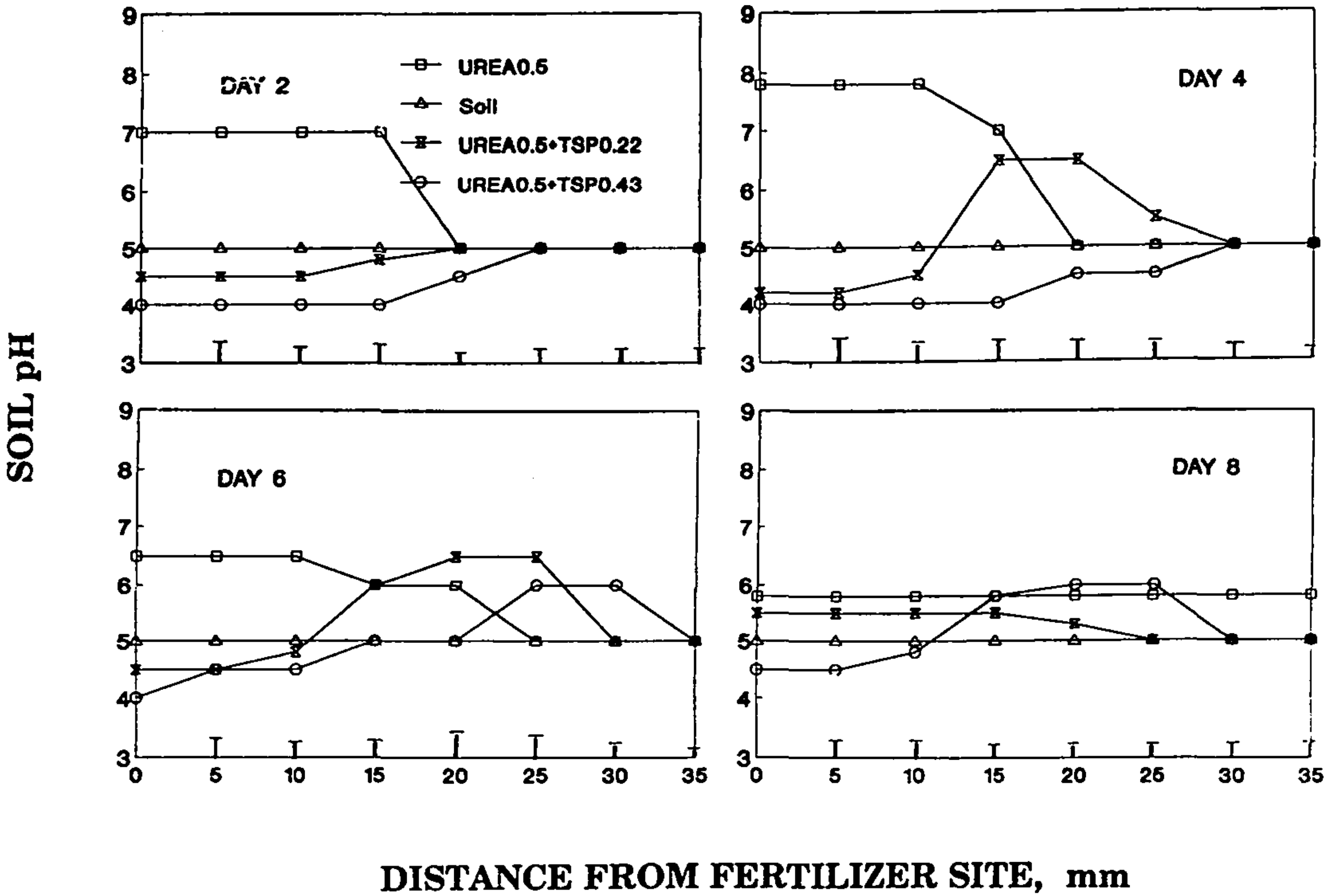
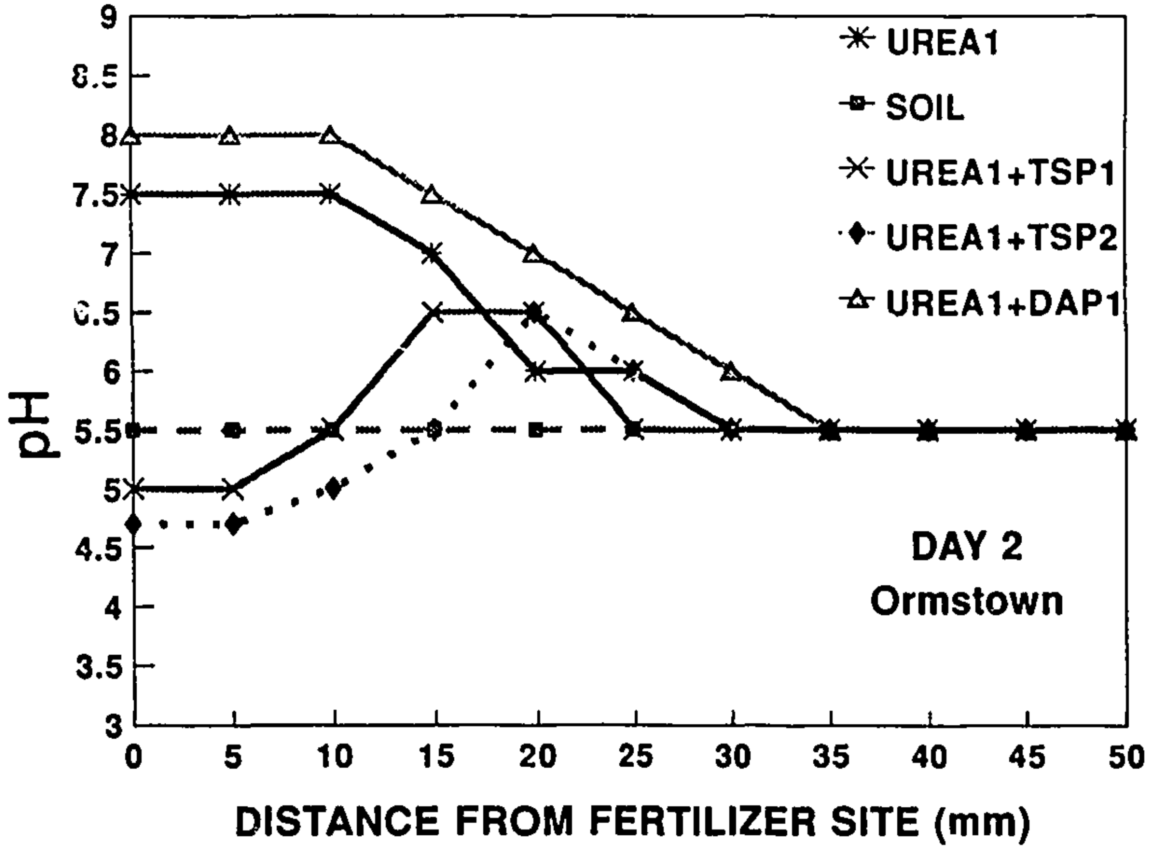
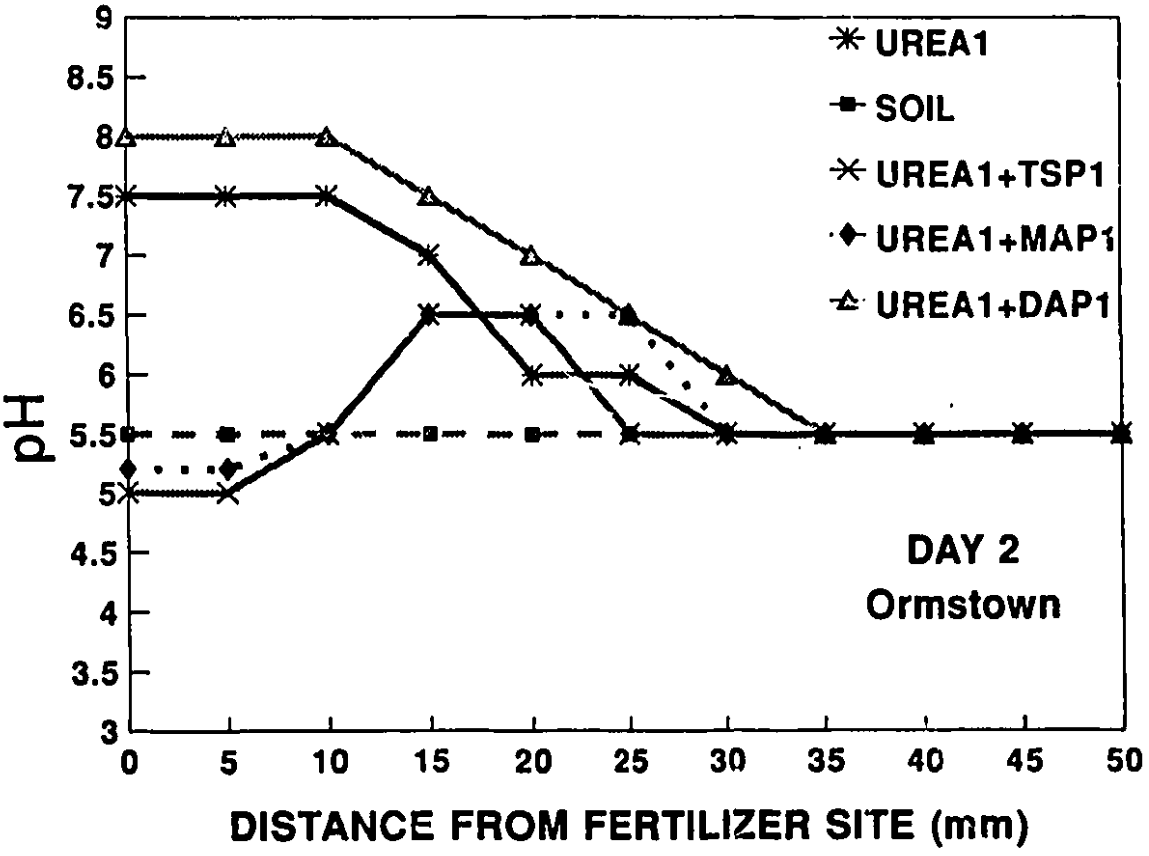

DAY 2
DAY 4
DAY 6
DAY 8
UREA0.5
Soil
UREA0.5+TSP0.22
UREA0.5+TSP0.43
SOIL pH
3
4
5
6
7
8
9
0
5
10
15
20
25
30
35
DISTANCE FROM FERTILIZER SITE, mm

Figure 4. Soil pH changes from fertilizer microsite after two days of application of urea, triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) on the Ormstown soil. Vertical bars represent LSD at 0.01 probability level.

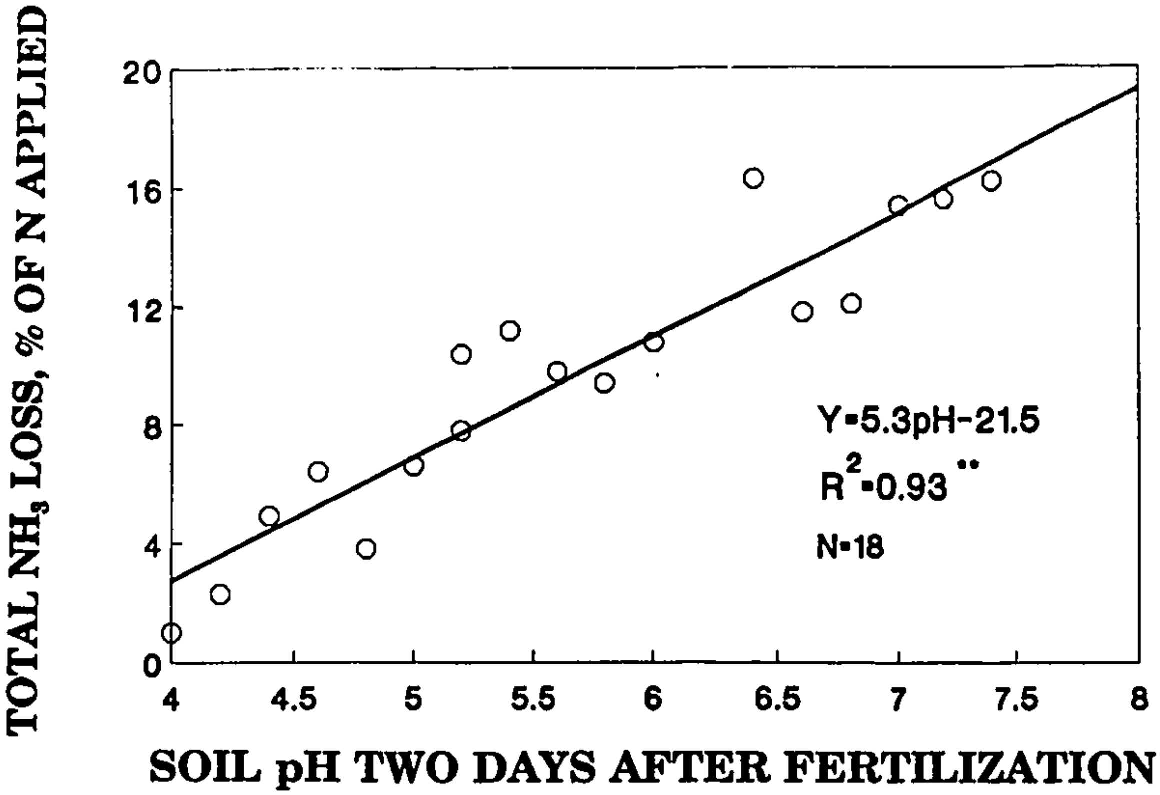


UREA1
SOIL
UREA1+TSP1
UREA1+TSP2
UREA1+DAP1
DAY 2
Ormstown
pH
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
0
5
10
15
20
25
30
35
40
45
50
DISTANCE FROM FERTILIZER SITE (mm)



UREA1
SOIL
UREA1+TSP1
UREA1+MAP1
UREA1+DAP1
DAY 2
Ormstown
pH
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
0
5
10
15
20
25
30
35
40
45
50
DISTANCE FROM FERTILIZER SITE (mm)

Figure 5. Relationship of pH in soil microsite measured two days after application of urea, triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) with total NH_3 loss from the Ste. Rosalie soil.



TOTAL NH_3 LOSS, % OF N APPLIED
20
16
12
8
4
0
4
4.5
5
5.5
6
6.5
7
7.5
8
SOIL pH TWO DAYS AFTER FERTILIZATION
Y=5.3pH-21.5
R^2=0.93 **
N=18

Table 1. Selected physical and chemical properties of soil samples

Soil	pH†			clay	silt	Organic Carbon‡	Exchangeable cations				
	H_2O	*M* KCl	SMP				Ca	Mg	K	Al	ECEC§
				-------- g kg^{-1}		---------	------ $cmol_c(+)$ kg^{-1} soil ------				
Ste. Rosalie	5.2	4.2	5.4	568	293	25	9.4	5.4	0.7	0.3	15.8
Ormstown	6.0	5.0	6.2	368	443	19	14.6	5.0	0.2	0.0	19.8

† McLean, 1982.

‡ Walkley-Black procedure (Nelson and Sommers, 1982)

§ Sum of exchangeable Ca,Mg,K and Al ($BaCl_2$ method; Rhoades, 1982).

Table 2. Ammonia volatilization after 24 d from urea-phosphate mixtures as related to amounts and source of added P at constant N rates

Treatments					Soils	
Urea	T-N†	TSP	MAP	DAP		
-------- N -------		------------ P ------------			Ste. Rosalie	Ormstown
---------------------- g kg^{-1} -------------------					------------- % applied N -------------	
2.0	2.0	0	0	0	16.3(2.1)‡	20.9(0.6)
2.0	2.0	0.43	0	0	10.4(0.9)	11.1(1.0)
2.0	2.0	0.86	0	0	6.4(0.8)	7.4(0.2)
2.0	2.0	1.72	0	0	3.0(0.1)	6.1(0.5)
1.8	2.0	0	0.43	0	11.2(1.5)	12.8(1.2)
1.6	2.0	0	0.86	0	6.6(0.4)	9.8(0.6)
1.2	2.0	0	1.72	0	1.6(0.1)	5.7(0.3)
1.6	2.0	0	0	0.43	16.6(0.8)	19.5(0.8)
1.2	2.0	0	0	0.86	17.7(0.8)	19.8(1.6)
0.4	2.0	0	0	1.72	8.7(8.7)	15.7(0.6)
P rate				d.f.: 3	**	**
P form				2	**	**
P rate * P form				3	**	*
P rate Lin. in TSP				1	**	NS
P rate Quad. in TSP				1	**	**
P rate Lin. in MAP				1	**	**
P rate Quad. in MAP				1	**	**
P rate Lin. in DAP				1	NS	NS
P rate Quad. in DAP				1	NS	NS

†. T-N = Total amount of N application.
‡. The numbers in the parentheses are standard errors.
Ns indicates no significant, and *, and ** indicate significant at 0.05 and 0.01 probability in Contrast, respectively.

Table 3. Ammonia volatilization after 24 d from urea-phosphate mixtures as related to amounts and source of added P at constant urea rates

Treatments					Soils	
Urea	T-N†	TSP	MAP	DAP		
-------- N --------		-------------- P --------------			Ste. Rosalie	Ormstown
------------------------ g kg^{-1} ------------------------					-------- % urea N‡--------	
0.5	0.5	0	0	0	4.7(0.6)§	9.8(0.6)
0.5	0.5	0.22	0	0	1.8(0.2)	4.9(0.5)
0.5	0.5	0.43	0	0	1.0(0.1)	2.4(0.5)
0.5	0.6	0	0.22	0	4.2(0.3)	4.1(0.4)
0.5	0.7	0	0.43	0	2.8(0.2)	3.0(0.2)
0.5	0.7	0	0	0.22	12.8(0.8)	14.2(1.0)
0.5	0.9	0	0	0.43	14.5(1.0)	22.8(1.4)
P rate				df: 2	**	**
P form				2	**	**
TSP vs MAP				1	*	NS
TSP, MAP vs DAP				1	**	**
P rate * P form				3	**	**
P rate Lin. in TSP				1	**	**
P rate Quad. in TSP				1	**	NS
P rate Lin. in MAP				1	**	NS
P rate Quad. in MAP				1	*	*
P rate Lin. in DAP				1	NS	**
P rate Quad. in DAP				1	*	**

†. T-N = Total amount of N application.
‡. Corrected for corresponding P only treatments.
§. The numbers in parentheses are standard errors.
Ns indicates no significant, and *, and ** indicate significant at 0.05 and 0.01 probability in Contrast, respectively.

Table 4. Effect of P form and rate on N recovery from added N after 24 days incubation

Treatment					Ste. Rosalie			Ormstown		
Urea-N	Total-N	TSP	MAP	DAP	NH_3 Loss	Soil NH_4+NO_3-N	Recovery	NH_3 Loss	Soil NH_4+NO_3-N	Recovery
- N g kg^{-1} -		-- P g kg^{-1} --			% applied N					
0.5	0.5	0	0	0	4.7	77	82	9.8	53	63
0.5	0.5	0.22	0	0	1.8	95	97	4.9	73	78
0.5	0.5	0.43	0	0	1.0	89	90	2.4	73	77
0.4	0.5	0	0.22	0	2.4	82	84	3.8	72	76
0.3	0.5	0	0.43	0	1.2	82	83	0.4	77	77
0.3	0.5	0	0	0.22	5.6	58	64	9.4	56	65
LSD 0.05					2.0	13	12	2.1	10	10
C.V.					35.0	9	7.9	28.4	13	7.4
P Rate					**	NS	NS	**	NS	*
P form					**	**	**	**	**	*
P rate*P form					NS	NS	NS	NS	NS	NS

Ns indicates no significant, and *, and ** indicate significant at 0.05 and 0.01 probability in Contrast, respectively.

Table 5. Influence of triple superphosphate (TSP) application rates on recovery of applied urea in two soils

Treatment		Recovery of urea in soil			
Urea-N	TSP-P	1 day	2 days	3 days	4 days
------- $g\ kg^{-1}$ soil -------		------------------- % -------------------			
			Ormstown		
0.5	0	48	29		13
0.5	0.22	52	35		18
0.5	0.43	60	34		31
LSD 0.05		15	5		3
			Ste. Rosalie		
0.5	0	95	72	53	33
0.5	0.22	95	89	66	38
0.5	0.43	95	89	72	63
LSD 0.05		29	21	23	12

CONNECTING PARAGRAPH

Chapter III demonstrated that adding acidic phosphates such as TSP and MAP to urea, reduced NH_3 losses on two soils. Ammonia loss decreased as P : urea-N ratios increased. Ammonia loss from urea was increased when urea was applied with DAP. The effect of acidic phosphates on NH_3 loss was related to a reduction in pH in fertilizer microsites and retarding urea hydrolysis. In consequence, soil NH_4- and NO_3-N contents were increased when acidic P fertilizers were applied as mixture with urea. On the other hand, urea hydrolysis increased pH and NH_4- and NO_3-N concentrations in soil-fertilizer microsite, which could affect soil chemical properties and P reactions in soils.

In Chapter IV, the effect of added urea on soil P sorption characteristics and fertilizer P distribution in different soil fractions was evaluated in two eastern Canadian soils using two electrolytes.

CHAPTER IV

PHOSPHATE SORPTION AS INFLUENCED BY ADDED UREA IN TWO EASTERN CANADIAN SOILS

1. ABSTRACT

The interaction of urea with P in soil-fertilizer microsites may have an important effect on P availability to crops. A laboratory study was conducted to evaluate the effect of urea on P reactions in two eastern Canadian soils (Typic Humaquepts). Phosphate sorption was studied by equilibrating soil samples pretreated with four levels of urea for 24 hours with six rates of P in either 0.01 *M* $CaCl_2$ or 0.03 *M* KCl solutions. Phosphate desorption was determined by sequentially extracting the residual soil with 0.01 *M* $CaCl_2$ or 0.03 *M* KCl, and 0.5 *M* $NaHCO_3$. Urea application increased the soil pH (0.01 *M* $CaCl_2$) in the fertilizer microsites from 5.2 to 7.3 in the Ste. Rosalie soil and from 5.9 to 7.4 in the Ormstown soil. These pH changes had variable effects on soil P sorption characteristics, depending on soil and electrolyte. Phosphate sorption increased with increasing urea and pH when using $CaCl_2$ as the electrolyte. Added urea and pH had little effect when KCl was used, indicating the urea effect on P sorption was influenced by Ca concentration in electrolyte. The effect of urea was not significant at P rates below 320 mg P kg^{-1} soil. The observed increase in P sorption and decrease in solution P with added urea was probably related to precipitation of Ca-P compounds and the shift from $H_2PO_4^-$ to HPO_4^{2-} at higher pH values. Urea application increased 0.5 *M* $NaHCO_3$ extractable P and reduced non-extractable P in both soils. It was concluded that for soils with high Ca content, urea application with P fertilizer could reduce P concentration in soil solution and P mobility because of the increase in P sorption and P buffer

capacity, but increase available P as expressed by $NaHCO_3$ extractable P.

2. INTRODUCTION

A major problem often found in acid soils is P deficiency for crop production (Engelstad and Terman, 1980). Applying P fertilizer to acid soils often results in low fertilizer efficiency because acid soils sorb large amounts of fertilizer P through P precipitation and adsorption (Lindsay et al., 1962; Eghball et al., 1990). Phosphorus is precipitated in acid soils by Fe and Al, and adsorption on Fe oxides is significant. Phosphate sorption by soils is influenced by pH (Haynes, 1982) and salt concentration (Bolan, et al., 1986). However, the effect can be highly variable. Reports have shown that P sorption decreased (Eze and Loganathan, 1990), increased (Chen and Barber, 1990) or was not affected (Reeve and Sumner, 1970) by an increase of pH.

The effect of pH on P precipitation may also be variable. In acid soils, variscite ($AlPO_4 \cdot 2H_2O$) and strengite ($FePO_4 \cdot 2H_2O$) are the dominant stable minerals. Their solubilities increase with pH (Lindsay and Moreno, 1960). Amorphous Fe- and Al-P compounds may also be present, with variable but generally higher solubility (Hsu, 1989). In slightly acid to alkaline conditions, P often forms poorly crystalline Ca minerals. Thus, increasing pH to or above neutrality can increase P precipitation because of the formation of relatively insoluble Ca-P compounds (White and Taylor, 1977).

Urea hydrolysis in soil increases the concentration of OH^- and HCO_3^- ions, which can neutralize soil acidity, raise soil pH, and could reduce acidity released from the dissolution of acidic P fertilizers. Such reactions could increase P availability in the soil (Kissel et al., 1988).

Lu et al.(1987) reported that urea applied with single superphosphate (SSP) to a calcareous soil increased soil Olsen-P and P uptake, compared to diammonium phosphate (DAP). Raun et al. (1987) found urea phosphate provided greater yield, grain P content and total P uptake than ammonium pyrophosphate and DAP on a calcareous soil.

There is, however, little information available on the effect of urea on P reactions in acid soils. Such information is necessary to develop effective fertilization practices. The objectives of this study were to determine the effect of added urea on P sorption and distribution in different fractions in two acid eastern Canadian soils.

3. MATERIALS AND METHODS

Surface soil samples (0 to 15 cm) from two Typic Humaquepts, a Ste. Rosalie clay (very fine silty, mixed, acid, frigid) and an Ormstown silty clay loam (fine silty, mixed, non-acid, frigid), differing in physical and chemical properties (Table 1) were used. Dominant clay minerals were mica, chlorite and vermiculite in the Ormstown soil, and mica and chlorite in the Ste. Rosalie soil (Chen and Mackenzie, 1992). These are important agricultural soils of eastern Canada. Samples were taken from soils used for corn production which had received little P fertilization. Samples were air-dried, ground and passed through a 1 mm sieve before use.

1). Phosphate sorption-desorption

Two g air-dry soil (<1 mm) was mixed with four urea-N levels in solution (0, 250, 500, and 1000 mg N kg^{-1} soil) in 50 mL centrifuge tubes and moistened to near field capacity, i.e. 200 g H_2O kg^{-1} soil for the Ormstown or 240 g H_2O kg^{-1} for the Ste. Rosalie soil. Soil samples treated with urea were incubated at 25 °C for four d. Following incubation, 25 mL of either 0.01 *M* $CaCl_2$ or 0.03 *M* KCl containing one of six P concentrations (0, 0.2, 0.4, 0.8, 1.2 and 1.6 m*M* P) was added to each soil. These were equivalent to 0, 80, 160, 320, 480 and 640 mg P kg^{-1} soil. Each treatment was replicated four times. Soil-solution mixtures were shaken at 25 °C for 24 h using an end-over-end shaker. After shaking, pH of suspensions was measured. Soil-solution mixtures were centrifuged at 5,000 g for 10 min, supernatant solutions were filtered through Whatman No. 5 filter paper, and P concentrations in the filtrates were determined using the method of Murphy and Riley (1962).

Residual soil in the centrifuge tube was used to determine P desorption by sequentially extracting with 25 mL of either 0.01 *M* $CaCl_2$ or 0.03 *M* KCl solution followed by an extraction with 25 mL of 0.5 *M* $NaHCO_3$ solution. For each extraction, samples were shaken on an end-over-end shaker for 20 h. Suspensions were centrifuged, filtered and P determined as described earlier for P sorption. Phosphorus retained in soil was determined and subtracted from subsequent fractions.

2). Analysis of data

The P sorbed on the solid phase (P_s), was calculated from the difference between added P (P_a) and increase in solution P (dP_l). The P_s was divided into 0.01 *M* $CaCl_2$ or 0.03 *M* KCl desorbed P (P_d), $NaHCO_3$-extractable-P (P_e) and non-extractable-P (P_n). The distribution of added P in soil was computed as:

$$P_a = dP_l + dP_d + dP_e + dP_n \qquad [1]$$

where $dP_l = P_l - P_{l(o)}$, $dP_d = P_d - P_{d(o)}$ and $dP_e = P_e - P_{e(o)}$; the suffix (o) refers to the value obtained at each urea level from a soil suspension without added P. The increment of non-extractable-P (dP_n), was computed as follows:

$$dP_n = P_a - (P_l - P_{l(o)}) - (P_d - P_{d(o)}) - (P_e - P_{e(o)}) \qquad [2]$$

Rearranging Equation 2 yields:

$$dP_n = P_a + [P_{l(o)} + P_{d(o)} + P_{e(o)}] - [P_l + P_d + P_e] \qquad [3]$$

For the relation of sorbed P with soil solution P after 24 h shaking, results obtained from the P sorption were fitted to the Langmuir equation $Q=kbC/(1+kC)$, where Q is the amount of P sorbed per unit weight of soil (P_s), C is the P concentration in soil solution (P_l); k is a constant, and b is a P adsorption maximum (Sample et al., 1980). Maximum P buffer capacity (PBC) was calculated from kb (Olsen and Khasawneh, 1980). Finally the effects of urea and pH of equilibrium solution on P sorption, buffer capacity and distribution were statistically analyzed using the GLM procedure of SAS (SAS Institute, 1985).

4. RESULTS AND DISCUSSION

1). Effect of urea on pH and P sorption isotherm

Four day incubation with different rates of urea generated a range in pH values (Table 2). Soil pH increased from 5.2 to 7.3 in the Ste. Rosalie soil, and from 5.9 to 7.4 in the Ormstown soil in the presence of 0.01 M $CaCl_2$ as electrolyte.

In both soils at all pH values, the relation of sorbed P ($Q=P_s$) to solution P concentration ($C=P_l$) conformed to the Langmuir sorption equation. The goodness-of-fit, as assessed by the coefficients of determination for the Langmuir linear plots ($C/Q = C/b+1/kb$) was highly significant (Table 2). Maximum P sorption capacities (b) in 0.01 M $CaCl_2$ electrolyte increased with pH for both soils. Sorbed P (mg kg^{-1} soil) was related to pH of equilibrium solutions for both soils (Q=33.3pH - 9.5; R^2=0.99). However, k decreased with increasing pH in Ste. Rosalie soil, but was not influenced by pH in the Ormstown soil.

In an attempt to separate the effect of pH from that of Ca, P sorption was studied using 0.03 M KCl solution as background electrolyte. In this case, P sorption isotherms were not significantly influenced by pH changes in either the Ste. Rosalie soil or at lower pH (<7.0) values of the Ormstown soil (Table 2). When pH increased to, or over 7, maximum P sorption capacity increased only in the Ormstown soil, which might be due to its higher exchangeable Ca^{2+} content (Table 1). The presence of Ca was associated with the apparent increase in P sorption at high pH values, probably due to the formation of insoluble Ca-P compounds and the affinity of Ca for adsorption surfaces (Barrow, 1985). Thus, Ca^{2+} concentration changes tend to modify the effect of added urea and pH on P sorption.

These results were similar to those of Fox (1986), Barrow (1979), and Naidu and Syers (1990). They found precipitation of Ca-P compounds was responsible for the increase of P sorption at higher pH values when either Ca was added in liming materials or was present in the background electrolyte. Helyar et al. (1976) and Smillie et al. (1987) suggested that Ca may play an important role in the formation of surface complexes with P.

Effect of urea on soil maximum P buffer capacity (PBC), calculated from P sorption isotherms ($PBC=kb$), also varied with soils and electrolytes. The maximum PBC of the Ormstown soil increased from 219 to 423 mg P kg^{-1} with pH increases from 5.9 to 7.4 in 0.01 M $CaCl_2$, but was not significantly changed when 0.03 M KCl was the electrolyte. In contrast, the PBC of the Ste. Rosalie soil increased at high pH with the 0.03 M KCl solution.

The effect of urea on P sorption was related to changes of pH and salt concentration in the soils. Regarding the effect of pH on P sorption, it is usually considered that increasing pH in acid soils may reduce the concentrations of soluble and exchangeable Fe and Al ions which otherwise could react with added P to form sparingly soluble Fe and Al phosphates. Surface charge would become more negative with the pH increase, thus decreasing the number of P-sorption sites and reducing the strength of P sorption (Sanchez and Uehera, 1980).

Increased P sorption with added urea and higher pH observed in this study may have been caused by one or more of following reasons. As pH is increased, the concentration of HPO_4^{2-} increases at the expense of $H_2PO_4^-$. Because HPO_4^{2-} is sorbed more readily on soil surfaces, Bowden et al. (1980) suggested that the increase in concentration of HPO_4^{2-} is sufficient to offset the decrease in electrostatic potential. Another possible explanation is precipitation of relatively insoluble Ca-P compounds, which are often formed in slightly acid to alkaline conditions (White and Taylor, 1977). Finally, the addition of large rates of urea can increase salt concentration in the sorption medium. At high pH, a high concentration of cations in the outer planes of adsorption can decrease the negative potential on the surface resulting in increased P sorption (Barrow, 1984).

2). Effect of P rates on solution P at different pH values

Solution P increased with increasing P addition in a significant quadratic relation (R^2=0.92 to 0.99) for all treatments in both soils (Fig. 1a-d). A higher proportion of the added P was adsorbed at the lower rates of P addition.

The effect of urea and pH on solution P as a function of added P was significant only for P rates of 320 mg kg^{-1} soil or more for both soils when 0.01 *M* $CaCl_2$ was used as the electrolyte. With $CaCl_2$, Ca and P concentrations in solution were significantly lower at higher urea and pH values compared to lower urea and pH values. White and Taylor (1977) found that, at high P concentrations (1 m*M*), dicalcium phosphate precipitated at pH values greater than 5.5.

3). Effect of urea on P distributions in different P fractions

Because soil solution P is usually very low (0.003-0.5 mg L^{-1}; Sample et al. 1980), crops depend on the release of solid phase P into the soil solution. Therefore, P dissolution or desorption capacities and distribution of added P in P fractions are important.

Urea application increased P sorption in both soils (Fig. 2). Most of the increase in sorbed P, averaged over six P rates, both soils and both electrolytes, was accounted for by increased P extracted with 0.5 *M* $NaHCO_3$. Phosphorus extracted with 0.5 *M* $NaHCO_3$ increased with added urea from 26.7% to 46.3% of total added P. Non-extractable P decreased with added urea from 40% to 31.8% of added P. Since the P extracted by 0.5 *M* $NaHCO_3$ can be considered as labile P in soil (Barrow, 1985), this suggested that pH increases from urea hydrolysis increased initial rapid sorption of P, but reduced conversion of P to non-extractable forms. The mechanism is unclear. Calcium-P precipitation at higher pH values with more urea may have been in an amorphous, more easily extracted form. Increased extractable P with increased urea might also be related to soil organic materials dissolved through pH increase from urea hydrolysis. In a recent study, we found that addition of urea increased the dissolution of soil organic matter (data not shown). The dissolved organic matter could inhibit the formation of stable calcium phosphates such as dicalcium phosphate dihydrate, and hydroxyapatite by blocking sites for new crystal growth (Grossl and Inskeep, 1991).

Desorbed P from 0.01 *M* $CaCl_2$ or 0.03 *M* KCl extracts accounted for about 7% of the added P, and was not affected by added urea. The effects of pH increase on the charge of the sorption surface may have been offset by either the increased salt effect from urea hydrolysis or the shift of $H_2PO_4^-$ to HPO_4^{2-}, thus nullifying any effects on easily desorbed P. Solution P and Ca, averaged over six P rates and both soils in the 0.03 *M* KCl extract, decreased with added urea, especially at higher rates of P. This indicated that solution P was controlled by the formation of Ca-P compounds.

The availability of P to crops is a function of P concentration in soil solution, mobility and the ability of soils to replenish the solution P as it is removed. Uptake of P by crops is significantly affected by both the amount of labile P and the P buffer capacity (Sahrawat and Warren, 1989). The pH increase from urea hydrolysis could reduce solution P and increase P sorption, but would also increase labile P and P buffer capacity. Thus, at equal amounts of P extracted in soil solution, a urea-treated soil would contain a greater reserve of desorbable P and thus a greater supply of P for crops. When urea is applied with P fertilizer, the pH and Ca content of soil should be considered to avoid a significant decrease of solution P. Such a decrease in P concentration of soil solution could be due to the increase of pH, Ca-P precipitation and any salt effect resulting from urea hydrolysis.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, through Operating Grant OGP0002957.

5. REFERENCES

Barrow, N.J. 1979. The description of desorption of phosphate from soil. J. Soil Sci. 30:259-263.

Barrow, N.J. 1984. Modelling the effect of pH on phosphate sorption by soils. J. Soil Sci. 35:283-297.

Barrow, N.J. 1985. Reaction of anions and cations with variable charge soils. Adv. Agron. 38:183-229.

Bolan, N.S., J.K. Syers, and R.W. Tillman. 1986. Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. J. Soil Sci. 37:379-388.

Bowden, N.J., S. Nagarajah, N.J. Barrow, A.M. Posner, and J.P. Quirk. 1980. Describing the adsorption of phosphate, citrate and selenite on a variable charge minerals surface. Aust. J. Soil Res. 18:49-60.

Chen Jen-Hshuan and S.A.Barber. 1990. Effect of liming and adding phosphate on predicted phosphorus uptake by maize on acid soils of three soil orders. Soil Sci. 150:844-850.

Chen, J.S. and A.F. Mackenzie. 1992. Fixed ammonium and potassium as affected by added nitrogen and potassium in three Quebec soils. Commun. Soil Sci. Plant Anal., 23:1145-1159.

Eghball, B., D.H. Sander and J. Skopp. 1990. Diffusion, adsorption, and predicted longevity of banded P fertilizer in three soils. Soil Sci. Soc. Am. J. 54:1161-1165.

Engelstad, O.P. and G.L. Terman. 1980. Agronomic effectiveness of phosphate fertilizers. p.311-332. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy. Madison. WS., USA.

Eze, O.C. and P. Loganathan. 1990. Effect of pH on phosphate sorption of some Paleudults of southern Nigeria. Soil Sci. 150:613-621.

Fox, R.L. 1986. Phosphorus - a basic nutrient for soil improvement. p.57-64. *In* Proceedings of the international conference on the management and fertilization of upland soils in the tropics and subtropics. Soil Res. Inst., Nanjing, P.R. of China.

Grossl, P.R. and W.P. Inskeep. 1991. Precipitation of dicalcium phosphate dihydrate in the presence of organic acids. Soil Sci. Soc. Am. J. 55:670-675.

Haynes, R.J. 1982. Effects of liming on phosphate availability in acid soils. Plant Soil. 68:289-308.

Helyar, K.R., Munns, D.N. and Burau, R.G. 1976. Adsorption of phosphate by gibbsite. 2. Formation of a surface complex involving divalent cations. J. Soil Sci. 27:315-323.

Hsu Pa Ho, 1989. Aluminum hydroxides and oxyhydroxides. p.331-378. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. SSSA. Madison. WS., USA.

Kissel, D.E., M.L. Cabrera and R.G. Ferguson. 1988. Reactions of ammonia and urea hydrolysis products with soil. Soil Sci. Soc. Am. J. 52: 1793-1796.

Lindsay, W.L. and E.C. Moreno. 1960. Phosphate phase equilibria in soils Soil Sci. Soc. Am. Proc. 24:177-182.

Lindsay, W.L., A.W. Frazier, and H.F. Stephenson 1962. Identification of reaction products from phosphate fertilizers in soils. Soil Sci. Soc. Am. Proc. 26:446-452.

Lu, D.Q., S.H. Chien, J. Henao, and D. Sompongse. 1987. Evaluation of short-term efficiency of diammonium phosphate versus Urea plus single superphosphate on a calcareous soil. Agron. J. 79:896-900

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphorus in nature waters. Anal. Chim. Acta. 27:31-36.

Mehlich, A. 1984. Mehlich-3 soil test extractant: A modification of Mehlich 2 extractant. Comm. Soil Sci. Plant Anal. 15:1409-1416.

Naidu, R. and J.K. Syers. 1990. Effect of liming on phosphate sorption by acid soil. J. Soil Sci. 41:163-175.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p.539-577. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Olsen, S.R. and F.E. Khasawneh. 1980. Use and limitation of physical-chemical criteria for assessing the status of phosphorus in soils. p.361-410. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy. Madison. WS., USA.

Raun, W.R., D.H.Sander, and R.A. Olson. 1987. Phosphorus fertilizer carrier and their placement for minimum till corn under sprinkler irrigation. Soil Sci. Soc. Am. J. 51:1055-1062.

Reeve, N.G. and M.E. Sumner. 1970. Effect of aluminium toxicity and phosphorus fixation on crop growth on oxisols in Natal. Soil Sci. Soc. Am. Proc. 34:263-267.

Rhoades, J.D. 1982. Cation exchange capacity. p.154-156. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Sahrawat, K.L. and G.P. Warren. 1989. Sorption of labelled phosphate by a Vertisol and Alfisol of the semi-arid zone of India. Fert. Res. 20:17-25.

Sample, E.C., R.J. Soper and G.J. Racz. 1980. Reactions of phosphate fertilizers in soils, p.263-304. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy. Madison. WS., USA.

Sanchez, P.A. and G. Uehara. 1980. Management considerations for acid soils with high phosphorus fixation capacity. p.472-514. *In* F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy. Madison. WS., USA.

SAS Institute Inc., 1985. SAS user's guide. 5 Edition. SAS Institute Inc. Cary, NC.

Smillie, G. W., D. Curtin, and J.K. Syers, 1987. Influence of exchangeable calcium on phosphate retention by weakly acid soils. Soil Sci. Soc. Am. J. 51:1169-1172.

White, R. E. and A.W.Taylor, 1977. Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high addition of soluble phosp2hate. J. Soil Sci. 28:48-61.

Figure 1. Effect of added P and urea-N on phosphorous concentration in soils suspended in 0.01 *M* $CaCl_2$ or 0.03 *M* KCl solutions (Vertical bars indicate LSD 0.05 level for N rates).

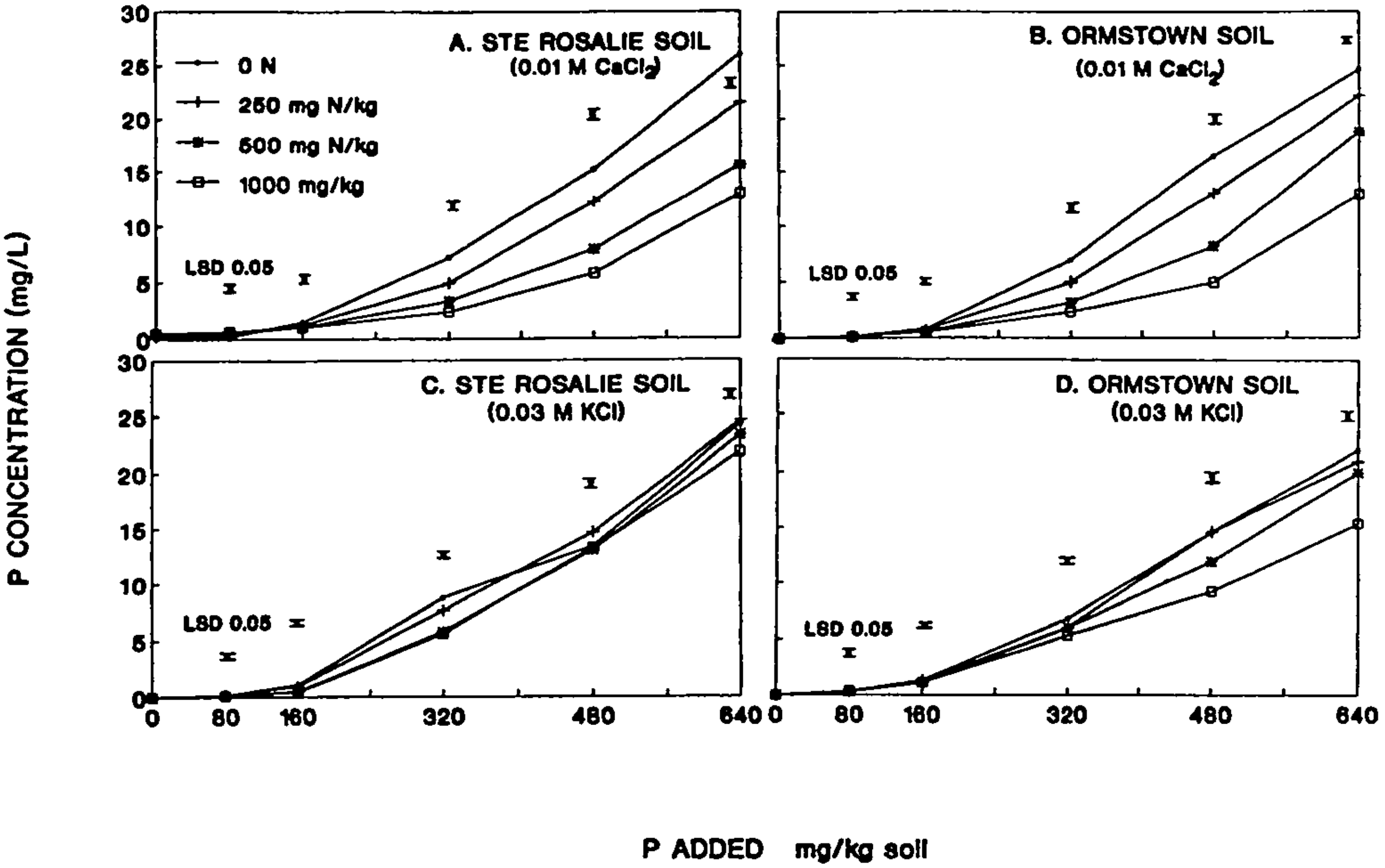

A. STE ROSALIE SOIL
(0.01 M $CaCl_2$)
B. ORMSTOWN SOIL
(0.01 M $CaCl_2$)
C. STE ROSALIE SOIL
(0.03 M KCl)
D. ORMSTOWN SOIL
(0.03 M KCl)
0 N
250 mg N/kg
500 mg N/kg
1000 mg/kg
LSD 0.05
LSD 0.05
LSD 0.05
LSD 0.05
P CONCENTRATION (mg/L)
0
5
10
15
20
25
30
0
80
160
320
480
640
P ADDED mg/kg soil

Figure 2. Effect of added urea on soil phosphorous fractions and calcium solution concentration in 0.03 *M* KCl solution (Values are averaged over all P rates and soils. P-Non is the P fraction retained in soil after 0.5 *M* $NaHCO_3$ extraction. Vertical bars indicate LSD 0.05 level for urea-N rates).

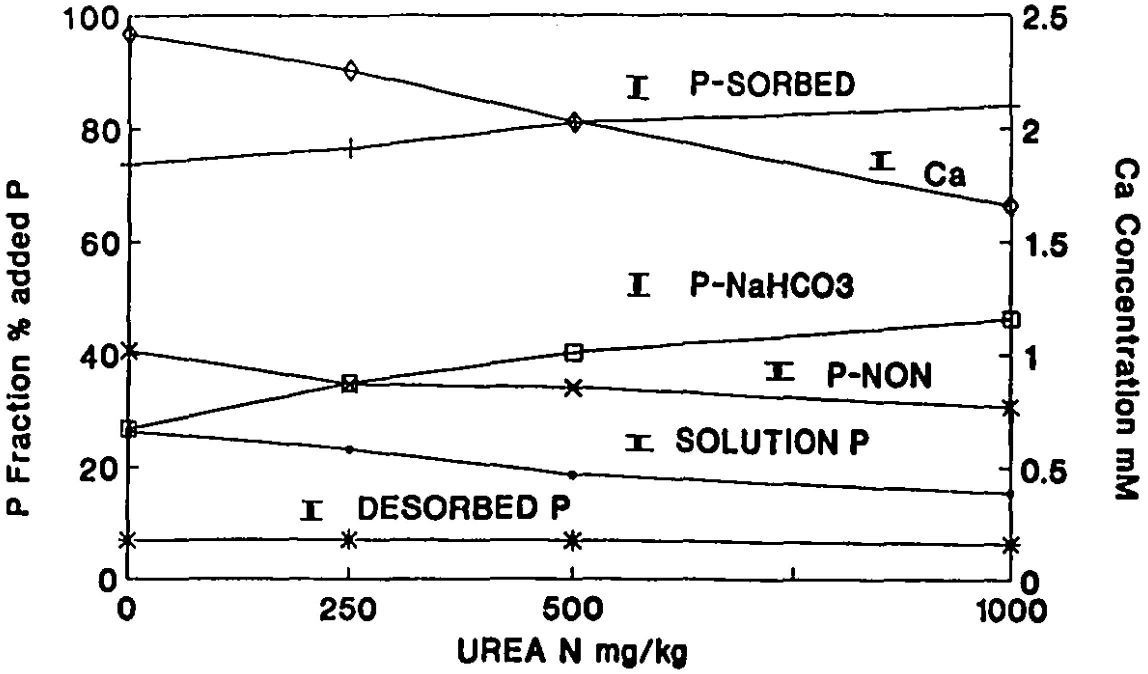

P Fraction % added P
0
20
40
60
80
100
Ca Concentration mM
0
0.5
1
1.5
2
2.5
UREA N mg/kg
0
250
500
1000
P-SORBED
Ca
P-NaHCO3
P-NON
SOLUTION P
DESORBED P

Table 1. Selected physical and chemical properties of the soils

Soil	pH		clay	silt	organic	Exchangeable cations					Soil P§
	H_2O	1 *M* KCl			matter†	Ca	Mg	K	Al	SUM‡	
			----- mg kg^{-1} -----			------ $cmol_c$ kg^{-1} soil -------					kg P ha^{-1}
Ste. Rosalie	5.2	4.1	568	293	43	9.4	5.4	0.7	0.3	15.8	18
Ormstown	6.0	5.0	368	443	33	14.6	5.0	0.2	0	19.8	26

† Walkley-Black procedure (Nelson and Sommers, 1982)

‡ Sum of exchangeable Ca, Mg, K and Al ($BaCl_2$ method; Rhoades, 1982).

§ Mehlich No.3 extractant (Mehlich, 1984).

Table 2. Effect of added urea on suspension pH and Langmuir isotherm parameters for two eastern Canadian soils

Soils	Added urea	Suspension pH	Langmuir parameters b	k	R^2	PBC *kb*
	mg N kg^{-1}		mg P kg^{-1}			mg P kg^{-1}
		------------ 0.01 M $CaCl_2$ as electrolyte -------				
Ste. Rosalie	0	5.2	308	0.59	0.98^{**}†	182
	250	6.1	380	0.48	0.98^{**}	181
	500	6.8	512	0.34	0.98^{**}	173
	1000	7.3	589	0.29	0.96^{**}	176
	LSD 0.05	0.3	48	0.10		31
Ormstown	0	5.9	310	0.71	0.96^{**}	219
	250	6.5	352	0.79	0.98^{**}	281
	500	7.0	403	1.03	0.98^{**}	417
	1000	7.4	500	0.83	0.98^{**}	423
	LSD 0.05	0.1	32	0.13		54
		---------- 0.03 M KCl as electrolyte ----------				
Ste. Rosalie	0	5.1	330	0.49	0.90^{**}	163
	250	5.9	323	0.60	0.96^{**}	193
	500	6.5	336	0.61	0.98^{**}	207
	1000	7.3	351	0.62	0.96^{**}	219
	LSD 0.05	0.1	27	0.10		39
Ormstown	0	6.2	360	0.40	0.94^{**}	143
	250	6.6	371	0.40	0.94^{**}	146
	500	7.0	400	0.40	0.96^{**}	160
	1000	7.5	493	0.30	0.90^{**}	147
	LSD 0.05	0.1	31	0.12		28

† ** indicates significant at 0.01 probability level by F test.

CONNECTING PARAGRAPH

In the previous Chapter, results of the P sorption experiment showed that adding urea had variable effects on soil P sorption characteristics, depending on soil and electrolyte characteristics. Phosphorous sorption increased, and P concentration in solution decreased with increasing urea and pH when using $CaCl_2$ as the electrolyte. But, added urea and pH had little effect when KCl was used, indicating the urea effect on P sorption was influenced by Ca content. Addition of urea to P fertilizer increased 0.5 *M* $NaHCO_3$ extractable P and reduced non-extractable P.

The availability and efficiency of applied P depend not only upon the content of available P, but also the rate and extent of P diffusion in the soil to plant roots. Rates and extent of diffusion are influenced by soil P sorption capacity, P concentration in soil solution and P reactions during diffusion processes. The following Chapter will look into the effect of the interaction between urea and P fertilizer on the movement of P from the fertilizer band into soil and subsequent P transformations in soil. This experiment was conducted in the same soils as previous experiments.

CHAPTER V

INTERACTION OF UREA WITH TRIPLE SUPERPHOSPHATE IN A SIMULATED FERTILIZER BAND

1. ABSTRACT

Fertilizer nutrient diffusion from fertilizer bands and transformations in soil affect fertilizer nutrient availability to crops. The interaction of urea and triple superphosphate (TSP) on urea hydrolysis and P transformations during diffusion processes from a fertilizer band was evaluated in a laboratory incubation experiment with two eastern Canadian soils (Ste. Rosalie clay, Typic Humaquept, pH 5.0; Ormstown silty clay loam, Typic Humaquept, pH 6.0). Two fertilizer sources (urea and TSP) and three N and P rates (0, 100 and 200 kg ha^{-1}) were combined in a factorial arrangement. Fertilizer combinations were placed on segmented soil columns, incubated and soil segments were analyzed for N and P content. Acidification from dissolution of TSP retarded urea hydrolysis, and curtailed the rise in soil pH surrounding the fertilizer band. Urea hydrolysis caused dissolution of soil organic matter, which might inhibit precipitation of insoluble phosphates. Banding urea with TSP increased 1 *M* KCl extractable P, soil solution P, sorbed P concentrations and total P diffused away from the band. Urea decreased 0.01 *M* $CaCl_2$ extractable P, indicating probable precipitation of calcium phosphates with $CaCl_2$ extraction. Banding urea with TSP could benefit P diffusion to plant roots and increase fertilizer P availability.

2. INTRODUCTION

Increased efficiency of applied phosphorous (P) fertilizer may depend upon increased soluble P, and increased P movement into the soil from fertilizer granules (Benbi, 1987). Phosphorous movement in soil is primarily by diffusion (Barber et al., 1963). The rate of P diffusion is influenced by the amount of applied P (Malcolm, 1986), soil water content, bulk density (Barraclough and Thinke, 1981; Bhadoria et al., 1991), and soil P adsorption capacity (Williams, 1971). These properties directly influence P concentration in soil solutions (C_l). In a sensitivity analysis, C_l was shown to be one of the most important soil variables that affect P diffusion to plant roots (Silberbush and Barber, 1984).

Phosphate reactions in soil may also be influenced by organic matter (O'Connor et al., 1986), pH changes (Lindsay and Stephenson, 1959; Kamprath, 1987; Fan et al., 1993), and electrolyte concentration in soil solutions (Barrow, 1985).

Urea and triple superphosphate (TSP) are now important fertilizers and common carriers in fertilizer programs. After application, hydrolysis of urea may raise the pH of noncalcareous soils and increase OH^-, HCO_3^- and NH_4^+ concentrations (Rachnpal-Sign and Nye, 1984; Fan and MacKenzie, 1993). The increase in soil pH and ionic strength has a significant effect on P adsorption (Barrow, 1985; Eze and Longanathan, 1990), P precipitation (Hanson, 1985), P concentrations in soil solution (Fan et al., 1993) as well as the solubility of soil organic matter (Myers and Thien, 1988). These soil changes with urea hydrolysis might influence P movement and reactions in soils. Urea hydrolysis and subsequent changes in soil pH and NH_4^+-N concentration also depend on soil type and fertilizer management. Adding TSP could reduce urea hydrolysis rates in acid soils (Fan and MacKenzie, 1993). Due to different diffusion rates of urea and TSP in soils, it is necessary to study urea-TSP interaction during diffusion processes.

While application of N with P in a band is known to increase fertilizer P efficiency in crop production (Lu et al., 1987; Eghball et al., 1990), little research is available on the interaction of urea and phosphate on the movement of P from fertilizer bands into soil and consequent P reactions in soils. The objectives of this experiment were to study the movement and reaction of varying quantities of urea and TSP in soil with distance from a simulated fertilizer band.

2. MATERIALS AND EXPERIMENTS

1). Soils

Surface soil samples (0-15 cm) from two soils, a Ste. Rosalie clay (very fine silty, mixed, acid, frigid, Typic Humaquept) and an Ormstown silty clay loam (fine silty, mixed, non-acid, frigid, Typic Humaquept), differing in physical and chemical properties (Table 1) were used. Samples were taken from soils which had received little fertilization. Samples were air-dried, and ground to pass a 2 mm sieve.

2). Measurement of phosphate and urea movement and transformation in soils

The experiment compared two fertilizer sources (urea and TSP) at three levels (0, 100 and 200 kg N or P ha^{-1}) calculated on a soil surface area basis. Treatments were arranged in a completely randomized design. Each treatment was replicated twice.

Soil-fertilizer cylinder preparation. The technique used was a modification of that of Lindsay and Stephenson (1959) and Moody (1989). Soil was packed into a polyvinylchloride (PVC) cylinder (7.5 cm internal diameter and 5 cm high) in 8 layers. Six layers were 5 mm deep (0-30 mm), 2 layers 10 mm (31-50 mm) deep. A bulk density of 1.07 g cm^{-3}, that of the soil in the field, was obtained by adding a calculated quantity of soil one layer at a time. The layers were separated by sets of three Whatman No. 2 filter papers, slightly smaller than the diameter of the PVC cylinder. After packing the cylinder, soil moisture was adjusted to 250 g kg^{-1} for Ste. Rosalie soil, and 200 g kg^{-1} for Ormstown soil. Two days later, fertilizers were applied uniformly as finely ground materials (< 1 mm) on the surface of the first set of filter papers on each cylinder. The top and bottom of the packed cylinder were covered with parafilm to prevent moisture loss. Following preparation, soil cylinders were incubated vertically at 25 °C.

Extraction and analysis of soil samples. After periods of 5, 10, and 20 days, filter papers and soil layers were separated and each soil layer was thoroughly mixed. Two g of moist soil sample from each layer was extracted with 50 mL 1 *M* KCL containing 5 mg L^{-1} of phenylmercuric acetate (PMA) for urea (Mulvaney and Bremner, 1979), NH_4, NO_3 and NO_2-N analyses (Keeney and Nelson, 1984). Soil sub-samples were oven dried at 90 °C for 24 hour to measure water content. Soil pH was measured in 1:20 (w:v) moist soil:0.01 *M* $CaCl_2$ suspensions.

Desorption of phosphate. One g moist soil, sampled from each layer, was first shaken for 24 hours at 25 °C with 0.01 *M* $CaCl_2$ at a solution:soil ratio of 20:1 (v:w). Suspensions were centrifuged at 5,000 g and supernatants filtered. Concentration of P in the filtrates was determined as soil solution P (Barrow 1979). Sulphuric acid soluble P in the residual soil samples in the centrifuge tubes was measured by shaking soil for 16 hours in 0.5 *M* H_2SO_4 (1:20, soil:solution) (Williams, 1971). Soil P extracted in *M* KCl (1:25, w:v) was determined on moist soil samples. Amounts of P above that for unfertilized soil were assumed to be from fertilizer P.

Concentration of P in soil solution adsorbed into the filter paper was determined. The center filter paper from each set of three was removed and weighed immediately. The increase in weight over that of an oven dried filter paper of the same size was taken as weight of solution in the filter paper. The moist filter paper was extracted with 20 mL of 0.5 *M* H_2SO_4 solution and analyzed for P.

An indication of the amount of dissolved soil organic matter (DOM) in the extract was obtained by measuring absorbence (ABS) of the filter paper extraction solution at 400 nm (Perrot, 1992).

3). Analysis of results

The data from each soil segment were analyzed in a completely randomized design. The effects of urea-N, TSP-P rate and their interaction on pH changes, DOM, urea hydrolysis and P fractions were tested with the GLM procedure of SAS for orthogonal contrasts (SAS Institute, 1985). Least significant differences (LSD) for means were computed using the GLM procedure. Where there was a similar tendency between two soils or treatments, only one soil or definitive treatment is discussed.

4. RESULTS AND DISCUSSION

1). Water movement (Ste. Rosalie soil)

When urea and TSP was applied to soils, soil water moved into fertilizer layer in response to moisture potential gradients. At 10 days, the water content of fertilizer layer increased from 50 g kg^{-1} to 318 g kg^{-1}. The water content of the soil adjacent to the fertilizer layer (0-5 mm distance) was reduced to 128 to 175 g kg^{-1} from about 210 g kg^{-1} in TSP or TSP plus urea treatments, and varied with TSP rate (Fig. 1a). Water content then increased gradually with distance up to approximately 17.5 mm from the fertilizer. This water distribution with P fertilizer was consistent with that of Lindsay and Stephenson (1959). The difference found in our studies was that water in the wetter zone did not move into the drier zone, but formed a sharp juncture at the boundary between the wetter and the drier zones. The formation of hard pan at the moist-dry juncture was noted, and might indicate the reprecipitation of P-dissolved soil minerals. With TSP treatments, water contents were consistent with a process of water vapour movement into fertilizer layer, with subsequent dissolution of the fertilizer and solution movement away from the fertilizer layer (Lindsay and Stephenson, 1959). With urea alone, there was an increase in soil water content near the fertilizer layer, with a gradual decrease in water content to the 17.5 mm distance (Fig. 1b). The water contents in the treatments with urea alone reflected a rapid dissolution of urea and rapid diffusion of the fertilizer solution from the fertilizer into the soil. Moisture movement with combinations of urea and TSP resulted in a combination of the two water movement processes.

2). Urea hydrolysis and pH changes

After five days, urea in treatments of 100 and 200 kg N ha^{-1} decreased linearly with distance from the fertilizer layer (Fig. 2a). Urea levels were proportional to the rate of added N. Diffusion of urea was found up to 37.5 mm from the fertilizer layer in the Ormstown and 27.5 mm in the Ste. Rosalie soil. Urea concentrations at 10 d in both soils decreased markedly from the 5 d values. Little urea remained at 10 d for 100 kg N ha^{-1} rates and at 20 days for all rates in the Ormstown soil and at 20 days for 100 kg N ha^{-1} rates in the Ste. Rosalie soil (not presented). Application of TSP with urea resulted in higher concentrations of urea in both the fertilizer layer and in adjacent soil layers than with treatments of urea alone in the ormstown soil at 5 and 10 d (Fig. 2a-c). After 5, and 10 d, the total amounts of urea remaining in the soil with TSP treatments were significantly higher than treatments without TSP in both soils (Table 2). Urea contents increased with increased P rates in both soil.

Results from 5 d and 10 d were consistent with findings of a study, in which adding TSP to urea increased urea recovery (Fan and MacKenzie, 1993). Fan and MacKenzie (1993) showed that the urea hydrolysis had been retarded by TSP in both the fertilizer layer and the soil into which urea diffused, even though phosphoric acid diffused at a slower rate than urea. Bremner and Douglas (1971) and Stumpe (1981) also found that urea hydrolysis was reduced by 14 to 50% with urea phosphate (UP) compared with urea alone, and the delay in urea hydrolysis was related to the N:P ratio of the UP (total acidity). The urease inactivation caused by acidity and the inhibition by orthophosphate of urea hydrolysis might be the main effects of TSP on retarding urea hydrolysis.

Urea hydrolysis resulted in an increase in soil pH (Fig. 3), but this increase was modified by added TSP. In Ste. Rosalie soil, urea alone at 200 kg ha^{-1} increased soil pH (0.01 M $CaCl_2$) from 4.5 to over 8.0 at distances of 0 to 25 mm after 5 d diffusion. Adding TSP reduced the pH in the 0 to 5 mm soil layer from 4.5 to 3.4 or 4.2, depending on P rate. Acidification from added TSP reduced the pH increase from urea hydrolysis as far as 7.5 mm from the fertilizer layer compared with urea alone. This effect of TSP on acidity might also result from retarded urea hydrolysis. Urea hydrolysis is usually slower in acid soils, which might result in less pronounced rise in pH from urea hydrolysis. Effects on soil pH from urea hydrolysis and TSP acidification decreased with time. At 20 d, the effect of TSP on urea treatments was eliminated probably due to acid neutralization by soil minerals during diffusion, or by urea hydrolysis.

3). Soil organic matter solubility

Dissolved soil organic matter, increased in the soil solution of all treatments with urea or urea plus TSP. As urea rates increased from 0 to 200 kg N ha^{-1}, ABS in the extractant increased from 0.05 to 0.30 in the Ste. Rosalie soil and to about 0.23 in the Ormstown soil at 10 mm distance from the fertilizer layer after 10 d (Fig. 4). Higher ABS values from treatments of urea or urea plus TSP could be identified up to a distance of 40 mm from the fertilizer site. This was consistent with the pH changes in the soil (Fig. 3), in that high pH can lead to dissolution of fulvic and humic acid components of organic matter (Schnitzer, 1978). Increased NH_4 concentration from urea hydrolysis could have increased DOM, as Myers and Thien (1988) found that DOM increased with increase in NH_4OH-N rates. The effect of urea on DOM was greater in the Ste. Rosalie soil than in the Ormstown soil, probably due to the higher organic matter content of the Ste. Rosalie soil.

4). Phosphorous movement and transformation

Because there were significant interactions among added urea and TSP treatments with distance, N and P effects as well as their interaction at each distance were considered separately (Table 3).

Adding urea with TSP increased P concentrations in $CaCl_2$ extractions at the 0 to 5 mm distance in both soils after 5 d (Tables 4 and 5), but reduced the $CaCl_2$ extractable P concentration at 0 to 5 and 5 to 10 mm distances after 10 d in Ste. Rosalie soil (Table 4), and at distances from 0 to 5 mm to 15 to 20 mm in the Ormstown soil after 10 d (Table 5). This effect of urea disappeared in both soils after 20 days of reaction. Decreased P concentration in $CaCl_2$ extract with added urea was probably related to the high pH, which caused Ca-P precipitation when both Ca and P concentrations in soil solution were high (Fan et al., 1993; Eze and Loganether, 1990).

In contrast, urea increased sorbed P and total P for both 10 and 20 d for both soils (Tables 4 and 5). Adding urea with TSP increased sorbed P concentrations and total amounts of P at 5 to 10 mm, 10 to 15 mm and 15 to 20 mm distances after 5 and 10 d diffusion, and at 20 to 25 mm distance after 20 d of diffusion in the Ste. Rosalie soil (Table 4). In Ormstown soil, however, urea effects on sorbed P and total P diffused were not as pronounced as those in the Ste. Rosalie soil (Table 5). Increases in sorbed P and total P diffused were found at the 0 to 5 mm and 15 to 20 mm distance after 5 d of diffusion; only in sorbed P at distance of 0 to 20 mm at 10 d; and in sorbed P and total P at 15 to 25 mm distance after 20 d. Because Ormstown soil has a higher pH and a higher exchangeable Ca content than the Ste. Rosalie soil, P diffusing into the soil might be transformed into non-extractable Ca-P compounds. Perrot (1992) reported that, where exchangeable Ca was present in soil samples, precipitation of Ca-P occurred during alkali extraction.

Adding urea with TSP increased the total P concentrations in solution sampled with filter paper (Fig. 5a-b) and in soil extraction with 1 *M* KCl (Fig. 5c-d). Higher P concentrations could be found in the solution of the treatment with urea plus TSP compared with TSP alone at all distances in both soils after 10 d. This contrasts with the urea effect on P concentration in $CaCl_2$ extraction where urea reduced P concentration. Naidu and Syers (1990) also found, in contrast with sorption of P from 0.01 *M* $CaCl_2$ by soils, that amounts of P sorbed decreased steadily with increasing pH when KCl was used as background electrolyte. This again implies precipitated Ca-P with $CaCl_2$ extracts of urea treatment. It has often been reported that whenever an increase in P sorption was observed at high pH values, either Ca^{+2} was present from the liming material, or was present in the background electrolyte. This led several authors (Fox et al., 1974; Barrow et al., 1985) to propose that the precipitation of Ca-P is responsible for the decrease in solution P concentration at high pH values. A similar role for Ca in the formation of surface complexes with P has been advanced by Smillie et al.(1987).

When large amounts of urea were banded with TSP, the rise in pH and NH_4^+ concentration in the layer dissolved organic matter as also noted by Bell and Black (1970), Tomasiewicz and Henry (1985), and Myers and Thien (1988). Dissolved organic matter could inhibit the precipitation of Ca-P compounds by adsorbing onto Ca-P surfaces, thus blocking sites for new crystal growth (Grossl and Inskeep, 1991). Inskeep and Silvertooth (1988) found that organic constituents inhibited the formation of thermodynamically stable Ca phosphates, thereby maintaining higher soluble P levels in soils. Moreover, in addition to ionic phosphate in soil solution, as much as half the phosphate may be present as soluble organic compounds, partically in soils containing appreciable organic matter (Barber, 1984). The high pH in soil solution resulting from urea hydrolysis might increase decomposition of the soluble organic compounds in soil solution. This high level of soluble P and the complexing of P precipitates with organic acids would account for increased P diffusion into the soil.

5. CONCLUSION

Banding TSP with urea affected both urea and P movements and transformations in soils. Acidification from TSP retarded urea hydrolysis in both soils, and therefore, curtailed the rise in pH of the soil surrounding the fertilizer layer. Urea hydrolysis caused dissolution of organic matter in soils, which might have inhibited precipitation of insoluble phosphates. Banded application of urea with TSP increased soluble P as measured in 1 *M* KCl and soil solution as measured in filter paper, sorbed P concentration and total amount of P diffusing into both soils. Adding urea decreased the P concentration in 0.01 *M* $CaCl_2$ extractions, indicating that the precipitation of Ca-P might occur at high pH values when $CaCl_2$ is used as the extractant, or in soils with high exchangeable Ca^{+2} contents. Therefore, banding urea with TSP could benefit P diffusion to plant roots in soil and increase fertilizer efficiency in low Ca soils.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, through Operating Grant OGP0002957.

6. REFERENCES

Barber, S.A., J.M. Walter, and E.H. Vasey. 1963. Mechanisms for the improvement of plant nutrients from the soil and fertilizer to the plant root. J. Agric. Food Chem. 11:204-207.

Barraclough, P.B. and P.B. Tinker. 1981. The determination of ionic diffusion coefficients in field soils. I. Diffusion coefficients in sieved soils relation to water content and bulk density. J. Soil Sci. 32: 225-236.

Barrow, N.J. 1979. The description of desorption of phosphate from soil. J. Soil Sci. 30:259-270.

Barrow, N.J. 1985. Reaction of anions and cations with variable charge soils. Adv. Agron. 38:183-229.

Bell, L.C. and C.A. Black. 1970. Comparison of methods for identifying crystalline phosphates produced by interaction of orthophosphate fertilizers with soils. Soil Sci. Soc. Am. Proc. 34:579-582.

Benbi, D.K., 1987. The movement into soil of P from superphosphate granules and its availability to plants. Fert. Res. 12:21-36.

Bhadoria, P.B.S., J. Kaselowsky, N. Claassen, and A. Jungk. 1991. Soil phosphate diffusion coefficients: their dependence on phosphorus concentration and buffer power. Soil Sci. Soc. Am. J. 55:56-60.

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

Eghball, B., D.H. Sander and J. Skopp. 1990. Diffusion, adsorption, and predicted longevity of banded P fertilizer in three soils. Soil Sci. Soc. Am. J. 54:1161-1165

Eze, O.C. and P. Loganathan. 1990. Effects of pH on phosphate sorption of some paleudults of southern nigeria. Soil Sci. 150:613-621.

Fan, M.X. and A.F. MacKenzie. 1993. Interaction of urea and phosphate in fertilizer microsites: Ammonia volatilization and pH changes. Soil Sci. Soc. Am. J. May-Jun. issue (in press; Chapter III).

Fan, M.X., A.F. MacKenzie and I.P. O'Halloran. 1993. Phosphate sorption as influenced by urea hydrolysis. Soil Sci. Soc. Am. J. Sept.-Oct. issue (in press; Chapter IV).

Fox, R.L., Nishimoto, R.K., Thompson, J.R. and De La Pena, R.S. 1974. Comparative external phosphorus requirements of plants growing in tropical soils. Transactions of 10th international soil science congress. New Delhi, India. 4:232-239.

Grossl, P.R. and W.P. Inskeep. 1991. Precipitation of dicalcium phosphate in the presence of organic acids. Soil Sci. Soc. Am. J. 55:670-675.

Inskeep, W.P. and J.C. Silvertooth. 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic and tannic acids. Soil Sci. Soc. Am. J. 52:941-946.

Kamprath, E.J. 1987. Enhanced phosphorus status of maize resulting from nitrogen fertilization of high phosphorus soil. Soil Sci. Soc. Am. J. 51:1522-1526.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen- inorganic forms. p.643-693. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

Lindsay, W.L. and H.F. Stephenson. 1959. Nature of the reactions of monocalcium phosphate in soils. Soil Sci. Soc. Am. Proc. 23:3-22.

Lu, D.Q., S.H. Chien, J. Henao, and D. Sompongse. 1987. Evaluation of short-term efficiency of DAP versus Urea plus single superphosphate on a calcareous soil. Agron. J. 79:896-900.

Mulvaney, R.L. and Bremner, J.M. 1979. A modified diacetyl monoxime method for colorimetric determination of urea in soil extracts. Commun. Soil Sci. Plant Anal. 10:1163-1140.

Malcolm, E. 1986. Phosphorus interaction with other nutrients and lime in field cropping system. Adv. Soil Sci. 5:201-251.

Mehlich, A. 1984. Mehlich-3 soil test extractant: A modification of Mehlich 2 extractant. Comm. Soil Sci. Plant Anal. 15:1409-1416.

Moody, P.W. 1989. Technique for determining effects of banded fertilizer on soil composition and root growth. Fert. Res. 18:251-256.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphorus in natural waters. Anal. Chim. Acta. 27:31-36.

Myers R.G. and S.J. Thien. 1988. Organic matter solubility and soil reaction in an ammonium and phosphorous application zone. Soil Sci. Soc. Am.

J. 52:516-522.

Naidu, R. and J.K. Syers. 1990. Effect of liming on phosphate sorption by acid soil. J. Soil Sci. 41:163-175.

Nelson, D.W. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. p.539-577. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

O'Connor, G.A., K.L. Kundtsen, and G.A. Connel. 1986. Phosphorus solubility in sludge-amended calcareous soils. J. Environ. Qual. 15:308-312.

Perrot, K.W. 1992. Effect of exchangeable calcium on fractionation of inorganic and organic soil phosphorus. Commun. Soil Sci. Plant Anal., 23:827-840.

Rachpal-Singh and P.H. Nye. 1984. The effect of soil pH and high urea concentration on urease activity in soil. J. Soil Sci. 35: 519-527.

Rhoades, J.D. 1982. Cation exchange capacity. p.149-157. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison. WS., USA.

SAS Institute. 1985. SAS user's guide: statistics. 5th ed. SAS Inst., Cary, NC.

Schnitzer, M. 1978. Some observations on the chemistry of humic substances. Agrochimica. 22:216-225.

Silberbush, M. and S.A. Barber. 1984. Phosphorus and potassium uptake of field-grown soybean cultivars predicted by a simulation model. Soil Sci. Soc. Am. J. 48:592-596.

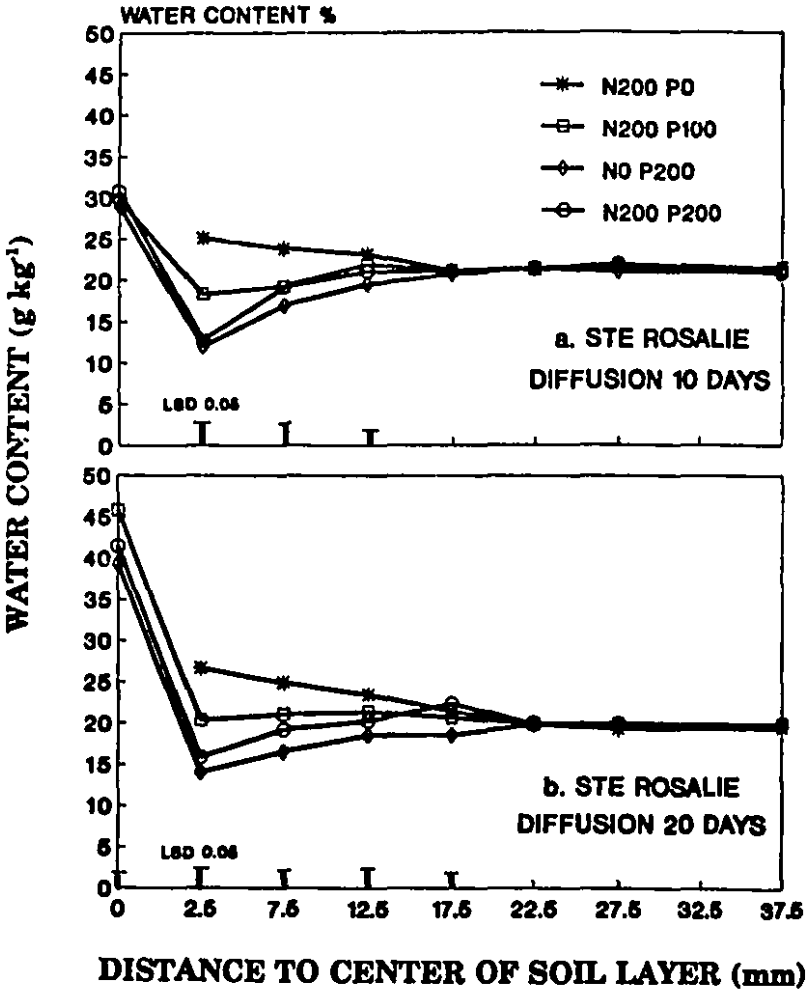
Smillie, G.W., D. Curtin, and J.K. Syers. 1987. Influence of exchangeable calcium on phosphate retention by weakly acid soils. Soil Sci. Soc. Am. J. 51:1169-1172.

Stumpe, J.M., 1981. Ammonia volatilization from urea and urea phosphates in calcareous soils. M.S. Thesis. Colorado State Univ., Fort Collins.

Tomasiewicz, D.J. and J.L. Henry. 1985. The effect of anhydrous ammonia application on the solubility of soil organic carbon. Can. J. Soil Sci. 65:737-747.

Williams, C.H. 1971. Reactions of surface applied superphosphate with soil. Aust. J. Soil Res. 9: 95-106.

Figure 1. Water content in soil as related to distance from urea and/or triple superphosphate layers after 10 days (a) and 20 days (b) in a Ste. Rosalie soil. Fertilizer layer is at 0 mm, and plotted values are the means of 5 or 10 mm soil layers.



WATER CONTENT %
WATER CONTENT (g kg⁻¹)
N200 P0
N200 P100
N0 P200
N200 P200
a. STE ROSALIE
DIFFUSION 10 DAYS
LSD 0.05
b. STE ROSALIE
DIFFUSION 20 DAYS
LSD 0.05
0
5
10
15
20
25
30
35
40
45
50
0
2.5
7.5
12.5
17.5
22.5
27.5
32.5
37.5
DISTANCE TO CENTER OF SOIL LAYER (mm)

Figure 2. Effect of triple superphosphate on urea concentration in Ormstown soil layers at increasing distances from the fertilizer layer. Vertical bars represent LSD at 0.05 probability level.

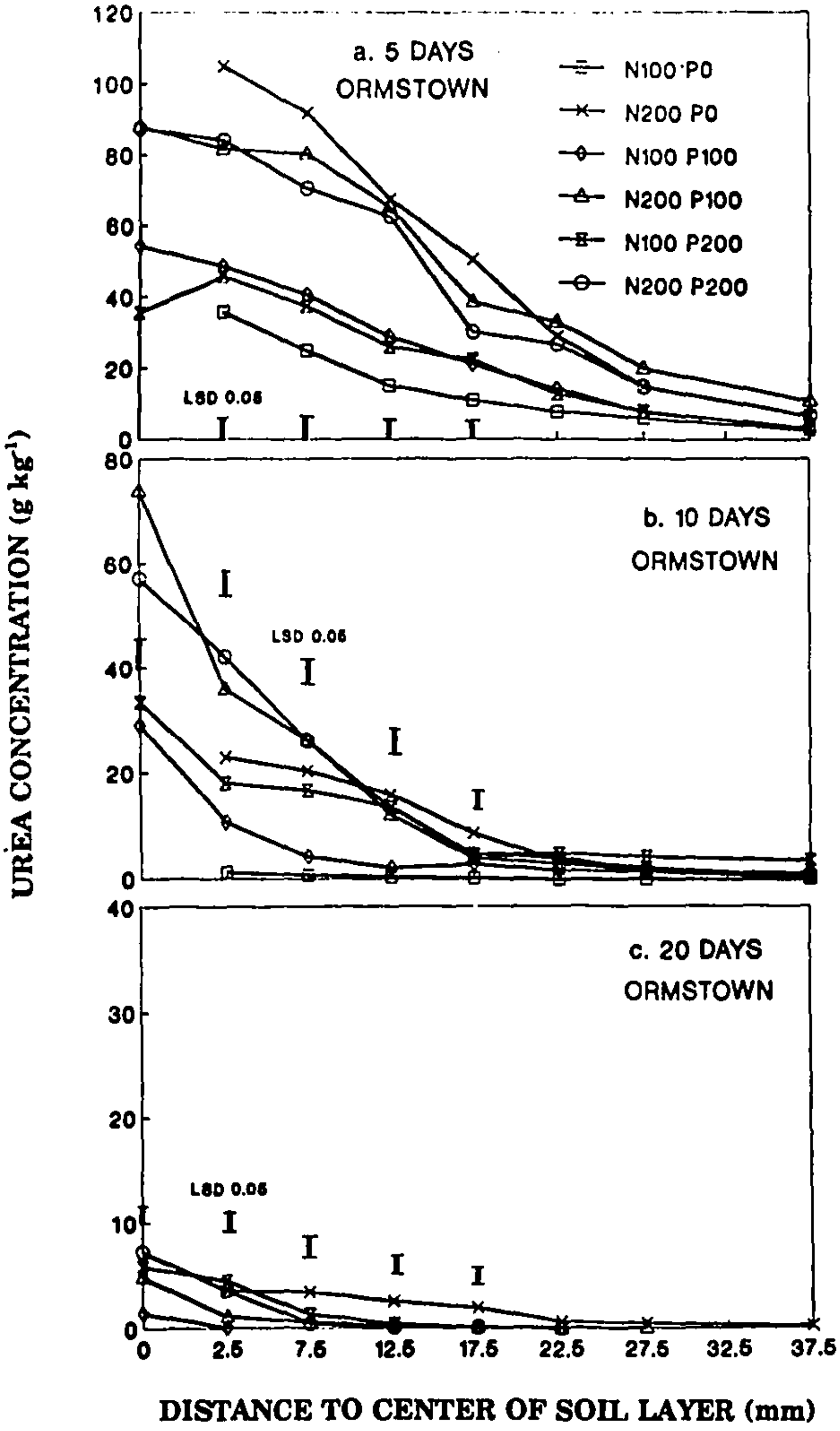

a. 5 DAYS
ORMSTOWN
N100 P0
N200 P0
N100 P100
N200 P100
N100 P200
N200 P200
LSD 0.05
b. 10 DAYS
ORMSTOWN
LSD 0.05
c. 20 DAYS
ORMSTOWN
LSD 0.05
120
100
80
60
40
20
0
80
60
40
20
0
40
30
20
10
0
0
2.5
7.5
12.5
17.5
22.5
27.5
32.5
37.5
UREA CONCENTRATION (g kg-1)
DISTANCE TO CENTER OF SOIL LAYER (mm)

Figure 3. pH changes in Ste. Rosalie soil as related to the distance from urea and/or triple superphosphate layers. Vertical bars represent LSD at 0.05 probability level.

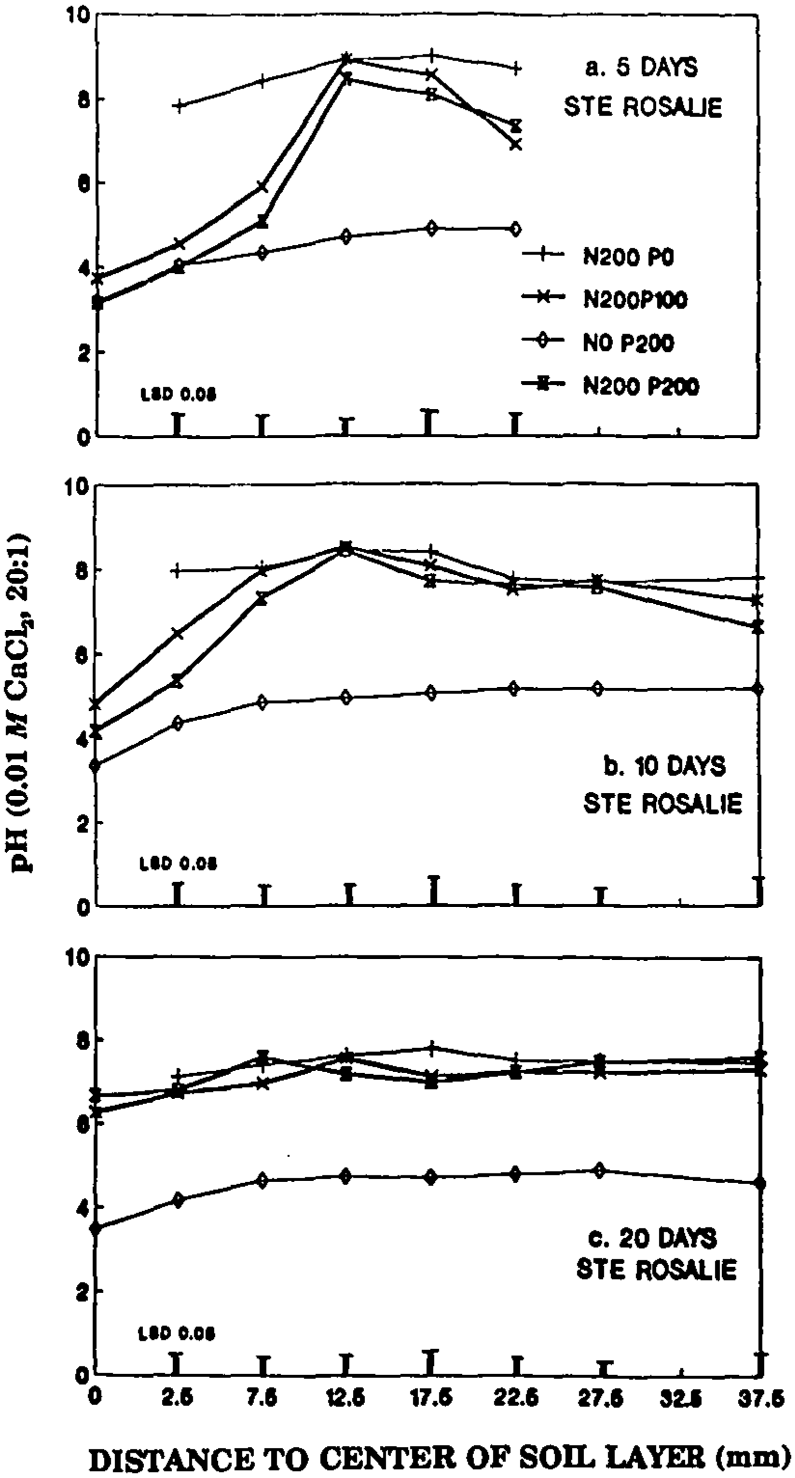

a. 5 DAYS
STE ROSALIE
N200 P0
N200P100
N0 P200
N200 P200
LSD 0.05
b. 10 DAYS
STE ROSALIE
LSD 0.05
c. 20 DAYS
STE ROSALIE
LSD 0.05
pH (0.01 M CaCl$_2$, 20:1)
0
2
4
6
8
10
0
2.5
7.5
12.5
17.5
22.5
27.5
32.5
37.5
DISTANCE TO CENTER OF SOIL LAYER (mm)

Figure 4. Effect of urea and/or triple superphosphate on dissolution of soil organic matter with distance from the fertilizer layer after ten days reaction. a). Ste. Rosalie soil; b). Ormstown soil. Vertical bars represent LSD at 0.05 probability level.

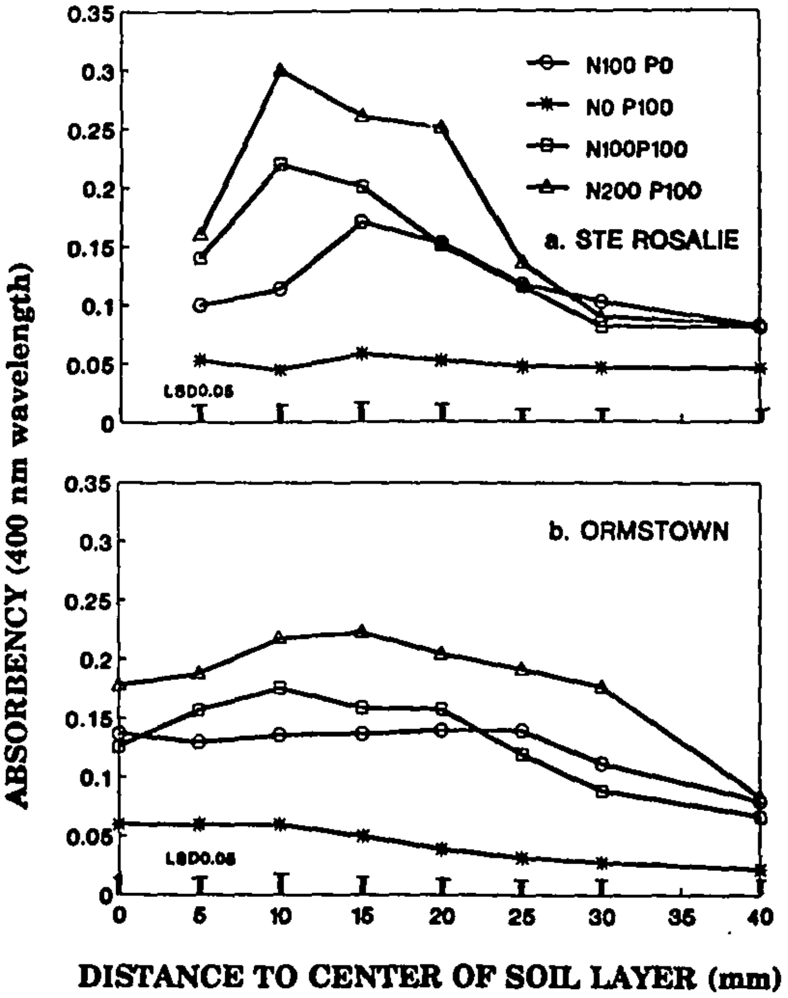

ABSORBENCY (400 nm wavelength)
DISTANCE TO CENTER OF SOIL LAYER (mm)
N100 P0
N0 P100
N100P100
N200 P100
a. STE ROSALIE
b. ORMSTOWN
LSD0.05
LSD0.05
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
40

Figure 5. Effect of urea and/or triple superphosphate on P concentration in soil solution sampled with filter paper (a and b) or extracted by 1 *M* KCl from soil layers (c and d) with distance from the fertilizer layer after ten days reaction. Vertical bars present LSD at 0.05 probability level.

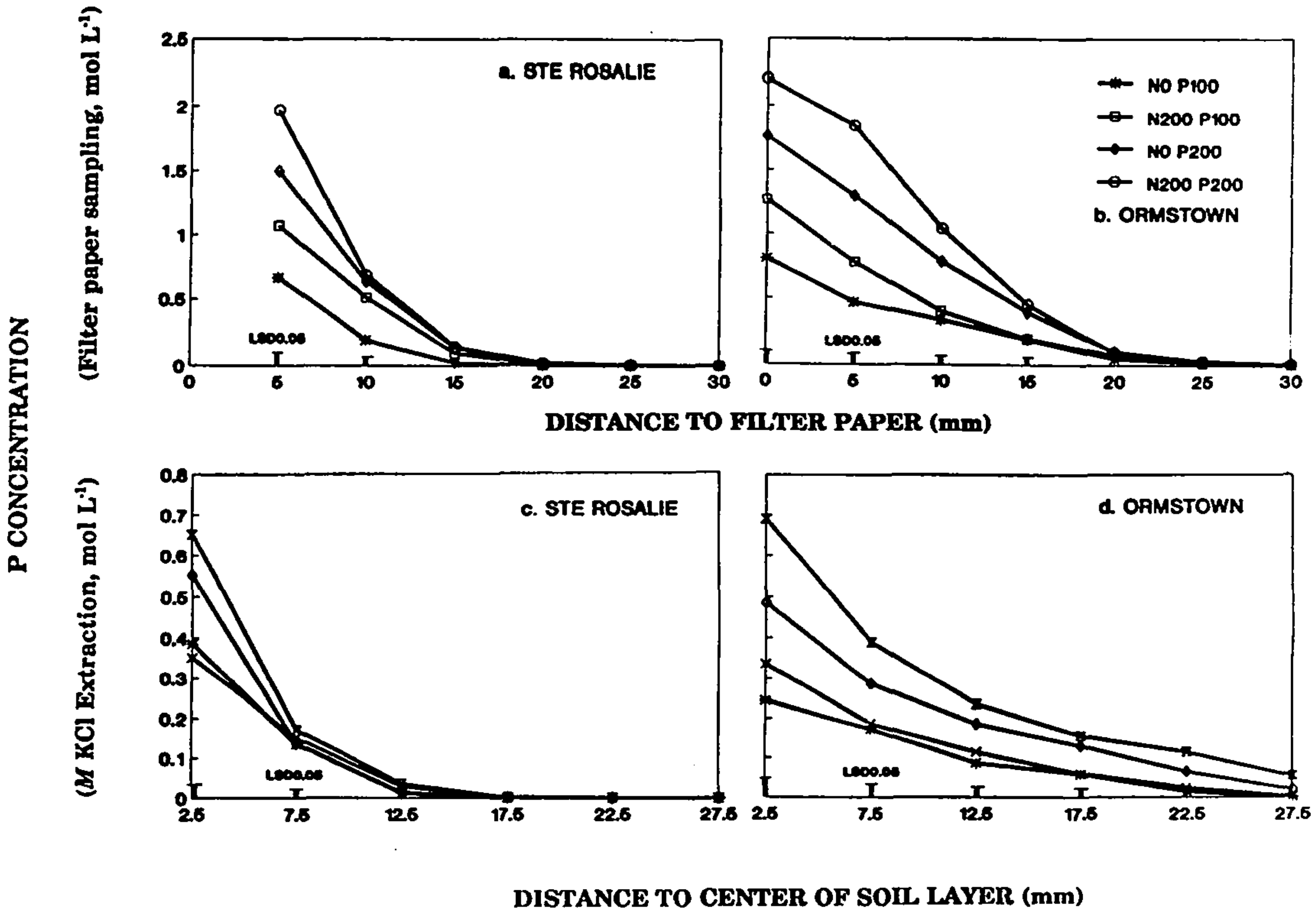
 P CONCENTRATION
(Filter paper sampling, mol L-1)
a. STE ROSALIE
b. ORMSTOWN
N0 P100
N200 P100
N0 P200
N200 P200
LSD0.05
0
0.5
1
1.5
2
2.5
0
5
10
15
20
25
30
DISTANCE TO FILTER PAPER (mm)
(M KCl Extraction, mol L-1)
c. STE ROSALIE
d. ORMSTOWN
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
2.5
7.5
12.5
17.5
22.5
27.5
DISTANCE TO CENTER OF SOIL LAYER (mm)

Table 1. Selected physical and chemical properties of the soils

Soil	pH		clay	silt	organic	Exchangeable cations					Soil P§
Series	H_2O	*M* KCl			matter†	Ca	Mg	K	Al	ECEC‡	
			------ g kg^{-1} -------			-------- $cmol_c(+)/kg$ soil --------					kg P/ha
Ste. Rosalie	5.0	4.0	568	293	43	9.4	5.4	0.7	0.3	15.8	18
Ormstown	6.0	5.1	368	443	33	14.6	5.0	0.2	0.0	19.8	26

† Walkley-Black procedure (Nelson and Sommers, 1982)

‡ Sum of exchangeable Ca,Mg,K and Al ($BaCl_2$ method; Rhoades, 1982).

§ Mehlich No.3 extractant (Mehlich, 1984).

Table 2. Influence of triple superphosphate (TSP) on the amount of applied urea remaining in the soil after 5, 10 and 20 d

Treatment		Ste. Rosalie			Ormstown		
Urea-N	TSP-P	5 days	10 days	20 days	5 days	10 days	20 days
--- kg ha^{-1} ---		--------------- The amount of urea in soil g kg^{-1} ---------------					
100	0	208(18)†	78(5)	9.5(1)	488(52)	12(2)	0
100	100	230(20)	83(5)	3.4(1)	811(68)	147(11)	1.2(0)
100	200	258(21)	163(12)	49(6)	823(43)	417(31)	37(3)
200	0	270(21)	139(8)	100(8)	847(76)	171(10)	32(4)
200	100	250(19)	200(11)	74(6)	808(90)	288(15)	6.4(1)
200	200	302(23)	175(7)	72(6)	820(95)	380(23)	15(2)
		------------------------ significance of F value ------------------------					
ANOVA	N	**	**	**	**	**	**
	P	**	**	**	**	**	**
	N*P	ns	**	**	**	**	**
LSD$_{0.05}$		39	23	8	210	37	5

† Numbers in parenthesis are standard deviations. ** and * indicate significance at $P<0.01$ and 0.05 level by F test respectively; ns indicates not significant at $P<0.05$ level. N=N rate, P=P rate.

Table 3. Significance of N and P effects on $CaCl_2$ extractable P, sorbed P and total P diffusing into soil after 10 and 20 d of fertilizer addition to Ste. Rosalie soil

	10 days			20 days		
Variables	P_{CaCl2}	Sorbed-P	Total-P	P_{CaCl2}	Sorbed-P	Toatl-P
At 0 - 5 mm distance						
N	*	ns	*	ns	ns	ns
Linear	**	ns	*	ns	ns	ns
Quadratic	**	ns	**	ns	ns	ns
P	**	**	**	**	**	**
Linear	**	**	**	**	**	**
N*P	ns	ns	ns	ns	ns	ns
C.V.%	49.3	30.1	25.6	49.9	8.9	23.5
At 5 - 10 mm distance						
N	**	**	*	**	ns	**
Linear	*	**	ns	ns	ns	**
Quadratic	*	**	**	*	ns	**
P	**	**	**	**	**	**
Linear	**	**	**	**	**	**
N*P	*	ns	ns	**	ns	ns
C.V.%	18.2	17.2	15.9	16.5	9.2	8.3
At 10 - 15 mm distance						
N	ns	**	*	**	*	*
Linear	ns	**	**	**	*	**
P	**	**	**	**	**	**
Linear	**	**	**	**	**	**
N*P	ns	ns	ns	**	ns	ns
C.V.%	38.7	27.1	27.5	8.6	12.3	10.8
At 15 - 20 mm distance						
N	ns	*	**	ns	*	*
Linear	ns	*	**	ns	*	*
P	ns	**	**	**	**	**
Linear	ns	**	**	**	**	**
N*P	ns	ns	ns	ns	ns	ns
C.V.%	58.4	70.0	72.2	37.8	34.2	32.7
At 20 - 25 mm distance						
N	ns	ns	**	ns	ns	*
Quadratic	ns	ns	**	ns	ns	*
P	ns	*	**	ns	**	**
Linear	ns	*	**	ns	*	*
N*P	ns	ns	ns	ns	ns	ns
C.V.%	52.9	10.2	58.0	62.3	40.8	48.1

† ns indicates no significant difference at $P < 0.05$ probability level; *, ** indicate significant difference at $P < 0.05$ and $P < 0.01$ probability level at respectively. N = N rate, P = P rate.

Table 4. Distribution of fertilizer-derived phosphorus with distance from the fertilizer layer in the Ste. Rosalie soil

Time	Distance from the layer	N_0P_{200}				$N_{200}P_{200}$			
		P_{CaCl_2}†	Sorb-P	Total-P	Retain -P	P_{CaCl_2}	Sorb-P	Total-P	Retain -P
days	mm	M	mol kg^{-1}	mg	%	M	mol kg^{-1}	mg	%
5	0	4.10	2.12	1930	48.2	4.17	1.94	1895	45.1
	0-5	0.59*	0.78	880	21.0	0.78*	0.75	986	23.5
	5-10	0.10	0.34*	278*	6.6	0.12	0.50*	395*	9.4
	10-15	0.01	0.08*	50*	1.2	0.01	0.14*	85*	2.0
	15-20	0.00	0.04*	17*	0.4	0.00	0.07*	35*	0.8
10	0	4.00	1.80	1813	43.2	3.47	1.88	1659	39.5
	0-5	0.72*	0.94*	1075	25.6	0.51*	1.21*	1122	26.7
	5-10	0.29*	0.34*	402	9.6	0.16*	0.52*	434	10.3
	10-15	0.03	0.12*	92*	2.2	0.03	0.27*	183*	4.4
	15-20	0.00	0.02*	11*	0.3	0.01	0.16*	101*	2.4
	20-25	0.00	0.01	0*	0.0	0.00	0.02	3.6*	0.1
20	0	2.36	3.19	1720	41.0	2.21	3.05	1632	38.8
	0-5	0.83	1.21*	1317*	31.0	1.06	1.41*	1609*	38.3
	5-10	0.33*	0.58*	595*	14.2	0.20*	0.65*	711*	16.9
	10-15	0.16*	0.23*	246	5.8	0.15*	0.29*	278	6.6
	15-20	0.02	0.13*	90*	2.2	0.06	0.16*	130*	3.1
	20-25	0.00	0.03*	9.6*	0.2	0.01	0.06*	37*	0.9

† P_{CaCl_2} = P concentration in 0.01 *M* $CaCl_2$ extraction, mole/L; Sorb-P = P concentration in extraction in 0.5 *M* H_2SO_4 mole/kg; Total-P = total amount of fertilizer P from various extractions in a soil layer, mg; Retain-P = P retained in a soil layer, as % of applied P.

* indicates there is a significant difference between the two treatments at 0.05% level of probability by LSD.

Table 5. Distribution of fertilizer-derived phosphorus with distance from the fertilizer layer in the Ormstown soil

Time	Distance from the layer	N_0P_{200}				$N_{200}P_{200}$			
		P_{CaCl2}†	Sorb-P	Total-P	Retain-P	P_{CaCl2}	Sorb-P	Total-P	Retain-P
Days	mm	M	mol kg^{-1}	mg	%	M	mol kg^{-1}	mg	%
5	0	4.13	1.42	1951	48.8	4.27	1.21	2339	55.7
	0-5	0.79*	0.27*	687*	16.4	0.97*	0.61*	1023*	24.4
	5-10	0.23	0.16	250	5.9	0.26	0.18	275	6.5
	10-15	0.12	0.09	134	3.3	0.14	0.14	176	4.2
	15-20	0.03	0.03*	33*	0.8	0.03	0.06*	49*	1.2
10	0	5.30	1.47	1838	43.7	4.66	1.37	1614	38.4
	0-5	1.13*	0.61*	1125	26.7	0.56*	0.74*	838	20.0
	5-10	0.40*	0.34*	477	11.4	0.23*	0.58*	519	13.0
	10-15	0.24*	0.18*	266	6.3	0.13*	0.32*	285	7.2
	15-20	0.15*	0.13*	176	4.2	0.04*	0.20*	148	3.7
	20-25	0.02	0.05	57	0.7	0.01	0.07	45	1.1
20	0	1.96	2.10	974	23.2	1.85	2.39	880	20.9
	0-5	0.48	0.87	874	20.8	0.46	0.82	830	19.8
	5-10	0.37	0.59	619	13.0	0.29	0.58	555	13.2
	10-15	0.27	0.34	390	7.2	0.20	0.42	392	9.4
	15-20	0.18	0.21*	246*	3.7	0.15	0.29*	278*	6.6
	20-25	0.04	0.05*	143*	1.1	0.10	0.18*	175*	4.2

† P_{CaCl2} = P concentration in 0.01 *M* $CaCl_2$ extraction, mole/L; Sorb-P = P concentration in extraction in 0.5 *M* H_2SO_4 mole/kg; Total-P = total amount of fertilizer P from various extractions in a soil layer, mg; Retain-P = P retained in a soil layer, as % of applied P.

* indicates a significant difference between the two treatments at 0.05% level of probability by LSD.

CONNECTING PARAGRAPH

Chapter II and III demonstrated that adding acidic phosphates such as TSP and MAP to urea reduced pH in fertilizer microsites and retarded urea hydrolysis and NH_3 loss from urea applied on both soils. Soil NH_4- and NO_3-N contents were increased when urea was applied as a mixture with acidic P fertilizers. In Chapter IV, results of the P sorption experiment showed that adding urea had variable effects on soil P sorption characteristics, depending on soil and electrolyte. Phosphate sorption increased, and P concentration in solution decreased with increasing urea and pH when using $CaCl_2$ as the electrolyte. The opposite occurred with KCl as the electrolyte. Urea application increased available P as expressed by 0.5 *M* $NaHCO_3$ extractable P and reduced non-extractable P in both soils. Chapter V further showed that acidification from TSP retarded the rate of urea hydrolysis during diffusion process in both soils, and curtailed the rise in pH of the soil surrounding the fertilizer layer. Urea hydrolysis caused dissolution of soil organic matter, increased sorbed P, and increased P diffusion into the soil. This experiment also confirmed that decreases of P concentration in soil solution with added urea were related to precipitation of Ca-P compounds when $CaCl_2$ was used as electrolyte or in soil with higher exchangeable Ca content. Adding urea with TSP increased P concentrations in soil solutions sampled with filter paper or in 1 *M* KCl extraction in both soils. These effects of the interaction between urea and acidic P fertilizers in soil-fertilizer microsites on pH, NH_3 production, NH_4- and NO_3-N content and on P availability and movement in soil would greatly benefit crop growth, especially in early growing season of corn in P deficient acid soils. Banding urea with acidic P fertilizers could result in the increase of both nutrient uptake and corn yield. In Chapter VI, the effect of banding urea with acidic P fertilizers in acid soils was evaluated on N and P uptake by corn, corn growth and grain yield under field conditions. In the two-year experiments in Ste. Rosalie and Ormstown soils, the efficiency of utilization of P fertilizers as affected by banding urea was studied.

CHAPTER VI

CORN (*Zea mays*,L.) YIELD AND PHOSPHOROUS UPTAKE AS INFLUENCED BY BANDING UREA AND PHOSPHATE MIXTURES IN TWO EASTERN CANADIAN SOILS

1. ABSTRACT

Low fertilizer P efficiency is a problem in agricultural production on acid soils, but efficiency may be affected by methods of fertilizer application. A field experiment was conducted on two eastern Canadian soils (very fine silty to fine silty, mixed, frigid Typic Humaquepts) to evaluate the effect of banding urea with acidic P fertilizers on corn (Zea mays L.) yield and fertilizer efficiency. Two sources of P(triple superphosphate, TSP; and monoammonium phosphate, MAP) and three rates of urea (0, 30, and 60 kg N ha^{-1}) banded with P fertilizers (90 kg P_2O_5 ha^{-1}) were studied in 1990. In 1991, three rates of TSP (0, 45, and 90 kg P_2O_5 ha^{-1}) were used in combination with the same three rates of urea to determine the effect of banding ratio of urea-N : TSP-P_2O_5. The residual fertilizer effects of the 1990 treatment were investigated in 1991. Banding urea with TSP or MAP increased soil extractable P (Mehlich-3). At the six-leaf stage, plant P concentrations and dry matter yields were increased linearly with both banded N and P in the Ste. Rosalie soil, and quadratically in the Ormstown soil. Total N and P uptake by corn was increased in both years by banding urea with TSP or MAP, and fertilizer P use efficiencies increased by 40 to 80%. Urea banded with P increased grain yield linearly with N rates in the Ste. Rosalie soil and quadratically in the Ormstown soil. No interactions were found between banded N rates and P sources in 1990, and between banded N rates and P rates in 1991. Greater residual effects of P fertilizer were found on grain yields and P uptake where P was banded with urea compared to P banded with no urea.

2. INTRODUCTION

Low fertilizer P efficiency often occurs in acid soils because acid soils sorb fertilizer P (Lindsay et al., 1962; Eghball et al., 1990), with reduced P availability to crops. Methods to increase efficiency of P fertilizer through reduced sorption or fixation are required for improved crop management.

It has been reported that in a greenhouse experiment (Lu et al., 1987) single superphosphate (SSP) applied with urea increased soil Olsen-P values and P uptake in a calcareous soil, compared to diammonium phosphate (DAP). Raun et al. (1987) found urea phosphoric acid (UP) provided greater yield, grain P concentration and total P uptake than ammonium pyrophosphates and DAP on a calcareous soil. Little information is available on the effect of urea on P availability from P fertilizers used in acid soils.

In a laboratory incubation experiment, extractable P levels and P movement were increased when urea was mixed with triple superphosphate (TSP) compared to TSP alone (Fan et al., 1993). The effect of urea on P availability was thought to be due to a pH rise, dissolution of soil organic matter, reduced acidification by TSP and reduced P precipitation.

The objective of this study was to determine the effect of mixing urea with acidic phosphates in the fertilizer band on P availability in terms of N and P uptake, corn growth, and grain yield.

3. MATERIALS AND METHOD

Field experiments were carried out on a Ste. Rosalie clay (very fine silty, mixed, acid, frigid, Typic Humaquept) and an Ormstown silty clay loam (fine silty, mixed, non-acid, frigid, Typic Humaquept), differing in physical and chemical properties (Table 1). Both soils were acid and had low soil test P values. In 1990 there were nine treatments at each site; two sources of P (TSP and monoammonium phosphate, MAP) banded with three rates of banded urea (0, 30, and 60 kg N ha^{-1}) plus urea alone treatments. Broadcast urea was applied before seeding to bring total N to 180 kg ha^{-1}. In 1991 the experiments were conducted in different locations from those in 1990, but on the same soils and sites. Because no significant differences were found between MAP and TSP in 1990, treatments were factorial combinations of three levels of TSP (0, 45, and 90 kg P_2O_5 ha^{-1}) with urea as in 1990. Treatments were arranged in a randomized complete block design with four replications.

Soil was ploughed 20 cm deep in the fall and disced to 10 cm in the spring before planting. Potassium fertilizer (KCl at 180 kg K_2O ha^{-1}) was broadcast on the soil surface in each plot prior to discing. Corn seed (Dekalb-403), pretreated with fungicide, was sown at 5 cm depth by a modified John Deere-7100 planter (ALMACO, Nevada, IA). Banded urea and P were placed 5 cm beside and 5 cm below the seed row at planting time, and band locations marked. Corn was planted at 80,000 seeds ha^{-1}. Plots were 5 by 3 m with four rows of corn spaced at 0.75 m.

At the six and nine leaf stages in 1990, and the eight leaf stage in 1991, 50% silking stage and harvest time in both years, soils were sampled as six cores a plot in the fertilizer band at a depth of one to 15 cm, and three plant samples were taken at the same period. Root samples were taken by pressing a metal cylinder (9.0 cm internal diameter and 10 cm high) into the soil, after the plant shoot had been cut, at the six leaf stage in 1990, and eight leaf stage in 1991. The metal cyclinder was removed, and excess soil trimmed from the cylinder. Roots were separated from soils by washing soil through a 1 mm ~~seive.~~ sieve Soil pH in 1 *M* KCl (1:1) was determined with a glass-electrode method. Soil extractable P was determined by using the Mehlich-3 extractant (Mehlich, 1984) and the ascorbic acid-ammonium molybdophosphate blue method (Watanabe and Olsen, 1965). Soil NH_4 and NO_2+NO_3 were extracted from fresh soil by shaking with 1 *M* KCl for 60 min. Ammonium-N was determined with the sodium salicylate/ sodium nitro-prusside method and nitrate was determined with the copperized cadmium reduction method (Keeney and Nelson, 1984) using a Technicon Autoanalyser system. Plant samples were digested with sulphuric acid-hydrogen peroxide method (Thomas et al., 1967), and analyzed for NH_4 and P using the same methods as for soil analyses.

Fertilizer P efficiency was calculated by subtracting P uptake in corresponding check treatments from P taken up in P fertilizer treatments and divided by applied P rates.

In order to study the residual effect of the P fertilizers banded in 1990, corn was sown in the same plots in 1991 in both soils. Fertilizer N and K (NH_4NO_3 180 kg N ha^{-1} and KCl 180 kg K_2O ha^{-1}) were broadcast on the surface of the plots and disced into soil before planting. Other analyses were obtained using the same methods as for the other field plots.

Statistical analyses were carried out for each soil-site based on the procedures of GLM, REG and contrast etc. in the Statistical Analysis System (SAS Institute, 1985).

4. RESULTS AND DISCUSSION

1). pH, nitrogen levels and soil test P

Banding urea with P fertilizers in both soils influenced soil chemical properties in the band. Added urea resulted in an increase in NH_4 concentrations and in pH in the fertilizer bands at the six leaf stage (Table 2). Exchangeable Ca and Mg concentrations were significantly lower for the urea plus P fertilizers treatments in the Ste. Rosalie soil compared to P alone (data not shown).

Added P increased Mehlich-3 extractable P levels in the band location of both soils for both years (Fig. 1). No significant difference in extractable P was found between TSP and MAP in 1990. Banding urea with P fertilizers increased soil extractable P concentrations in both soils at each P level or P source in soils sampled at the six and nine leaf stages. A significant regression was found between Mehlich-3 extractable P at the six leaf stage and banded N and P rates in both soils in 1991 (Table 3). The extractable soil P from soils treated with equivalent P application rates decreased less with time in the Ormstown soil vs. the Ste. Rosalie soil. Urea effects were significant at harvest time in the

Ormstown soil. This may be due to higher pH and extractable P in the Ormstown soil, which could lead to the formation of more soluble P reaction products (Hanson and Westfall, 1985). Banding urea with P fertilizers did not increase 0.03 *M* KCl extractable P in either soil (data not shown), indicating that banding urea with P fertilizers increased soil P capacity but not P intensity. These results are consistent with an incubation experiment where urea incubated with P was found to increase 0.5 *M* $NaHCO_3$ extractable P but not 0.01 *M* $CaCl_2$ or 0.03 *M* KCl extractable P in either Ste. Rosalie or Ormstown soil (Fan et al., 1993). Hanson and Westfall (1985) noted that fertilizer P availability was enhanced by placement of ammonium-N in direct contact with P. When ammonium-N concentrations were increased to 89 kg N ha^{-1} in a P fertilizer band, reaction products tended toward more available Ca-P forms than with P fertilizer alone. Chien et al. (1987) found that urea was much better than NH_4Cl in increasing P availability from Pesca phosphate rock and TSP for maize. They concluded that the better performance of urea was due to the interaction of urea hydrolysis and soil organic matter that resulted in a greater dissolution of phosphate rock in the soil.

2). Phosphorous uptake by plant

Banded urea with P generally increased plant P conentrations in both soils and years (Table 4). Banded urea increased plant P concentrations at the six leaf stage quadratically in the Ste. Rosalie soil in 1990 and at the eight leaf stage in both soils in 1991, with calculated maximum banded urea rates at the six or eight leaf stages of 38 to 58 kg N ha^{-1} across all P sources and rates. At later stages, N effects on P concentrations were linear, indicating optimum N levels at or above 60 kg N ha^{-1}. Thus, although higher urea N rates may have been unnecessary, or detrimental in some cases to six leaf seedlings, such effects were temporary. Increased P concentrations in 1991 were linear with added P at the eight leaf stage, and quadratic at the silking stage. This implied that P was more deficient at the eight leaf stage than at the silking stage. Perhaps this was due to greater soil P availability at or prior to silking due to warmer soil temperatures and enhanced biological activities compared to soils up to the eight leaf stage. Without added P, shoot P concentrations were below the critical level of 3.5 to 4.0 g P kg^{-1} for both soils as noted by Barry et al. (1989). Adding P fertilizer, regardless of the P source, increased P concentrations in plant into the sufficient range, 4.0 to 8.0 g P kg^{-1} at six leaf stages; and 2.5 to 4.0 g P kg^{-1} at the silking stages in both soils. An exception was found in the P concentration at silking stage in the Ste Rosalie in 1991, which was less than 2.5 g kg^{-1} indicating a possible P deficiency even with added P.

At the eight leaf stage, plant P concentration and dry matter yield were significantly related to rates of banded N and P in the Ste. Rosalie soil, and to P rate in the Ormstown soil (Table 3). This means the effect of urea banded with P fertilizers was greater in the Ste. Rosalie soil, which is not consistent with the effect of urea on soil Mehlich-3 P values. The lower pH and lower Ca concentration in the Ste. Rosalie soil may have resulted in a greater impact of pH change on soil P availability, or less P precipitation at higher pH than in the Ormstown soil. Further, the greater buffer capacity in the Ste. Rosalie could mean a reduced magnitude of pH change (Table 2), therefore a reduced impact on root physiology.

Total P uptake, which represent the total P concentration of the above ground plant parts, was significantly increased by banding urea with P fertilizers in all site-years (Tables 5 and 6). There was no significant interaction between urea-N rates and P sources on P uptake in either soil in 1990. There was an interaction between banded urea-N rate and P rate on total P uptake in both soils in 1991 (Table 6). Urea effects on total P uptake were only noted when P was also added in the band, and the quadratic response to added urea indicated that rates near or below 60 kg N ha^{-1} were optimum. The maximum banded urea rates for total P uptake in 1991 were calculated at 38 to 40 kg N ha^{-1} at the low P rate, and 58 to 60 kg N ha^{-1} at the high P rate.

Increases of P uptake from banding urea with P fertilizers indicate increased P availability. Total P uptake was significantly related to soil Mehlich-3 P levels in both soils (R^2=0.68***, n=72 in Ste. Rosalie soil and R^2=0.63***, n=72 in Ormstown soil). Added urea also increased root growth at the 30 kg N ha^{-1} rate when applied with TSP (Fig. 2), which permitted the roots access to larger soil volumes. Duncan and Ohlrogge (1958) reported a greater root mass and more fine silky roots resulted when N was placed in, rather than separated from the P fertilizer band.

Average P efficiencies obtained were from 22.0% to 41.4% in 1990, and 18.8% to 39.5% in 1991. These fertilizer P recovery estimates varied with banded N and P rates. Increased banded urea with P fertilizers increased linearly P efficiencies in 1990 and 1991 with high rates of P (90 kg P_2O_5 ha^{-1}) treatments, and quadratically in 1991 with low rates of P (45 kg P_2O_5 ha^{-1}; Tables 5 and 6). This indicates that there may be an optimum N:P_2O_5 ratio with respect to P efficiency.

3). Plant growth and grain yield

Among P treatments, banding urea with P improved plant growth and grain yields. Generally, plants in the urea plus MAP/TSP treatments had greater root and seedling dry matter yields at early stages in both soils and both years (Fig.2). Banding urea with P did not affect the stover yield in 1990 in either soil, nor in the Ormstown soil in 1991. Banded urea with P fertilizer increased grain yields linearly in the Ste. Rosalie soil and quadratically in Ormstown soil in both years (Table 7). Both plant growth and P concentration at the six leaf stage, and grain yield and total P uptake were linearly related to banded N and P rates for Ste. Rosalie soil, but were linearly related only to the P rates on the Ormstown soil in 1991 (Table 3). Effects of banding urea with P fertilizer on yield were greater in the Ste. Rosalie soil than the Ormstown soil. In the Ormstown soil, the maximum banded urea rates for grain yield in both 1990 and 1991 were calculated at 33 to 45 kg N ha^{-1} over all P sources and rates. No interactions were found between banded N rate and P source in 1990, and between banded N rate and P rate in 1991.

Banding urea with P fertilizer improved corn development. Corn reached tasselling and silking stages about five to eight days earlier with urea plus TSP/MAP compared to treatments with P alone (data not shown). The dry matter content in grain and dry matter weight per 100 grains were increased quadratically with increasing rates of urea banded with P fertilizers (Table 8). The effect of banding urea with P on hastened maturity is of practical importance in corn production in temperate climates.

4). Residual effect in 1991 of P fertilizers banded in 1990

Residual effects of P fertilizer banded in 1990 were found in 1991 with stover yields, grain yields, and total P uptake in both soils (Table 9). Inclusion of urea with P fertilizer bands increased grain yield and P uptake for both soils, and stover yield in Ormstown soil. Average P residual efficiencies were 12.0%, 17.0% and 19.0%, respectively, at 0, 30, and 60 kg N ha^{-1} rates of urea banded with P fertilizers in 1990. This was consistent with the soil Mehlich-3 P concentrations at the harvest time of 1990, where added urea increased soil extractable P.

5. CONCLUSIONS

The addition of urea to acidic phosphates in banded applications increased P fertilizer efficiencies and crop yields by improving fertilizer nutrient availabilities in acid soils.

Hydrolysis of urea increased NH_4 concentration and pH in the soil around the fertilizer band, reduced P precipitation in acid soil or favoured precipitation as more soluble P compounds. Banding urea with P increased soil extractable P (Mehlich-3), plant growth and N and P uptake of corn, resulting in higher fertilizer efficiencies. Banding urea with P fertilizer resulted in a greater residual effects of P fertilizers on grain yield and P uptake in the following year.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, through Operating Grant OGP0002957, for their support of the project.

6. REFERENCES

Barry, D.A.J., M.H. Miller and T.E. Bates. 1989. Ear leaf and seedling P concentration and DRIS indices as indicators of P nutrition for maize. Commun. Soil Sci. Plant Anal. 20:1397-1412.

Chien, S.H., Sompongse L., J. Henao and D.T. Hellums. 1987. Greenhouse evaluation of P availability from compacted phosphate rocks with urea or urea and triple superphosphate. Fert. Res. 14:245-256.

Duncan, W.G. and J.A. Ohlrogge. 1958. Principles of nutrient uptake from fertilizer bands II. Root development in the band. Agron. J. 50:605-608.

Eghball, B., D.H. Sander and J. Shopp. 1990. Diffusion,adsorption, and predicted longevity of banded P fertilizer in three soils. Soil Sci. Soc. Am. J. 54:1161-1165

Fan, M.X., A.F. MacKenzie, and I.P. O'Halloran. 1993. Phosphate sorption as influenced by added urea in two eastern Canadian soils. Soil Sci. Soc. Am. J. (in press).

Hanson, R.L. and D.G.Westfall. 1985. Orthophosphate solubility transformations and availability from dual applied N and P. Soil Sci. Soc. Am. J. 49:1283-1289.

Keeney, D.R. and D.W. Nelson. 1984. Nitrogen-inorganic forms. p.643-698 *In* A.L.Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison, WS., USA.

Lindsay, W.L., A.W. Frazier, and H.F. Stephenson. 1962. Identification of reaction products from phosphate fertilizers in soils. Soil Sci. Soc. Am. Proc. 26:446-452.

Lu, D.Q., S.H. Chien, J. Henao, and D. Sompongse. 1987. Evaluation of short-term efficiency of DAP versus urea plus single superphosphate on a calcareous soil. Agron.J. 79:896-900.

Mehlich, A. 1984. Mehlich-III soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15:1409-1416.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-577. *In* A.L.Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison, WS., USA.

Raun, W.R., D.H. Sander, and R.A. Olson. 1987. P fertilizer carrier and their placement for minimum till corn under sprinkler irrigation. Soil Sci.Soc.Am.J. 51:1055-1062.

Rhoades, J.D. 1982. Cation exchange capacity. p. 149-157. *In* A.L.Page (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd edition. ASA. Madison, WS., USA.

SAS Institute Inc. 1985. SAS user's guide: Statistics. 5th ed. SAS Inst., Cary, NC.

Thomas, R.L., R.W. Sheard, and J.R. Moyer. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorus and potassium analysis of plant material using a single digestion. Agron. J. 59:240-243.

Watanabe, F.S. and S.R.Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extractants for soil. Soil Sci Soc.Am.Proc. 29:677-678.

Figure 1. The changes of soil extractable P (Mehlich-3) as influenced by banded urea and P fertilizers in Ste. Rosalie and Ormstown soils. The CK, U1, and U2 represent the treatments with 0, 30, and 60 kg N ha^{-1} of banded urea rates. AP and TP represent banded monoammonium phosphate and triple superphosphate. TP1 and TP2 represent the treatment with 45 and 90 kg P_2O_5 ha^{-1} of banded triple superphosphate rates.

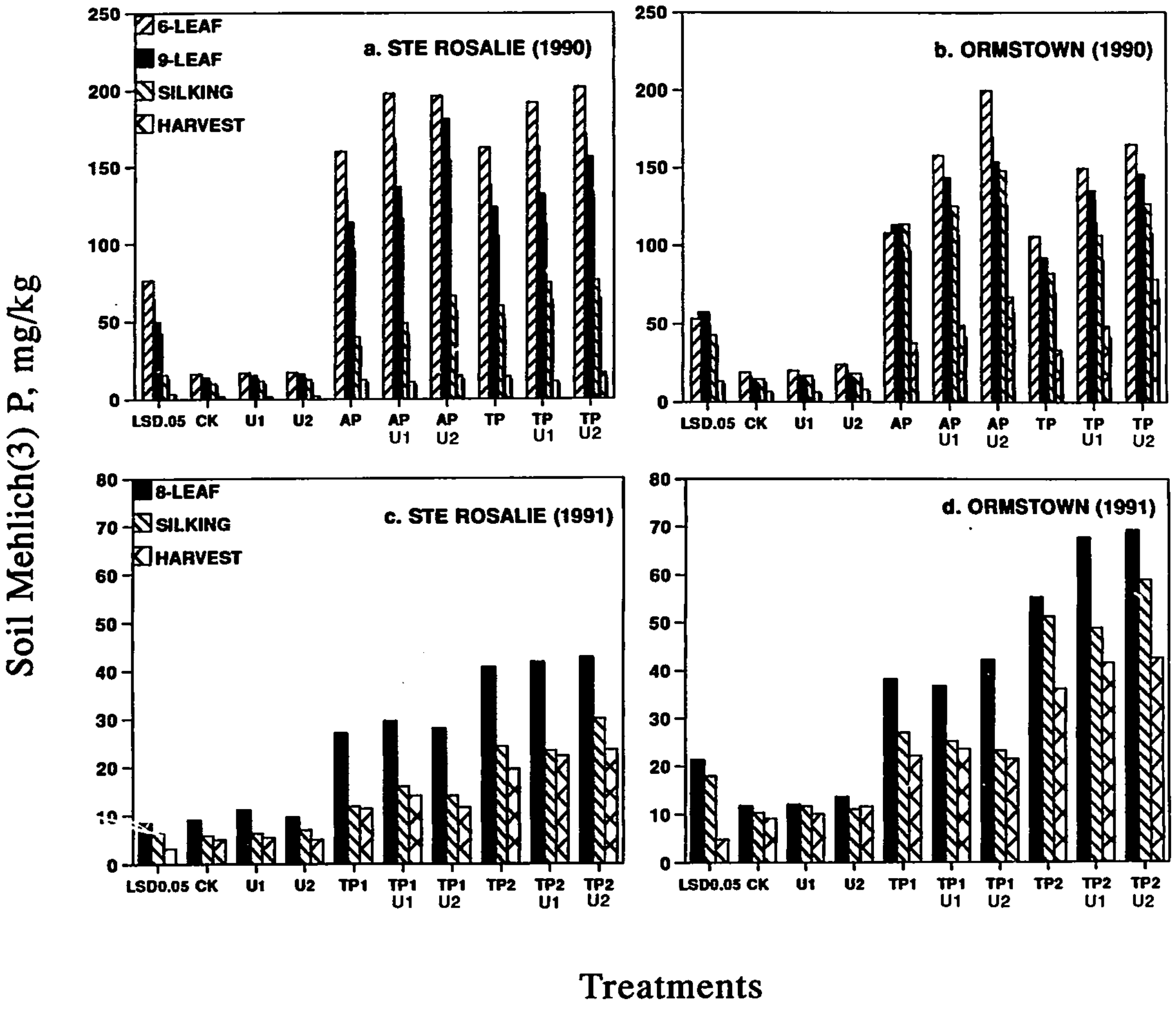

Soil Mehlich(3) P, mg/kg
Treatments
a. STE ROSALIE (1990)
6-LEAF
9-LEAF
SILKING
HARVEST
0
50
100
150
200
250
LSD.05
CK
U1
U2
AP
AP U1
AP U2
TP
TP U1
TP U2
b. ORMSTOWN (1990)
0
50
100
150
200
250
LSD.05
CK
U1
U2
AP
AP U1
AP U2
TP
TP U1
TP U2
c. STE ROSALIE (1991)
8-LEAF
SILKING
HARVEST
0
10
20
30
40
50
60
70
80
LSD0.05
CK
U1
U2
TP1
TP1 U1
TP1 U2
TP2
TP2 U1
TP2 U2
d. ORMSTOWN (1991)
0
10
20
30
40
50
60
70
80
LSD0.05
CK
U1
U2
TP1
TP1 U1
TP1 U2
TP2
TP2 U1
TP2 U2

Figure 2. The dry matter weight of corn shoot and roots at six-leaf stage in 1990 and eight leaf-stage in 1991 as affected by banded urea with P fertilizers in Ste. Rosalie and Ormstown soils. The CK, U1, and U2 represent the treatments with 0, 30, and 60 kg N ha^{-1} of banded urea rates. AP and TP represent banded monoammonium phosphate and triple superphosphate. TP1 and TP2 represent the treatment with 45 and 90 kg P_2O_5 ha^{-1} of banded triple superphosphate rates.

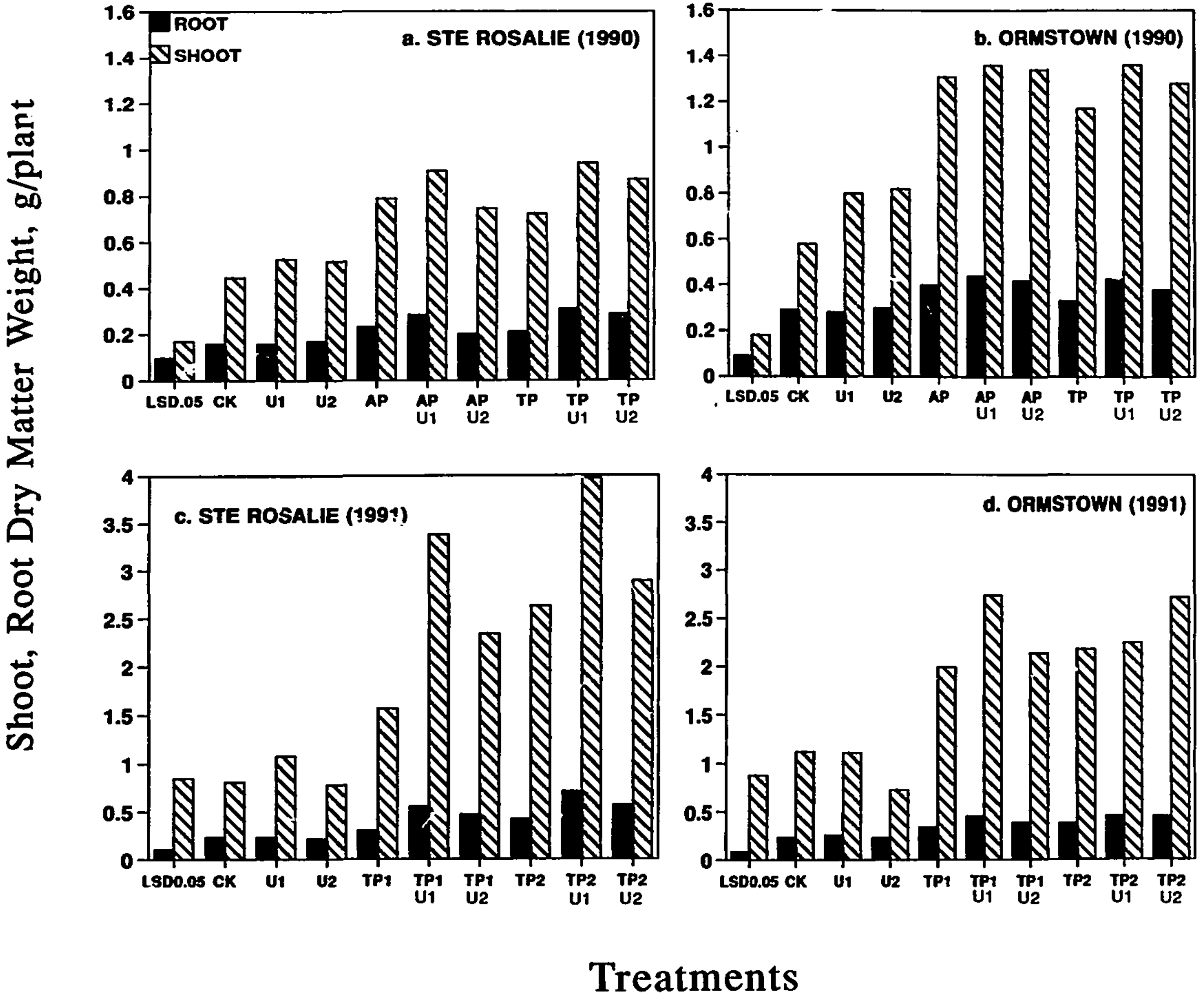

Shoot, Root Dry Matter Weight, g/plant
ROOT
SHOOT
a. STE ROSALIE (1990)
b. ORMSTOWN (1990)
c. STE ROSALIE (1991)
d. ORMSTOWN (1991)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0.5
1.5
2
2.5
3
3.5
4
LSD.05
LSD0.05
CK
U1
U2
AP
AP U1
AP U2
TP
TP U1
TP U2
TP1
TP1 U1
TP1 U2
TP2
TP2 U1
TP2 U2
Treatments

Table 1. Selected physical and chemical properties of the soils

Soil Series	pH		clay	silt	organic matter†	Exchangeable cations					Soil P§
	H_2O	*M* KCl				Ca	Mg	K	Al	ECEC‡	
			---------- g kg^{-1}	---------		------ $cmol_c(+)/kg$ soil	-------				kg P ha^{-1}
Ste. Rosalie(1990)	5.0	4.0	568	293	48	9.4	5.4	0.7	0.3	15.8	18
Ste. Rosalie(1991)	5.4	4.1	402	354	43						16
Ormstown(1990)	6.0	5.1	368	443	33	14.6	5.0	0.2	0.0	19.8	26
Ormstown(1991)	6.2	5.3	309	419	39						28

† Walkley-Black procedure (Nelson and Sommers, 1982)

‡ Sum of exchangeable Ca,Mg,K and Al ($BaCl_2$ method; Rhoades, 1982).

§ Mehlich No.3 extractant (Mehlich, 1984).

Table 2. Effect of banded phosphorous sources and urea rates on soil pH, nitrate and ammonium concentration at the six leaf stage in 1990

	Ste. Rosalie			Ormstown		
	pH (H_2O)	NO_3-N	NH_4-N	pH (H_2O)	NO_3-N	NH_4-N
P Source		------- mg kg^{-1} ------			------ mg kg^{-1} ------	
0 P†	5.0^{A}‡	37	195^{B}	6.6^{A}	59	200
MAP	4.9^{B}	31	259^{A}	6.5^{A}	54	216
TSP	4.8^{C}	40	180^{B}	6.3^{B}	57	188
N rates kg N ha^{-1}						
0	4.7	26	56	6.3	37	19
30	4.9	39	246	6.5	66	222
60	5.0	48	330	6.7	66	365
Trend	Q^{**}	L^{**}	L^{*}	L^{**}	Q^{*}	L^{**}

† 0 P, MAP, and TSP values are the average of over three N rates.
Values under any one N rate are the average over P sources and control treatments.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

*, and ** indicate significant at 0.05 and 0.01 probability levels, respectively.

Table 3. Regressions relating corn plant dry matter, stover and grain yield, phosphorous concentration, and soil Mehlich-3 extractable phosphorus to banded nitrogen and phosphorous rates at the eight-leaf stage and at harvest for Ste. Rosalie and Ormstown soils in 1991

Sources	Intercept	N rate coefficient	P rate coefficient	R^2
Ste. Rosalie		**Eight leaf stage**		
P concentration(g kg^{-1})	26.5***†	0.081**	0.12***	0.70***
Dry matter(g)	0.85*	0.0061**	0.026**	0.61***
Soil extractable P (mg kg^{-1})	14.25***	0.087**	0.278***	0.63***
		Harvest		
Stover yield(kg ha^{-1})	4910***	15.25	26.57***	0.52***
Grain yield(kg ha^{-1})	7180***	10.12*	20.46***	0.65***
Total P uptake(kg ha^{-1})	16.69***	0.052**	0.099***	0.79***
Ormstown		**Eight leaf stage**		
P concentration(g kg^{-1})	34.1***	0.032	0.061***	0.46***
Dry matter(g)	1.14***	0.0012	0.016***	0.51***
Soil extractable P (mg kg^{-1})	13.71**	0.264*	0.51***	0.68***
		Harvest		
Stover yield(kg ha^{-1})	8065***	4.43	14.22*	0.25*
Grain yield(kg ha^{-1})	9286***	6.08	11.71***	0.40**
Total P uptake(kg ha^{-1})	26.4***	0.051*	0.12***	0.69***

† *, ** and *** indicate significant at 0.05, 0.01 and 0.001 probability levels by F test, respectively.

Table 4. Effects of banded phosphorous sources and urea rates (1990), and banded triple superphosphate (TSP) rates and urea rates on phosphorous concentration of corn plant at different growth stages

Treatment		P concentration in plant tissue					
		Ste. Rosalie			Ormstown		
		6-leaf	9-leaf	silking	6-leaf	9-leaf	silking
1990	P Source	g P kg^{-1} DM					
	0 P†	3.2^{C}‡	1.9^{C}	2.3^{B}	3.2^{C}	2.9^{B}	3.5^{B}
	MAP	4.9^{A}	2.8^{A}	2.7^{A}	5.8^{A}	3.3^{A}	3.8^{A}
	TSP	4.5^{B}	2.5^{B}	2.7^{A}	5.3^{B}	3.3^{A}	3.9^{A}
	N rates kg N ha^{-1}						
	0	3.9	2.3	2.4	4.6	3.0	3.6
	30	4.5	2.5	2.6	4.9	3.2	3.7
	60	4.2	2.4	2.7	4.9	3.3	3.8
	Trend	Q^{*}	NS	L^{**}	NS	L^{*}	L^{*}
1991	P rates kg P_2O_5 ha^{-1}	8-leaf		silking	8-leaf		silking
	0	3.1		1.5	4.2		2.4
	45	3.8		1.8	4.6		2.6
	90	4.2		1.9	4.9		2.7
	Trend	L^{**}		Q^{**}	L^{**}		Q^{**}
	N rates kg N ha^{-1}						
	0	3.4		1.6	4.4		2.5
	3C	3.8		1.7	4.7		2.6
	60	3.9		1.8	4.6		2.6
	Trend	Q^{**}		L^{*}	Q^{*}		NS

† 0 P, MAP, and TSP values are the average of over three N rates. Values under any one N rate are the average over P sources and control(1990) or P rates (1991) treatments. Values under any one P rate are the average over three N rates.

‡ Means in 1990 in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

NS, *, and ** indicate not significant, significant at 0.05 and 0.01 probability levels, respectively.

Table 5. Effects of banded phosphorous sources and urea rates on phosphorous and nitrogen uptake and phosphorous efficiency with corn in 1990.

Treatments		Ste. Rosalie			Ormstown		
		N uptake	P uptake	P efficiency	N uptake	P uptake	P efficiency
1990	P Source	------ kg ha^{-1} -----		- % -	----- kg ha^{-1} -----		- % -
	0 P†	158^{B}‡	26.8^{B}		180^{B}	31.6^{B}	
	MAP	209^{A}	39.5^{A}	32.1	211^{A}	42.7^{A}	27.4
	TSP	209^{A}	39.1^{A}	30.3	211^{A}	42.1^{A}	26.0
	N rates kg N ha^{-1}						
	0	176	31.3	22.0	185	35.1	24.3
	30	188	34.8	31.1	207	38.9	14.6
	60	203	39.4	40.6	207	42.3	41.4
	Trend	L^{**}	L^{**}	L^{**}	Q^{**}	L^{**}	L^{*}

† 0 P, MAP, and TSP values are the average of over three N rates.
Values under any one N rate are the average over P sources and control(1990).

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

*, and ** indicate significant at 0.05 and 0.01 probability levels, respectively.

Table 6. Effect of banding urea with phosphorous fertilizer on phosphorous uptake and phosphorous efficiency by corn in 1991.

	P Rate kg P_2O_5 ha^{-1}	Rate of Urea-N banded kg ha^{-1} 0		60	Trend
		Ste. Rosalie			
Total P	0	17.5	17.6	18.6	NS
Uptake	45	21.7	24.2	23.9	Q*
kg ha^{-1}		24.1	25.9	30.3	L**
	Trend	L**	L**	L**	
P efficiency	45	21.0	33.4	26.2	Q*
%	90	16.6	21.0	29.1	L**
		Ormstown			
Total P	0	27.1	28.2	26.3	NS
Uptake	45	32.7	36.1	35.2	Q*
kg ha^{-1}		33.7	39.0	40.9	Q**
	Trend	Q**	L*	L**	
P efficiency	45	27.8	39.5	44.9	Q*
%	90	16.4	27.0	36.0	L**

*, ** indicate significant at 0.05 and 0.01 probability levels.

Table 7. Effect of banded phosphorous sources and urea rates in 1990; banded triple superphosphate (TSP) rates and urea rates in 1991 on stover and grain yields of corn

Treatment		Ste. Rosalie		Ormstown	
		stover yield	grain yield	stover yield	grain yield
1990	P Source	------------ Mg ha^{-1} -----------		------------ Mg ha^{-1} -----------	
	0 P†	6.4^{B}‡	7.8^{B}	11.0	8.6^{B}
	MAP	8.6^{A}	9.6^{A}	11.9	10.0^{A}
	TSP	8.0^{A}	9.8^{A}	11.4	9.9^{A}
	N rates kg N ha^{-1}				
	0	7.5	8.8	10.9	9.1
	30	7.4	9.1	11.9	9.7
	60	8.1	9.4	11.5	9.7
	Trend	NS	L^{*}	NS	Q^{*}
1991	P rates kg P_2O_5 ha^{-1}				
	0	5.4	7.4	8.0	9.4
	45	6.6	8.6	9.3	10.2
	90	7.7	9.2	9.2	10.4
	Trend	Q^{**}	Q^{**}	Q^{**}	Q^{**}
	N rates kg N ha^{-1}				
	0	6.3	8.0	8.5	9.7
	30	6.1	8.5	9.2	11.2
	60	7.2	8.7	8.8	10.1
	Trend	L^{*}	L^{*}	NS	Q^{*}

† 0 P, MAP, and TSP values are the average of over three N rates.

Values under any one N rate are the average over P sources and control(1990) or P rates (1991) treatments. Values under any one P rate are the average over three N rates.

‡ Means in 1990 in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

NS, *, and ** indicate not significant, significant at 0.05 and 0.01 probability levels, respectively.

Table 8. Effects of banded phosphorous sources and urea rates on grain weight and dry matter content on Ste. Rosalie soil in 1990.

Treatment	grain weight	dry matter content in grain
P Source	g 100^{-1} grains	g kg^{-1}
0 P†	4.96^{B}‡	233^{B}
MAP	8.31^{A}	417^{A}
TSP	9.08^{A}	390^{A}
N rates kg N ha^{-1}		
0	6.53	310
30	8.35	355
60	7.48	375
Trend	Q^{*}	Q^{*}

† 0 P, MAP, and TSP values are the average of over three N rates. Values under any one N rate are the average over P sources and control treatments.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

* indicate significant at 0.05 probability level.

Table 9. Effect of banded phosphorous sources and urea rates in 1990 on phosphorous uptakes, phosphorous residual efficiency by corn and stover and grain yield of corn in 1991.

	Ste. Rosalie				Ormstown			
	stover yield	grain yield	P uptake	P efficiency	stover yield	grain yield	P uptake	P efficiency
P Source	----- Mg ha^{-1} -----		kg ha^{-1}	%	--- Mg ha^{-1} ---		kg ha^{-1}	%
0 P†	5.9^{B}‡	7.4^{B}	15.0^{B}		8.4^{B}	8.5^{B}	22.9	
MAP	6.8^{A}	8.1^{A}	19.0^{A}	9.9	9.3^{A}	9.5^{A}	23.5	18.1
TSP	6.8^{A}	8.3^{A}	19.7^{A}	11.6	9.3^{A}	9.3^{A}	24.3	13.9
N rates kg N ha^{-1}								
0	6.7	7.7	16.5	10.5	8.5	8.8	24.6	12.0
30	6.5	7.9	17.9	9.5	9.1	9.2	27.8	17.0
60	6.3	8.2	19.3	12.4	9.4	9.3	29.1	19.0
Trend	NS	L^{*}	L^{*}	NS	L^{*}	L^{*}	L^{**}	Q^{*}

† 0 P, MAP, and TSP values are the average of over three N rates.

Values under any one N rate are the average over P sources and control treatments.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

NS, *, and ** indicate not significant, significant at 0.05 and 0.01 probability levels, respectively.

CHAPTER VII

SUMMARY OF RESULTS AND GENERAL CONCLUSIONS

Ammonia volatilization is a significant mechanism of N loss when urea and urea plus DAP mixtures are surface applied to acid soils, because of the high pH in soil-fertilizer microsites from urea hydrolysis and DAP dissolution. Adding acidic phosphates such as TSP and MAP to urea reduced pH in soil-fertilizer microsites and retarded urea hydrolysis. Therefore, the total NH_3 loss and maximum daily rates of NH_3 loss were reduced and the time of maximum NH_3 loss rates were delayed by applying TSP or MAP with urea on both Ste. Rosalie and Ormstown soils. Ammonia loss decreased as P_2O_5 : urea-N ratios increased. Soil NH_4- and NO_3-N concentrations were increased. It is suggested that applying mixtures of acidic phosphate fertilizer with urea can increase the efficiency of surface-applied urea fertilizer.

The interaction of urea with P in soil-fertilizer microsites also affects P sorption, transformation, movement and availability to crops. Based on the results of the P sorption experiment, adding urea to P fertilizer increased soil pH, but had variable effects on soil P sorption characteristics, depending on soil and electrolyte. Phosphate sorption increased, and P concentration in solution decreased with increasing urea and pH when using $CaCl_2$ as the electrolyte. Added urea and pH increase had little effect on soil P sorption when KCl was used as the electrolyte, indicating that the urea effect on P sorption was influenced by soil solution Ca concentration. The effect of urea on reducing P concentration in solution was not significant at P rates below 320 mg P kg^{-1} soil. The observed increase in P sorption and decrease in solution P with added urea was probably related to precipitation of Ca-P compounds and the shift from $H_2PO_4^{-1}$ to HPO_4^{-2} at higher pH values. However, it was found in subsequent P fractionation experiments that urea application increased 0.5 *M* $NaHCO_3$ extractable P and reduced non-extractable P in both soils. In an incubation experiment studying urea and phosphate movement and their reactions in soil during the diffusion from fertilizer band into soils, it was confirmed that the acidification from TSP retarded the rate of urea hydrolysis in both fertilizer bands and soil layers into which urea diffused. This curtailed the rise in pH of the soil surrounding fertilizer bands. Banding of urea with TSP caused dissolution of organic matter in soils, and increased sorbed P concentrations and total amounts of P diffused into soils.

The effect of urea on P movement was found to be greater in Ste. Rosalie than in Ormstown soils, though the P diffusion rate was greater in Ormstown soil. This might be due to the higher organic matter content and lower initial pH in the Ste. Rosalie soil, and higher initial pH and exchangeable Ca concentration in the Ormstown soil. The effect of urea on P concentration in soil solutions during diffusion varied with methods of extraction or electrolyte. Adding urea decreased P concentration in 0.01 *M* $CaCl_2$ extraction after 10 days of diffusion. However, it increased the P concentration in soil solution sampled with filter papers or with 1 *M* KCl extractions in both soils. These results indicate that precipitation of calcium phosphates might have occurred at high pH values when $CaCl_2$ was used as electrolyte or in soils with higher exchangeable Ca concentrations.

The results obtained in the two years' field experiments conducted in the Ste. Rosalie and Ormstown soil supported the supposition that the interaction of urea and phosphate mixtures can increase fertilizer efficiency and crop yield by improving fertilizer nutrients availability in acid soils. The results demonstrated that banding suitable rate of urea with TSP or MAP (about $N:P_2O_5$ ratio of 1:1.5 to 3) increased soil extractable P (Mehlich-3), N and P nutrient uptake, plant growth and development in acid Quebec soils. Greater P fertilizer efficiencies and higher yields were achieved by banding urea with acidic P fertilizers to acid soils, and the increase was greater in the Ste. Rosalie soil than in Ormstown soil. Greater residual effect of P fertilizer was also found on grain yield and P uptake in the second year following fertilization. Therefore, banding applications of mixtures of urea with acidic P fertilizers such as TSP or MAP (when banding urea-N is limited under 60 kg N ha^{-1}) can be considered as a good technique for increasing both crop yield and fertilizer efficiency in acid Quebec soils, and also for minimizing environmental pollution through NH_3 volatilization.

SUGGESTIONS FOR FUTURE WORK

1. One of the major problems of banding application of urea is the toxicity to seed germination and root growth of seedlings. In the light of the fact that acidic P fertilizer could retard urea hydrolysis and reduce the pH increase from urea hydrolysis, the NH_3 concentration and toxicity to seed germination

and root growth should be reduced. Future research should study the effect of acidic P fertilizers on the toxicity to seed germination and root growth from urea in the soils with different acidity and buffering capacities. This is important for designing suitable fertilizer recommendations of banding ratios for urea-N and P_2O_5.

2. Adding acidic phosphates such as TSP and MAP to urea reduced NH_3 loss from urea on both Ste. Rosalie and Ormstown soils and suggested that applying mixtures of acidic phosphate fertilizer with urea had potential to increase the efficiency of surface-applied urea fertilizer. Future research should study the possibility of producing urea plus acidic P fertilizer granules and evaluating their effect on N efficiency under field conditions where surface-application of urea is the only way of fertilization.

3. pH effects on P sorption and movement are influenced by soil mineral composition, especially Fe and Al oxides and $CaCO_3$ content, soil clay and organic matter contents. The major effect of the interaction between urea and TSP in soil-fertilizer microsites was found on pH changes in soil-fertilizer microsites. Therefore, future studies should employ a greater variety of soils varying in soil mineralogy, soil texture and organic matter content.

APPENDICES

Figure 1. Effect of P_2O_5 : N ratio in the mixtures of triple superphosphate(TSP), or monoammonium phosphate (MAP) with urea on NH_3 loss from Ste Rosalie and Ormstown soils at a two rates of total urea plus phosphate N in the first experiment.

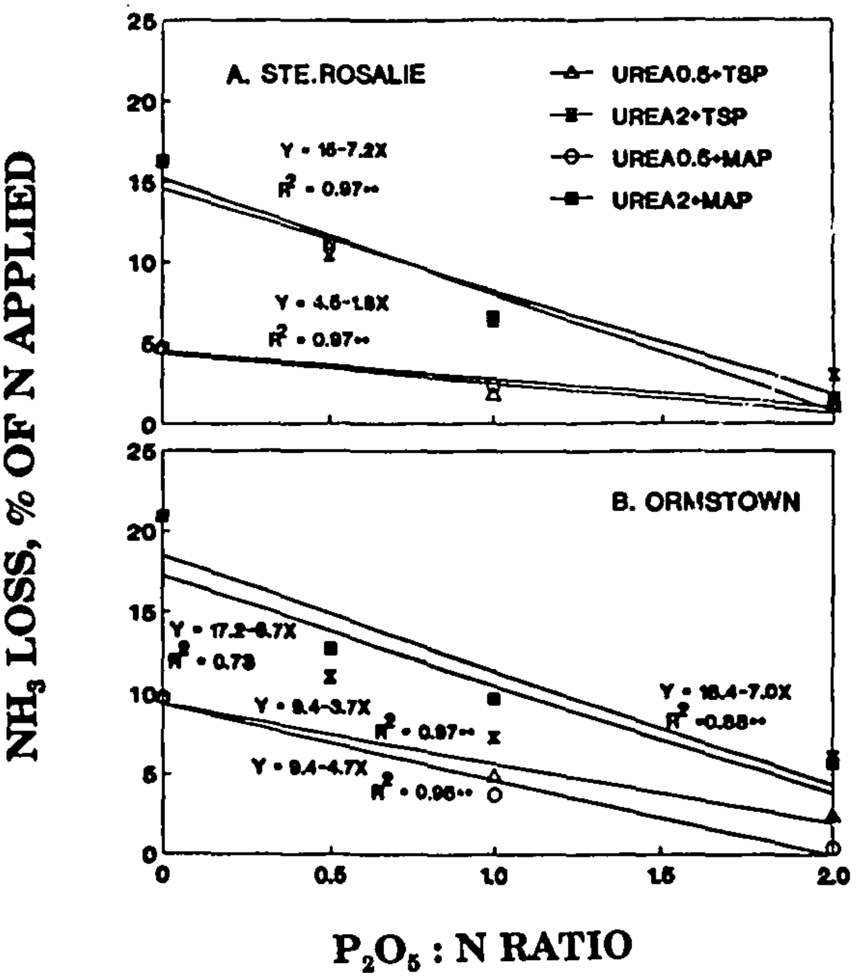

A. STE.ROSALIE
UREA0.5+TSP
UREA2+TSP
UREA0.5+MAP
UREA2+MAP
Y = 15-7.2X
R² = 0.97**
Y = 4.5-1.8X
R² = 0.97**
B. ORMSTOWN
Y = 17.2-6.7X
R² = 0.73
Y = 9.4-3.7X
R² = 0.97**
Y = 9.4-4.7X
R² = 0.96**
Y = 18.4-7.0X
R² =0.88**
0
5
10
15
20
25
0
0.5
1.0
1.5
2.0
NH3 LOSS, % OF N APPLIED
P2O5 : N RATIO

Figure 2. Effect of P_2O_5 : urea-N ratio in the mixtures of triple superphosphate(TSP), monoammonium phosphate (MAP), or diammonium phosphate (DAP) with urea on NH_3 loss from Ste Rosalie and Ormstown soils in the second experiment at the application rate of 0.5 g urea-N kg^{-1}.

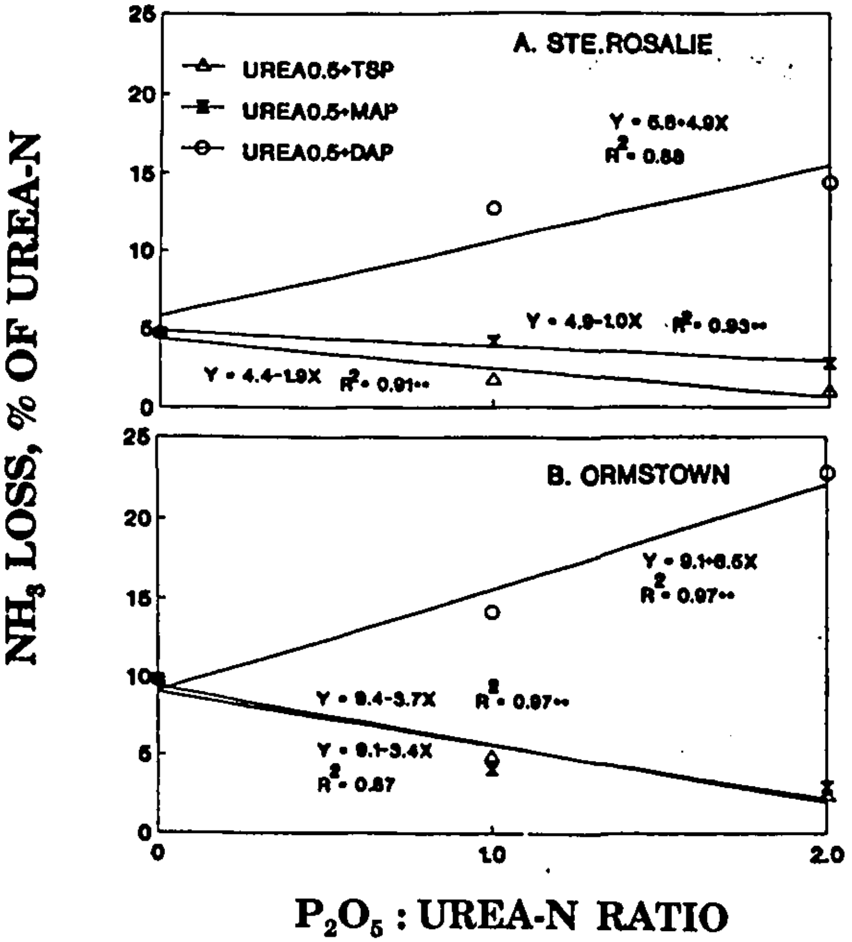
A. STE.ROSALIE
UREA0.5+TSP
UREA0.5+MAP
UREA0.5+DAP
Y = 5.8+4.9X
R2 = 0.88
Y = 4.9-1.0X R2 = 0.93**
Y = 4.4-1.9X R2 = 0.91**
B. ORMSTOWN
Y = 9.1+6.5X
R2 = 0.97**
Y = 9.4-3.7X R2 = 0.97**
Y = 9.1-3.4X
R2 = 0.87
25
20
15
10
5
0
0
1.0
2.0
NH3 LOSS, % OF UREA-N
P2O5 : UREA-N RATIO

Figure 3. Effect of urea and/or triple superphosphate on P concentration extracted by 0.5 **M** H_2SO_4 from soil layers with distance from fertilizer layer after five and ten days on the Ste Rosalie (A and B) and the Ormstown soil (C and D).

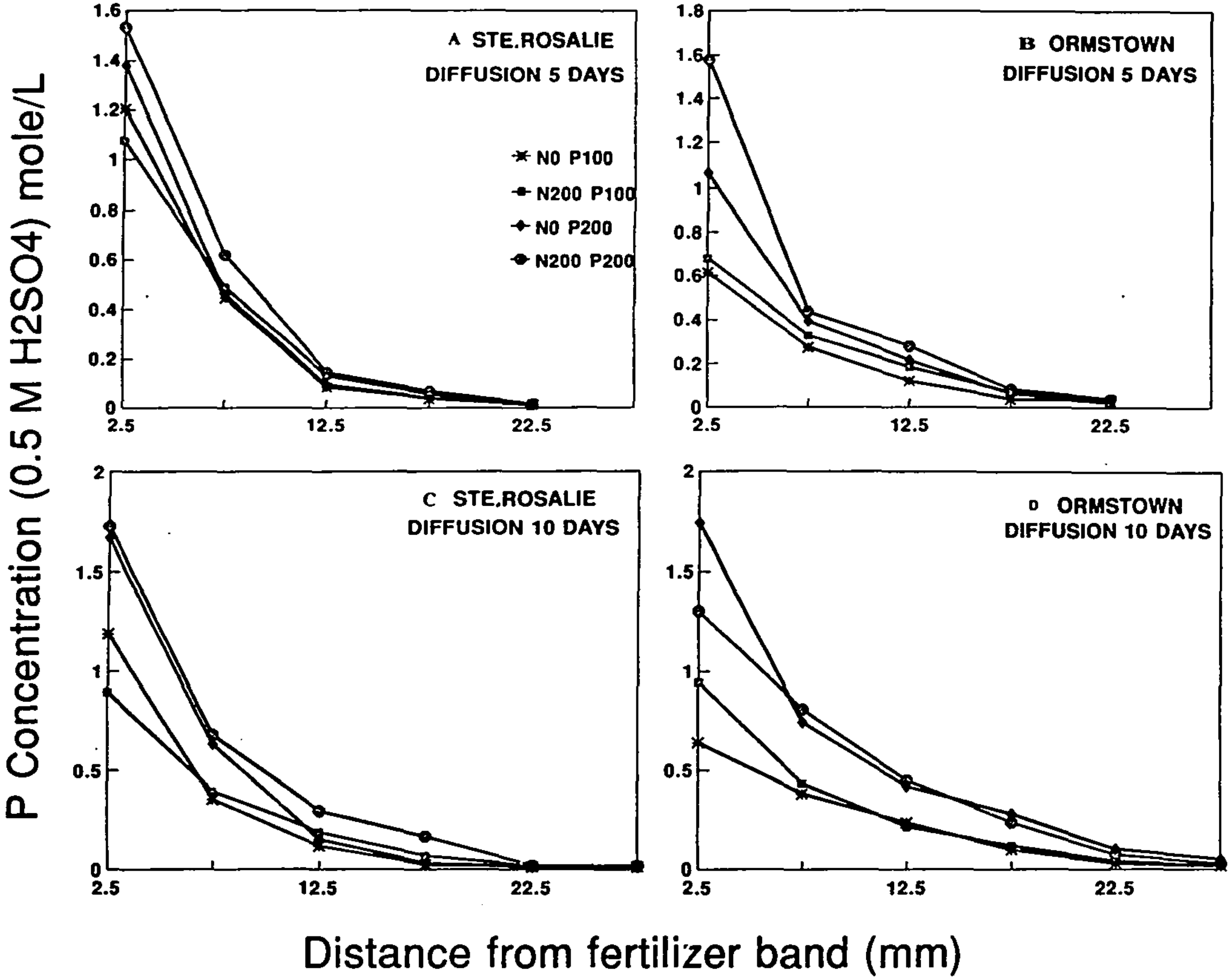

P Concentration (0.5 M H2SO4) mole/L
A STE.ROSALIE
DIFFUSION 5 DAYS
N0 P100
N200 P100
N0 P200
N200 P200
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
2.5
12.5
22.5
B ORMSTOWN
DIFFUSION 5 DAYS
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
2.5
12.5
22.5
C STE.ROSALIE
DIFFUSION 10 DAYS
2
1.5
1
0.5
0
2.5
12.5
22.5
D ORMSTOWN
DIFFUSION 10 DAYS
2
1.5
1
0.5
0
2.5
12.5
22.5
Distance from fertilizer band (mm)

Table 1. Parameters(A,B) and correlation coefficient (R^2) of the exponential equation relating cumulative NH_3 loss to time for Ste Rosalie and Ormstown soils.

Treatment					Parameters		R^2	Parameters		R^2
Urea	T-N†	TSP	MAP	DAP	A	B		A	B	
-- N --		--- P_2O_5 ---								
------- g/kg -------					----- Ste Rosalie -----			------- Ormstown -------		
2.0	2.0	0	0	0	0.580	0.232	0.72	0.164	0.105	0.068
2.0	2.0	1.0	0	0	0.110	0.289	0.81	0.113	0.245	0.83
2.0	2.0	2.0	0	0	0.058	0.224	0.91	0.092	0.243	0.80
2.0	2.0	4.0	0	0	0.049	0.295	0.81	0.057	0.252	0.84
1.8	2.0	0	1.0	0	0.127	0.291	0.77	0.140	0.246	0.84
1.6	2.0	0	2.0	0	0.094	0.295	0.81	0.113	0.245	0.81
1.2	2.0	0	4.0	0	0.056	0.301	0.81	0.082	0.238	0.75
1.6	2.0	0	0	1.0	4.26	0.118	0.79	5.53	0.102	0.59
1.2	2.0	0	0	2.0	7.26	0.091	0.66	7.33	0.088	0.58
0.4	2.0	0	0	4.0	9.28	0.073	0.63	10.2	0.057	0.64
0.5	0.5	0	0	0	0.058	0.125	0.46	0.046	0.108	0.07
0.5	0.5	0.5	0	0	0.044	0.158	0.66	0.035	0.221	0.73
0.5	0.5	1.0	0	0	0.023	0.146	0.65	0.016	0.225	0.76
0.4	0.5	0	0.5	0	0.053	0.162	0.69	0.029	0.215	0.75
0.3	0.5	0	1.0	0	0.032	0.145	0.69	0.026	0.115	0.61
0.3	0.5	0	0	0.5	1.13	0.089	0.61	1.18	0.076	0.68

†. T-N = Total amount of N application.

The daily cumulative NH_3 losses for each soil (Table 1) were fitted to a exponential model which described a sigmoidal curve constrained to go through the origin. This curve had the equation:

$$Y = A\,e^{Bt}$$

where Y = cumulative NH_3 volatilized as mg N/jar, t = time in days, A, B = equation constants.

The high values of the coefficient of determination (R^2) for each equation indicate that the model was a good fit for the experimental data for each soil. The constants (A) increased with increasing of urea and DAP rates; and decreased with increasing of TSP and MAP rates.

Table 2. NH_3 volatilization from urea-phosphate mixtures with increasing amount of added P at constant total N rates

Treatment					NH_3 Loss	
Urea	T-N†	TSP	MAP	DAP	Soils	
---- N ----		------ P_2O_5 ------			Ste Rosalie	Ormstown
----------- g/kg ----------					----- % applied N ------	
0.5	0.5	0	0	0	4.7	9.8
0.5	0.5	0.5	0	0	1.8	4.9
0.5	0.5	1.0	0	0	1.0	2.4
0.4	0.5	0	0.5	0	2.4	3.8
0.3	0.5	0	1.0	0	1.2	0.4
0.3	0.5	0	0	0.5	5.6	9.4
P rate					**	**
Source					**	**
P rate * Source					**	**
P rate Lin. in TSP					NS	**
P rate Quad. in TSP					**	NS
P rate Lin. in MAP					**	**
P rate Quad. in MAP					NS	NS

†. T-N = Total amount of N application.

Table 3. Effect of P source and rate on the maximum NH_3 volatilization rate (Rmax) and time to reach Rmax(Tmax) at 0.5 g N/kg soil application rate

Treatment					Ste Rosalie		Ormstown	
Urea-N	T-N†	TSP	MAP	DAP	Rmax	Tmax	Rmax	Tmax
---- N ----		---- P_2O_5 ---						
---------- g/kg ---------					N mg/jar/d	day	N mg/jar/d	day
0.5	0.5	0	0	0	0.32	7	0.59	7
0.5	0.5	0.5	0	0	0.14	9	0.21	12
0.5	0.5	1.0	0	0	0.04	9	0.11	12
0.4	0.5	0	0.5	0	0.14	8	0.19	12
0.3	0.5	0	1.0	0	0.05	8	0.04	8
0.3	0.5	0	0	0.5	0.26,0.3‡	1, 5‡	0.58,0.46	1, 6
LSD 0.05					0.06	2	0.08	2
C.V.					28.7	17.3	35.9	23.2

† T-N = Total amount of N application.

† The first number represents the first peak and the second represents the second peak of NH_3 volatilization.

Table 4. Effect of P source and rate on the maximum NH_3 volatilization rate(Rmax) and time to reach Rmax(Tmax) at 2.0 g N/kg soil application rate

Treatment					Ste Rosalie		Ormstown	
Urea-N	T-N†	TSP	MAP	DAP	Rmax	Tmax	Rmax	Tmax
---- N ----		----- P_2O_5 ----						
---------- g/kg ---------					N mg/jar/d	day	N mg/jar/d	day
2.0	2.0	0	0	0	4.4	8	4.5	6
2.0	2.0	1.0	0	0	1.8	14	1.8	14
2.0	2.0	2.0	0	0	1.3	16	1.3	16
2.0	2.0	4.0	0	0	1.1	16	1.1	16
1.8	2.0	0	1.0	0	2.1	14	1.9	15
1.6	2.0	0	2.0	0	1.8	14	1.9	16
1.2	2.0	0	4.0	0	1.2	16	1.5	16
1.6	2.0	0	0	1.0	1.2, 4.1‡	1, 4‡	1.4, 4.7	1, 4
1.2	2.0	0	0	2.0	1.6, 4.0	1, 4	2.1, 5.0	1, 4
0.4	2.0	0	0	4.0	2.0, 3.4	1, 4	4.9, 4.3	1, 5
			LSD 0.05		0.4	2	0.5	2
			C.V.		33.5	18.5	23.6	27.3

† T-N = Total amount of N application.

† The first number represents the first peak and the second represents the second peak of NH_3 volatilization.

Table 5. Effect of P source and rate on the maximum NH_3 volatilization rate (Rmax) and time to reach Rmax(Tmax) at 0.5 g urea-N/kg soil application rate

Treatment					Ste Rosalie		Ormstown	
Urea-N	T-N†	TSP	MAP	DAP	Rmax	Tmax	Rmax	Tmax
---- N ----		---- P_2O_5 ---						
---------- g/kg ---------					N mg/jar/d	day	N mg/jar/d	day
0.5	0.5	0	0	0	0.32	7	0.59	7
0.5	0.5	0.5	0	0	0.14	9	0.21	12
0.5	0.5	1.0	0	0	0.04	9	0.11	12
0.5	0.6	0	0.5	0	0.17	12	0.24	12
0.5	0.7	0	1.0	0	0.08	12	0.20	14
0.5	0.7	0	0	0.5	0.54,1.3‡	1, 4‡	0.6, 1.4	1, 4
0.5	0.9	0	0	1.0	1.0, 1.3	1, 4	1.3, 1.9	1, 3
		LSD 0.05			0.1	2	0.1	2
		C.V.			31.5	26.7	36.8	23.7

† T-N = Total amount of N application.
† The first number represents the first peak and the second represents the second peak of NH_3 volatilization.

Table 6 Regression equations between sorbed P (Y; mg P/kg soil) and equilibrium P concentration (X; mg P/L) for two eastern Canadian soils

Soil	Treatment urea-N mg/kg	Regression Equations	R^2
		--- 0.01 M $CaCl_2$ as electrolyte ---	
Ste Rosalie	0	$Y = 91.3 + 20.11X - 0.48X^2$	0.97
	250	$Y = 96.8 + 30.47X - 0.88X^2$	0.95
	500	$Y = 97.1 + 55.15X - 2.21X^2$	0.96
	1000	$Y = 90.4 + 94.23X - 5.35X^2$	0.97
Ormstown	0	$Y = 107.3 + 15.55X - 0.33X^2$	0.91
	250	$Y = 106.9 + 26.26X - 0.72X^2$	0.93
	500	$Y = 103.5 + 49.19X - 1.83X^2$	0.95
	1000	$Y = 85.9 + 91.22X - 4.83X^2$	0.98
		--- 0.03 M KCl as electrolyte ---	
Ste Rosalie	0	$Y = 57.9 + 24.35X - 0.56X^2$	0.89
	250	$Y = 62.3 + 24.19X - 0.57X^2$	0.89
	500	$Y = 70.3 + 30.36X - 0.84X^2$	0.88
	1000	$Y = 72.2 + 29.95X - 0.87X^2$	0.87
Ormstown	0	$Y = 55.6 + 26.87X - 0.65X^2$	0.92
	250	$Y = 56.0 + 29.48X - 0.76X^2$	0.90
	500	$Y = 53.1 + 35.41X - 0.99X^2$	0.94
	1000	$Y = 43.7 + 47.21X - 1.46X^2$	0.96

Table 7. Effect of Urea on Ca and P concentration in solution and the significances of the F test for thr analysis of variance (0.03 M KCl as electrolyte, 25 ml/2 g soil)

			P potential	Lime potential
Soil	$pH_2PO_4^+$	pCa	$pH_2PO_4+0.5pCa$	pH-0.5pCa'
Ste Rosalie soil				
N	**	**	**	**
Lin.	**	**	**	**
Qua.	**	**	**	*
P	**	**	**	**
Lin.	**	**	**	**
Qua.	**	NS	**	NS
N*P	**	NS	**	**
Ormstown soil				
N	**	**	**	**
Lin.	**	**	**	**
Qua.	**	**	**	*
P	**	**	**	**
Lin.	**	**	**	**
Qua.	**	NS	**	NS
N*P	**	NS	**	**

*,** significant at 0.05 and 0.01 probability level respectively.
+ pH_2PO_4 and pCa are the negative logarithm of $H_2PO_4^-$ and Ca^{++} ion activities.

Table 8 Correlation coefficients between phosphorus potential and lime potential for two eastern Canadian soils

Treatment urea-N mg/kg	R^2 Ste Roaslie	 Ormstown
0	0.29	0.88
250	0.66	0.90
500	0.91	0.87
1000	0.81	0.99

Table 9. Analysis of variances for phosphorus and nitrogen diffusion and transformation in five days in Ormstown soil

Source	DF	Urea g/kg	NH_4-N g/kg	Pl-FP M	Pl_{CaCl2} M	TPl_{CaCl2} mg/set	Ps mg/set	T-P mg/set
R	1	ns†	ns	ns	ns	ns	ns	ns
N	2	**	**	ns	ns	ns	*	ns
P	2	**	**	**	**	**	**	**
D	8	**	**	**	**	**	**	**
N*P	4	**	**	ns	ns	ns	*	ns
N*P*D	29	**	**	**	ns	ns	ns	ns
C.V.%		16.5	41.6	22.6	46.5	50.3	71.7	53.4
<u>N Effect</u>	0	0^{c}‡	0.0^{c}	0.45	0.36	140	50	191
	100	19.1^{b}	1.5^{b}	0.39	0.33	117	49	166
	200	43.5^{a}	0.9^{a}	0.38	0.31	128	62	190
<u>P Effect</u>	0	22.5	2.0^{a}	0^{c}	0^{c}	0^{c}	0^{c}	0^{c}
	100	23.7	0.5^{b}	0.43^{b}	0.32^{b}	84^{b}	55^{b}	138^{b}
	200	21.4	0.4^{b}	0.72^{a}	0.60^{a}	271^{a}	96^{a}	366^{a}

† ** and * indicate significant at P<0.01 and 0.05 level by the Duncan test; ns indicates not significant at P<0.05 level.

‡ Different letters in each column indicates a difference between treatments by Duncan test at 0.05 significance level; absence of letters indicates no difference.

Table 10. Analysis of variances for phosphorus and nitrogen diffusion and transformation in ten days in Ormstown soil

Source	DF	Urea g/kg	NH_4-N g/kg	Pl-FP M	Pl_{CaCl2} M	TPl_{CaCl2} mg/set	Ps mg/set	T-P mg/set
R	1	ns†	ns	ns	ns	ns	ns	ns
N	2	**	**	**	*	**	**	*
P	2	**	**	**	**	**	**	**
D	8	**	**	**	**	**	**	**
N*P	4	**	**	*	ns	ns	**	*
N*P*D	29	*	*	ns	*	*	**	*
C.V.%		42.6	26.8	37.8	95.4	85.5	23.1	42.4
<u>N Effect</u>	0	0^{c}‡	0^{c}	0.35^{b}	0.35^{a}	135^{a}	102^{a}	226^{a}
	100	6.1^{b}	7.5^{a}	0.39^{b}	0.23^{b}	74^{b}	88^{b}	161^{b}
	200	414.7^{a}	6.5^{b}	0.45^{a}	0.27^{b}	78^{b}	90^{b}	180^{b}
<u>P Effect</u>	0	4.2^{c}	7.3^{a}	0^{c}	0^{c}	0^{c}	0^{c}	0^{c}
	100	7.8^{b}	3.2^{c}	0.37^{b}	0.21^{b}	47^{b}	100^{b}	146^{b}
	200	9.4^{a}	5.4^{b}	0.68^{a}	0.54^{a}	204^{a}	153^{a}	356^{a}

† ** and * indicate significant at $P<0.01$ and 0.05 level by the Duncan test; ns indicates not significant at $P<0.05$ level.

‡ Different letters in each column indicates a difference between treatments by Duncan test at 0.05 significance level; absence of letters indicates no difference.

Table 11. Analysis of variances for phosphorus and nitrogen diffusion and transformation in five days in Ste Rosalie soil

Source	DF	Urea M	NH_4-N M	pH_{CaCl2} 20:1	Pl_{CaCl2} M	Pl-FP M	Ps M	T-P M
R	1	ns†	ns	ns	ns	ns	ns	ns
N	2	**	**	**	**	ns	*	**
P	2	**	**	**	**	**	**	**
D	8	**	**	**	**	**	**	**
N*P	4	ns	**	**	**	ns	**	*
N*P*D	29	**	**	**	**	**	**	**
C.V.%		12.0	15.5	3.9	7.2	27.8	9.1	22.0
<u>N Effect</u>	0	0^{c}‡	0.0^{c}	4.5^{c}	0.48	0.25	0.44^{a}	0.92^{a}
	100	0.18^{b}	0.28^{b}	6.7^{b}	0.45	0.23	0.39^{b}	0.84^{b}
	200	0.42^{a}	0.25^{a}	6.9^{a}	0.45	0.24	0.38^{b}	0.83^{b}
<u>P Effect</u>	0	0.22	0.14^{a}	7.8^{a}	0^{c}	0.01^{c}	0.01^{c}	0.01^{c}
	100	0.21	0.13^{b}	5.8^{b}	0.41^{b}	0.28^{b}	0.52^{b}	0.92^{b}
	200	0.20	0.26^{b}	5.3^{c}	0.83^{a}	0.40^{a}	0.56^{a}	1.39^{a}

† ** and * indicate significant at P<0.01 and 0.05 level by F test;
ns indicates not significant at P<0.05 level.

‡ Different letters in each column indicates a difference between treatments by Duncan test at 0.05 significance level; absence of letters indicates no difference.

Table 12. Analysis of variances for phosphorus and nitrogen diffusion and transformation in ten days in Ste Rosalie soil

Source	DF	Urea M	NH_4-N M	pH_{CaCl2} 20:1	Pl_{CaCl2} M	Pl-FP M	Ps M	T-P M
R	1	ns†	ns	ns	ns	ns	ns	ns
N	2	**	**	**	**	**	*	**
P	2	**	**	**	**	**	**	**
D	8	**	**	**	**	**	**	**
N*P	4	**	**	**	*	*	**	**
N*P*D	29	**	**	**	**	**	**	**
C.V.%		16.4	7.5	3.1	23.1	31.3	18.1	13.1
N Effect	0	0^{c}‡	0.0^{c}	5.0^{c}	0.39^{a}	0.18^{b}	0.35	0.74^{a}
	100	0.07^{b}	0.38^{b}	7.1^{b}	0.29^{b}	0.18^{b}	0.33	0.61^{b}
	200	0.2^{a}	0.40^{a}	7.4^{a}	0.29^{b}	0.22^{a}	0.32	0.61^{b}
P Effect	0	0.09	0.33^{a}	7.3^{a}	0^{c}	0^{c}	0.01^{c}	0.01^{c}
	100	0.11	0.33^{b}	6.5^{b}	0.29^{b}	0.18^{b}	0.44^{b}	0.73^{b}
	200	0.10	0.23^{b}	6.1^{a}	0.57^{a}	0.37^{a}	0.49^{a}	1.04^{a}

† ** and * indicate significant at $P<0.01$ and 0.05 level by F test; ns indicates not significant at $P<0.05$ level.

‡ Different letters in each column indicates a difference between treatments by Duncan test at 0.05 significance level; absence of letters indicates no difference.

Table 13. Analysis of variances for phosphorus and nitrogen diffusion and transformation in twenty days in Ste Rosalie soil

Source	DF	Urea M	NH_4-N M	pH$_{\mathrm{CaCl2}}$ 20:1	Pl$_{\mathrm{CaCl2}}$ M	Pl-FP M	Ps M	T-P M
R	1	ns†	ns	ns	ns	ns	ns	ns
N	2	**	**	**	*	ns	ns	ns
P	2	**	**	ns	**	**	**	**
D	8	**	**	**	**	**	**	**
N*P	4	**	**	*	ns	ns	ns	**
N*P*D	29	**	**	*	**	**	**	**
C.V.%		4.4	9.4	5.7	55.7	32.5	21.3	24.8
N Effect	0	0^{c}‡	0.0^{c}	4.7^{b}	0.29^{a}	0^{b}	0.59^{a}	0.88^{a}
	100	0.015^{b}	0.5^{b}	7.2^{a}	0.15^{b}	0.23^{a}	0.41^{b}	0.56^{b}
	200	0.10^{a}	0.7^{a}	7.3^{a}	0.18^{b}	0.26^{a}	0.40^{b}	0.59^{b}
P Effect	0	0.049	0.37^{b}	7.4^{a}	0^{c}	0^{c}	0.01^{c}	0.01^{c}
	100	0.04	0.51^{a}	6.4^{b}	0.13^{b}	0.23^{b}	0.55^{b}	0.67^{b}
	200	0.044	0.48^{a}	6.3^{b}	0.39^{a}	0.51^{a}	0.63^{a}	1.01^{a}

† ** and * indicate significant at $P<0.01$ and 0.05 level by F test; ns indicates not significant at $P<0.05$ level.

‡ Different letters in each column indicates a difference between treatments by Duncan test at 0.05 significance level; absence of letters indicates no difference.

Table 14. The cumulated amount of P that diffused from the fertilizer layer to soil at different distance in ten days in Ste Rosalie soil

Treatment		Total cumulated P at distance from fertilizer layer(mm)					
N	P	0	2.5	7.5	12.5	17.5	22.5
kg ha^{-1}		mg P					
0	100	1036	301	73	6.3	0	0
100	100	902	468	96	18.2	1.0	0
200	100	981	409	160	43	1.9	0
0	200	1582	506	104	11.5	0.65	0
100	200	1699	694	166	31	5.1	0
200	200	1813	726	292	109	5.9	0
N	effect	ns†	+	*	**	**	
	Lin.	ns	+	ns	**	**	
	Quad.	ns	*	**	**	**	
P	effect	**	**	**	**	**	
	Lin.	**	**	**	**	**	
	Quad.	**	**	**	ns	ns	
N*P		ns	ns	ns	ns	ns	
C.V.	%	18.2	16.4	15.9	27.5	72.2	

† +, * and ** indicate significant at P<0.1, 0.05 and 0.01 level, respectively; ns indicates not significant at P<0.05 level by contrast test.

Table 15. The cumulated amount of P that diffused from the fertilizer layer to soil at different distance in twenty days in Ste Rosalie soil

Treatment		Total cumulated P at distance from fertilizer layer(mm)					
N	P	0	2.5	7.5	12.5	17.5	22.5
kg ha^{-1}		mg P					
0	100	1338	441	139	18.9	0.9	0.3
100	100	1188	509	181	50.0	4.3	1.8
200	100	1273	566	262	112	13.0	2.7
0	200	2447	941	347	101	10.5	1.9
100	200	2452	788	340	124	27.1	6.2
200	200	2604	1262	452	175	44.6	8.0
N	effect	ns†	ns	**	*	*	*
	Lin.	ns	ns	ns	*	*	*
	Quad.	ns	ns	**	*	ns	ns
P	effect	**	**	**	**	**	**
	Lin.	**	**	**	**	**	*
	Quad.	ns	ns	**	**	**	**
N*P		ns	ns	**	ns	ns	ns
C.V.	%	27.2	23.5	8.3	10.8	32.7	48.1

† ns indicates not significant at $P<0.05$ level;
*, and ** indicate significant at $P<0.05$; 0.01 level by contrast, respectively.

Table 16. The cumulated amount of P that diffused from the fertilizer layer to soil at different distance in ten days in Ormstown soil

Treatment		Total cumulated P at distance from fertilizer layer(mm)					
N	P	0	2.5	7.5	12.5	17.5	22.5
kg/ha		mg P					
0	100	878	468	226	78	18.2	4.6
100	100	1077	525	278	102	31	4.3
200	100	1123	518	242	106	33.7	9.0
0	200	2143	1023	544	274	98.2	35
100	200	1869	1023	572	295	117	38
200	200	1773	936	411	171	50	13.3
N	effect	ns†	ns	ns	ns	ns	*
	Lin.	ns	ns	ns	ns	ns	*
	Quad.	ns	ns	ns	ns	ns	ns
P	effect	**	**	**	**	**	**
	Lin.	**	**	**	**	**	**
	Quad.	ns	ns	ns	ns	ns	**
N*P		ns	ns	ns	ns	ns	ns
C.V.	%	34.6	21.3	10.9	11.7	6.8	33.2

† ns indicates not significant at P<0.05 level;
*, and ** indicate significant at P<0.05, 0.01 level, respectively by contrast.

Table 17. The cumulated amount of P that diffused from the fertilizer layer to soil at different distance in twenty days in Ormstown soil

Treatment		Total cumulated P at distance from fertilizer layer(mm)					
N	P	0	2.5	7.5	12.5	17.5	22.5
kg/ha		mg P					
0	100	1228	756	451	252	118	52
100	100	1192	714	422	208	86	41
200	100	1243	719	440	237	118	53
0	200	2371	1497	878	488	242	99
100	200	2171	1337	758	385	200	81
200	200	2357	1526	972	580	301	127
N	effect	ns†	ns	ns	ns	ns	ns
	Lin.	ns	ns	ns	ns	ns	ns
	Quad.	ns	ns	ns	ns	ns	ns
P	effect	**	**	**	**	**	**
	Lin.	**	**	**	**	**	**
	Quad.	ns	ns	ns	ns	ns	**
N*P		ns	ns	ns	ns	ns	ns
C.V.	%	12.6	9.8	15.9	27.0	14.1	10.4

† ns indicates not significant at P<0.05 level;
*, and ** indicate significant at P<0.05, 0.01 level, respectively by contrast.

Table 18. The main effect of banded P sources and urea-N rates (1990); Banded TSP-P rates and urea-N rates on P content of corn plant in different growth stages.

Main effect		P content in plant tissue					
		Ste Rosalie			Ormstown		
		6-leaf	9-leaf	silking	6-leaf	9-leaf	silking
1990		------------------------------- g/kg DM	-------------------------------				
P Source	0 P†	3.2^{C}‡	1.9^{C}	2.3^{B}	3.2^{C}	2.9^{B}	3.5^{B}
	MAP	[illegible]^{A}	2.8^{A}	2.7^{A}	5.8^{A}	3.3^{A}	3.8^{A}
	TSP	[illegible]	2.5^{B}	2.7^{A}	5.3^{B}	3.3^{A}	3.9^{A}
N Rates	N0	3.8	2.3	2.4	4.6	3.0	3.6
	N30	4.5	2.5	2.6	4.9	3.2	3.7
	N60	4.2	2.4	2.7	4.9	3.3	3.8
	Trend	Q^{*}	NS	L^{**}	NS	L^{*}	L^{*}
1991							
P Rates	TSP0	3.1		1.5	4.2		2.4
	TSP45	3.8		1.8	4.6		2.6
	TSP90	4.2		1.9	4.9		2.7
	Trend	L^{**}		Q^{**}	L^{**}		Q^{**}
N rates	N0	3.4		1.6	4.4		2.5
	N30	3.8		1.7	4.7		2.6
	N60	3.9		1.8	4.6		2.6
	Trend	Q^{**}		L^{*}	Q^{*}		NS

† 0 P, MAP, and TSP indicate the average of four replications and three N rates banded with no P, MAP, and TSP, respectively.

N0, N30, and N60 indicate the average of four replications and three P sources (1990) or P rates (1991) banded with no urea, 30 kg N/ha, and 60 kg N/ha urea, respectively.

TSP0, TSP45, and TSP90 indicate the average of four replications and three N rates banded with no TSP, 45 kg P_2O_5/ha, and 90 kg P_2O_5/ha TSP, respectively.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test. NS, *, and ** indicate no significant, significant at 0.05 and 0.01 probability levels in Contrast, respectively.

Table 19. Regressions relating plant dry matter,P content, and P uptake to soil Mehlich-3 extractable P at 6-leaf and silking stage for Ste Rosalie and Ormstown soil

Sources	Intercept	Soil P coefficient (mg kg^{-1})	R^2
	6-leaf stage	(Ste Rosalie)	
shoot P content(%)	3.388***†	0.006***	0.43***
P uptake(mg plant^{-1})	1.574***	0.013***	0.68***
dry matter(g plant^{-1})	4.596***	0.022***	0.67***
		(Ormstown)	
shoot P content(%)	3.420***	0.015***	0.46***
P uptake(mg plant^{-1})	2.784***	0.003***	0.63***
dry matter(g plant^{-1})	7.957***	0.032***	0.52***
	silking stage	(Ste Rosalie)	
ear-leaf P content(%)	34.575**	0.030***	0.62***
	silking stage	(Ormstown)	
ear-leaf P content(%)	22.26***	0.076***	0.35***

† *, ** and *** indicate the probability of a greater F are at 0.05, 0.01 and 0.001 level respectively.

Table 20. Analysis of variance and contrasts for N and P uptake and corn yield in 1990

Source of variation	df	Total Uptake N	Total Uptake P	yield stover	yield grain
		Ste Rosalie soil			
N rate	2	**	*	NS	*
Linear	1	**	*	NS	*
Quadratic	1	NS	NS	NS	NS
P sources	2	**	**	**	**
P0 vs MAP, TSP	1	**	**	**	**
MAP vs TSP	2	NS	NS	NS	NS
N rate x P sources	4	NS	NS	NS	NS
		Ormstown soil			
N rate	2	**	*	NS	*
Linear	1	**	*	NS	NS
Quadratic	1	**	NS	NS	*
P sources	2	**	**	NS	**
P0 vs MAP, TSP	1	**	**	NS	**
MAP vs TSP	1	NS	NS	NS	NS
N rate*P sources	4	NS	NS	NS	NS

**, * = significant at 0.01 and 0.05 probability levels. NS = not significant. df = degree of freedom.

Table 21. Analysis of variance and contrasts for N and P uptake and corn yield in 1991

Source		Total Uptake		yield	
of variation	df	N	P	stover	grain
		Ste Rosalie soil			
N rate	2	**	*	*	*
Linear	1	**	**	*	*
Quadratic	1	NS	NS	NS	NS
N0 vs N1, N2	1	**	*	NS	*
N1 vs N2	1	**	*	*	NS
P rate	2	**	**	**	**
Linear	1	**	**	**	**
Quadratic	1	NS	NS	**	**
P0 vs P1, P2	1	**	**	**	**
P1 vs P2	1	**	**	*	*
N rate x P rate	4	*	*	NS	NS
		Ormstown soil			
N rate	2	**	**	NS	*
Linear	1	NS	NS	NS	NS
Quadratic	1	**	*	NS	*
N0 vs N1, N2	1	**	**	NS	*
N1 vs N2	1	NS	NS	NS	NS
P rate	2	*	**	**	**
Linear	1	NS	*	NS	NS
Quadratic	1	**	*	**	**
P0 vs P1, P2	1	**	**	**	**
P1 vs P2	1	NS	**	NS	NS
N rate*P rate	4	*	*	NS	NS

**, * = significant at 0.01 and 0.05 probability levels. NS = not significant. df = degree of freedom.

Table 22. The main effect of banded P sources and urea-N rates (1990); Banded TSP-P rates and urea-N rates on P and N uptakes and P use efficiency by corn in 1990 and 1991.

Main Effects		Ste Rosalie			Ormstown		
		N uptake	P uptake	P efficiency	N uptake	P uptake	P efficiency
1990		----- kg/ha -----		g/kg	----- kg/ha -----		g/kg
P Source	0 P†	158^{B}‡	26.8^{B}		180^{B}	31.6^{B}	
	MAP	209^{A}	39.5^{A}	321	211^{A}	42.7^{A}	274
	TSP	209^{A}	39.1^{A}	303	211^{A}	42.1^{A}	260
N Rates	N0	176	31.3	220	185	35.1	243
	N30	188	34.8	311	207	38.9	146
	N60	203	39.4	406	207	42.3	414
	Trend	L^{**}	L^{**}	L^{**}	Q^{**}	L^{**}	L^{*}
1991							
P Rates	TSP0	157	17.8		220	27.2	
	TSP45	188	23.2	268	263	34.7	368
	TSP90	215	26.7	222	269	37.9	264
	Trend	L^{**}	L^{**}	NS	Q^{**}	Q^{**}	L^{**}
N rates	N0	175	21.1	188	224	31.2	221
	N30	185	22.5	272	264	34.5	332
	N60	201	24.2	276	262	34.2	395
	Trend	L^{**}	L^{**}	Q^{*}	Q^{*}	Q^{*}	Q^{*}

† 0 P, MAP, and TSP indicate the average of four replications and three N rates banded with no P, MAP, and TSP, respectively.

N0, N30, and N60 indicate the average of four replications and three P sources (1990) or P rates (1991) banded with no urea, 30 kg N/ha, and 60 kg N/ha urea, respectively.

TSP0, TSP45, and TSP90 indicate the average of four replications and three N rates banded with no TSP, 45 kg P_2O_5/ha, and 90 kg P_2O_5/ha TSP, respectively.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test. NS, *, and ** indicate no significant, significant at 0.05 and 0.01 probability levels in Contrast, respectively.

Table 23. The main effect of banded P sources and urea-N rates (1990); Banded TSP-P rates and urea-N rates on stover and grain yields of corn in 1990 and 1991.

Main Effects		Ste Rosalie		Ormstown	
		stover yield	grain yield	stover yield	grain yield
1990		------------ Mg/ha -----------		------------ Mg/ha -----------	
P Source	0 P†	6.4^{B}‡	7.8^{B}	11.0	8.6^{B}
	MAP	8.6^{A}	9.6^{A}	11.9	10.0^{A}
	TSP	8.0^{A}	9.8^{A}	11.4	9.9^{A}
N Rates	N0	7.5	8.8	10.9	9.1
	N30	7.4	9.1	11.9	9.7
	N60	8.1	9.4	11.5	9.7
	Trend	NS	L^{*}	NS	Q^{*}
1991					
P Rates	TSP0	5.4	7.4	8.0	9.4
	TSP45	6.6	8.6	9.3	10.2
	TSP90	7.7	9.2	9.2	10.4
	Trend	Q^{**}	Q^{**}	Q^{**}	Q^{**}
N rates	N0	6.3	8.0	8.5	9.7
	N30	6.1	8.5	9.2	11.2
	N60	7.2	8.7	8.8	10.1
	Trend	L^{*}	L^{*}	NS	Q^{*}

† 0 P, MAP, and TSP indicate the average of four replications and three N rates banded with no P, MAP, and TSP, respectively.

N0, N30, and N60 indicate the average of four replications and three P sources (1990) or P rates (1991) banded with no urea, 30 kg N/ha, and 60 kg N/ha urea, respectively.

TSP0, TSP45, and TSP90 indicate the average of four replications and three N rates banded with no TSP, 45 kg P_2O_5/ha, and 90 kg P_2O_5/ha TSP, respectively.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test. NS, *, and ** indicate no significant, significant at 0.05 and 0.01 probability levels in Contrast, respectively.

Table 24. The main effect of banded P sources and urea-N rates in the 1990 on P and N uptakes and P residual efficiency by corn and stover and grain yield of corn in 1991.

Main Effects		Ste Rosalie				Ormstown			
		stover yield	grain yield	P uptake	P efficiency	stover yield	grain yield	P uptake	P efficiency
1990		----- Mg/ha -----		kg/ha	g/kg	----- Mg/ha -----		kg/ha	g/kg
P Source	0 P†	5.9^{B}‡	7.4^{B}	15.0^{B}		8.4^{B}	8.5^{B}	22.9	
	MAP	6.8^{A}	8.1^{A}	19.0^{A}	99	9.3^{A}	9.5^{A}	23.5	181
	TSP	6.8^{A}	8.3^{A}	19.7^{A}	116	9.3^{A}	9.3^{A}	24.3	139
N Rates	N0	6.7	7.7	16.5	105	8.5	8.8	24.6	120
	N30	6.5	7.9	17.9	95	9.1	9.2	27.8	170
	N60	6.3	8.2	19.3	124	9.4	9.3	29.1	190
	Trend	NS	L^{*}	L^{*}	NS	L^{*}	L^{*}	L^{**}	Q^{*}

† 0 P, MAP, and TSP indicate the average of four replications and three N rates banded with no P, MAP, and TSP, respectively.

N0, N30, and N60 indicate the average of four replications and three P sources banded with no urea, 30 kg N/ha, and 60 kg N/ha urea, respectively.

‡ Means in the same column with different letters are significantly different at the 0.05 level based on Duncan's Multiple Range Test. NS, *, and ** indicate no significant, significant at 0.05 and 0.01 probability levels in Contrast, respectively.

Table 25. Analysis of variance and contrasts for the effect of banded phosphorous sources and urea rates in the 1990 on phosphorous uptake and
corn stover and grain yield in 1991

Source of variation	df	Total P uptake	yield stover	 grain
		Ste Rosalie soil		
N rate	2	*	NS	*
Linear	1	**	NS	*
Quadratic	1	NS	NS	NS
P sources	2	**	*	**
P0 vs MAP, TSP	1	**	*	**
MAP vs TSP	2	NS	NS	NS
N rate x P sources	4	NS	NS	NS
		Ormstown soil		
N rate	2	**	*	*
Linear	1	**	*	*
Quadratic	1	NS	NS	NS
P sources	2	**	NS	**
P0 vs MAP, TSP	1	**	*	**
MAP vs TSP	1	NS	NS	NS
N rate*P sources	4	NS	NS	NS

**, * = significant at 0.01 and 0.05 probability levels. NS = not significant.
df = degree of freedom.

Table 26. Regressions of soil pH (H_2O), and soil buffer pH (SMP) with final agar-soil pH rises in urea (0.5 g kg^{-1} treatment) fertilizer microsites after application

Soil	soil pH†	soil pH†	agar-soil pH near urea microsite		
	(H_2O)	(SMP)	day 2	day 4	day6
Ste Rosalie	5.0	5.5	7.0	7.7	6.5
Ormstown	5.5	6.2	7.5	8.0	7.0
Upland Tope soil	4.2	5.3	6.5	6.5	6.5
Upland Subsoil	4.0	4.5	5.5	5.5	5.5

Regressions of soil pH with pH near fertilizer microsite (n=4)

pH(day 2) vs pH(H_2O)	$Y = 1.33 + 1.13X$	$R^2 = 0.86^*$
pH(day 2) vs pH(SMP)	$Y = 0.21 + 1.20X$	$R^2 = 0.96^{**}$
pH(day 4) vs pH(H_2O)	$Y = 0.78 + 1.29X$	$R^2 = 0.79^*$
pH(day 4) vs pH(SMP)	$Y = 0.16 + 1.24X$	$R^2 = 0.76^*$
pH(day 6) vs pH(H_2O)	$Y = 2.91 + 0.74X$	$R^2 = 0.68$
pH(day 6) vs pH(SMP)	$Y = 1.66 + 0.88X$	$R^2 = 0.95^{**}$

Y = final agar-soil pH; X = original soil pH(H_2O) or pH(SMP).
* and ** indicate significant at 0.05 and 0.01 probability level by F test.
† Soil pH(H_2O) and pH(SMP) methods: McLean, E.O. 1982.

Table 27 Nitrogen uptake And N use efficiency by Corn in 1991

	P Rate (kg P_2O_5/ ha)	Rate of Urea-N banded (kg/ha)			
		0	30	60	Means
Total N	0	148(9)	155(17)	167(20)	157^{C}
Uptake	45	180(30)	186(22)	197(16)	188^{B}
kg / ha	90	195(32)	210(22)	239(23)	215^{A}
(Ste Rosalie)	MEANS	175^{B}	185^{B}	201^{A}	
N use Efficiency	45	32.4(33)	30.9(28)	30.0(31)	31.1^{B}
%	90	47.6(26)	54.5(13)	72.4(35)	58.1^{A}
(Ste Rosalie)	MEANS	40.0	42.7	51.2	
Total N	0	214(12)	235(13)	210(15)	220^{B}
Uptake	45	240(9)	271(30)	276(15)	263^{A}
kg / ha	90	219(62)	285(25)	301(11)	269^{A}
(Ormstown)	MEANS	224^{B}	264^{A}	262^{A}	
N use Efficiency	45	25.2(11)	36.5(32)	66.1(13)	42.6
%	90	4.6(3)	50.5(20)	91.1(13)	48.8
(Ormstown)	MEANS	14.9^{C}	43.5^{B}	78.6^{A}	

Means in the same column or row with the different letter are significantly different at the 0.05 level based on Duncan's Multiple Range Test.

The values in the bracket are standard deviations.

N use efficiency=(N uptake in treatment with banded N - N uptake in corresponding treatment without banded N fert.)*100/N applied.