

**EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION
ON THE PERFORMANCE OF UREA FERTILIZERS AMENDED WITH THE
UREASE INHIBITOR N-(N-BUTYL) THIOPHOSPHORIC TRIAMIDE**

BY

CHRISTINE D. L. RAWLUK

A Thesis Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

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

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

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

0-612-51790-X

**THE UNIVERSITY OF MANITOBA
FACULTY OF GRADUATE STUDIES

COPYRIGHT PERMISSION PAGE**

**EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION
ON THE PERFORMANCE OF UREA FERTILIZERS AMENDED WITH THE
UREASE INHIBITOR N-(N-BUTYL) THIOPHOSPHORIC TRIAMIDE**

by

Christine D.L. Rawluk

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University
of Manitoba in partial fulfillment of the requirements of the degree
of
MASTER OF SCIENCE**

Christine D.L. Rawluk © 2000

Permission has been granted to the Library of The University of Manitoba to lend or sell copies of this thesis/practicum, to the National Library of Canada to microfilm this thesis/practicum and to lend or sell copies of the film, and to Dissertations Abstracts International to publish an abstract of this thesis/practicum.

The author reserves other publication rights, and neither this thesis/practicum nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

ABSTRACT

Rawluk, Christine Dawn Lyons. M.Sc. The University of Manitoba, May 2000.
Effect of Soil Texture, Temperature and Irrigation on the Performance of Urea Fertilizers Amended with the Urease Inhibitor N-(n-butyl) Thiophosphoric Triamide (NBPT).
Major professors; Cynthia A. Grant and Geza J. Racz.

Ammonia volatilization can decrease the efficiency of surface-applied urea fertilizers by decreasing the amount of fertilizer N available in the soil for plant utilization. Three field experiments using lysimeters were conducted to investigate the ability of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) to reduce volatile losses of N from surface-applied urea fertilizers under soil texture, temperature and moisture regimes representative of Western Manitoba. Urea and UAN were amended with NBPT and surface-applied under modified zero tillage. The effectiveness of NBPT was assessed relative to unamended urea fertilizers by measuring NH_3 volatilization from urea and UAN fertilizers over a 2 and 3 week period after fertilization and measuring the amount of soil N in the 0-30 cm depth of soil. The ability of NBPT to reduce NH_3 volatilization from urea was evaluated for varying rates of NBPT. The impact of NBPT use with urea and UAN on N availability to wheat plants and recovery in soil after plant growth was also assessed.

N-(n-butyl) thiophosphoric triamide delayed the onset of NH_3 volatilization and reduced the total NH_3 loss under all soil texture and temperature conditions in the field. Total NH_3 volatilization decreased in the order of non-irrigated > irrigated > non-irrigated +NBPT > irrigated+NBPT and was greater from urea than UAN. Amendment of urea

with NBPT at rates of 0.05 to 0.15% significantly reduced NH_3 volatilization with greater suppression of NH_3 loss with the 0.10 and 0.15% rates than with the 0.05% rate, particularly in the second and third weeks after fertilization. The inhibitor was most effective during periods of peak NH_3 loss from unamended urea where NH_3 losses were reduced by about 82-96% when averaged for all studies.

The NH_3 conserved through use of NBPT resulted in increased soil N as a proportion of total N measured in the soil plus the air. Soil N was concentrated within 10 cm of the soil surface with greater NO_3^- for irrigated NBPT treatments and greater exchangeable NH_4^+ and urea for non-irrigated NBPT treatments. Soil N was greater in May on the Newdale CL soil where soil and temperature conditions were less conducive to NH_3 volatilization. In contrast, when plants were grown and soil sampling was delayed until 6 to 8 weeks after fertilization, NBPT amendment and irrigation had minimal effect on N form and distribution in soil for the different soil texture and temperature conditions. Delayed time to soil sampling and elevated background soil N likely masked any initial effects of irrigation or NBPT on urea hydrolysis and distribution of hydrolysis products in the soil. Plant biomass and N content were increased when urea was treated with NBPT as compared to unamended urea. Averaged for all studies, plant N content increased by 24% when urea was amended with NBPT but decreased by 4% when NBPT was applied with UAN. However, these effects were not significant because modified growing conditions within the lysimeter resulted in uneven emergence and excessive moisture and heat stress.

Results of this research indicate NBPT is suitable for use in Western Manitoba to reduce NH_3 volatilization from surface-applied urea fertilizers and to increase the amount of fertilizer N in soil for plant utilization.

ACKNOWLEDGMENTS

I am eternally grateful to my co-advisors Dr. Cynthia Grant and Dr. Geza Racz for presenting me with the opportunity to pursue this Masters Degree in Soil Science. Dr. Racz, you have unselfishly given me many hours of your time, providing expert insight and advice. You instilled my appreciation for 'all things soil'. Dr. Grant, through your guidance, generosity and confidence in my abilities you have cultivated an earnest interest in agricultural research, providing an environment where I can hone my skills and continue to develop and advance intellectually.

Dr. D. N. Flaten and Dr. M. K. Pritchard, I greatly appreciate the thoroughness of your review and the helpful suggestions you have provided during the writing of this thesis and during the oral defense.

Thank you to Teresa Visser, Kim Brown, Brian Hadley, Mike Svistovski, Ian Murchison, Cheryl Dooley and Gregg Morden for their technical assistance and support in the field and in the laboratory. For their constant friendliness and willingness to help, I thank Carol Enns, Helen Nemeth and Pearl Novotny.

The graduate students and staff in the Department of Soil Science are unrivaled, where community spirit abounds and all are welcome. I am confident the quality of education I have received through this department will assist me in all my future endeavors. The Agriculture and Agri-Food Canada Brandon Research Centre, where I conducted my field research, is a centre of excellence of which I am proud to be

affiliated.

I would like to acknowledge the financial support of IMC-Global, Sherritt Fertilizers and the Matching Investment Initiative of Agriculture and Agri-Food Canada.

To my parents Gwen Lyons and Beverly and Raymond Rawluk, thank you for your faith, confidence and continuous support.

Finally, my deepest appreciation for my husband Chris and his insurmountable patience. Thank you for your well timed words of encouragement and constant support through the, at times, seemingly endless period during which I have pursued this degree. We have seen many changes (since our days in Environmental Science) through which this thesis has been a constant. Now as we enter into the next exciting phase of our lives, Parenthood, we close this chapter.

FOREWARD

This thesis was written in manuscript style as outlined in the Department of Soil Science *Guide to Thesis Preparation for Graduate Students*. Manuscripts entitled “Ammonia volatilization and soil N following surface application of urea fertilizers with and without NBPT: Effect of soil texture, temperature and irrigation” and “Ammonia loss from urea amended with varying rates of NBPT applied to soils of differing texture and temperature” will be submitted for publication to the Canadian Journal of Soil Science.

TABLE OF CONTENTS

	Page
ABSTRACT.....	i
ACKNOWLEDGMENTS.....	iii
FOREWARD.....	v
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
LIST OF ABBREVIATIONS.....	xii
1. INTRODUCTION.....	1
2. LITERATURE REVIEW.....	4
2.1 Introduction.....	4
2.2 The Urease Enzyme.....	5
2.2.1 Urease Structure and Hydrolysis Mechanism.....	5
2.2.2 Urease in Soil.....	7
2.2.3 Urease Activity.....	9
2.3 Reactions of Urea and Urea Hydrolysis Products in Soil.....	10
2.4 Factors Affecting Urea Hydrolysis and Ammonia Volatilization.....	13
2.4.1 Soil Properties.....	13
2.4.2 Environmental Conditions.....	16
2.4.2.1 Soil and Air Temperature.....	17
2.4.2.2 Soil Water Flux.....	18
2.4.3 Management Factors.....	21
2.4.3.1 Tillage Practice and Residue Management.....	21
2.4.3.2 Urea Fertilizer Placement, Quantity, Timing and Form....	23
2.5 The Urease Inhibitor N-(n-butyl) Thiophosphoric Triamide.....	25
2.5.1 Mechanism of Urease Inhibition.....	26
2.5.2 Performance and Suitability of NBPT for Agricultural Use.....	27
2.6 Distribution of Urea and Nitrogen Reaction Products in Soil.....	31
2.7 Plant Yield and Recovery of Urea-N Surface-Applied with NBPT.....	34

3. AMMONIA VOLATILIZATION AND SOIL N FOLLOWING SURFACE APPLICATION OF UREA FERTILIZERS WITH AND WITHOUT NBPT: EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION.....	37
3.1 Abstract.....	37
3.2 Introduction.....	38
3.3 Materials and Methods.....	39
3.4 Results and Discussion.....	44
3.4.1 Ammonia Volatilization.....	44
3.4.2 Soil Nitrogen Content.....	52
3.5 Conclusions.....	66
4. AMMONIA LOSS FROM UREA AMENDED WITH VARYING RATES OF NBPT APPLIED TO SOILS OF DIFFERING TEXTURE AND TEMPERATURE.....	67
4.1 Abstract.....	67
4.2 Introduction.....	68
4.3 Materials and Methods.....	69
4.4 Results.....	72
4.5 Discussion.....	76
4.6 Conclusions.....	78
5. PLANT RESPONSE AND SOIL N FOLLOWING SURFACE APPLICATION OF UREA FERTILIZERS WITH AND WITHOUT NBPT: EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION.....	80
5.1 Abstract.....	80
5.2 Introduction.....	81
5.3 Materials and Methods.....	83
5.4 Results and Discussion.....	87
5.4.1 Plant Biomass and N Accumulation.....	87
5.4.2 Soil Mineral N.....	91
5.5 Conclusions.....	99
6. GENERAL DISCUSSION.....	100
7. SUMMARY AND CONCLUSIONS.....	104
8. CONTRIBUTION TO KNOWLEDGE.....	107
9. REFERENCES.....	109

10. APPENDICES.....	118
Ia. Daily meteorological data for the May study on the Newdale clay loam soil, 1996.....	118
Ib. Daily meteorological data for the July study on the Newdale clay loam soil, 1996.....	118
Ic. Daily meteorological data for the May study on the Stockton fine sandy loam soil, 1996.....	119
Id. Daily meteorological data for the July study on the Stockton fine sandy loam soil, 1996.....	119
Ie. Daily meteorological data for the May study on the Newdale clay loam soil, 1997	120
If. Daily meteorological data for the July study on the Newdale clay loam soil, 1997	120
Ig. Daily meteorological data for the May study on the Stockton fine sandy loam soil, 1997.....	121
Ih. Daily meteorological data for the July study on the Stockton fine sandy loam soil, 1997.....	122
IIa. Cumulative $\text{NH}_3\text{-N}$ loss (% of applied N) minus control for 1996 (Manuscript 3).....	123
IIb. Cumulative $\text{NH}_3\text{-N}$ loss (% of applied N) minus control for 1997 (Manuscript 3).....	124
IIIa. Variable NBPT rate study $\text{NH}_3\text{-N}$ (% of applied N) minus control in 1996 (Manuscript 4).....	125
IIIb. Variable NBPT rate study $\text{NH}_3\text{-N}$ (% of applied N) minus control in 1997 (Manuscript 4).....	126
IV. LS means total N as NO_3^- , exchangeable NH_4^+ and plant N (g N m^{-2}) for the 1996 and 1997 studies (Manuscript 5).....	127

LIST OF TABLES

Table	Page
2.1 Conceptual view of components of soil enzymes.....	8
3.1 Selected chemical and physical characteristics of soils used.....	40
3.2 $Pr > F$, F and LS means standard error values for log-transformed NH_3 -N data.....	43
3.3 Probability values and LS means standard error for log-transformed soil N data.....	44
3.4 Contrast analysis and LS means standard error values for log-transformed 1996 NH_3 -N data.....	47
3.5 Contrast analysis and LS means standard error values for log-transformed 1997 NH_3 -N data.....	48
3.6 Soil urea-N, exchangeable NH_4 -N and NO_3 -N content ($kg\ N\ ha^{-1}$) with depth for the Newdale clay loam soil, 1996.....	53
3.7 Soil urea-N, exchangeable NH_4 -N and NO_3 -N content ($kg\ N\ ha^{-1}$) with depth for the Stockton fine sandy loam soil, 1996.....	54
3.8 Soil urea-N, exchangeable NH_4 -N and NO_3 -N content ($kg\ N\ ha^{-1}$) with depth for the Newdale clay loam soil, 1997.....	55
3.9 Soil urea-N, exchangeable NH_4 -N and NO_3 -N content ($kg\ N\ ha^{-1}$) with depth for the Stockton fine sandy loam soil, 1997.....	56
3.10 Contrast analysis and LS means standard error values for log-transformed soil N data for the Newdale clay loam soil.....	59
3.11 Contrast analysis and LS means standard error values for log-transformed soil N data for the Stockton fine sandy loam soil.....	60
3.12 Contrast analysis and LS means standard error values for log-transformed NH_3 -N, exchangeable NH_4 -N, NO_3 -N and urea-N as a percent of total N measured for the Newdale clay loam soil.....	63

3.13	Contrast analysis and LS means standard error values for log-transformed $\text{NH}_3\text{-N}$, exchangeable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and urea-N as a percent of total N measured for the Stockton fine sandy loam soil.....	63
4.1	Selected chemical and physical characteristics of soils used.....	70
4.2	Probability, F values and LS means standard error for log-transformed $\text{NH}_3\text{-N}$ data.....	72
4.3	Contrast analysis and standard error values for log-transformed 1996 $\text{NH}_3\text{-N}$ data.....	74
4.4	Contrast analysis and standard error values for log-transformed 1997 $\text{NH}_3\text{-N}$ data.....	74
5.1	Study periods for the 1996 and 1997 studies.....	83
5.2	Selected chemical and physical characteristics of soils used.....	84
5.3	Meteorological data collected during each study period.....	84
5.4	Probability values and standard errors of effect of treatment, irrigation, temperature and soil on total plant N and biomass of wheat.....	87
5.5	Plant biomass (g m^{-2}), contrast analysis values and LS means standard error for wheat.....	89
5.6	Plant N accumulation (g N m^{-2}), contrast analysis values and LS means standard error for wheat.....	90
5.7	Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Newdale clay loam soil, 1996.....	92
5.8	Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Stockton fine sandy loam soil, 1996.....	93
5.9	Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Newdale clay loam soil, 1997.....	94
5.10	Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Stockton fine sandy loam soil, 1997.....	95
5.11	Statistical analyses for log-transformed soil $\text{NO}_3\text{-N}$ and exchangeable $\text{NH}_4\text{-N}$ data, and $\text{NO}_3\text{-N}$ as percent of total soil N for 1996.....	97
5.12	Statistical analyses for log-transformed soil $\text{NO}_3\text{-N}$ and exchangeable $\text{NH}_4\text{-N}$ data, and $\text{NO}_3\text{-N}$ as percent of total soil N for 1997.....	98

LIST OF FIGURES

Figure	Page
2.1 Proposed mechanism of urease-catalyzed hydrolysis.....	6
2.2 Chemical structure of NBPT and NBPTO.....	27
3.1 Cumulative NH_3 -N loss from urea and UAN with and without irrigation and NBPT for two soils in May and July in 1996, minus controls.....	45
3.2 Cumulative NH_3 -N loss from urea and UAN with and without irrigation and NBPT for two soils in May and July in 1997, minus controls.....	46
3.3 Recovery of NH_3 -N, NO_3 -N, exchangeable NH_4 -N and urea-N as percent of total N measured in soil plus air for the Newdale clay loam soil.....	64
3.4 Recovery of NH_3 -N, NO_3 -N, exchangeable NH_4 -N and urea-N as percent of total N measured in soil plus air for the Stockton fine sandy loam soil.....	65
4.1 Cumulative NH_3 -N loss from urea fertilizer amended with NBPT (0.0, 0.05, 0.10 and 0.15% w/w), minus control for 1996 and 1997 studies.....	75

LIST OF ABBREVIATIONS

CWRS	Canadian Western Red Spring
NBPT	N-(n-butyl) thiophosphoric triamide
NBPTO	N-(n-butyl) phosphoric triamide
DAF	Days after fertilization
UAN	Urea ammonium nitrate
I	Irrigated
NI	Non-irrigated
NI+NBPT	Non-irrigated with N-(n-butyl) thiophosphoric triamide
I+NBPT	Irrigated with N-(n-butyl) thiophosphoric triamide
PVC	poly vinyl chloride

1. INTRODUCTION

Urea is currently the most popular nitrogen fertilizer in Western Canada (Agriculture and Agri-Food Canada 1999) as it is comparatively safe to handle and readily available in either liquid or granular form. However, NH_3 derived from surface-applied urea may be volatilized to the atmosphere if urea hydrolysis proceeds at or near the soil surface, thereby reducing total fertilizer N in the soil. In addition to reducing the efficiency of the fertilizer N application, NH_3 volatilization may affect air quality. Urea is the primary fertilizer source of NH_3 emissions to the atmosphere in Canada, estimated at 71 Gg N or 15% of total NH_3 emissions from agriculture in 1990 (Janzen 1999). The majority of volatilized NH_3 returns to the surface with rainfall as it is readily soluble in water, having a mean residence time in the troposphere of only 14 days (Schlesinger 1991). Ammonia can contribute to soil and surface water acidification, may induce toxicity in aquatic organisms and plants, or may stimulate eutrophication of water bodies and nutrient competition or exclusion in plants (Janzen 1999; McGinn et al. 1997). At high atmospheric concentrations ammonia may form NO_x (Isermann 1994) or be converted to the greenhouse gas nitrous oxide (Janzen 1999). Although approximately 80% of total agriculture NH_3 emissions are from livestock animals, contributions from mismanagement of urea fertilizers should also be considered as a source of atmospheric contamination.

The dynamics of NH_3 volatilization from surface-applied urea and the soil,

weather and management factors controlling NH_3 loss have been thoroughly investigated separately. However, the actual magnitude of a volatilization event under non-static field conditions where these factors interact is difficult to quantify and predict. Generally the potential for ammonia volatilization from surface application of urea increases with i) increases in soil temperature, ii) slow to moderate drying of a moist soil, iii) decreases in clay and organic matter content, or increased coarseness of soil texture, and iv) increases in soil pH (McInnes et al. 1986; Hargrove 1988; Clay et al. 1990; Watson et al. 1994b).

Zero or reduced tillage is increasing in popularity, practiced on an estimated 2.3 million acres of total seeded acres of cereals, oilseeds and peas in Manitoba in 1998¹. The payment of protein premiums for CWRS wheat has rekindled interest in in-crop N applications to elevate protein content (Grant and Flaten 1998). In-crop fertilization of perennial and forage crops is also practiced. Surface application of N fertilizer is preferred under these cropping systems as it avoids risk of seedling damage, does not disrupt root systems, compromise seed-bed quality or lead to loss of soil moisture, and reduces time, labour and energy costs compared to incorporation, subsurface banding or seed-row placement (Grant et al. 1996a). The potential for NH_3 loss may be increased with surface application of urea under these conditions where accumulation of organic material on soil surfaces may support high urease activity and may impede movement of urea into the soil with infiltrating water (Byrnes and Freney 1995).

The susceptibility of surface-applied urea to reduced use efficiency due to NH_3 volatilization and the declining availability of NH_4NO_3 in Western Canada have created the need for an alternate N source suitable for surface application under a range of

¹ Personal communication. B. Bradley. Manitoba North Dakota Zero Tillage Association. 7 - 31st Street. Brandon, MB. R7B 2J5

weather, soil and management conditions in the field. The potential risk of excessive NH_3 emissions to the atmosphere in localized areas from urea and manures is an additional incentive to identify an alternative N source.

Research spanning the last decade has shown amendment of urea with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) to be an effective means of improving the efficiency of surface-applied urea (Byrnes and Freney 1995; Bremner 1995). The inhibitor reduces the rate of urea hydrolysis and NH_3 formation, thereby decreasing the potential for NH_3 volatilization to the atmosphere. However, the contribution of NBPT to improved retention of fertilizer N in the soil, and hence availability to plants, is more difficult to evaluate and define due to the inherent variability in weather and soil conditions in the field.

In our studies, field experiments using lysimeters were conducted to evaluate the performance of NBPT under modified zero tillage management and under soil and weather conditions representative of the Black Soil Zone of Western Manitoba to assess the suitability of NBPT for use in Manitoba and similar areas. Studies were designed to investigate the capacity of NBPT to reduce NH_3 loss from surface applications of granular urea and liquid UAN when applied to two texturally different soils at two soil temperature and moisture regimes. The performance of NBPT was evaluated to determine its effect on i) the distribution and form of urea hydrolysis products in soil and ii) the amount of soil N available for crop uptake and growth. An additional component of this research was to identify an appropriate rate of application of NBPT when surface-applied with urea under variable field conditions.

2. LITERATURE REVIEW

2.1 Introduction

Urea is currently the most popular nitrogen fertilizer worldwide and has been for over two decades. The dominant fertilizer N sources in Canada are urea and anhydrous ammonia with 6×10^5 tonnes urea and 6.6×10^5 tonnes anhydrous ammonia used in the 1996/1997 calendar year (International Fertilizer Industry Association 1998). In Western Canada, 1998 retail sales of urea exceeded all other N sources, including anhydrous ammonia (Agriculture and Agri-Food Canada 1999).

Urea is an inert molecule ($\text{CO}(\text{NH}_2)_2$) which is enzymatically or chemically hydrolyzed to ammonium and carbon dioxide. The urease enzyme catalyses urea hydrolysis and is the typical pathway of urea degradation because chemical hydrolysis proceeds very slowly in comparison. Ammonium can convert to NH_3 which may be lost to the atmosphere if present near the soil surface. The activity of urease defines the rate of urea hydrolysis which establishes the extent of NH_3 formation in soil. Amendment of urea fertilizers with an urease inhibitor may reduce NH_3 volatilization losses from surface-applied urea by interfering with urease activity to slow the rate of urea hydrolysis (Yeomans 1991). The potential magnitude and duration of NH_3 volatilization and urease inhibitor performance are governed by soil physicochemical properties, environmental conditions and management practices.

2.2 The Urease Enzyme

2.2.1 Urease Structure and Hydrolysis Mechanism

Soil urease is inherently heterogeneous, composed of urease from plants, microorganisms and soil fauna (Skujins 1978). Microorganisms are commonly viewed as the dominant contributors to soil urease (Bremner and Mulvaney 1978; Lai and Tabatabai 1992). To understand the origin and properties of soil urease, it is useful to review the composition of microbial and plant ureases. The structure and catalysis mechanism of the urease enzyme (urea amidohydrolase EC 3.5.1.5) have been identified through comprehensive study of purified extracts of soybean and jack bean urease and several microbial ureases. The most extensively studied urease enzyme is that of jack bean (*Canavalia ensiformis*), first crystallized in 1926 by James Sumner (Andrews et al. 1984).

Blakeley and Zerner (1984) and co-workers (1980) as cited in Kolodziej (1994) developed the best available model for urease structure, identifying the essential constituents, hydrolysis catalysis mechanism and the catalytic role of nickel (Andrews et al. 1984) (Figure 2.1). Essential components of each active urease subunit at resting state are two Ni(II) ions, a carboxylate ion, a general base and a unique thiol of the cysteine residue. Modification of any single one of these essential components may render the entire enzyme inactive (Andrews et al. 1984) as observed with nickel removal from urease enzymes of some bacteria (Mobley and Hausinger 1989).

According to the model, the two Ni ions, a water coordinated Ni(II)_a and an OH-coordinated Ni(II)_b, are oriented opposite to each other at a maximal spacing of 6Å. Initially urea displaces the Ni(II)_a-coordinated water from the active site to form an O-coordinated complex with Ni(II)_a. During this step, the carboxylate ion stabilizes the

positively charged nitrogen of the urea-Ni(II)_a complex, promoting nucleophilic attack of the complex by the Ni(II)_b co-ordinated hydroxide ion. A general base aids in hydroxide addition to urea, resulting in the formation of a tetrahedral intermediate among urea and the two nickel ions, and the release of NH₄⁺. The active thiol group may serve as a general acid catalyst to release carbamate from the active site. Water then enters the active site and the enzyme resting state is reestablished (Kolodziej 1994).

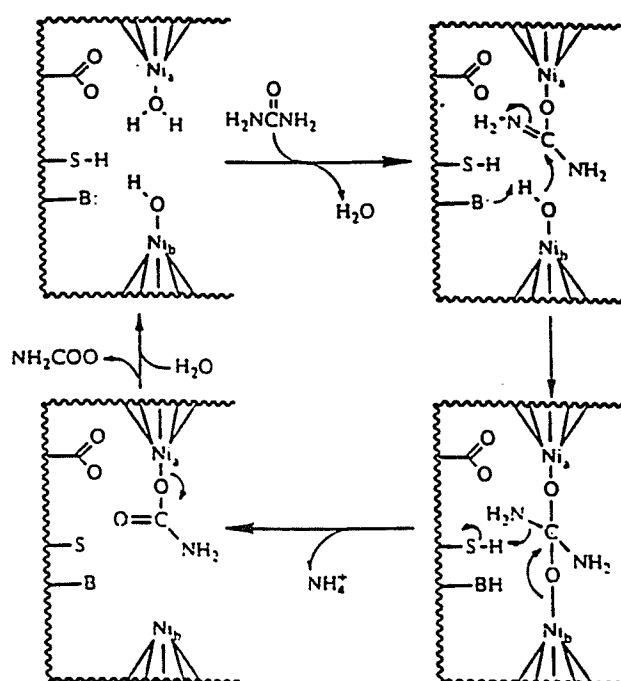


Figure 2.1 Proposed mechanism of urease-catalyzed hydrolysis (From Kolodziej 1994).

Purified microbial and plant ureases have a similar structural composition and therefore are likely to exhibit similar catalytic mechanisms. The purified jack bean urease is a homopolymeric hexamer of weight $M_r = 590,000$ arranged as two stacked trimers, having a total of 6 identical subunits of molecular weight $M_r = 90,777$ with one active site per subunit (Kolodziej 1994). By comparison, purified microbial ureases are generally lower in molecular weight, typically in the range $M_r = 200,000$ to $250,000$

(Mobley and Hausinger 1989) and are commonly heteropolymeric, composed of three non-identical subunits ($\alpha\beta\gamma$) of different molecular weights: $Mr_\alpha = 60,000-70,000$, $Mr_\beta = 10,000-17,000$ and $Mr_\gamma = 8,000-12,000$, with generally two Ni atoms per each α subunit (Kolodziej 1994). This heteromeric structure is typical for many bacteria, particularly gram negative bacteria, while some gram positive bacteria appear to contain only a single subunit type (Mobley and Hausinger 1989).

Similarities between plant (jack bean and soybean) and several bacterial urease protein sequences may be evidence that plant protein sequences evolved from bacterial protein sequences. Homology of aligned plant and bacterial protein sequences supports the concept that fusion of bacterial structural genes preceded formation of plant urease genes (Kolodziej 1994). The similarities in active sites and enzyme chemistry of both urease sources may also be evidence of this evolution.

2.2.2 Urease in Soil

The individual fractions of urease in soil, namely endocellular enzymes, free exoenzymes and bound enzymes, comprise the total potential urease activity in soil (Burns 1977). The relative contribution of each fraction depends on microbial activity and associated production of urease, rate of enzyme degradation, and the capacity of the soil to stabilize and protect the enzyme. The capacity of the soil to stabilize urease depends largely on soil structure and clay and organic matter content. For example, Paulson and Kurtz (1969) found bound, stable urease comprised 79-89% of the total soil urease present in the soils examined. Table 2.1 provides a conceptual overview of the components of soil urease.

Table 2.1 Conceptual view of components of soil enzymes (From Skujins 1978).

Origin	Enzymatic activity in soil							Endocellular enzymes of proliferating microorganisms, plant roots, soil fauna
	Abiotic enzymes							
	Accumulated enzymes					Continuously released extracellular enzymes		
	Bound to microbial cellular components			Not associated with cellular components		From microorganisms	From plant roots	
	IN NON-PROLIFERATING CELLS	In intact dead cells	In cellular fragments	Originating from microorganisms and soil fauna				
				Endocellular enzymes from disrupted cells	Extracellular enzymes			
In liquid phase								
Location in soil	BOUND TO SOIL COMPONENTS						IN ORGANISMS	

Major components found experimentally in soils are capitalized.

Urease is continually added to the soil via excretion from microorganisms or release upon cell lysis, and via plant root exudation or plant residue additions to soil. At the same time, urease is continuously removed from the soil environment. Endocellular urease is present in viable cells and non-lysed dead cells. Cell lysis or cellular excretion results in free (in soil solution) or extracellularly attached urease. Free extracellular urease is subject to enzymatic proteolysis, microbial degradation and physicochemical-induced denaturation. Extracellular urease may also be chemically and physically altered and assimilated within soil organo-clay complexes. Endocellular urease may also be intimately associated with soil colloids through occlusion of intact microbial cells (Lai and Tabatabai 1992). Bound or occluded urease is typically more recalcitrant and stable as the colloid pore structure provides protection from larger proteolytic enzymes and microorganisms while permitting substrate diffusion to bound urease (Burns 1977).

Urease-soil-organic matter colloid bonds may be chemical or physical in nature (Weetall 1975 in Lai and Tabatabai 1992). Ionic, covalent or hydrogen bonding,

adsorption, and cross linking are means of chemical enzyme immobilization. Physical mechanisms include entrapment and microencapsulation of urease or microbes in the complex during humus formation (Burns et al. 1972 in Pettit et al. 1976). The presence of coatings such as aluminum hydroxides on clay surfaces may reduce the capacity of a mineral to bind urease by limiting enzyme access to structural "holes" or reactive surfaces (Gianfreda et al. 1992). Conversely, the association of organic matter with soil may enhance the suitability of the surface for urease stabilization (Lai and Tabatabai 1992).

2.2.3 Urease Activity

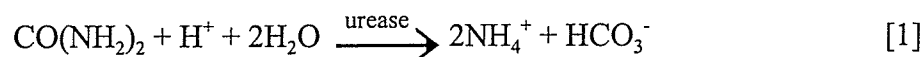
Urease activity is defined as the amount of urea hydrolyzed per unit soil per unit time. This measurement represents the potential urease activity for a specific urea concentration applied under a unique set of soil, environment and management conditions. The potential activity of each soil urease fraction is a function of both time and soil characteristics (Pettit et al. 1976). For example, consistent microbial activity over time maintains a constant supply of urease to the soil. Properties of the soil environment, both stable and variable, regulate urease production, persistence, functioning, and thus overall potential urease activity in the soil (Kissel and Cabrera 1988). Changes in weather and management will lead to changes in substrate (urea) concentration, organic matter content and distribution, soil pH, soil temperature, and soil moisture (Kissel and Cabrera 1988). Cation exchange capacity, sand, silt and clay fractions, clay-organo complexes, and soil surface area are more stable properties of the soil environment, being a product of the soil mineralogy and parent material (Bremner and Mulvaney 1978). Detailed statistical analyses for numerous soils repeatedly identified organic carbon, total nitrogen and cation exchange capacity as the soil factors most

strongly related to potential urease activity (Reynolds et al. 1985; Baligar et al. 1991; Bremner and Mulvaney 1978).

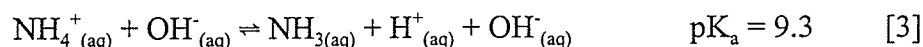
Response of soil urease to substrate follows a first order reaction, increasing as substrate concentration increases until substrate is no longer limiting. Therefore, soils with relatively high potential urease activity, such as fine textured soils, require more substrate to achieve enzyme saturation. Urease activity may initially be lower in localized areas of urea fertilizer application, increasing over time as urea diffuses outward and becomes more accessible to the soil urease (Kissel and Cabrera 1988). Uniform mixing of urea with soil improves the substrate-urease contact (Singh and Nye 1984; Tabatabai and Bremner 1972), increasing the rate of activity.

2.3 Reactions of Urea and Urea Hydrolysis Products in Soil

The urease catalyzed hydrolysis of urea yields two ammonium ions:

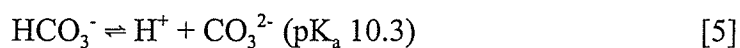


Ammonium and ammonia establish equilibrium in soil solution:



$$[\text{NH}_3] = K \frac{[\text{NH}_4^+]}{[\text{H}^+]} \quad [4]$$

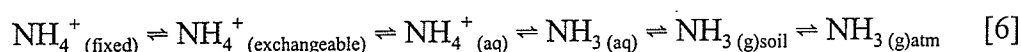
In soil, inorganic C from urea can react to generate proton(s), reducing the total proton consumption of urea hydrolysis (Koelliker and Kissel 1988). Above pH 8.2, the majority of urea-derived inorganic C is present as HCO_3^- and a portion is present as CO_3^{2-} as illustrated in Eq. [5], reducing the total H^+ consumption from two to less than 1 H^+ per mole urea hydrolyzed (Kissel et al. 1988).



The tendency towards Eq. [5] also increases if $[\text{CO}_3^{2-}]$ and $[\text{Ca}^{++}]$ in soil solution are sufficient to exceed the CaCO_3 solubility product and CaCO_3 precipitates, decreasing net consumption of H^+ even further. The net result is a reduction in the pH increase accompanying urea hydrolysis once pH exceeds 8.2 which should reduce the extent of NH_3 formation according to Eq. [3] and Eq. [4].

Equation [4] illustrates $[\text{NH}_4^+]$ and soil pH as the dominant forces driving NH_3 formation. Rapid hydrolysis of urea results in localized areas of high $[\text{NH}_4^+]$ and thus a high potential for NH_3 formation. Initially following urea hydrolysis the soil pH increases and approaches the ammoniacal-N equilibrium pK_a favouring increased $[\text{NH}_3]$. The potential for NH_3 formation gradually diminishes with outward diffusion of NH_4^+ and pH decrease via proton release during ammoniacal N oxidation to NO_3^- and urea-derived CO_2 reaction with water (Eqs. [2] and [5]). The soil pH is also reduced as H^+ generated during NH_3 formation accumulates in the soil.

Ammonium in soil is subject to various physical transformations and transport reactions (Eq. [6]) (Sherlock and Goh 1985). The nature or chemistry of the soil solution as well as transport processes in the soil and at the soil/air interface govern the extent of ammonia volatilization.



Ammonium in soil is fixed in clay matrices, held in an exchangeable form on the surfaces of clay and clay-organo complexes, and present in the soil solution [6]. Exchangeable NH_4^+ and solution NH_4^+ are removed from the equilibrium system via plant uptake, and microbial immobilization and nitrification. An equilibrium between $[\text{NH}_4^+_{(\text{aq})}]$ and $[\text{NH}_3_{(\text{aq})}]$, $[\text{NH}_3_{(\text{aq})}]$ and $[\text{NH}_3_{(\text{g})\text{soil}}]$, and between soil and atmospheric gaseous NH_3 establishes. Removal of NH_4^+ from the system reduces $[\text{NH}_4^+_{(\text{aq})}]$ and $[\text{NH}_3_{(\text{aq})}]$. The lower concentration of $\text{NH}_3_{(\text{aq})}$ reduces $[\text{NH}_3_{(\text{g})\text{soil}}]$, and thus the concentration gradient between gaseous NH_3 in the soil and the atmosphere.

The difference between $[\text{NH}_3_{(\text{g})\text{soil}}]$ and $[\text{NH}_3_{(\text{g})\text{atm}}]$ determines NH_3 volatilization losses (Koelliker and Kissel 1988). Volatilization occurs along a positive diffusion gradient driven by high $[\text{NH}_3_{(\text{g})\text{soil}}]$ located a short distance from the soil/air interface. Thus, a decrease in the concentration gradient between $\text{NH}_3_{(\text{g})\text{soil}}$ and $\text{NH}_3_{(\text{g})\text{atm}}$ results in decreased NH_3 volatilization. The ultimate control of NH_3 loss is the partial pressure difference between $\text{NH}_3_{(\text{g})\text{soil}}$ and $\text{NH}_3_{(\text{g})\text{atm}}$ at the soil/air interface with high NH_3 volatilization when the pressure difference is high (Nelson 1982).

2.4 Factors Affecting Urea Hydrolysis and Ammonia Volatilization

The potential for NH_3 volatilization is established by the rate of urea hydrolysis or urease activity and subsequent conversions, and by the factors governing ammonia volatilization. The combination of soil physicochemical parameters, weather or environmental components, and management practices at the application site establishes what percentage of urea-N may be lost via NH_3 volatilization (Tisdale et al. 1993).

2.4.1 Soil Properties

The fundamental soil characteristics influencing urea hydrolysis and NH_3 volatilization dynamics are cation exchange capacity (CEC), organic matter content, urease activity, soil pH, titratable acidity and soil texture (Nelson, 1982; Hargrove 1988; Kissel and Cabrera 1988; Watson et al. 1994b). Urease activity, soil pH and titratable acidity control the rate of urea hydrolysis and NH_3 formation. Titratable acidity, or H^+ buffering capacity, is the capacity of a soil to resist pH increase via H^+ release to soil solution. Soil texture, CEC and organic matter affect the movement of urea and ammoniacal N in soil and NH_4^+ retention. Toews and Soper (1978) found losses were greatest from a high pH soil with a low CEC and observed higher loss in the presence of free carbonates. Watson et al. (1994b) explained 90.6% of total variation in NH_3 loss from 16 soils with the soil properties titratable acidity, pH in water, urease activity and CEC. Urease activity was positively and highly significantly correlated with organic C, total N and CEC and to a lesser degree with clay, sand and surface area for 21 diverse Iowa soils where organic matter content explained most variation in urease activity (Zantua et al. 1977). Organic matter content may indicate if urease is primarily in the

form of stabilized urease-organic matter complexes, or as free living endocellular or exocellular urease.

The CEC, which is dependent on soil texture and organic matter content, provides a sink for NH_4^+ and reduces $[\text{NH}_{3(\text{aq})}]$ [6]. Coarse textured soils characteristically have a lower CEC and organic matter content, larger more uniformly distributed soil pores, and lower water holding capacity than clay-rich soils. Low CEC and organic matter content favour increased NH_4^+ concentration in the soil solution which drives the equilibrium towards NH_3 formation. The resultant elevated NH_3 levels, in combination with the large pore size, uniform pore matrix and low water holding capacity of coarse soils, create a positive gradient for NH_3 diffusion to the atmosphere. Drying of a coarse textured soil results in upward movement of urea and water towards the surface as water evaporates from the soil surface. As evaporation continues, urea and NH_3 concentrate near the soil surface, increasing the positive gradient between $\text{NH}_{3(\text{g})\text{soil}}$ and $\text{NH}_{3(\text{g})\text{atm}}$ and the potential for volatilization. Fine textured soils with increased clay content have smaller pores, higher CEC, organic matter content and water holding capacity than coarse textured soils and are subsequently less conducive to volatile loss of ammonia than sandy soils. Al-Kanani et al. (1991) found differences between losses from a moist and a dry soil were reduced with higher clay content, because NH_4^+ absorption capacity increases with clay content. However, the higher tortuosity of fine textured soils can lead to a reduced rate of infiltration of surface-applied urea and its reaction products, which may result in significant NH_3 loss from the surface. The reduction in loss as a function of ability of urea to diffuse away from the point of application has been observed by others (Christianson et al. 1993; Carmona et al. 1990).

Soils with high clay content support a high and more stable urease activity. High

organic matter content and microbial activity, a stable oxygen and water environment, and a complex pore matrix provide an optimal environment for urease production, protection, stabilization and hence, activity. Conversely, a coarse textured soil with low clay content would support a more dynamic urease activity, corresponding to periods of improved soil moisture, which stimulates microbial activity and urease production. The urease activity of this soil type would likely be more sporadic as the bulk of urease would be unprotected endocellular and extracellular urease due to the low capacity of a coarse soil for enzyme protection and stabilization.

Urease activity may vary with soil pH. Generally, urease activity is maximal in the pH range 6.5-7.5 (Bremner and Mulvaney 1978; Kolodziej 1994). Free extracellular urease is more sensitive to pH fluctuation than stabilized soil urease, as the soil and organic matter moderate the environment in which bound urease functions (Baligar et al. 1991). Urea concentration may complicate the effect of pH on urease activity. Singh and Nye (1984) observed greatest rates of urea hydrolysis at a pH of 7.8 and pH of 4.9 for low and high urea concentrations, respectively.

Soil solution pH and rate of NH_4^+ conversion, consumption or diffusion from point of application will influence the rate and duration of NH_3 formation (Singh and Nye 1984). Soil pH establishes the ratio of NH_3 to NH_4^+ in soil solution (Eqs. [3] and [4]) and the persistence of ammoniacal N in soil solution in the fertilizer microsite. Proton consumption during urea hydrolysis restricts NO_3^- formation as high $[\text{NH}_3]$ inhibits nitrification of NO_2^- to NO_3^- . Also, as pH increases, $[\text{NH}_3]$ and the potential for NH_3 volatilization increase if NH_3 concentrates near the soil surface.

High pH soils are more prone to NH_3 loss than low pH soils (Hendrickson and Douglass 1993). High buffering capacity, or high $[\text{H}^+]$ of low pH soils restricts pH

increase of urea hydrolysis by releasing protons to soil solution as they are consumed during hydrolysis. Conversely, on a high pH soil, abundant base cations such as Ca^{++} and Mg^{++} restrict the pH decrease accompanying $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$, increasing the extent of NH_3 formation. However, findings are not always consistent and may be affected by other soil properties such as texture (Christianson et al. 1993).

2.4.2 Environmental Conditions

Weather conditions affect both the soil and atmospheric environment, and often produce short term fluxes in soil temperature and water content. Temperature, relative humidity, wind speed, soil water content and rainfall patterns (timing, duration, frequency and quantity of precipitation) (Hargrove 1988; Kissel and Cabrera 1988) establish the extent of granular urea dissolution, potential urease activity and associated rate of hydrolysis, as well as the magnitude, duration and pattern of NH_3 volatilization. The magnitude of NH_3 loss ultimately depends on soil water conditions and the influence of temperature on these conditions.

The influence of environmental factors on urea hydrolysis and NH_3 loss has been intensely studied in laboratory settings, but the complex interactions and inherent interrelatedness of these factors in the field is more difficult to elucidate and limits the ability to accurately predict the potential magnitude of NH_3 volatilization from a field (Ferguson and Kissel 1986; McInnes et al. 1986; Black et al. 1987; Reynolds and Wolf 1987; Clay et al. 1990; Al-Kanani et al. 1991; Watson et al. 1994a; Grant et al. 1996b). For example, a similar rainfall pattern may either amplify or minimize the extent of NH_3 loss, depending on the initial soil water content (Bouwmeester et al. 1985). Frequent small rainfall events on a soil that was initially dry may prolong the duration of NH_3

volatilization with loss occurring in bursts. In contrast, small rainfall events on a wet soil may increase downward movement of urea and ammoniacal N, reducing total NH_3 loss.

2.4.2.1 Soil and Air Temperature. Temperature influences urea hydrolysis and NH_3 loss a number of different ways. 1) Urease activity, and thus rate of urea hydrolysis and NH_3 formation, increase with increases in temperature within the range encountered during the growing season. Moyo et al. (1989) and Xu et al. (1993) found the Arrhenius equation appropriately described the urease activity/temperature relationship in the 5 to 45°C temperature range. Soil urease activity has been observed at -10 and -20°C (Bremner and Zantua 1975), which may have ramifications for NH_3 loss from fall-applied urea fertilizer. 2) The diffusion, and thus mobility of urea and ammoniacal N, increases with increases in temperature. The direction of diffusion may be upward under moderate soil drying or downward if the soil is moist or receives rainfall. Zhengping et al. (1996) observed some upward NH_4^+ diffusion when urea was placed 3-4 cm below the soil surface at 10%, but not 20% soil moisture content. 3) Both the $\text{NH}_4^+/\text{NH}_3$ equilibrium [3] and the ammoniacal N transformation/transport reactions [6] shift toward $\text{NH}_{3(g)}$ formation as temperature increases. The higher concentration of $\text{NH}_{3(g)\text{soil}}$ creates a large concentration gradient between $\text{NH}_{3(g)\text{soil}}$ and $\text{NH}_{3(g)\text{atm}}$ leading to significant NH_3 volatilization (Nelson 1982; O'Deen and Follet 1992). 4) Water evaporation or water flux from the soil surface increases with increases in temperature. McInnes et al. (1986) and Clay et al. (1990) reported diurnal patterns of maximum NH_3 loss during periods of higher temperature and lower soil water content. As increased temperature dries the soil, soil water carries NH_3 and urea upwards. When the water evaporates, ammonia concentrates near the surface, creating a positive gradient between $\text{NH}_{3(g)\text{soil}}$ and $\text{NH}_{3(g)\text{atm}}$.

Cumulative ammonia loss and rate of loss are greater under warm moist conditions than under hot dry conditions which promote slow drying and rapid drying, respectively (Beyrouthy et al. 1988).

2.4.2.2 Soil Water Flux. Relative humidity, wind velocity, soil water content and rainfall patterns are dynamic and closely related components of the soil and atmospheric environment, defining the soil water flux of a system. Soil water content, or water potential, sets the stage for urea dissolution and hydrolysis. Sufficient soil moisture is required for granular dissolution which must occur for urea hydrolysis to proceed. Urease activity is inversely proportional to negative water potential. As negative water potential decreases, that is as the soil moisture increases, the rate of hydrolysis increases. Kissel and Cabrera (1988) observed optimal urease activity around -20 kPa soil water potential, lowering slightly as the soil approached saturation and decreasing markedly as the soil neared dryness for both a very fine sandy loam and a clay soil. Incident rain transports urea downward. Fenn and Miyamoto (1981) observed urea movement to lag behind water movement only slightly. The depth of downward movement is proportional to the rate, amount and duration of rain intercepting the soil. Conversely, evaporation of water from the soil induces mass flow of urea towards the soil surface (Ferguson and Kissel 1986) to increase the amount of urea near the soil surface. Relative humidity and wind velocity establish the rate of soil drying or water evaporation, and thus the extent of upward transport of urea.

Volatile loss of NH_3 is maximum under conditions conducive to urea dissolution and hydrolysis but not to transport of urea and NH_3 away from soil surface, or when conditions promote upward movement of water and urea or NH_3 along an evaporative

stream. Such conditions occur when 1) initial soil water content is adequate for urea dissolution and hydrolysis but insufficient for downward diffusion of urea, or is subject to moderate drying (McInnes et al. 1986). Dissolution and hydrolysis occur at water contents ranging from above field capacity (-0.1 MPa) to near permanent wilting point, with hydrolysis proceeding until near dryness is reached (-1.4 MPa) (Black et al. 1987; Al-Kanani et al. 1991); 2) initial soil water content is low and relative humidity is high (80-95%) or rainfall events are small and frequent. Specific humidity, or actual water content in air may be a more important indicator of atmospheric moisture than relative humidity. Beyrouthy et al. (1988) observed increased urea hydrolysis and NH_3 loss once specific humidity was high enough for dissolution, while relative humidity did not accurately reflect air moisture status.

If heightened evaporation or moderate drying occurs after an accumulation of NH_3 , volatilization losses may be very high (Bouweemester et al. 1985; Reynolds and Wolf 1987). Ammonia has an extremely high affinity for water. In soil solution NH_3 is closely associated with water through hydrogen bonding, being present as $2\text{NH}_3 \cdot \text{H}_2\text{O}$ or $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Cotton and Wilkinson 1962). Due to this strong affinity, NH_3 preferentially moves with soil water. As soil water evaporates into the atmosphere, $\text{NH}_{3(g)}$ transported with water concentrates near the soil surface. Wind at the soil surface also reduces the thickness of the boundary layer directly above the surface which reduces $[\text{NH}_{3(g)\text{atm}}]$ at the soil/air interface. The overall result is a high $[\text{NH}_{3(g)}]$ in soil a short distance from the soil/air interface creating a strong positive gradient for NH_3 volatilization.

Conversely, NH_3 volatilization is minimal if environmental conditions either prevent urea dissolution and hydrolysis, or facilitate downward movement of urea and hydrolysis products to depth in soil (McInnes et al. 1986) such as when 1) the soil is

initially dry followed by a prolonged or heavy rainfall where dissolution is prevented prior to soil wetting; 2) the soil is initially wet, permitting urea and ammoniacal N diffusion into the soil; 3) a large rainfall event or a number of smaller successive events occur directly following urea application; or 4) a moist soil dries rapidly before granule dissolution or hydrolysis proceeds, where intact granules are stranded on the soil surface, or where upward movement of urea with water ceases. Bouwmeester et al. (1985) found a 2.4 cm rain immediately following urea surface application was equivalent to banding urea at a depth of 2.5 cm. However, the benefits of a rainfall event diminish with increased delay following urea application if initial soil moisture content is sufficient for hydrolysis and NH_3 formation to proceed (Black et al. 1987).

The extent of NH_3 volatilization following a rainfall event may also be related to soil diffusion and retention characteristics (Christianson et al. 1993). The rate of urea hydrolysis and NH_3 volatilization is more extreme in coarse textured soils due to the rapid wetting/drying capacity or water flux and lower capacity for NH_4^+ retention. The large uniformly distributed pores of a coarse textured soil permit rapid movement of water and air and extend the depth of soil subject to air and water fluxes. If urea is transported far enough with incident rain or irrigation water to limit upward movement of urea and NH_3 with soil drying, urea hydrolysis proceeds at depth and NH_3 volatilization losses are negligible. Conversely, a light rainfall may be insufficient to move urea beyond the "flux" zone and urea is rapidly transported back to the surface with soil drying where NH_3 concentrates as soil water evaporates, leading to high NH_3 loss. The complex pore matrix of a fine textured soil holds water and ammoniacal N more tightly in the soil and restricts water flux. Consequently NH_3 is less susceptible to loss on a clay soil than a coarse soil, as soil drying is restricted to the surface layer due to the high matric potential of clay

soils. However, urea and NH_3 must diffuse below this drying layer for losses to be low.

2.4.3 Management Factors

Management practices in agricultural systems such as tillage frequency, residue management, and the quantity, placement, timing and form of urea fertilizer applied influence ammonia volatilization potential as they modify the soil environment both physically and chemically.

2.4.3.1 Tillage Practice and Residue Management. Urease activity is a function of soil organic matter content and the amount and distribution of organic residue additions, the extent and duration of which is influenced by residue management practices (Reynolds et al. 1985). Cultivation distributes plant residues within the soil to the depth of tillage, improving soil-residue contact. Microbial activity also increases with residue incorporation as organic material is a microbial substrate. Both plants and microbes are primary sources of urease; therefore, increasing the concentration of each at depth with tilling also increases urease concentration and activity within the depth of tillage. In a cultivated soil, urease activity is predominantly associated with free extracellular and endocellular urease, as repeated disturbance and aggregate destruction limits the extent of stable urease-colloid bonding.

Urease activity in non-cultivated soils is greater than that of cultivated soils, but is concentrated in the upper 0 to 10 cm of soil. Dick (1984) observed 3 to 5 times higher urease activity at the surface of non-cultivated versus cultivated soils for two different soils. Under zero tillage, crop residues and plant roots accumulate on and below the soil surface, respectively. Microbial activity and hence urease production and activity

concentrates near the soil surface where labile organic material accumulates. Limited disturbance of soil colloids and aggregates leads to a greater proportion of protected soil urease. Soil aggregates and colloids protect the enzymes and microbes from predators, which in turn encourages elevated urease activity.

Retaining crop residues on the soil surface modifies the temperature and moisture environment of the surface where urea is applied, supports high urease activity, and obstructs movement of surface-applied urea into the soil, particularly solution urea as it is absorbed by the residue, all of which may promote rapid hydrolysis and substantial NH_3 loss (Hargrove 1988). Residue urease activity, associated with organic matter and microorganisms, is much greater than urease activity in soil. Urease activity in corn and wheat residues have been reported to exceed soil urease activity by approximately 47 (Beyrouthy et al. 1988) and 20 (McInnes et al. 1986) times, respectively. Beyrouthy et al. (1988) measured NH_3 losses of 35 and 7% during a 20 day study from urea surface-applied to a no-till and conventional till soil, respectively.

If urea moves or is placed below the residue cover to be in direct contact with the soil surface, NH_3 volatilization potential is reduced (Clay et al. 1990). The residue-covered soil environment is cooler, moister and less dynamic than that of a bare soil, with the extended boundary layer creating a more static atmospheric environment directly above the soil surface. The residue layer creates a physical boundary which restricts the exchange of NH_3 formed in the interlayer air with the greater atmospheric air. Also, accumulation of $\text{NH}_{3(g)}$ in the interlayer is limited as the cool, moist soil environment promotes downward movement of urea.

2.4.3.2 Urea Fertilizer Placement, Quantity, Timing and Form. Ammonia losses from urea fertilizers can be avoided by subsurface placement which reduces the volatilization gradient between $\text{NH}_{3(g)\text{soil}}$ and $\text{NH}_{3(g)\text{atm}}$ (Bouwmeester et al. 1985).

Subsurface placement also provides an opportunity for most of the ammoniacal N to be adsorbed as NH_4^+ . Zhengping et al. (1996) reported limited NH_4^+ at the soil surface from urea placed in soil columns 3-4 cm below the soil surface, particularly under moist soil conditions. However, under reduced or zero tillage, subsurface placement of urea is undesirable due to the accompanying soil disturbance.

Concentrating surface applications of urea granules in bands as opposed to broadcasting may reduce NH_3 volatilization. Applying urea fertilizer in bands restricts urease contact and increases the total amount of water required per given area for granule dissolution and hydrolysis. As a result, the rate of hydrolysis and NH_3 formation is reduced which allows more time for incident rainfall to transport urea away from the soil surface. In support of this, Toews (1971) observed in laboratory experiments that as the concentration of urea increased, the percent of N lost as NH_3 decreased. Losses at 24 hours were 85, 65 and 42% of applied N at 25, 100 and 300 ppm urea-N. In their review, Mulvaney and Bremner (1981) reported larger quantities of water were required to completely hydrolyze higher concentrations of urea in some studies. Surface band placement in zero tillage, where surface residues accumulate, may also reduce immobilization losses of N by decreasing microbial contact with the fertilizer. However, if surface soil moisture is adequate for urea hydrolysis to proceed at the soil surface, the duration and total magnitude of NH_3 loss may be higher with this placement as NH_3 is concentrated in a smaller area and thus is more susceptible to loss if formed near or at the soil surface.

Patterns of ammonia loss from liquid urea ammonium nitrate (UAN) are similar to loss patterns from granular urea, although on a smaller scale, likely because UAN is only 50% urea-N. Unlike granular urea, dissolution of UAN is not required and hydrolysis can commence immediately after UAN application, even under dry conditions. Under zero tillage, surface-applied UAN may be readily absorbed by surface residues. This process may increase NH_3 volatilization as hydrolysis then occurs on the residue surface where environmental conditions are more conducive to NH_3 volatilization than at the soil surface below the residue cover. Concentrating UAN in surface bands ("dribble" application) may reduce NH_3 loss as losses tend to be higher with spray applications of liquid N sources (Hargrove 1988). Fairlie and Goos (1986) found NH_3 loss from dribble applications were consistently lower than from spray applications of UAN applied at rates ranging from 170 to 190 kg N ha⁻¹. Al-Kanani and MacKenzie (1992) reported NH_3 losses from UAN of 0.8 to 9.5% of applied N, with lower losses from conventional tillage than zero tillage due to residue accumulation in the latter. The NH_4NO_3 component of UAN has an acidic reaction zone which should restrict the pH increase accompanying urea hydrolysis and thus should also contribute to reducing overall NH_3 loss from UAN.

Timing fertilizer applications to coincide with periods of adequate rainfall, moderately high soil moisture and cool soil temperature may reduce NH_3 volatilization by promoting diffusion of urea and ammonia away from the point of application and slowing the rate of hydrolysis, while reducing soil drying at surface (Malhi et al. 1996). Irrigation immediately following surface application will be similarly effective by moving urea into the soil.

The efficiency of urea surface applications may also be improved by modifying urea fertilizer or by co-application with various compounds to directly interfere with

urease-urea contact, urease activity or the soil chemistry. Coating urea granules with substances such as sulphur restricts urease-urea contact and slows granule dissolution (Gould et al. 1986), thereby slowing the rate of hydrolysis. Increasing the size of urea granules (Nommik 1973) may have an effect similar to increasing urea concentration by slowing dissolution and hydrolysis. Applying urea with acidic compounds such as phosphates (Fan and Mackenzie 1993) or highly soluble Ca and Mg salts (Evangelou 1990) can modify soil pH to restrict the pH increase accompanying urea hydrolysis which in turn restricts NH_3 formation. However, the suitability of this practice depends on soil chemical properties. For example, phosphate is immobile and readily precipitates with Ca in alkaline soils; thus, plant availability of surface-applied P will be limited and the pH effect will be of short duration.

Treating urea with a urease inhibitor may reduce NH_3 loss by delaying and/or lengthening the hydrolysis process, thereby retarding NH_3 formation and enabling downward movement of urea. A vast array of herbicides, insecticides, fungicides and other compounds, such as hydroquinone, have been tested as urease inhibitors (Mulvaney and Bremner 1981; Medina and Radel 1988; Yeomans 1991; Bremner 1995). To date, the most promising compound for inhibition of soil urease activity is the phosphoroamide N-(n-butyl) thiophosphoric triamide (Bremner 1995).

2.5 The Urease Inhibitor N-(n-butyl) Thiophosphoric Triamide

Manipulating the dynamics of urea hydrolysis with urease inhibitors has attracted much interest, with recent developments identifying phosphoroamides as an effective group of inhibitors (Yeomans 1991), particularly N-(n-butyl) thiophosphoric triamide

(NBPT) (Chai and Bremner 1987; Bremner et al. 1991; Byrnes and Freney 1995). The high capacity of NBPT to reduce NH_3 loss from surface applications of urea fertilizers has been reported in a number of field and laboratory studies across a range of concentrations (Christianson et al. 1990; Carmona et al. 1990; Christianson et al. 1993; Watson et al. 1994ab; Vittori Antisari et al. 1996; Grant et al. 1996b). Bremner and Chai (1989) reported NBPT (0.47% w/w) on average decreased NH_3 loss from 52 to 5% when soils were incubated for 14 days, where 59% urea-N remained with NBPT but 0% with unamended urea. For NBPT to significantly reduce NH_3 loss, there must exist a strong potential for NH_3 volatilization in the absence of the inhibitor. Therefore, NBPT benefit is more readily observed with controlled experiments where conditions are optimal for high NH_3 loss as compared to evaluation in the field where conditions are not always conducive to NH_3 volatilization.

2.5.1 Mechanism of Urease Inhibition

N-(n-butyl) thiophosphoric triamide itself is a weak inhibitor of urease activity. Once in contact with soil, NBPT converts to its oxon analog N-(n-butyl) phosphoric triamide (NBPTO), which is a strong inhibitor of urease activity in soil (Creason et al. 1990). Oxygen is required for this conversion which does not proceed under saturated or anaerobic conditions (Keerthisinghe and Freney 1994). McCarty et al. (1989) found NBPT was a poor inhibitor of pure microbial and plant urease in purified extracts but an effective inhibitor of soil urease. In the soil, inhibition persisted as NBPT degraded to NBPTO, while the absence of oxygen in the purified extracts prevented NBPTO formation and thus any pronounced urease inhibition.

N-(n-butyl) thiophosphoric triamide and NBPTO are classified as structural

analogs of urea, possessing bond angles and lengths similar to urea which enable the compounds to occupy the urease enzyme active site to inhibit urea hydrolysis (Byrnes and Freney 1995) (Figure 2.2). Urease inhibition is complete with the formation of a diamidophosphate-urease complex where NBPT occupies the enzyme active site, inactivating the enzyme and precluding urea hydrolysis. N-(n-butyl) thiophosphoric triamide restricts hydrolysis for several days, delaying the period of maximum NH_3 loss (Watson et al. 1994a; Grant et al. 1996b) and improving the opportunity for rainfall to move urea into the soil to restrict NH_3 loss (Hendrickson 1992).

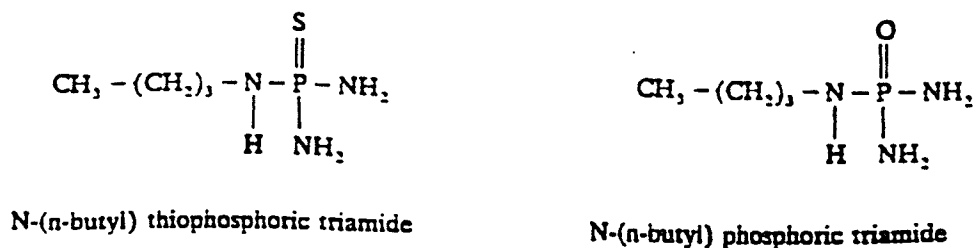


Figure 2.2 Chemical structure of NBPT and NBPTO.

2.5.2 Performance and Suitability of NBPT for Agricultural Use

To qualify as an urease inhibitor for agricultural purposes, a compound must satisfy a set of criteria (Medina and Radel 1988; Grant and Bailey 1997). The compound must 1) specifically and persistently inhibit urease activity and be stable in urea fertilizer, 2) not adversely affect environment health, crop health or crop consumer health, 3) inhibit urease activity over a range of soil and environment conditions for a suitable duration at a reasonable concentration, and 4) be cost effective over the long-term. N-(n-butyl) thiophosphoric triamide, marketed as Agrotain by IMC-Global, meets the criteria, is registered for agricultural use in the USA, and was registered for use in Canada in

March 1999.

The effectiveness of NBPT is a function of both the rate of conversion to NBPTO, which is affected by soil constituents which catalyze the thio-oxon conversion, and the stability of NBPT and its derivative in soil (Christianson et al. 1990). Although NBPTO is the dominant inhibitory compound and inhibition by NBPTO is of greater magnitude than that of NBPT when tested in pure enzyme assays (Keerthisinghe and Blakeley 1995), the total capacity for urease inhibition is greater with NBPT than with NBPTO. Hendrickson and Douglass (1993) related this inhibitory capacity to the enhanced persistence of a larger quantity of NBPTO derived from NBPT than pure NBPTO. Although NBPT conversion to NBPTO commences almost immediately following application to soil (McCarty et al. 1989), the disappearance of pure NBPTO is more rapid than that of NBPTO formed from NBPT degradation. Also, because NBPT is more persistent in soil than NBPTO, NBPT-derived NBPTO and inhibitory performance will persist in the soil for a longer time, as it is formed over time in the soil. Hendrickson and Douglass (1993) recovered NBPT (0.5% w/w) and NBPTO from NBPT up to 2 weeks after application to an incubated soil (pH 6.9), while NBPTO degradation was complete within 8 days after application. The rate of disappearance decreased as initial NBPT concentration increased.

The persistence of urease inhibition may also be related to the similarity of urea and NBPT/NBPTO movement in soil. Christianson and Howard (1994) observed movement of NBPT and NBPTO closely matched that of urea on soil thin-layer chromatography plates in the laboratory. Over time NBPT movement lagged slightly behind urea, which the authors attributed to the concurrent conversion of NBPT to NBPTO.

The relatively rapid degradation of NBPT and NBPTO in soil limits the duration of any negative health effects on the environment, phytotoxic effects, or health effects to crop consumers. N-(n-butyl) thiophosphoric triamide toxicity, as presented in the commercial product information guide, is very low for aquatic organisms and does not affect soil bacterial populations (Anonymous 1996). Incidence of leaf-tip necrosis at higher concentrations of NBPT appears to be due to accumulation of toxic levels of urea in plant tissue rather than NBPT-induced toxicity (Bremner and Krogmeier 1988; Krogmeier et al. 1989).

As NBPT interferes with the actual hydrolysis process, soil and environmental factors which affect urea hydrolysis and movement of urea and NH_4^+ will also impact on the performance of NBPT as a urease inhibitor. For example, a rainfall event in conjunction with NBPT use would likely reduce NH_3 loss to a greater extent than if precipitation did not occur before the inhibitor degraded by moving unhydrolyzed urea into the soil. In the absence of urea and NH_3 movement away from the surface, use of NBPT would merely sustain a reduced rate of NH_3 loss for a longer duration and not reduce total NH_3 loss (Christianson et al. 1993).

The greatest positive benefit of NBPT will likely be observed on high pH soils which are more prone to ammonia loss than soils of low pH (Beyrouy et al. 1988). Hendrickson and Douglass (1993) observed a greater magnitude and duration of urease inhibition with NBPT on a neutral soil than an acid soil, even when the pH of the acid soil was artificially increased to that of the neutral soil by the addition of $\text{Ca}(\text{OH})_2$. Clay et al. (1990) found NBPT decreased the rate of urea hydrolysis and the accompanying pH increase. Use of NBPT (0.5% w/w) restricted the soil pH increase from 6.5 to 7.2 versus the observed increase from 6.5 to 9.0 without NBPT. N-(n-butyl) thiophosphoric

triamide has also been more effective in soils with high NH_3 loss from unamended urea, specifically those with low titratable acidity, low moisture content, low organic matter and high pH (Watson et al. 1994b).

The magnitude and persistence of NBPT in soil depends on the rate of NBPTO formation and the stability of NBPTO in soil relative to the urea hydrolysis rate. For successful urease inhibition, the rate of NBPT conversion to NBPTO must exceed the rate of urea hydrolysis (Keerthisinghe and Blakeley 1995). N-(n-butyl) thiophosphoric triamide may be less effective in soils amended with residues and at higher temperatures, as increased residue content and temperature coincide with increased urease activity. Use of NBPT with urea reduced NH_3 loss from 26% to 1% when applied to soil plus residue and from 92 to 39% when applied to residue without soil (Beyrouly et al. 1988). Carmona et al. (1990) observed a decrease in relative NBPT performance as soil temperature increased from 18 to 32°C. At higher temperatures and increased residue content, the rate of urease activity and urea hydrolysis may exceed the rate of NBPT conversion to NBPTO, or the rate of inhibitor degradation may be more rapid, requiring a higher rate of NBPT to suppress NH_3 losses.

The amount of product required for optimal suppression of loss is also a key consideration in evaluating an inhibitor. Watson et al. (1994a) calculated an optimum NBPT rate of 0.1% w/w, achieving 93% inhibition of NH_3 loss for their site conditions. In their studies, the magnitude of NH_3 volatilization reduction decreased with increasing rates beyond 0.1%, illustrating diminishing returns at higher rates. At very low concentrations the disappearance rate of NBPT is more rapid, somewhat reducing the persistence of inhibition (Hendrickson and Douglass 1993). However, effective inhibition has been observed even at concentrations as low as 0.005% to 0.01% w/w

(Carmona et al. 1990; Watson et al. 1994a). Christianson et al. (1990) observed 1.5 to 3 times lower NH_3 losses at an NBPT concentration of 0.1% versus 0.01% although urea hydrolysis was still inhibited by about 68% at the lower concentration.

Improving the efficiency of urea surface applications alone is insufficient to justify use of NBPT. The conservation of N with NBPT use must be translated to increased yield and plant uptake of N to achieve a return on input investment. Conditions are not conducive to NH_3 volatilization every year; therefore, NBPT is a long-term management tool, maintaining yield potential in years when considerable NH_3 loss in the absence of NBPT would limit N supply to the crop and significantly detract from yield. It is important to remember NBPT does not completely and indefinitely prevent urea hydrolysis but rather slows the conversion, the extent of delay and concentration of NBPT applied being positively related (Carmona et al. 1990) and dependent on soil, environmental and management conditions.

2.6 Distribution of Urea and Nitrogen Reaction Products in Soil

The extent and pattern of NH_3 loss are not necessarily solely related to the pattern of urea hydrolysis (Carmona et al. 1990). Urea movement and subsequent conversions and equilibrium reactions of urea-derived ammoniacal N in soil also alter the potential for NH_3 volatilization. The capacity of the soil for movement and retention determine the spatial and temporal distribution of surface-applied urea and successive N reaction products in soil, combined with environmental conditions following urea fertilization. Amendment of urea with NBPT may alter the distribution pattern of urea and reaction products with depth in soil and may interfere with N conversions (Christianson et al.

1993; Vittori Antisari et al. 1996; Zhengping et al. 1996). N-(n-butyl thiophosphoric triamide slows urea hydrolysis and the accompanying pH and $[\text{NH}_4^+]$ increase in soil, permitting downward movement with soil water or incident rain. Irrigation, a single rainfall event or multiple small consecutive rainfalls equivalent to about 2 to 2.5 cm (Bouwmeester et al. 1985; Anonymous 1996) should induce a similar scenario. Reduced NH_3 volatilization and rapid nitrification are more likely with increased water infiltration prior to urea hydrolysis because the movement of NH_4^+ in soil water is much slower than that of urea.

Urea movement and ammoniacal N diffusion rates increase as water content and soil temperature increase. Nitrate accumulates with increased outward diffusion of urea and NH_4^+ from the application zone as high $[\text{NH}_3]$ and high pH inhibit nitrate formation (Schmidt 1982). Zhengping et al. (1996) found low soil moisture content (10%) limited movement of urea and ammoniacal N from the zone of placement, restricting NO_3^- formation to the periphery of the fertilizer reaction zone, all of which was delayed with use of NBPT. However, at 20% moisture content, more rapid diffusion and hydrolysis led to more rapid NO_3^- accumulation. At the higher moisture content, NBPT slowed hydrolysis but prevented NH_4^+ accumulation. Ammonium was quickly nitrified to NO_3^- as NBPT eliminated pH- and NH_3 - induced inhibition of NO_3^- formation.

Soil properties also influence distribution and formation of urea-N and N hydrolysis products in soil. Bremner and Chai (1989) observed the proportion of urea-N present as exchangeable NH_4^+ was markedly greater in soils with higher organic matter, clay content and CEC, perhaps because these soils could retain more NH_4^+ on their greater total surface area and exchange sites to limit the extent of subsequent N conversions in soil solution as in Eq. [6]. Christianson et al. (1993) found the capacity of

a soil to permit diffusion dictated the effectiveness of NBPT in reducing NH_4^+ and pH accumulation in the fertilizer microsite as reduced $[\text{NH}_4^+]$ and greater diffusion was detected on a sandy textured soil (pH 5.2) than on a clay soil (pH 8.2) when urea treated with NBPT was surface-applied. Nitrification was most rapid at 0.5% NBPT where the time to pH and NH_4^+ accumulation was delayed the most. Nitrate accumulated where NH_4^+ concentration was the lowest and decreased inward towards the zone of urea placement. However, initial soil pH may have partially confounded these findings as the maximum pH associated with hydrolysis is lower on an acid soil versus an alkaline soil. Soil pH is highly correlated with NH_4^+ , NO_2^- and NO_3^- formation from urea with and without NBPT (Watson et al. 1994b).

The rate of NBPT applied with urea may affect the formation and distribution of urea-N and hydrolysis products in soil. Christianson et al. (1990) reported increased recovery of urea in the 0-5 cm depth with increased NBPT rate from 0 to 0.1% over a 10 day period when downward movement was prevented. Watson et al. (1994a) found the quantity of urea and NH_4^+ remaining increased with increased rate of NBPT while nitrification was significantly reduced at 0.28% NBPT. Bremner and Chai (1989) reported NBPT (0.47% w/w) on average decreased nitrite formation from 11 to 1% when soils were incubated for 14 days. Research by Vittori Antisari et al. (1996) showed the ratio of $\text{NO}_3^-:\text{NO}_2^-$ from urea increased as NBPT concentration increased. Use of NBPT may have reduced the inhibition of nitrate formation because of resulting lower $[\text{NH}_3]$.

The influence of NBPT application on formation and distribution of urea hydrolysis products in soil is temporary, merely delaying the conversion of urea-N to nitrate. Watson et al. (1994a) found no significant effect of NBPT on recovery to 15 cm at 5 cm depth increments 6 weeks after application. Christianson et al. (1990) measured

greater levels of NH_4^+ at 0.01% NBPT than at 0.10% in the 0-5 cm depth mid way through a 10 day laboratory study although final NH_4^+ content was similar.

2.7 Plant Yield and Recovery of Urea-N Surface-Applied with NBPT

N-(n-butyl) thiophosphoric triamide has been shown to be a proficient inhibitor of soil urease, improving the efficiency of urea-N fertilizer applications by reducing the extent of NH_3 loss to the atmosphere. However, for NBPT to be economically viable, the savings in fertilizer nitrogen availability must result in increased plant uptake of fertilizer N and increased yield or improved crop quality (Grant and Bailey 1997).

Effects of NBPT on grain yield and plant uptake of fertilizer N has predominantly been studied with corn and is dependent on the overall capacity of the crop to benefit from the increased quantity of available N. Crop response to NBPT will generally occur when conditions are conducive to large NH_3 or immobilization losses and N is limiting to crop production (Murphy and Ferguson 1997) in the absence of NBPT, so that the conserved fertilizer N is utilized by the crop (Hendrickson 1992). Use of NBPT with urea shows most promise when surface-applied to a soil with an accumulated layer of residue and/or to a moist soil subject to evaporation or drying (Murphy and Ferguson 1997) where loss of fertilizer N may be detrimental to yield. For example, corn yield in a ridge till system responded positively to NBPT applied with urea (5.6 bu acre⁻¹ increase) in only one year of a 3 year field study. The authors concluded conditions were not conducive to NH_3 loss, or N was not limiting to yield, in the other 2 years (Murphy and Ferguson 1997). Results from 78 trials conducted in the USA over a 5 year period showed on average NBPT increased grain yields by 4.3 bu acre⁻¹ and 1.6 bu acre⁻¹ when

applied with urea and UAN, respectively (Hendrickson 1992). Fox and Piekielek (1993) found amendment of urea with NBPT significantly improved corn yield and N uptake with broadcast urea and significantly increased N uptake with sprayed UAN.

A limited number of field experiments evaluating yield response to NBPT-amended urea in crops other than corn have been conducted. Gezgin and Bayraklı (1995) reported winter wheat grain yield increased from 3763 kg ha⁻¹ with unamended urea to 4443 and 4313 kg ha⁻¹ with amendment of urea with NBPT at rates of 0.25 and 0.5% w/w, respectively. Field experiments with surface applications of urea to perennial ryegrass (Watson et al. 1994a) showed N conserved through use of NBPT amended-urea (0.05% w/w) was utilized by the plant and translated into a 9% increase in dry matter yield. Percent N utilization also significantly increased from 32 to 39% with use of NBPT.

Some preliminary studies in Manitoba indicate there is potential for increased crop response when urea is amended with NBPT. In a 3 year study, NBPT consistently increased grain yield of barley under zero tillage when surface broadcast with urea (Grant and Bailey 1997). In a growth chamber experiment, vegetative yield and plant nitrogen accumulation of wheat increased with increased rates of NBPT from 0 to 0.25% w/w surface-applied with urea, indicating transference of N conserved from volatilization to plant growth (Xiaobin et al. 1995).

A legitimate concern with the use of urease inhibitors is the potential plant physiological impact which may accompany use of elevated rates of NBPT with urea, where intact urea may be taken up by the plant (Watson et al. 1994a; Yeomans 1991). Watson et al. (1994a) found reduced dry matter yield response at NBPT rates greater than 0.1% where the higher rates perhaps induced plant damage. Leaf tip necrosis,

accompanied by urea accumulation in plant tissue, has been observed in sorghum and wheat with foliar applications of NBPT-treated urea (Bremner and Krogmeier 1988; Krogmeier et al. 1989), indicating urea toxicity as opposed to direct NBPT toxicity.

Use of NBPT will only improve crop productivity when soil, environment and management conditions result in significant NH_3 volatilization from surface applications of unamended urea creating an N deficiency to the growing crop. A heightened understanding of conditions contributing to NBPT effectiveness will assist in predicting whether there will be economic benefits to using NBPT on the Eastern Canadian prairies.

3. AMMONIA VOLATILIZATION AND SOIL N FOLLOWING SURFACE APPLICATION OF UREA FERTILIZERS WITH AND WITHOUT NBPT: EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION

3.1 Abstract

Field studies using lysimeters were conducted under modified zero tillage conditions on two Orthic Black Chernozemic soils, a Stockton fine sandy loam and a Newdale clay loam, to assess the effect of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) on NH_3 volatilization and distribution of urea hydrolysis products in the soil from surface-applied urea and urea ammonium nitrate (UAN) with and without irrigation. The studies were ran in May and again in July to evaluate NBPT performance under varying temperature regimes. Ammonia losses were measured to 12 days after fertilization (DAF) in 1996 and to 21 DAF in 1997, after which soil exchangeable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and urea-N content were determined. Total NH_3 volatilization decreased in the order of non-irrigated > irrigated > non-irrigated+NBPT > irrigated+NBPT and was greater from urea than UAN. Ammonia loss varied from 16.9 to 36.2 % and 8.0 to 31.5% of applied N for unamended urea and UAN, respectively with rate and amount of loss being greatest for the Stockton fine sandy loam soil fertilized in July. N-(n-butyl) thiophosphoric triamide was most effective in reducing NH_3 loss during periods of peak NH_3 loss from unamended urea, reducing NH_3 loss by 83-98% and delaying the period of

maximum loss until at least 8 DAF. For each study, soil nitrogen content to 30 cm decreased in the order of $\text{NO}_3\text{-N} > \text{NH}_4\text{-N} > \text{urea-N}$ for most treatments. Nitrogen form and distribution in soil was influenced more by irrigation than by NBPT as irrigation enhanced downward movement of NO_3^- and nitrification of NH_4^+ to NO_3^- . Urea and NH_4^+ content at 0-5 cm were greatest for non-irrigated urea and UAN amended with NBPT whereas soil NO_3^- varied inconsistently with treatment. The proportion of total N measured (soil N plus volatilized $\text{NH}_3\text{-N}$) that was present in the soil was greater with NBPT than without, indicating that the reduction in NH_3 volatilization resulted in increased soil N.

3.2 Introduction

Urea fertilizer is rapidly hydrolyzed by urease enzymes in soil and organic material to 2NH_4^+ and HCO_3^- (Koelliker and Kissel 1988). The efficiency of urea fertilizer applications is reduced if this ammonia is lost through volatilization. Volatilization of NH_3 is a function of: i) urea hydrolysis rate or rate of NH_4^+ formation, ii) equilibrium among NH_3 and NH_4^+ in soil solution and NH_3 in soil air ($\text{NH}_4^+_{(\text{aq})} \rightleftharpoons \text{NH}_{3(\text{aq})} \rightleftharpoons \text{NH}_{3(\text{g})\text{soil}}$), iii) NH_3 exchange between soil and atmosphere ($\text{NH}_{3(\text{g})\text{soil}} \rightleftharpoons \text{NH}_{3(\text{g})\text{atm}}$), and iv) exchange between NH_4^+ in solution and soil exchange sites ($\text{NH}_4^+_{(\text{ex})} \rightleftharpoons \text{NH}_4^+_{(\text{aq})}$) (Sherlock and Goh 1985). The amount of $\text{NH}_4^+_{(\text{aq})}$ present is also altered by removal of NH_4^+ from the soil via plant uptake, immobilization and nitrification. Ammonia volatilization proceeds when there is a sufficient difference in the partial pressure between $\text{NH}_{3(\text{g})\text{soil}}$ and $\text{NH}_{3(\text{g})\text{atm}}$ at the soil/air interface due to an elevated concentration of $\text{NH}_{3(\text{g})\text{soil}}$ near the soil surface (Koelliker and Kissel 1988). The potential for NH_3 loss is greatest when urea is

surface-applied to residue covered soil, such as under zero tillage where urease activity is elevated and movement of urea into the soil prior to hydrolysis may be impeded (Byrnes and Freney 1995). Since a relatively large land area in Manitoba is zero-tilled, an efficient means of providing fertilizer N under these conditions is needed.

The urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) may slow NH_3 formation from surface-applied urea by inactivating urease enzymes (Kolodziej 1994) to delay the period of maximum NH_3 loss (Clay et al. 1990; Carmona et al. 1990). N-(n-butyl) thiophosphoric triamide decreases NH_4^+ accumulation and pH increase accompanying urea hydrolysis (Schmidt 1982) and lengthens the time frame over which urea can move into the soil with infiltrating water to reduce the potential for NH_3 volatilization (Grant et al. 1996b). Amendment of urea with NBPT may alter the distribution pattern of urea and hydrolysis products with depth in soil and may interfere with N conversions. Use of NBPT with urea has been shown in laboratory studies to increase diffusion of urea from the placement zone, slow conversion of urea and decrease accumulation of $\text{NH}_4\text{-N}$ versus $\text{NO}_3\text{-N}$ when studied under varying soil and moisture conditions (Christianson et al. 1993; Vittori Antisari et al. 1996; Zhengping et al. 1996).

The objective of this study was to characterize the effect of NBPT applied with urea and UAN fertilizers on ammonia volatilization, and the spatial distribution and dominant species of urea hydrolysis products in soil as influenced by variable weather and soil parameters of zero tilled fields in Manitoba.

3.3 Materials and Methods

Field experiments using lysimeters were conducted in 1996 and 1997 on Stockton

fine sandy loam (FSL) and Newdale clay loam (CL) Orthic Black Chernozemic soils (Table 3.1) (Goh et al. 1993; Hendershot et al. 1993ab; Janzen 1993). Field trials were run in mid-May and mid-July for each year and for each soil. Volatilized NH_3 was measured for 12 DAF in 1996 and for 21 DAF in 1997. Studies in 1996 trials commenced May 21 and July 16 on the Newdale CL and May 28 and July 17 on the Stockton FSL. Trials in 1997 began May 20 and July 24 on the Newdale CL and May 6 and July 24 on the Stockton FSL. Soil moisture contents determined at seeding in May from a directly adjacent study were 33% and 22% for the Newdale CL and Stockton FSL soil, respectively in 1996 and 34% and 18%, respectively in 1997. Daily air temperature and soil temperature within the cylinders at 1 cm below the soil surface were recorded throughout each trial period. Data recording in May 1997 was delayed until 7 DAF and 3 DAF on the Newdale CL and the Stockton FSL soil, respectively, and ended at 9 DAF in July 1997 on the Newdale CL due to equipment failure (Figures 3.1 and 3.2).

Table 3.1 Selected chemical and physical characteristics of soils used^z.

Soil Name	Sand %	Silt %	Clay %	FC %	BD g cm ⁻³	CEC cmol kg ⁻¹	OC %	CaCO ₃ %	pH	EC μS/cm
Newdale (1996)	32.2	36.3	31.5	30	1.17	49.8	4.3	1.6	8.0	896
Stockton (1996)	76.0	11.8	12.2	23	1.15	23.1	2.7	0.3	7.6	1092
Newdale (1997)	35.8	32.2	32.0	32	1.31	46.7	4.9	3.6	8.2	740
Stockton (1997)	75.5	11.4	13.1	19	1.34	23.2	2.1	1.4	8.2	756

^z All determinations made using 0-15 cm depth composite samples.

^y FC = field capacity; BD = bulk density; CEC = cation exchange capacity; OC = organic carbon; pH in water; EC = electrical conductivity saturated paste method.

Each individual experiment was set up as a randomized complete block design having three replicates with 10 treatments occurring once in each block. The treatments were an irrigated and a non-irrigated control (no fertilizer or NBPT), 100 kg N ha⁻¹ as urea with and without NBPT (0.14% w/w) both with and without irrigation, and 100 kg N ha⁻¹ as UAN with and without NBPT (0.14% w/w) both with and without irrigation.

Irrigation consisted of adding the equivalent of 2 cm of deionized water at 2 and 8 DAF.

Study design and ammonia capture and analysis procedures followed that of Grant et al. (1996b), derived from the methodologies of Nommik (1973) and Fairlie and Goos (1986). White polyvinyl chloride (PVC) cylinders (lysimeters), 20 cm in length by 15 cm diameter, were inserted into the soil to a depth of 5 cm with minimal disturbance of the soil. Prior to treatment application, surface residue was cleared from the immediate area of fertilizer placement within each cylinder to allow direct contact of fertilizer with soil and to eliminate any direct effects of residue on urea hydrolysis and ammonia volatilization. Filter paper was placed on the soil surface in each lysimeter and 150 mL distilled water added 24 hrs prior to fertilizer addition to attain equivalent soil surface moisture content within all lysimeters at a site. Fertilizer treatments were dispensed on the soil surface within a 2 cm diameter area at the centre of each PVC cylinder.

Immediately following fertilization, each cylinder was fitted with two polyfoam discs, 2.5 cm thick and 16 cm in diameter, previously double washed with distilled water, 0.001M H₂SO₄ and a glycerol-phosphoric acid solution (100 ml 14.7 M H₃PO₄, 125 ml glycerol and 2275 ml deionized water), thoroughly wrung after each washing. The lower disc was inserted in the cylinder at 5 cm above the soil surface to trap volatilized NH₃ and the second disc placed 5 cm below the top of the cylinder to prevent drying and atmospheric ammonia contamination of the lower disc. Each disc was designed to fit

tightly within the cylinder to minimize escape of gaseous NH_3 . Clear plexiglass sheets were positioned atop four corner-placed reinforcing bars approximately 30 cm above the lysimeters in each block to provide protection from rainfall but permit incident sunlight.

On specified DAF during each trial (at 1, 2, 5, 8, 12 DAF in 1996 and extended to 15, 19 and 21 DAF in 1997) the lower disc was removed, immediately replaced by a fresh disc and placed in a sealed, airtight plastic bag containing 250 ml 2M KCl. Each disc was thoroughly rinsed in the KCl solution to extract the trapped ammonia, and the solution decanted into vials, sealed and stored frozen until analysis. The KCl extract was analyzed at room temperature for ammonium-nitrogen content using a Technicon Autoanalyzer (Technicon Industrial Systems 1977).

At the end of each trial period all soil at the 0-5 cm and 5-10 cm depths was removed and three soil cores taken from each lysimeter at 10-20 and 20-30 cm increments and composited by depth. Field moist samples were extracted and analyzed for exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (Maynard and Kalra 1993) and urea-N (Bremner 1982) using a Technicon Autoanalyzer (Technicon Industrial Systems 1980). Technical difficulties rendered $\text{NH}_4\text{-N}$ data in 1996 below 0.25 mg kg^{-1} as unreliable. Values below this limit are reported as "nd".

Statistical analyses were conducted on log-transformed data ($\log + 1$) (Little and Hills 1978) using the MIXED models procedure of the SAS Institute, Inc. (Littell et al. 1998) as the design supported both fixed and random effects. Ammonia volatilization and soil nitrogen data were analysed separately. As significant interactions occurred between year, soil, study and treatment for $\text{NH}_3\text{-N}$ (Table 3.2) and for soil exchangeable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and urea-N data (Table 3.3), the data was analysed separately by study, soil and year. Least squares means standard error and contrast analysis probabilities are

reported. Statistical analysis of ammonia volatilization data was performed on date groupings for the period prior to initial irrigation at 2 DAF, and from 2 to 5 DAF, 5 to 12 DAF, 12 to 21 DAF (1997 only) and on total NH_3 loss. Soil nitrate, ammonium and urea-nitrogen data were analyzed separately by depth. For some depths and times, particularly at lower depths and in July, there were insufficient data values to statistically analyze $\text{NH}_4\text{-N}$ and urea-N data. Statistical analyses were also performed on log-transformed data ($\log + 1$) of total soil N measured in soil as a percent of total N recovered (soil N plus volatilized $\text{NH}_3\text{-N}$). Data was log-transformed as the variance of non-transformed data was not homogeneous as determined using the $F_{\max}$ -test (Sokal and Rohlf 1981).

Table 3.2 $\text{Pr} > F$, F and LS means standard error values for log-transformed $\text{NH}_3\text{-N}$ data.

Source	Sum to 2 DAF		Sum 2 to 5 DAF		Sum 5 to 12 DAF		Sum 12 to 21 DAF	
	F value	$\text{Pr} > F$	F value	$\text{Pr} > F$	F value	$\text{Pr} > F$	F value	$\text{Pr} > F$
Soil	0.82	ns	36.45	ξ	53.72	**	58.66	ξ
Study	252.24	ξ	678.27	ξ	45.84	ξ	6.77	**
Soil*Study	0.00	ns	11.58	***	26.24	ξ	4.35	*
Year	72.99	ξ	63.70	ξ	9.02	**	84.56	ξ
Year*Soil	31.81	ξ	11.85	***	1.23	ns	0.51	ns
Year*Study	121.12	ξ	33.96	ξ	1.03	ns	23.72	ξ
Year*Soil*Study	6.05	*	7.8	**	4.96	*	26.58	ξ
Treatment	73.03	ξ	211.66	ξ	207.96	ξ	111.9	ξ
Soil*Treatment	0.54	ns	1.79	ns	2.95	***	6.8	ξ
Study*Treatment	32.09	ξ	17.93	ξ	26.48	ξ	10.43	ξ
Soil*Study*Treatment	0.95	ns	2.41	**	3.11	***	3.07	***
Year*Treatment	14.33	ξ	11.22	ξ	13.51	ξ	19.15	ξ
Year*Soil*Treatment	7.23	ξ	5.90	ξ	3.50	***	2.98	***
Year*Study*Treatment	7.96	ξ	3.63	ξ	3.67	ξ	12.07	ξ
Year*Soil*Study*Treatment	2.89	***	3.63	ξ	3.3	***	4.09	ξ
LS Means Std Error	0.09		0.09		0.15		0.01	

*, **, ***, ξ = significant at $p = 0.05, 0.01, 0.001$ and 0.0001 levels, respectively; DAF = Days After Fertilization; Study = May or July trial period.

Table 3.3 Probability values and LS means standard error for log-transformed soil N data.

Source	0-5 cm Depth			5-10 cm Depth			10-20 cm Depth			20-30 cm Depth		
	NO ₃ -N	NH ₄ -N	Urea-N	NO ₃ -N	NH ₄ -N	Urea-N	NO ₃ -N	NH ₄ -N	Urea-N	NO ₃ -N	NH ₄ -N	Urea-N
Soil	ξ	ξ	ns	*	ξ	ns	ns	ξ	ns	ns	ξ	ns
Study	ns	ξ	ξ	ξ	ξ	***	ξ	ξ	ξ	ξ	ξ	ξ
Soil*Study	ns	ξ	ns	ns	***	ns	ns	ns	ns	ns	ns	ns
Year (Y)	***	ns	ξ	ns	ξ	***	ns	ξ	ns	ns	ξ	ns
Y*Soil	ns	**	ns	ns	***	ns	**	ξ	*	**	ξ	*
Y*Study	ns	ξ	**	ns	ξ	**	*	ξ	ns	*	ξ	ns
Y*Soil*Study	ns	ns	ns	ns	ns	ns	*	ns	ns	*	ns	ns
Treatment (T)	ξ	ξ	ξ	ξ	*	ns	ξ	*	ns	ξ	*	ns
Soil*T	ns	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns
Study*T	***	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns
Soil*Study*T	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns	ns
Y*T	ns	*	ns	ns	ξ	ns	*	ξ	ns	*	ξ	ns
Y*Soil*T	ns	ns	*	ns	ns	**	ns	ns	ns	ns	ns	ns
Y*Study*T	**	ns	**	ns	***	***	ns	ns	ns	ns	ns	ns
Y*Soil*Study*T	**	ns	ns	ns	*	ns	ns	ξ	ns	ns	ξ	ns
LS Means SE	0.09	0.17	0.11	0.1	0.08	0.1	0.11	0.09	0.08	0.11	0.09	0.08

*, **, ***, ξ = significant at p = 0.05, 0.01, 0.001 and 0.0001 levels, respectively; DAF = Days After Fertilization; Study = May or July trial period.

3.4 Results and Discussion

3.4.1 Ammonia Volatilization

Volatilization of ammonia from surface-applied urea and UAN decreased in the order of non-irrigated > irrigated > non-irrigated plus NBPT (NI+NBPT) > irrigated plus NBPT (I+NBPT) for all trials. The only exception was the study on the Stockton FSL soil in July 1997 where NH₃ volatilization beyond the 8 DAF sampling period from NI+NBPT urea and UAN exceeded loss from irrigated treatments without NBPT (Figures 3.1 and 3.2). Both irrigation and NBPT significantly decreased NH₃ volatilization. Ammonia volatilization from irrigated treatments plus NBPT ranged from 1.2 to 24.1% for urea and 3.2 to 13.2% for UAN as compared to 16.9 to 36.8% and 7.2 to 31.5% for unamended urea and UAN, respectively.

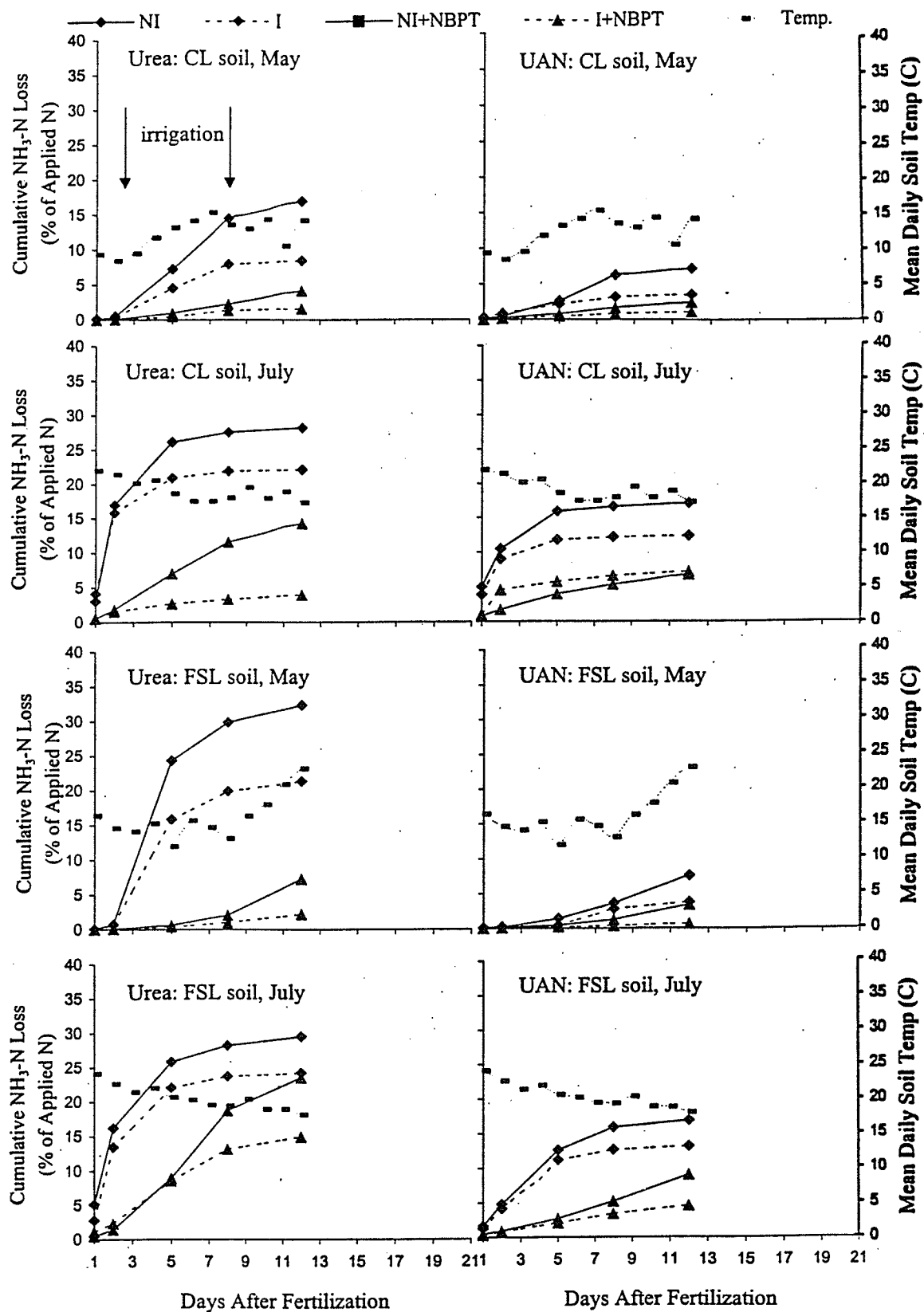


Figure 3.1 Cumulative $\text{NH}_3\text{-N}$ loss from urea and UAN with and without irrigation and NBPT for two soils in May and July in 1996, minus controls (I = irrigated, NI = non-irrigated).

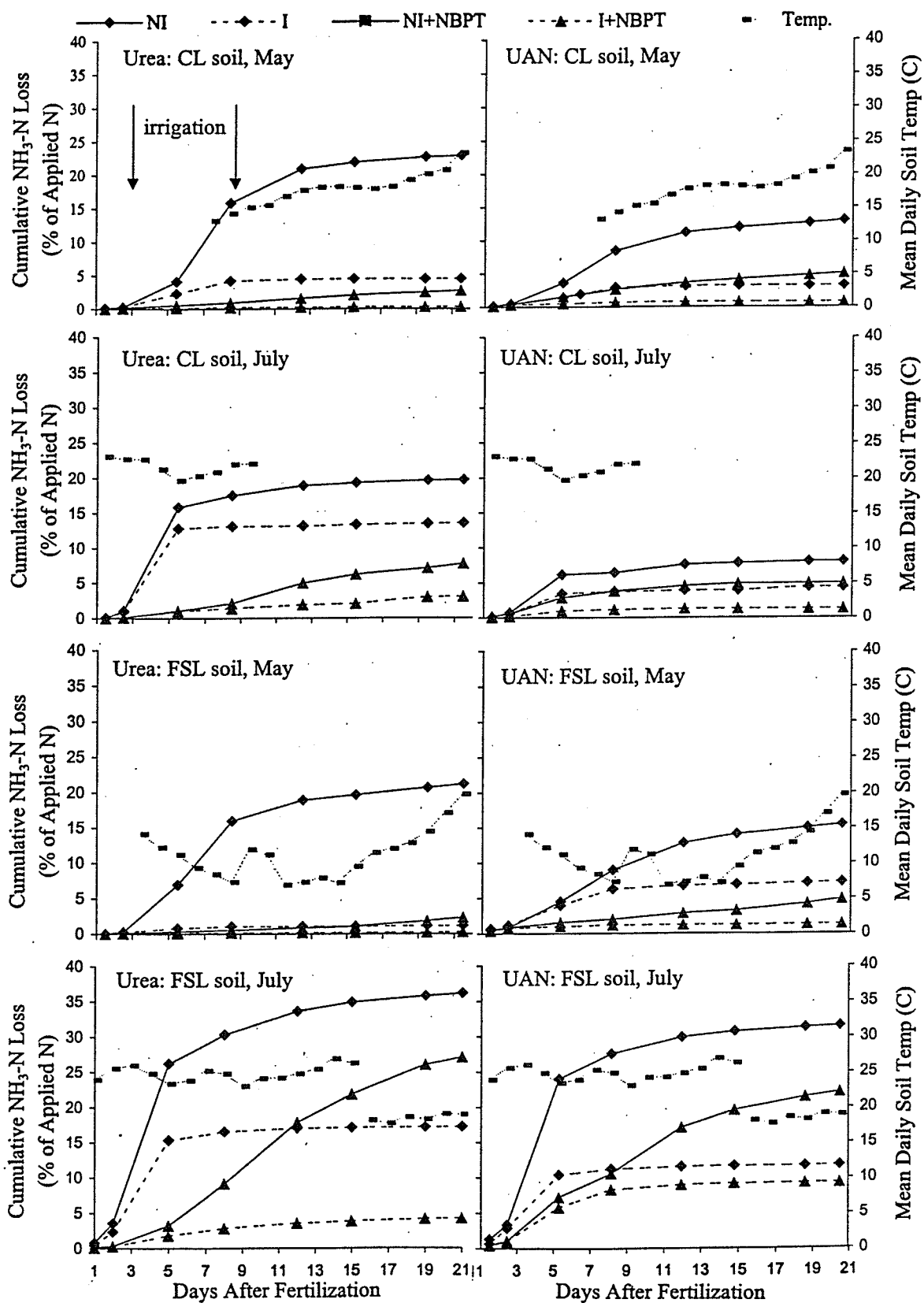


Figure 3.2 Cumulative $\text{NH}_3\text{-N}$ loss from urea and UAN with and without irrigation and NBPT for two soils in May and July in 1997, minus controls (I = irrigated, NI = non-irrigated).

Volatilization was lowest during the first week with NI+NBPT, with irrigation in the second week and with I+NBPT throughout the study duration. For all treatments, total NH_3 loss and rate of loss were consistently greater in July than May and greater for the Stockton FSL than for the Newdale CL soil. Ammonia loss from urea treatments generally exceeded loss from corresponding UAN treatments (Tables 3.4 and 3.5) where the difference was greater for the unamended treatments than the treatments with NBPT.

Table 3.4 Contrast analysis and LS means standard error values for log-transformed 1996 NH_3 -N data.

Contrast	Sum to 2 DAF				Sum 2 to 5 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treat. vs Cont.	ξ	ξ	***	ξ	ξ	ξ	ξ	ξ
Urea vs UAN	*	ns	***	***	**	***	ξ	ξ
1 vs 2	ns	ns	ns	ns	**	ξ	ns	ns
7 vs 8	ns	ns	ns	ns	ns	ns	ns	ns
1 and 2 vs 3 and 4	ξ	ξ	ξ	ξ	ξ	ξ	ξ	ξ
7 and 8 vs 9 and 10	ξ	ξ	ns	***	ξ	ξ	ξ	ξ
2 vs 3	**	ξ	***	***	***	ξ	ξ	***
8 vs 9	ξ	ξ	ns	*	**	ξ	***	ξ
LS Means Std Err	0.11	0.28	0.11	0.51	0.24	0.23	0.23	0.31

Contrast	Sum 5 to 12 DAF				Sum to 12 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treat. vs Cont.	ξ	ξ	ξ	ξ	ξ	ξ	ξ	ξ
Urea vs UAN	ξ	ξ	ξ	ξ	***	**	ξ	ξ
1 vs 2	ξ	ξ	*	***	ξ	ξ	*	**
7 vs 8	***	***	ns	ξ	**	ns	ns	**
1 and 2 vs 3 and 4	ξ	ns	ξ	ξ	ξ	ξ	ξ	ns
7 and 8 vs 9 and 10	ξ	ns	**	*	ξ	***	ξ	ξ
2 vs 3	ns	ξ	***	ξ	*	ns	ξ	ns
8 vs 9	ns	*	ns	ns	ns	ns	ns	ns
LS Means Std Err	0.48	0.40	0.57	0.30	0.54	0.51	0.58	0.53

*, **, ***, ξ = significant at $p = 0.05, 0.01, 0.001$ and 0.0001 levels, respectively; DAF = Days After Fertilization; Treat. = Treatment; Cont. = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea; 3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN; 8 = I UAN; 9 = NI UAN+NBPT and 10 = I UAN+NBPT.

Table 3.5 Contrast analysis and LS means standard error values for log-transformed 1997 NH₃-N data.

Contrast	Sum to 2 DAF				Sum 2 to 5 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treat. vs Cont.	ξ	ξ	ξ	ξ	ξ	ξ	ξ	ξ
Urea vs UAN	ξ	ns	ξ	**	ns	*	ξ	*
1 vs 2	ns	ns	ns	ns	***	ns	ξ	ns
7 vs 8	ns	ns	ns	ns	ξ	**	*	ns
1 and 2 vs 3 and 4	*	ξ	*	ξ	ξ	ξ	ξ	ξ
7 and 8 vs 9 and 10	ns	ns	ns	ξ	ξ	***	ξ	***
2 vs 3	ns	***	ns	***	ξ	ξ	***	ξ
8 vs 9	ns	ns	ns	**	ns	ns	ξ	ns
LS Means Std Err	0.08	0.14	0.11	0.28	0.14	0.30	0.11	0.41

Contrast	Sum 5 to 12 DAF				Sum 12 to 21 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treat. vs Cont.	ξ	ξ	ξ	ξ	ξ	***	ξ	ξ
Urea vs UAN	ns	***	ξ	ns	ns	**	**	*
1 vs 2	ξ	ξ	ξ	ξ	ξ	***	ξ	ξ
7 vs 8	ξ	***	ξ	ξ	ξ	ns	ξ	ξ
1 and 2 vs 3 and 4	ξ	***	ξ	**	ξ	**	**	ξ
7 and 8 vs 9 and 10	ξ	ns	ξ	ns	***	ns	***	ξ
2 vs 3	ξ	ns	ns	**	ξ	ξ	ξ	ξ
8 vs 9	**	ns	ξ	***	ξ	ns	***	ξ
LS Means Std Err	0.17	0.45	0.2	0.57	0.22	0.55	0.31	0.37

Contrast	Sum to 21 DAF			
	Newdale CL		Stockton FSL	
	May	July	May	July
Treat. vs Cont.	ξ	ξ	ξ	ξ
Urea vs UAN	ns	**	ξ	ns
1 vs 2	ξ	***	ξ	ξ
7 vs 8	ξ	***	ξ	ξ
1 and 2 vs 3 and 4	ξ	ξ	ξ	ξ
7 and 8 vs 9 and 10	ξ	ns	ξ	ns
2 vs 3	ξ	ns	ns	ns
8 vs 9	*	ns	ξ	ns
LS Means Std Err	0.22	0.55	0.27	0.62

*, **, ***, ξ = significant at p = 0.05, 0.01, 0.001 and 0.0001 levels, respectively; DAF = Days After Fertilization; Treat. = Treatment; Cont. = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea; 3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN; 8 = I UAN; 9 = NI UAN+NBPT and 10 = I UAN+NBPT.

N-(n-butyl) thiophosphoric triamide markedly decreased the rate and total cumulative amount of NH_3 volatilized from urea and UAN fertilizers for the 12 d studies in 1996 and the 21 d studies in 1997 (Figures 3.1 and 3.2). The inhibitor was most effective during periods of peak loss from unamended treatments, delaying the onset of loss until 2 to 5 DAF in July and until 5 to 8 DAF in May, and postponing the period of peak NH_3 loss until the second and third weeks after fertilization. In contrast, peak loss from unamended urea and UAN occurred within the first 2 to 5 DAF in May and 5 to 8 DAF in July. Cumulative NH_3 loss during the first 5 days after fertilization ranged from 0.4% to 26.2% for unamended fertilizer treatments but from only 0.1% to 8.9% for NBPT-amended treatments, while losses from 12 to 21 DAF in 1997 were 0.1 to 2.6% and 0.0 to 9.3%, for treatments without and with NBPT, respectively. Thus, significant probability values of NBPT treatments versus unamended fertilizer treatments for the cumulative loss during the 12 to 21 DAF period for the 1997 studies represent increased rate of NH_3 loss from NBPT-treated urea and UAN relative to unamended treatments (Tables 3.4 and 3.5). Significant differences at other periods were due to lower loss from urea and UAN with NBPT than without NBPT. Others have reported temperature and NBPT suppression of ammonia loss similar to that which we observed (Watson et al. 1994a; Clay et al. 1990; McInnes et al. 1986; Carmona et al. 1990).

The extent of NH_3 loss is dependent on soil and air temperature, initial surface soil moisture status, timing and duration of rainfall events, relative humidity, wind velocity and soil properties. These variables establish the rate of soil drying (Ferguson and Kissel 1986; Reynolds and Wolf 1987) and infiltration of urea (Black et al. 1987), and provide the environment within which NBPT performs. The addition of water prior to fertilizer application and the warmer soil temperatures in July likely accelerated the rate of urea

dissolution and increased urease activity to overcome urease inhibition prior to sufficient downward movement of urea. Beyrouthy et al. (1988) measured accelerated NH_3 loss under warm, moist conditions. Similarly, Bremner et al. (1991) observed decreased persistence of urease inhibition when temperatures were increased from 15 to 30°C for a "field-moist" soil.

Although the pattern of loss with and without irrigation was similar, the addition of water to the soil reduced NH_3 volatilization for both fertilizers under all field conditions. The product information guide for Agrotain, the commercial source of NBPT, states use of NBPT at the prescribed rate of 0.14% w/w provides control of NH_3 loss equivalent to 2 cm of rain (Anonymous 1996). However, results of this experiment show timing of the rainfall event is critical. If rain does not occur for a few days following urea application, NH_3 loss can be reduced to a greater extent with use of NBPT than with rainfall. Irrigation (2 cm) at 2 DAF depressed, but did not consistently eliminate NH_3 volatilization both in the presence and absence of NBPT, particularly under warm soil temperatures. An additional 2 cm irrigation was required to prevent further NH_3 loss. Irrigation in combination with NBPT provided the greatest control of NH_3 volatilization, restricting total NH_3 loss to less than 14.9% from urea and 9.3% from UAN, most notably for the July studies on the Stockton FSL soil where loss potential was the greatest.

The relative humidity was elevated in this experiment by use of moist polyfoam discs which impeded drying of the soil surface, especially on the Newdale CL soil which has a greater water holding capacity. Ferguson and Kissel (1986) measured greater NH_3 loss when humid air was passed over soil near field capacity versus dry air. In addition, the modified conditions of our studies likely created an artificially large NH_3

concentration gradient between the soil surface and the air directly above, where $[\text{NH}_{3(\text{air})}]$ was kept low by the polyfoam disc simulating wind removal of NH_3 to maintain the gradient for NH_3 loss. As such, NH_3 losses likely proceeded for an extended duration in this modified field study as compared to what might occur under true field conditions where wind would dry the soil surface. More rapid drying of the soil surface would have created a barrier layer, particularly on the Newdale CL soil, which would have restricted NH_3 movement to the surface, resulting in reduced NH_3 loss.

The potential magnitude of an NH_3 volatilization event and hence NBPT effectiveness, depend on soil factors which affect urea and NH_4^+ movement and NH_4^+ retention (Sherlock and Goh 1985; Christianson et al. 1993; Carmona et al. 1990). These factors include soil texture, cation exchange capacity (CEC), organic matter content, urease activity and soil pH (Nelson 1982; Koelliker and Kissel 1988). These properties determine the soil's capacity for diffusion, air and water flux and for retention of ammoniacal N and water. Soil pH, or more specifically the H^+ -buffering capacity against a pH increase or, in calcareous soils, soil buffering capacity against a pH decrease due to CaCO_3 (Hargrove 1988), is the most important factor. The volatilization potential is greatest on high pH soils which are not buffered against hydrolysis pH increase or maintain an elevated pH for a longer duration (Watson et al. 1994b), such as the soils used in our experiment.

The greatest loss of NH_3 for all treatments was observed on the Stockton FSL soil, particularly in July when the soil was warmer, where loss from NI+NBPT averaged 25.3% for urea and 15.6% for UAN. The Stockton FSL had low CEC, organic matter content and water holding capacity and likely had uniformly distributed pores with a high soil water flux, conditions ideal for NH_3 formation and volatilization. The Newdale CL

had higher CEC and organic matter content and greater water holding capacity, and likely supported smaller pores with more complex distribution and lower soil water flux, and therefore was less conducive to NH_3 formation and volatilization. As a result, cumulative NH_3 loss from the Stockton FSL ranged from 0.2 to 32.3% in May and from 4.2 to 36.2% in July, with lower ranges of 0.3 to 23.0% and 1.3 to 28.1% for the Newdale CL in May and July, respectively.

3.4.2 Soil Nitrogen Content

For all treatments urea, exchangeable NH_4^+ and NO_3^- were most abundant at 0-5 cm and decreased with depth (Tables 3.6 to 3.9). Nitrate was more abundant than exchangeable NH_4^+ at all depths with the exception of the non-irrigated treatments for the Stockton FSL studies where exchangeable NH_4^+ and NO_3^- content were similar. The total amount of soil N measured was greater in May than July where exchangeable NH_4^+ content was higher for the Stockton FSL than the Newdale CL soil, and NO_3^- higher for the CL than the FSL soil (FSL: mean exchangeable $\text{NH}_4\text{-N} = 37.2 \text{ kg N ha}^{-1}$, mean $\text{NO}_3\text{-N} = 58.66 \text{ kg N ha}^{-1}$; CL: mean exchangeable $\text{NH}_4\text{-N} = 11.9 \text{ kg N ha}^{-1}$, mean $\text{NO}_3\text{-N} = 83.4 \text{ kg N ha}^{-1}$). The amount of soil urea measured was markedly lower than other N species, particularly in July, ranging from 0.0 to 16.0 kg N ha^{-1} . Significant but inconsistent differences in soil N content were observed between urea and UAN treatments. Differences between the 1996 and 1997 trials may have resulted from variations in weather and previous site management, the one week difference in study period length or a combination of both.

Table 3.6 Soil urea-N, exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg N ha^{-1}) with depth for the Newdale clay loam soil, 1996.

Newdale Clay Loam Soil May											
Irrigation Fertilizer Depth	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	13.6	26.5	15.9	1.2	1.1	1.8	20.4	5.2	7.4	9.0	1.18
5-10 cm	3.0	0.2	2.9	0.9	0.7	1.6	5.0	4.2	3.0	3.9	1.18
10-20 cm	4.1	0.5	2.6	2.0	1.0	6.2	7.8	9.9	5.6	4.5	1.32
20-30 cm	6.3	0.5	1.1	1.6	1.6	4.7	7.4	6.9	6.9	1.1	1.37
Total	26.9	27.8	22.4	5.7	4.4	14.4	40.6	26.2	22.8	18.5	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	75.3	52.0	64.1	55.0	10.1	4.6	85.7	55.1	56.7	58.7	1.18
5-10 cm	6.5	13.0	7.1	17.0	5.5	3.7	14.8	16.1	7.7	13.3	1.18
10-20 cm	8.4	20.9	8.7	19.3	6.6	7.2	13.1	20.7	8.8	25.3	1.32
20-30 cm	7.0	12.9	7.5	12.3	6.2	7.1	8.3	11.2	6.9	13.6	1.37
Total	97.2	98.9	87.4	103.6	28.3	22.6	122.0	103.0	80.1	110.9	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	4.0	2.1	5.4	2.4	1.0	0.7	1.4	0.5	2.9	0.6	1.18
5-10 cm	0.1	1.2	1.6	0.8	1.3	0.7	2.3	1.6	1.9	2.3	1.18
10-20 cm	2.9	2.7	2.0	3.8	2.2	1.9	2.3	4.1	1.7	1.6	1.32
20-30 cm	1.6	1.8	6.6	3.6	3.4	4.5	1.0	1.0	1.9	1.3	1.37
Total	8.6	7.7	15.7	10.8	7.9	7.8	7.0	7.3	8.3	5.8	
Newdale Clay Loam Soil July											
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	4.2	0.9	7.5	3.6	nd	nd	2.4	5.0	4.0	8.1	1.18
5-10 cm	nd	nd	nd	nd	nd	nd	nd	nd	0.5	nd	1.18
10-20 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.32
20-30 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.37
Total	4.2	0.9	7.5	3.6	0.0	0.0	2.4	5.0	4.5	8.1	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	64.0	44.8	68.7	46.2	10.1	8.0	72.1	48.9	88.2	44.3	1.18
5-10 cm	4.9	6.7	4.9	12.0	3.9	3.4	8.1	15.2	4.3	8.8	1.18
10-20 cm	2.6	7.3	2.1	14.3	2.5	3.3	5.5	12.8	3.2	13.9	1.32
20-30 cm	1.2	3.3	0.8	4.8	1.4	1.9	3.3	7.9	0.8	5.0	1.37
Total	72.7	62.1	76.4	77.3	17.9	16.6	88.9	84.7	96.5	72.1	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	0.6	0.4	1.3	0.0	0.0	0.4	0.2	0.4	0.8	0.0	1.18
5-10 cm	0.0	0.0	0.1	0.0	0.4	0.1	0.0	0.2	0.4	0.0	1.18
10-20 cm	0.0	0.0	0.0	0.8	0.0	0.3	0.0	0.0	0.0	0.4	1.32
20-30 cm	1.0	0.0	0.0	0.8	0.0	0.0	0.0	0.7	0.0	0.5	1.37
Total	1.7	0.4	1.4	1.6	0.4	0.7	0.2	1.2	1.2	0.9	

Table 3.7 Soil urea-N, exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg N ha^{-1}) with depth for the Stockton fine sandy loam soil, 1996.

Stockton Fine Sandy Loam Soil May											
Irrigation Fertilizer Depth	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	34.5	29.4	58.8	40.9	2.3	4.4	38.9	30.9	42.1	24.7	1.15
5-10 cm	4.7	4.0	5.5	4.6	2.8	2.5	5.3	5.7	5.7	9.0	1.15
10-20 cm	3.5	3.1	7.5	5.1	1.9	2.3	5.6	5.9	4.1	4.1	1.21
20-30 cm	2.0	3.4	2.9	2.9	1.4	1.5	5.5	7.4	2.5	2.5	1.29
Total	44.7	40.0	74.7	53.5	8.4	10.7	55.3	49.8	54.3	40.3	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	38.8	42.8	30.8	36.9	12.2	7.7	45.3	37.6	43.8	36.7	1.15
5-10 cm	6.6	7.7	7.1	8.3	5.3	4.1	5.7	11.7	7.3	11.3	1.15
10-20 cm	4.8	8.7	7.5	8.1	6.0	3.8	4.0	10.4	7.7	9.6	1.21
20-30 cm	4.3	7.4	5.4	5.1	4.7	3.7	4.5	8.1	6.2	7.1	1.29
Total	54.4	66.5	50.7	58.4	28.2	19.3	59.5	67.9	65.0	64.6	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	1.4	2.1	5.3	1.7	0.3	1.5	1.1	0.4	1.0	0.0	1.15
5-10 cm	1.0	0.7	1.5	1.1	0.2	0.3	0.4	0.7	0.1	0.0	1.15
10-20 cm	0.4	1.6	0.0	0.5	0.2	0.9	0.9	0.0	0.0	0.0	1.21
20-30 cm	0.8	1.0	0.6	0.0	0.5	2.5	0.7	0.0	0.0	0.0	1.29
Total	3.5	5.4	7.3	3.3	1.3	5.2	3.1	1.2	1.1	0.0	
Stockton Fine Sandy Loam Soil July											
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	5.2	3.8	11.8	1.1	nd	nd	9.9	11.0	46.0	14.1	1.15
5-10 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.15
10-20 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.21
20-30 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.29
Total	5.2	3.8	11.8	1.1	0.0	0.0	9.9	11.0	46.0	14.1	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	30.4	38.4	39.2	40.2	7.0	8.1	40.1	47.7	42.6	39.1	1.15
5-10 cm	5.1	5.5	3.2	6.4	2.1	2.5	3.2	4.6	4.0	7.7	1.15
10-20 cm	1.9	2.9	1.4	4.6	1.4	2.0	1.2	3.8	2.1	4.6	1.21
20-30 cm	2.1	3.9	1.3	9.5	1.2	1.6	1.2	2.2	1.9	2.1	1.29
Total	39.4	50.7	45.1	60.7	11.7	14.2	45.7	58.3	50.6	53.6	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	0.0	0.2	2.7	0.1	0.5	0.0	0.0	0.0	0.2	0.8	1.15
5-10 cm	0.3	0.2	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.1	1.15
10-20 cm	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	1.21
20-30 cm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.29
Total	0.3	0.7	2.7	0.1	0.5	0.0	0.2	0.1	0.5	1.1	

Table 3.8 Soil urea-N, exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg N ha^{-1}) with depth for the Newdale clay loam soil, 1997.

Newdale Clay Loam Soil May											
Irrigation Fertilizer Depth	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	3.3	1.6	12.6	2.0	1.8	1.4	3.1	1.2	6.1	1.1	1.22
5-10 cm	1.4	1.5	1.7	1.9	1.9	1.1	0.7	1.2	0.8	0.7	1.22
10-20 cm	2.7	3.3	3.9	3.8	3.0	1.3	2.1	1.1	1.3	1.5	1.27
20-30 cm	3.8	2.2	3.0	4.4	2.3	1.2	1.9	1.8	1.6	1.7	1.3
Total	11.2	8.4	21.1	12.1	9.0	4.9	7.7	5.4	9.8	4.9	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	47.1	43.0	86.7	35.4	16.4	11.0	70.5	44.9	71.4	28.1	1.22
5-10 cm	8.8	16.3	10.8	17.6	7.4	6.9	10.6	13.2	9.0	21.3	1.22
10-20 cm	9.2	13.9	14.4	18.8	11.3	13.2	7.3	14.1	13.9	19.0	1.27
20-30 cm	7.2	14.3	13.2	9.5	12.3	16.5	6.7	16.8	13.9	9.8	1.3
Total	72.2	87.5	125.0	81.4	47.4	47.5	95.2	89.1	108.2	78.2	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	2.2	0.9	7.7	1.1	0.9	1.7	1.1	0.4	3.3	1.6	1.22
5-10 cm	0.8	0.8	1.2	1.5	0.8	1.1	0.5	0.8	1.0	1.0	1.22
10-20 cm	1.2	1.5	2.0	2.1	1.9	1.8	1.1	1.2	2.2	2.0	1.27
20-30 cm	2.2	1.5	1.4	2.0	1.9	1.9	0.9	1.1	1.4	1.7	1.3
Total	6.5	4.7	12.2	6.6	5.5	6.5	3.6	3.6	7.9	6.2	
Newdale Clay Loam Soil July											
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	8.5	1.5	18.3	1.3	1.0	1.5	2.6	4.4	3.8	1.5	1.22
5-10 cm	0.8	0.5	1.6	0.9	1.2	1.3	0.8	0.9	0.7	1.1	1.22
10-20 cm	1.6	1.6	2.4	0.8	1.5	1.8	1.8	1.7	1.0	1.1	1.27
20-30 cm	1.4	1.4	1.5	1.9	1.3	1.6	1.6	0.6	1.5	1.0	1.3
Total	12.4	5.1	23.8	4.9	5.0	6.2	6.7	7.6	7.0	4.7	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	49.5	34.0	31.5	62.5	4.8	6.4	64.3	64.5	77.4	45.9	1.22
5-10 cm	5.4	3.3	2.7	6.2	1.5	2.3	7.2	6.5	9.9	13.2	1.22
10-20 cm	1.3	1.0	0.9	0.6	1.0	1.2	2.3	1.1	1.8	2.1	1.27
20-30 cm	0.3	0.3	0.4	0.5	0.5	0.3	0.4	0.0	0.0	0.2	1.3
Total	56.5	38.6	35.4	69.7	7.9	10.2	74.1	72.1	89.1	61.4	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	2.9	1.9	9.5	1.7	0.0	0.0	1.1	0.9	0.7	0.3	1.22
5-10 cm	1.5	1.8	1.1	0.5	0.0	0.0	1.5	1.1	0.5	0.3	1.22
10-20 cm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.27
20-30 cm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3
Total	4.5	3.8	10.6	2.2	0.0	0.0	2.6	2.0	1.1	0.6	

Table 3.9 Soil urea-N, exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg N ha^{-1}) with depth for the Stockton fine sandy loam soil, 1997.

Stockton Fine Sandy Loam Soil May											
Irrigation Fertilizer Depth	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	43.3	8.8	31.1	7.6	4.4	5.6	33.7	27.7	49.5	11.7	1.34
5-10 cm	6.0	8.2	5.7	12.7	4.7	4.8	4.9	5.8	5.9	6.1	1.34
10-20 cm	14.4	9.7	9.7	10.6	9.7	10.2	11.1	10.0	10.4	8.5	1.33
20-30 cm	15.1	9.1	8.8	8.6	8.4	8.6	6.4	8.9	11.6	9.5	1.27
Total	78.7	35.8	55.4	39.4	27.2	29.2	56.1	52.5	77.5	35.8	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	35.6	37.0	27.0	23.2	5.7	2.2	49.5	35.3	38.4	33.2	1.34
5-10 cm	7.8	25.8	5.3	27.6	5.1	3.7	7.7	10.9	7.6	21.8	1.34
10-20 cm	9.6	12.9	8.7	15.0	9.2	8.9	9.9	14.6	9.3	14.1	1.33
20-30 cm	10.7	7.4	9.7	14.2	11.3	17.1	9.6	11.0	12.2	10.6	1.27
Total	63.6	83.2	50.8	80.1	31.3	31.9	76.7	71.9	67.5	79.6	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	1.7	1.5	11.3	1.0	0.8	1.0	1.1	0.4	8.6	1.9	1.34
5-10 cm	1.2	1.2	1.2	0.7	1.1	0.8	1.0	0.2	0.9	1.5	1.34
10-20 cm	2.1	2.7	2.1	1.6	1.6	1.5	0.5	0.7	2.2	3.3	1.33
20-30 cm	2.2	2.7	1.4	1.1	1.7	2.2	0.8	0.7	2.2	2.3	1.27
Total	7.2	8.1	16.0	4.4	5.2	5.5	3.4	2.1	13.9	9.1	
Stockton Fine Sandy Loam Soil July											
$\text{NH}_4\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	20.3	4.4	30.4	5.1	3.9	2.5	8.2	3.3	11.8	3.9	1.34
5-10 cm	4.9	4.6	4.0	5.5	4.3	2.8	3.3	3.1	3.3	2.8	1.34
10-20 cm	10.7	8.3	13.6	10.4	7.8	4.7	6.1	6.7	6.5	5.7	1.33
20-30 cm	8.3	7.9	9.0	8.5	8.3	4.6	5.0	6.0	7.8	6.0	1.27
Total	44.2	25.2	57.0	29.6	24.4	14.7	22.5	19.1	29.3	18.3	
$\text{NO}_3\text{-N (kg N ha}^{-1}\text{)}$											
0-5 cm	29.1	22.8	23.5	48.7	5.8	5.5	32.8	26.5	38.5	57.7	1.34
5-10 cm	5.1	6.3	4.5	12.6	2.8	4.0	5.6	16.5	4.3	15.1	1.34
10-20 cm	4.8	6.7	6.1	14.0	3.2	4.6	1.7	3.5	2.0	10.7	1.33
20-30 cm	2.5	2.2	2.0	1.7	1.8	2.5	0.5	1.5	0.9	2.1	1.27
Total	41.5	38.0	36.1	77.1	13.6	16.6	40.7	48.0	45.7	85.6	
$\text{Urea-N (kg N ha}^{-1}\text{)}$											
0-5 cm	1.8	0.6	3.1	0.6	0.0	1.5	2.2	2.2	2.2	2.0	1.34
5-10 cm	1.0	1.0	1.0	1.5	0.0	0.7	1.4	2.3	1.9	2.1	1.34
10-20 cm	0.6	0.5	0.7	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.33
20-30 cm	0.6	0.6	0.7	0.0	0.4	0.0	0.0	0.0	0.0	0.0	1.27
Total	4.0	2.7	5.4	2.6	0.4	2.3	3.6	4.6	4.1	4.2	

Bremner and Chai (1989) reported a greater proportion of urea-N present as exchangeable NH_4^+ in soils with higher organic matter, clay content and CEC. In contrast to these findings, a higher relative proportion of mineral N was present as exchangeable NH_4^+ for the Stockton FSL soil than for the Newdale CL soil for all studies and all treatments (Tables 3.6 to 3.9), although soil pH was similar (7.8-8.2) and the CEC, organic matter content and clay content of the Stockton FSL soil was markedly lower than that of the Newdale CL soil (Table 3.1). Ammonium content in soils of the control treatments was elevated for the Stockton FSL relative to the Newdale CL soil in 1997. Nitrification of NH_4^+ may have been restricted to a greater extent on the Stockton FSL soil than on the Newdale CL soil. Higher immobilization of NH_4^+ and NH_4^+ fixation by organic matter (Vittori Antisari et al. 1996) or interlayer clays (Mamo et al. 1993; Tisdale et al. 1993) of the clay loam soil may also have contributed to differences in exchangeable NH_4^+ content, as the total N measured in soil was lower for the clay loam soil than the fine sandy loam soil in 1997. An alternate possibility is that mineralization may have been greater for the 1997 Stockton FSL soil than for the Newdale CL soil due to differences in substrate quality (Moulin and Beckie 1994; Smith et al. 1993), as the preceding crop was barley for the fine sandy loam soil and canola for clay loam soil. The Stockton FSL may also have contained a more labile pool of organic material associated with more frequent wet/dry cycles of this soil (Killham 1994). The presence of urea in control samples is less easily explained and may indicate an error in analysis procedures. The lower levels of soil N measured in July relative to May may be due to enhanced immobilization, movement either laterally or vertically out of the sample area or greater volatilization losses accompanying increased soil temperature in July.

Differences between irrigated and non-irrigated treatments were more consistently

significant than differences due to the presence or absence of NBPT (Tables 3.10 and 3.11). A higher percent of total soil N measured was present as NO_3^- , and a lower percent as urea and exchangeable NH_4^+ , with irrigation than without for both urea and UAN, particularly with NBPT. There was lower exchangeable NH_4^+ at 0-5 cm and greater downward movement of NO_3^- for irrigated treatments than for corresponding non-irrigated treatments. Irrigation or increased water content enhances the rate of N transformations in soil (Singh and Beauchamp 1988) via dilution and distribution to improve N accessibility to soil microorganisms and enzymes. The impact of NBPT on urea-N distribution in soil is more subtle but can be enhanced when used in conjunction with irrigation or when soil water content is higher (Zhengping 1996). The actual impact of irrigation on N form and distribution in soil may have been confounded by increased total soil N with use of NBPT.

N-(n-butyl) thiophosphoric triamide with urea or UAN did not always influence final N form and distribution when measurement was restricted to the conclusion of the 2 and 3 week field studies. The relative proportion of exchangeable NH_4^+ , NO_3^- and urea likely changed during the course of the studies and final recoveries may not have reflected intermediate N levels. Laboratory studies have shown NBPT to only temporarily impact N transformations in soil (Zhengping 1996; Christianson et al. 1990; Christianson et al. 1993) where final urea, exchangeable NH_4^+ and NO_3^- content were similar for urea with and without NBPT, particularly at higher moisture content and alkaline pH.

Table 3.10 Contrast analysis and LS means standard error values for log-transformed soil N data for the Newdale clay loam soil.

Contrast ^z	0-5 cm Depth												5-10 cm Depth											
	May						July						May						July					
	NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	***	***	***	*	*	ns	***	***	**	ns	ns	***	***	***	ns	ns	ns	ns	**	**	ns	ns	ns	***
Urea vs UAN	ns	ns	ns	ns	**	ns	ns	ns	ns	ns	*	***	ns	ns	***	***	*	ns	ns	*	ns	ns	ns	ns
1 vs 2	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	*	**	ns	ns	ns	ns	ns	ns	ns	ns	ns
7 vs 8	**	*	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns
3 vs 4	ns	***	**	***	ns	***	ns	*	ns	***	***	***	***	ns	ns	ns	ns	ns	***	ns	ns	*	ns	ns
9 vs 10	ns	***	ns	**	*	ns	**	ns	ns	ns	***	ns	ns	**	ns	ns	ns	ns	***	ns	*	ns	**	ns
1 vs 3	ns	**	ns	**	ns	**	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	ns
7 vs 9	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	**	ns	ns	ns	ns	ns	**	ns	*	ns	**	ns
2 vs 4	ns	ns	***	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns
8 vs 10	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns
LS Means SE	0.12	0.19	0.44	0.31	0.39	0.32	0.19	0.26	0.72	0.42	0.15	0.31	0.17	0.18	0.37	0.19	0.42	0.24	0.16	0.39	0.13	0.14	0.11	0.33

Contrast	10-20 cm Depth												20-30 cm Depth											
	May						July						May						July					
	NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N		NO ₃ -N		Exch. NH ₄ -N		Urea-N	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	***	ns	ns	ns	ns	ns	*	ns	-	ns	ns	-	***	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	-
Urea vs UAN	*	ns	***	***	ns	ns	ns	ns	-	ns	ns	-	ns	ns	**	**	ns	ns	ns	ns	-	ns	ns	-
1 vs 2	***	ns	*	ns	ns	ns	ns	ns	-	ns	ns	-	**	*	**	ns	ns	ns	ns	ns	-	ns	*	-
7 vs 8	**	**	ns	ns	ns	ns	*	ns	-	ns	ns	-	ns	*	ns	ns	ns	ns	ns	**	-	ns	ns	-
3 vs 4	***	ns	ns	ns	ns	ns	***	ns	-	**	**	-	**	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	-
9 vs 10	***	ns	ns	ns	ns	ns	**	ns	-	ns	ns	-	**	ns	**	ns	ns	ns	ns	ns	-	ns	ns	-
1 vs 3	ns	*	ns	ns	ns	ns	ns	ns	-	ns	ns	-	ns	ns	**	ns	ns	ns	ns	ns	-	ns	*	-
7 vs 9	*	**	ns	ns	ns	ns	ns	ns	-	ns	ns	-	ns	ns	ns	ns	ns	ns	ns	**	-	ns	ns	-
2 vs 4	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	**	-	ns	ns	ns	*	ns	ns	ns	ns	-	ns	ns	-
8 vs 10	ns	ns	*	ns	ns	ns	ns	ns	-	ns	ns	-	ns	ns	**	ns	ns	ns	ns	ns	-	ns	ns	-
LS Means SE	0.13	0.17	0.34	0.20	0.46	0.24	0.38	0.24	-	0.20	0.11	-	0.12	0.21	0.31	0.19	0.48	0.26	0.44	0.08	-	0.19	0.14	-

*, **, *** Significant at p = 0.05, 0.01 and 0.001 levels, respectively; ns = not significant at p < 0.05 level and '-' = insufficient non-zero values for statistical analysis.

^z Treat = N Treatments; C = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea; 3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN; 8 = I UAN; 9 = NI UAN+NBPT; 10 = I UAN+NBPT and SE = Standard Error.

Table 3.11 Contrast analysis and LS means standard error values for log-transformed soil N data for the Stockton fine sandy loam soil.

Contrast ²	0-5 cm Depth												5-10 cm Depth											
	May						July						May						July					
	NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	***	***	***	***	ns	ns	***	***	**	***	ns	**	**	***	***	ns	ns	ns	**	***	-	ns	ns	***
Urea vs UAN	ns	***	ns	***	***	ns	ns	ns	ns	***	ns	**	ns	ns	*	*	**	ns	ns	ns	-	**	ns	**
1 vs 2	ns	ns	ns	***	ns	ns	ns	ns	ns	***	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	-	ns	ns	ns
7 vs 8	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	**	ns	ns	ns	ns	***	ns	ns	-	ns	ns	ns
3 vs 4	ns	ns	ns	***	ns	***	ns	ns	ns	***	**	**	ns	***	ns	**	ns	ns	*	ns	-	ns	ns	ns
9 vs 10	ns	ns	ns	***	ns	ns	ns	ns	ns	***	ns	ns	ns	*	ns	ns	ns	ns	ns	*	-	ns	ns	ns
1 vs 3	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	***	ns	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns
7 vs 9	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	-	ns	ns	ns
2 vs 4	ns	**	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	-	ns	ns	ns
8 vs 10	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	***	ns	ns	-	ns	ns	ns
LS Means SE	0.16	0.12	0.30	0.22	0.38	0.37	0.19	0.48	0.90	0.28	0.31	0.28	0.17	0.31	0.18	0.17	0.34	0.19	0.25	0.40	-	0.34	0.15	0.33

Contrast	10-20 cm Depth												20-30 cm Depth											
	May						July						May						July					
	NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N		NO ₂ -N		Exch. NH ₄ -N		Urea-N	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	***	ns	**	ns	ns	ns	ns	ns	-	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
Urea vs UAN	ns	ns	ns	ns	ns	ns	ns	ns	-	**	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	-	*	-	*
1 vs 2	*	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
7 vs 8	***	ns	ns	ns	ns	ns	**	ns	-	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
3 vs 4	ns	*	ns	ns	ns	ns	**	ns	-	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	-	ns	-	ns
9 vs 10	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
1 vs 3	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
7 vs 9	**	ns	ns	ns	ns	*	ns	ns	-	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	-	ns	-	ns
2 vs 4	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
8 vs 10	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-	ns	-	ns
LS Means SE	0.16	0.24	0.34	0.14	0.24	0.25	0.35	0.53	-	0.38	0.09	0.18	0.18	0.32	0.40	0.25	0.30	0.23	0.47	0.40	-	0.39	-	0.18

*, **, *** Significant at p = 0.05, 0.01 and 0.001 levels, respectively; ns = not significant at p < 0.05 level and '-' = insufficient non-zero values for statistical analysis.

² Treat = N Treatments; C = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea; 3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN;

8 = I UAN; 9 = NI UAN+NBPT; 10 = I UAN+NBPT and SE = Standard Error.

The most consistent treatment difference for the various N forms at the different depths occurred between NBPT treatments with and without irrigation. Urea and exchangeable NH_4^+ at 0-5 cm were significantly increased by the use of NBPT with urea and UAN in the absence of irrigation, averaging 5.8 and 23.3 kg N ha⁻¹, respectively for urea, and 2.5 and 21.4 kg N ha⁻¹, respectively for UAN. With irrigation, NBPT did not generally significantly alter final soil urea, exchangeable NH_4^+ and NO_3^- content relative to unamended urea and UAN. Although use of NBPT increased the proportion of soil N present as urea and exchangeable NH_4^+ in the first 5 cm of soil, NBPT did not increase downward movement of urea, exchangeable NH_4^+ or NO_3^- . Irrigation was required to transport fertilizer N to the lower depths. Movement of N may have been better assessed under controlled laboratory conditions using smaller depth increments to reveal subtle effects of NBPT on diffusion of N from the placement zone as observed by others (Christianson et al. 1993; Zhengping et al. 1996).

The effects of irrigation and NBPT were more pronounced on the Newdale CL soil than on the Stockton FSL soil. In the latter, use of NBPT in the absence of irrigation resulted in increased urea and exchangeable NH_4^+ at 0-5 cm depth and significantly lower NO_3^- , as a percent of the total N measured in the soil, relative to other treatments. Conversely, Christianson et al. (1993) found a less pronounced effect of NBPT on a clay soil (46% clay) which restricted movement of urea and NH_4^+ from the placement zone. However, the different pH of the soils of their studies may also have been a contributing factor (silty loam: 5.2; clay: 8.2).

The proportion of all N measured in each study (soil N plus volatilized NH_3 recovered in the lysimeters) that was present in the soil was greater with NBPT than without (Tables 3.12 and 3.13 and Figures 3.3 and 3.4), indicating soil N was increased

by the conservation of fertilizer N from NH_3 loss. This increase in soil N as a proportion of all N measured was lower in July than in May ($p < 0.0001$) and for the Stockton FSL soil than for the Newdale CL soil ($p = 0.0044$). The total amount of N measured in the soil (kg N ha^{-1}), although variable, was also greatest for NBPT treatments for all periods except May 1996 for the Newdale CL and 1997 for the Stockton FSL soil. This nitrogen was localized within 10 cm of the soil surface, even with irrigation, and therefore would have been readily accessible to plants, were they grown. Increased plant N accumulation and positive crop yield response to surface applications of NBPT-amended urea have been observed, for example with corn (Hendrickson 1992), perennial ryegrass (Watson et al. 1994a), wheat (Xiabon et al. 1995) and barley (Grant and Bailey 1997).

Table 3.12 Contrast analysis and LS means standard error values for log-transformed $\text{NH}_3\text{-N}$, exchangeable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and urea-N as a percent of total N measured for the Newdale clay loam soil.

Contrast ²	May										July									
	$\text{NO}_3\text{-N}$		Exch. $\text{NH}_4\text{-N}$		Urea-N		Total Soil-N		$\text{NH}_3\text{-N}$		$\text{NO}_3\text{-N}$		Exch. $\text{NH}_4\text{-N}$		Urea-N		Total Soil-N		$\text{NH}_3\text{-N}$	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	**	ns	ns	ns	**	**	ξ	ξ	ξ	ξ	ξ	ns	-	ξ	***	-	ξ	**	ξ	***
Urea vs UAN	ns	**	**	*	ns	ns	ξ	*	ξ	ns	**	***	-	ns	ns	-	ξ	***	**	***
1 vs 2	ns	ξ	ns	ns	ns	ns	ξ	ξ	*	ξ	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
7 vs 8	ns	ns	ns	ns	ns	ns	ns	**	ns	ξ	ns	ns	ns	ns	**	ns	ns	ns	ns	ns
3 vs 4	ns	ns	***	ns	ns	ns	ns	ns	*	***	**	ξ	ns	**	ns	ns	**	ns	ξ	ns
9 vs 10	ns	ns	ns	ns	ns	ns	ns	ns	*	ξ	ns	ns	-	ns	ns	-	ns	ns	ns	ns
1 vs 3	ns	***	ns	ns	ns	ns	ξ	ξ	ξ	ξ	*	*	ns	ns	ns	*	***	ns	*	ns
7 vs 9	ns	ns	ns	ns	ns	ns	ns	**	ns	ξ	ns	ns	-	ns	**	-	**	ns	***	ns
2 vs 4	ns	ns	***	ns	ns	ns	***	ns	ξ	ξ	***	ns	ns	ns	*	ns	ξ	***	ξ	**
8 vs 10	ns	ns	ns	ns	ns	ns	ns	ns	**	ξ	ns	ns	-	ns	ns	-	ns	ns	ns	ns
LS Means SE	0.09	0.06	0.29	0.31	0.56	0.42	0.01	0.49	0.26	0.16	0.05	0.12	0.69	0.44	0.45	0.37	0.03	0.04	0.17	0.36

² Total Soil-N = $\text{NH}_4\text{-N}$ + $\text{NO}_3\text{-N}$ + urea-N; Exch. = Exchangeable; Treat = N Treatments; C = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea;

3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN; 8 = I UAN; 9 = NI UAN+NBPT; 10 = Irrigated UAN+NBPT and SE = Standard Error.

*, **, ***, ξ = significant at p = 0.05, 0.01, 0.001 and 0.0001 levels, respectively; ns = not significant at p < 0.05 level; '-' = not available.

Table 3.13 Contrast analysis and LS means standard error values for log-transformed $\text{NH}_3\text{-N}$, exchangeable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and urea-N as a percent of total N measured for the Stockton fine sandy loam soil.

Contrast ²	May										July									
	$\text{NO}_3\text{-N}$		Exch. $\text{NH}_4\text{-N}$		Urea-N		Total Soil-N		$\text{NH}_3\text{-N}$		$\text{NO}_3\text{-N}$		Exch. $\text{NH}_4\text{-N}$		Urea-N		Total Soil-N		$\text{NH}_3\text{-N}$	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Treat vs C	ξ	ns	***	*	-	*	***	ξ	ξ	ξ	ξ	ns	-	**	-	ns	***	ξ	ξ	ξ
Urea vs UAN	***	ns	ns	ns	-	*	ξ	ns	ξ	ξ	ns	**	-	**	-	ns	ξ	ns	ξ	ns
1 vs 2	ns	ξ	ns	***	ns	ns	*	ξ	ns	ξ	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
7 vs 8	ns	ns	ns	ns	ns	ns	ns	***	ns	**	ns	ns	ns	ns	ns	ns	***	ns	ns	ns
3 vs 4	**	ξ	ns	**	ns	**	ns	ns	ns	ξ	***	ξ	ns	ns	ns	ns	***	ns	ξ	ns
9 vs 10	ns	***	ns	***	-	ns	ns	ns	**	**	***	**	-	ns	-	ns	ns	**	ns	**
1 vs 3	ns	ns	ns	ns	ns	**	ξ	ξ	ξ	ξ	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
7 vs 9	ns	ns	ns	ns	**	*	ns	ξ	ns	ξ	*	ns	-	ns	ns	ns	*	**	ns	ns
2 vs 4	ns	ns	ns	ns	ns	ns	***	ns	ξ	**	ns	**	ns	ns	ns	ns	**	ns	ξ	ns
8 vs 10	ns	ns	ns	**	-	ns	ns	**	ξ	ξ	ns	ns	-	ns	-	ns	ns	**	ns	ns
LS Means SE	0.08	0.10	0.21	0.10	0.58	0.41	0.03	0.01	0.32	0.21	0.08	0.14	0.45	0.34	0.98	0.39	0.07	0.04	0.28	0.26

² Total Soil-N = $\text{NH}_4\text{-N}$ + $\text{NO}_3\text{-N}$ + urea-N; Exch. = Exchangeable; Treat = N Treatments; C = Control; NI = Non-irrigated; I = Irrigated; 1 = NI Urea; 2 = I Urea;

3 = NI Urea+NBPT; 4 = I Urea+NBPT; 7 = NI UAN; 8 = I UAN; 9 = NI UAN+NBPT; 10 = Irrigated UAN+NBPT and SE = Standard Error.

*, **, ***, ξ = significant at p = 0.05, 0.01, 0.001 and 0.0001 levels, respectively; ns = not significant at p < 0.05 level; '-' = not available.

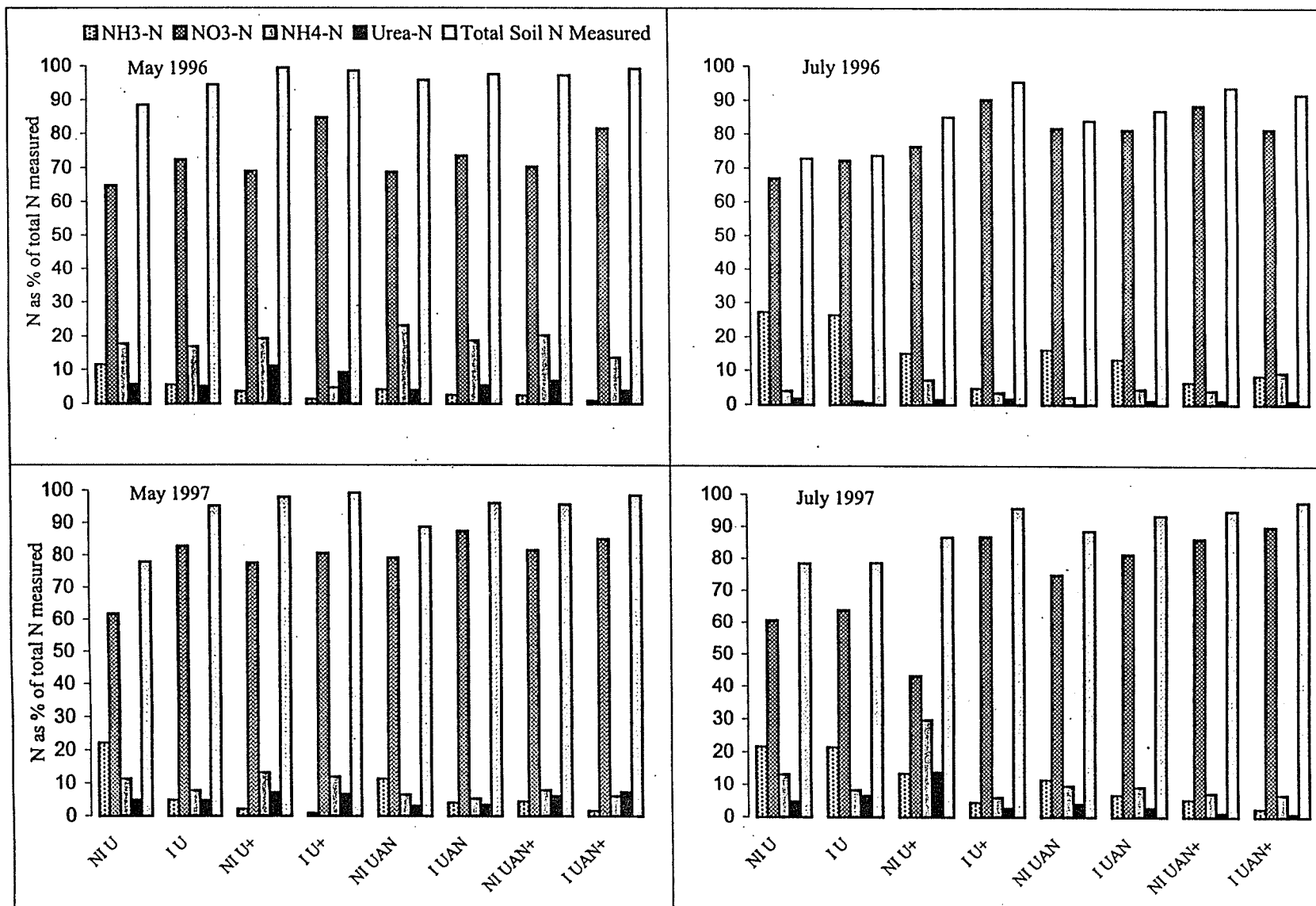


Figure 3.3 NH₃-N, NO₃-N, exchangeable NH₄-N and urea-N as a percent of total N measured in soil plus air for the Newdale clay loam soil.

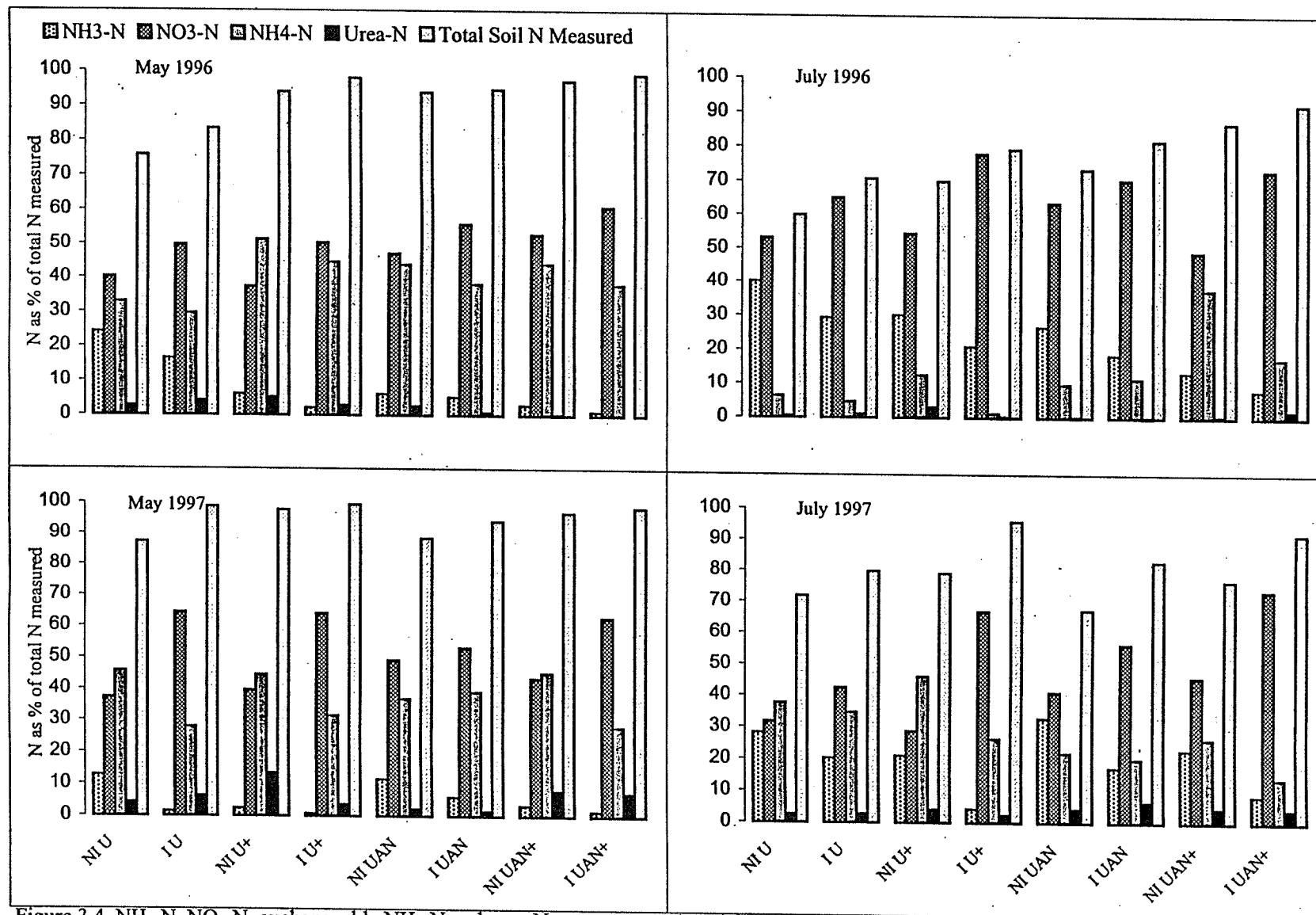


Figure 3.4 NH₃-N, NO₃-N, exchangeable NH₄-N and urea-N as a percent of total N measured in soil plus air for the Stockton fine sandy loam soil.

3.5 Conclusions

Use of NBPT resulted in a reduction in volatile losses of NH_3 from urea and UAN and an accumulation of urea-N and exchangeable NH_4 -N near the soil surface relative to unamended treatments. Ammonia-N conserved through use of NBPT with urea and UAN increased the proportion of total N measured in soil (NH_4 -N, NO_3 -N, urea-N) plus in air (NH_3 -N) that was present as soil N. This conserved N was readily available for plant uptake as it was generally localized in the upper 10 cm of soil.

How effective NBPT will be in a particular soil will be determined by the ability of urea to diffuse away from the surface and of NH_4^+ to be retained on exchange surfaces or be nitrified to NO_3^- . Unless rainfall within 24 hrs of application is imminent, or soils are very moist and cool, NBPT will improve the efficiency of surface-applied urea and UAN. If rainfall does not occur within approximately two weeks and conditions for NH_3 loss persist, NH_3 volatilization from NBPT-treated urea may approach a magnitude similar to loss from unamended urea. Thus, the timing and amount of rainfall following urea fertilizer application may be the most critical factor determining the magnitude of NH_3 loss and the transformation and distribution of urea and hydrolysis products in the soil, and hence NBPT effectiveness. These studies demonstrate the urease inhibitor NBPT can be used to mitigate NH_3 loss, and to an extent, alter the distribution of urea-derived N in soil under a range of conditions, particularly in the absence of a timely rainfall.

4. AMMONIA LOSS FROM UREA AMENDED WITH VARYING RATES OF NBPT APPLIED TO SOILS OF DIFFERING TEXTURE AND TEMPERATURE

4.1 Abstract

Field studies using lysimeters were conducted in 1996 and 1997 under modified zero tillage to compare the amount of ammonia volatilized from surface applications of granular urea (100 kg N ha^{-1}) treated with varying concentrations of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) (0.00, 0.05, 0.10 and 0.15% NBPT w/w). The studies were conducted on two Orthic Black Chernozemic soils, a Stockton fine sandy loam and a Newdale clay loam, in May and again in July to determine the influence of soil texture and temperature on NBPT performance at the varying rates. Ammonia losses were measured at various times to 12 days after fertilization (DAF) in 1996 and to 21 DAF in 1997. Total NH_3 losses decreased in the order of $0.00\% > 0.05\% > 0.15\% \geq 0.10\%$ where NBPT delayed peak NH_3 volatilization until the second and third weeks of the studies. The NH_3 loss did not always differ significantly among the various rates of NBPT although consistently greater suppression of NH_3 loss was achieved at the 0.10 and 0.15% rates than at the 0.05% rate. Use of NBPT with urea reduced total NH_3 loss by 28-88% over the entire study duration, and by 82 to 96% during periods of peak loss from unamended urea. Ammonia volatilization losses from NBPT-amended urea treatments were lower in May than in July with similar performance in both soils while total NH_3 loss in July was lower for the clay loam soil than the fine sandy loam soil.

4.2 Introduction

Urea is the dominant form of fertilizer nitrogen produced, transported and consumed world-wide as it is economical to manufacture and distribute, and is an efficient nitrogen source if properly managed (Harre and Bridges 1988; Byrnes and Freney 1995). In Western Canada, 1998 retail sales of urea fertilizer exceeded sales of all other N sources (Agriculture and Agri-Food Canada 1999). Once applied to the soil, urea is rapidly hydrolyzed by urease enzymes in the soil and organic material to yield 2 NH_4^+ per $\text{CO}(\text{NH}_2)_2$ (Sherlock and Goh 1985). This ammonium is susceptible to volatile loss to the atmosphere as $\text{NH}_{3(g)}$ if present in sufficient concentration near the soil surface (Koelliker and Kissel 1988). The potential for NH_3 volatilization is greatest under zero tillage where urea fertilizer is surface-applied to residue-enriched soil. Grant et al. (1996b) observed NH_3 loss from urea surface-applied to zero tillage at 38 and 83% of applied N in May and August, respectively, while Watson et al. (1994a) reported a maximum loss of 20.8% for a temperate grassland.

Treating urea fertilizer with the urease inhibitor NBPT may reduce the magnitude of NH_3 loss from surface applications of urea (Clay et al. 1990; Bremner et al. 1991). Once applied to the soil, NBPT converts to its oxon analog N-(n-butyl) phosphoric triamide (NBPTO) which is the actual inhibitor of urease activity (McCarty et al. 1989; Creason et al. 1990). The inhibitor occupies the urease active site, inactivating the enzyme (Mobley and Hausinger 1989; Kolodziej 1994) and delaying the period of maximum NH_3 loss (Watson et al. 1994a). The delay in hydrolysis reduces the concentration of NH_3 present near the soil surface which decreases the potential for NH_3 volatilization (Grant et al. 1996b) and improves the opportunity for rainfall to move urea

into the soil (Hendrickson 1992).

The performance of NBPT at varying concentrations has been studied under controlled laboratory conditions which showed increased inhibition of urease activity with increasing rate of NBPT applied with urea (Watson et al. 1994a; Carmona et al. 1990). Christianson et al. (1990) observed 68% inhibition of urea hydrolysis at 0.01% NBPT w/w with 1.5 to 3 times lower NH_3 losses when the rate was increased to 0.1%.

Field trials addressing this issue are limited (Watson et al. 1994a) and although results tend to agree with laboratory studies, the extension and applicability of these results to the Chernozemic soils of the Eastern Canadian Prairies is restricted. Field studies were conducted in 1996 and 1997 on two Black Chernozemic soils of different textures under zero tillage at two temperature regimes to assess the influence of various rates of NBPT on NH_3 volatilization.

4.3 Materials and Methods

Field experiments were conducted in 1996 and 1997 in mid-May and mid-July on two Orthic Black Chernozemic soils of differing physical and chemical properties (Table 4.1) (Goh et al. 1993; Hendershot et al. 1993ab; Janzen 1993). The 1996 trials commenced May 21 and July 16 on the Newdale clay loam (CL) soil and May 28 and July 17 on the Stockton fine sandy loam (FSL) soil. Trials in 1997 began May 20 and July 24 on the Newdale CL soil and May 6 and July 24 on the Stockton FSL soil. Soil moisture contents determined at seeding in May from a directly adjacent study were 33% and 22% for the Newdale CL and Stockton FSL soil, respectively, in 1996, and 34% and 18% for the Newdale CL and Stockton FSL soil, respectively, in 1997.

Table 4.1 Selected chemical and physical characteristics of soils used^{zy}.

Soil Name	Sand %	Silt %	Clay %	FC %	BD g cm ⁻³	CEC cmol kg ⁻¹	OC %	CaCO ₃ %	pH	EC μ S/cm
Newdale (1996)	32.2	36.3	31.5	30	1.17	49.8	4.3	1.6	8.0	896
Stockton (1996)	76.0	11.8	12.2	23	1.15	23.1	2.7	0.3	7.6	1092
Newdale (1997)	35.8	32.2	32.0	32	1.31	46.7	4.9	3.6	8.2	740
Stockton (1997)	75.5	11.4	13.1	19	1.34	23.2	2.1	1.4	8.2	756

^z All determinations made using 0-15 cm depth composite samples.

^y FC = field capacity; BD = bulk density; CEC = cation exchange capacity; OC = organic carbon; pH in water; EC = electrical conductivity saturated paste method.

Each experiment was arranged as a randomized complete block design having three replicates with 5 treatments occurring once in each block. The treatments consisted of a control (no fertilizer or NBPT) and 100 kg urea N ha⁻¹ at rates of 0.0, 0.05, 0.10 and 0.15% NBPT w/w. Study design and ammonia capture and analysis procedures followed that of Grant et al. (1996b), derived from the methodologies of Nommik (1973) and Fairlie and Goos (1986). White polyvinyl chloride (PVC) cylinders, 20 cm in length by 15 cm diameter, were inserted 5 cm into the soil with minimal soil disturbance. Prior to treatment application, surface residue was cleared from the immediate area of fertilizer placement within each cylinder to allow direct contact of fertilizer with soil to eliminate any direct effects of residue on urea hydrolysis and ammonia volatilization. Filter paper was placed on the soil surface in each cylinder and 150 mL distilled water added 24 hrs prior to fertilizer addition to attain equivalent soil surface moisture content within all lysimeters at a site. Fertilizer treatments were dispensed on the soil surface within a 2 cm diameter area at the centre of each PVC cylinder.

Immediately following fertilization, each cylinder was fitted with two polyfoam discs, 2.5 cm thick and 16 cm in diameter, previously double washed with distilled water, 0.001M H_2SO_4 and a glycerol-phosphoric acid solution (100 ml 14.7 M H_3PO_4 , 125 ml glycerol and 2275 ml deionized water), thoroughly wrung after each washing. The lower disc was inserted in the cylinder at 5 cm above the soil surface to trap volatilized NH_3 and the second disc placed 5 cm below the top of the cylinder to prevent drying and atmospheric NH_3 contamination of the lower disc. Each disc was designed to fit tightly within the cylinder to minimize escape of gaseous ammonia. Clear plexiglass sheets were positioned atop four corner-placed reinforcing bars approximately 30 cm above the cylinders in each block to provide protection from rainfall but permit incident sunlight.

On specified days after fertilization (DAF) during each trial (at 1, 2, 5, 8, 12 DAF in 1996 and extended to 15, 19 and 21 DAF in 1997) the lower disc was removed, immediately replaced by a fresh disc and placed in a sealed, airtight plastic bag containing 250 ml 2M KCl. Each disc was thoroughly rinsed in the KCl solution to extract the trapped ammonia and the solution decanted into vials, sealed and stored frozen until analysis. The KCl extract was analyzed at room temperature for ammonium-nitrogen content using a Technicon Autoanalyzer (Technicon Industrial Systems 1977).

Daily minimum, maximum and average air temperature, and soil temperature within the cylinders at 1 cm below the soil surface, were recorded throughout each study period on each soil in both study years. Data recording in May 1997 was delayed until 7 DAF on the Newdale CL and until 3 DAF on the Stockton FSL, and in July 1997 on the Newdale CL soil, data recording ended at 9 DAF due to equipment failure (Figure 4.1).

Statistical analyses were conducted on log-transformed data ($\log + 1$) (Steel et al. 1997) using the MIXED models procedure of the SAS Institute, Inc. (Littell et al. 1998)

as the design supported both fixed and random effects. Analyses were performed on cumulative gaseous ammonia loss to 5 DAF, from 5 DAF to 12 DAF, from 15 to 21 DAF (1997 only) and on total NH_3 loss. Data was analysed separately by trial and year as significant interactions occurred between year, soil, study period and treatment (Table 4.2). Least squares means standard error and contrast analysis probabilities are reported.

Table 4.2 Probability, F values and LS means standard error for log-transformed NH_3 -N data.

Source ^x	Sum to 5 DAF ^z				Sum 5 to 12 DAF				Sum 15 to 21 DAF ^y			
	NDF	DDF	F value	Pr > F	NDF	DDF	F value	Pr > F	NDF	DDF	F value	Pr > F
Soil (S)	1	16	18.34	0.0006	1	16	33.30	0.0001	1	8	14.33	0.0054
Study (St)	1	16	290.41	0.0001	1	16	60.59	0.0001	1	8	0.01	ns
Soil*Study	1	16	4.51	0.0496	1	16	24.64	0.0001	1	8	12.00	0.0085
Year (Y)	1	16	19.35	0.0004	1	16	3.55	ns	0	-	-	-
Year*Soil	1	16	3.20	ns	1	16	0.01	ns	0	-	-	-
Year*Study	1	16	6.53	0.0212	1	16	8.39	0.0105	0	-	-	-
Year*Soil*Study	1	16	15.07	0.0013	1	16	12.45	0.0028	0	-	-	-
Treatment (T)	4	64	265.91	0.0001	4	64	223.60	0.0001	4	32	28.58	0.0001
Soil*Treatment	4	64	1.57	ns	4	64	5.99	0.0004	4	32	3.22	0.0251
Study*Treatment	4	64	26.65	0.0001	4	64	32.58	0.0001	4	32	4.03	0.0093
S*St*T	4	64	1.09	ns	4	64	3.29	0.0163	4	32	4.54	0.0051
Year*Treatment	4	64	3.26	0.0169	4	64	4.63	0.0024	0	-	-	-
Y*S*T	4	64	0.93	ns	4	64	1.13	ns	0	-	-	-
Y*St*T	4	64	0.46	ns	4	64	3.57	0.0109	0	-	-	-
Y*S*St*T	4	64	2.02	ns	4	64	4.47	0.0030	0	-	-	-
LS Means Std Error			0.11				0.17				0.22	

^z DAF = Days After Fertilization.

^y Data available for 1997 only.

^x Study = May or July trial period.

4.4 Results

Total NH_3 volatilization loss from untreated urea during the 12 d studies in 1996 and the 21 d studies in 1997 was similar for each trial, in the range of 20 to 26%, with the exception of the July 1997 trial on the Stockton FSL soil where NH_3 loss was 50% of applied urea-N (Figure 4.1). Ammonia loss from untreated urea began within 2 DAF in

the July trials but not until 5 DAF in the May trials. The peak rate of NH_3 volatilization from untreated urea was generally reached by 5 DAF in July and 12 DAF in May.

N-(n-butyl) thiophosphoric triamide applied with urea at rates of 0.05, 0.10 and 0.15% significantly reduced NH_3 volatilization (Tables 4.3 and 4.4). Use of NBPT delayed the period of peak NH_3 loss until the second or third week after fertilization and reduced total NH_3 loss by 28-88% in the 1996 and 1997 studies. The pattern of NH_3 loss over the 12 and 21 d studies was best described by a quadratic equation (Tables 4.3 and 4.4). Extending the study period by 9 d in 1997 showed loss from NBPT-treated urea continued to gradually increase for the duration of the study. Ammonia volatilization losses from NBPT treatments were generally lower at the end of the 21 d studies in 1997 than at the end of 12 d studies in 1996.

N-(n-butyl) thiophosphoric triamide performance was significantly different for the two soils and the two trial dates (Table 4.2). The inhibitory effect was less persistent in the July trials where NH_3 loss from treated urea occurred by 5 DAF, whereas NH_3 loss from NBPT-amended urea during the May trials was negligible until at least 8 DAF (Figure 4.1). The rate and extent of NH_3 loss from NBPT-treated urea was lower on the Newdale CL than the Stockton FSL soil, particularly in July where rate of loss from all treatments was accelerated due to increased soil temperatures. In July, the various rates of NBPT reduced ammonia losses by about half as much on the Stockton FSL soil as on the Newdale CL soil in both years.

The duration and magnitude of urease inhibition was slightly higher at the 0.10 and 0.15% rates than at the 0.05% rate although the differences were predominantly significant for the May studies in 1997 (Table 4.4). Ammonia volatilization throughout each study was very similar at the 0.10 and 0.15% rates. Use of NBPT at 0.05, 0.10 and

0.15% w/w reduced NH_3 loss by i) May Newdale CL soil: 77.4, 84.2 and 84.7%, ii) July Newdale CL soil: 69.1, 74.4 and 75.0%, iii) May Stockton FSL soil: 64.2, 80.7 and 81.0%, and iv) July Stockton FSL soil: 31.0, 43.7 and 36.8%, respectively.

Table 4.3 Contrast analysis and standard error values for log-transformed 1996 NH_3 -N data.

Source	Sum to 5 DAF				Sum 5 to 12 DAF				Sum to 12 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July	May	July	May	July
Treatment	0.0001	0.0001	0.0001	0.0007	0.0001	0.0033	0.0001	0.0006	0.0001	0.0003	0.0001	0.0004
LS Means SE	0.18	0.36	0.16	0.59	0.39	0.78	0.44	0.57	0.43	0.82	0.6	1.02
<u>Contrast</u>												
U vs NBPT U	0.0001	0.0001	0.0001	0.0003	ns	ns	0.0002	ns	0.0001	0.0037	0.0001	0.0288
0.05% vs 0.15%	0.0136	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
0.10% vs 0.15%	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
quadratic	0.0001	0.0001	0.0001	0.0006	0.0001	0.0098	0.0001	0.0019	0.0001	0.0004	0.0001	0.0003

DAF = Days After Fertilization; SE = Standard Error and U = Urea.

Table 4.4 Contrast analysis and standard error values for log-transformed 1997 NH_3 -N data.

Source	Sum to 5 DAF				Sum 5 to 12 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treatment	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
LS Means SE	0.07	0.25	0.12	0.31	0.25	0.37	0.23	0.59
<u>Contrast</u>								
U vs NBPT U	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	ns
0.05% vs 0.15%	0.0016	ns	ns	ns	0.0386	0.0294	0.0077	ns
0.10% vs 0.15%	0.0087	ns	ns	ns	ns	ns	ns	ns
quadratic	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

Source	Sum 15 to 21 DAF				Sum to 21 DAF			
	Newdale CL		Stockton FSL		Newdale CL		Stockton FSL	
	May	July	May	July	May	July	May	July
Treatment	0.0005	ns	0.0001	0.0036	0.0001	0.0001	0.0001	0.0001
LS Means SE	0.24	0.44	0.23	0.69	0.37	0.61	0.44	0.97
<u>Contrast</u>								
U vs NBPT U	ns	ns	ns	0.0078	0.0001	0.0002	0.0001	ns
0.05% vs 0.15%	ns	ns	0.0009	ns	0.0359	ns	0.0012	ns
0.10% vs 0.15%	ns	ns	0.0415	ns	ns	ns	ns	ns
quadratic	0.0004	ns	0.0001	ns	0.0001	0.0001	0.0001	0.0001

DAF = Days After Fertilization; SE = Standard Error and U = Urea.

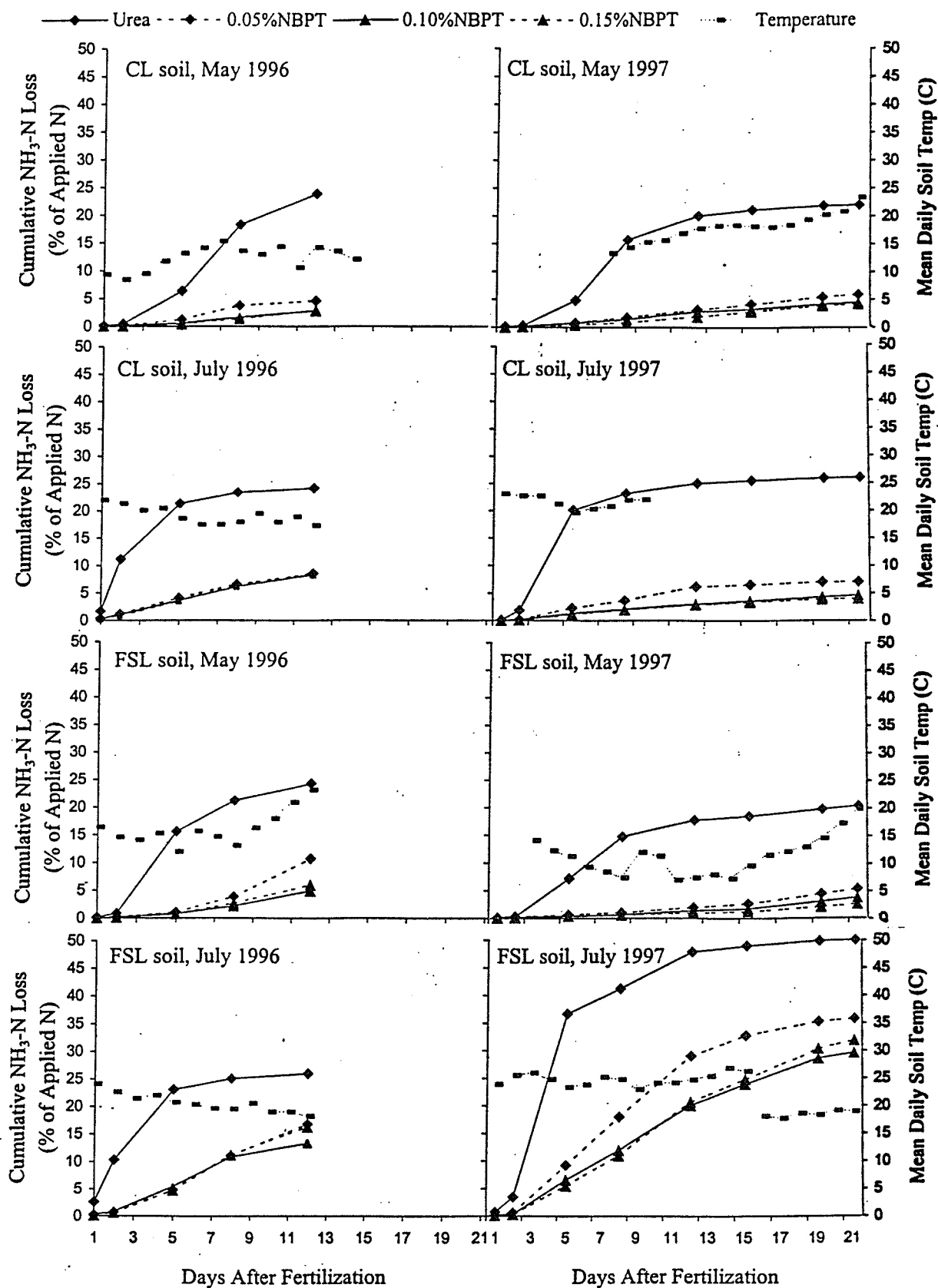


Figure 4.1 Cumulative $\text{NH}_3\text{-N}$ loss from urea fertilizer amended with NBPT (0.0, 0.05, 0.10 and 0.15% w/w), minus control for 1996 and 1997 studies.

4.5 Discussion

The pattern and magnitude of NH_3 loss from NBPT-treated urea varied between soils and between the May and July trials, being related to soil and weather factors. Soil factors predominantly establish the potential for NH_3 production and volatilization while the actual magnitude of a volatilization event is determined by weather conditions (Hargrove 1988). As temperature increases, the increased rate of hydrolysis favours NH_3 formation (Nelson 1982) and subsequent losses via NH_3 volatilization can be high if soil and moisture conditions are also conducive to loss. Soil temperatures were similar in both years with the exception of the Stockton FSL soil in May 1997 where temperatures were exceptionally low, ranging from 5 to 15°C during the first 19 days of the trial. Total NH_3 volatilization at the 0.00 to 0.15% NBPT rates were lowest in this trial demonstrating the predominant role of weather conditions on the magnitude of NH_3 volatilization from surface-applied urea.

The exceptionally high losses measured in 1997 on the Stockton FSL July trial for all treatments are most likely due to the high soil temperatures (20-25°C) and moist soil conditions (60 mm rain prior to start of study), which resulted in rapid granular dissolution and urea hydrolysis. The accelerated rate of urea dissolution provided the urease enzyme with abundant substrate while the warm soil temperatures promoted increased urease activity to more rapidly overcome the NBPT inhibitory effect. Ammonia would have concentrated near the soil surface, creating a high gradient for NH_3 volatilization in the initial days of the study as the soil surface dried, before sufficient downward movement of urea and hydrolysis products into the soil profile could proceed to decrease the potential for NH_3 loss.

There is a maximum number of enzyme active sites that can be occupied at a given concentration of NBPT. Therefore if urease activity and concentration of dissolved urea increase such as under warm, moist soil conditions, then there exists a lower percentage of total enzyme active sites that can be occupied by NBPT. Under these conditions a greater concentration of NBPT is required to achieve a level of inhibition equivalent to when loss potential is low such as when the soil is cool and dry. This scenario may explain the slightly more persistent inhibition observed for all studies at the 0.10 and 0.15% rates than at the 0.05% rate of NBPT and the gradual increase in NH_3 volatilization from all rates of NBPT-treated urea as urea hydrolysis progressed over the duration of the experiment. Hendrickson and Douglass (1993) found minimal amounts of NBPT and NBPTO remained at the conclusion of a 14 d laboratory experiment.

The duration of NBPT activity is shorter at higher temperatures (Clay et al. 1990; Bremner et al. 1991; Watson et al. 1994a; Grant et al. 1996b) which promote greater urease activity. Therefore, at higher temperatures the hydrolysis rate may surpass the rate of NBPT conversion to NBPTO or the rate of inhibitor degradation may be more rapid. Enhanced loss at all rates of NBPT in the July trials relative to the May trials for both soils coincided with elevated soil temperatures. In addition, the 0.05% rate was less persistent than the higher rates in the July trials.

The greatest potential for positive effects of NBPT will likely be observed on soils with high potential for loss from unamended urea such as coarse textured soils with warm temperatures or elevated urease activity, high soil water flux or drying conditions, low CEC, low organic matter, and high pH (Watson et al. 1994b). Under these conditions downward diffusion of urea and NH_4^+ and retention of NH_4^+ on the soil is limited, and NH_3 formation is rapid (Sherlock and Goh 1985). In our studies NBPT was most

effective during the first week after fertilization and on the soils most prone to NH_3 loss. The potential for NH_3 volatilization from urea was greatest on the Stockton FSL soil in the July trial, where soil physical and chemical conditions in combination with soil environment conditions, namely warm soil temperatures and moist, drying soil, were conducive to NH_3 formation and volatilization. In the May trials, control was greatest at 5 and 8 DAF in 1996 and 5 to 12 DAF in 1997, which coincided with periods of peak loss from unamended urea.

The 0.10 and 0.15% NBPT rates were similar in effectiveness; therefore, the 0.10% rate provided optimal performance per economic investment. In agreement with findings of this experiment, Watson et al. (1994a) calculated an optimum NBPT rate of 0.10% w/w based on the observation of diminishing returns.

4.6 Conclusions

Ammonia loss from surface-applied urea was significantly reduced with use of NBPT at rates of 0.05, 0.10 and 0.15%. Suppression of NH_3 loss was slightly greater and of longer duration at the 0.10 and 0.15% rates than at the 0.05% rate. The greatest reduction in NH_3 loss occurred during the first week of the studies when NH_3 losses were greatest from unamended urea. Use of NBPT delayed the peak period of loss until the second and third weeks of the studies. Ammonia loss from all treatments was greatest in July when warm soil temperatures would have resulted in rapid granular dissolution, elevated urease activity, and upward movement of urea and NH_3 to the soil surface in the evaporation stream, resulting in high concentrations of NH_3 near the soil surface. Ammonia losses at this time were greater on the Stockton FSL soil versus the Newdale

CL soil likely because of greater aeration of the FSL soil due to characteristic continuous pore structure, and lower capacity for retention of NH_4^+ due to the lower organic matter content and CEC.

The commercial rate of NBPT application to urea is 0.14% w/w. This research indicates a lower rate of NBPT may be suitable for surface applications of urea under zero tillage field conditions in Western Manitoba. Further field research is required to evaluate performance of NBPT with surface applications of urea to residue-covered soil and to determine the potential yield benefit at lower rates of NBPT.

5. PLANT RESPONSE AND SOIL N FOLLOWING SURFACE APPLICATION OF UREA FERTILIZERS WITH AND WITHOUT NBPT: EFFECT OF SOIL TEXTURE, TEMPERATURE AND IRRIGATION

5.1 Abstract

Field studies using lysimeters were conducted in May and July of 1996 and 1997 on two Orthic Black Chernozems, a Stockton fine sandy loam and a Newdale clay loam, under modified zero tillage to investigate the influence of irrigation, soil texture and temperature on total N uptake and biomass of CWRS wheat, and soil N as NO_3^- and exchangeable NH_4^+ following surface-application of urea (60 kg N ha^{-1}) and UAN (60 kg N ha^{-1}) with and without the urease inhibitor NBPT. Fertilization and irrigation had little or no effect on plant biomass and N accumulation of wheat grown on either soil. Growing conditions within the lysimeters resulted in uneven emergence and poor plant growth, possibly due to heat and moisture stress. Use of NBPT with urea generally increased plant biomass and N accumulation whereas NBPT-amended UAN tended to slightly decrease biomass and total N uptake. Forms and distribution of N in the soil were not significantly affected by N source, NBPT amendment or irrigation, but varied significantly with year, soil type, study period and depth to 10 cm. There were no consistent patterns of soil N distribution with depth for the various treatment combinations. Nitrogen removal by plants, extended time between fertilizer application

any initial effects of irrigation or NBPT on urea hydrolysis and distribution of hydrolysis products in the soils evaluated. Overall this experiment failed to meet the objective of identifying a possible crop response to NBPT-amended urea and UAN as the design and environmental conditions restricted plant growth and uptake of N. In addition, high residual soil N was not limiting to plant growth as had been intended.

5.2 Introduction

Urea is currently the most important agricultural nitrogen fertilizer worldwide (International Fertilizer Industry Association 1998) and is the major granular fertilizer for agricultural use in Western Canada (Agriculture and Agri-Food Canada 1998). Once applied to the soil, urea hydrolyzes to NH_4^+ which can further dissociate to NH_3 . Ammonia present near the soil surface may be volatilized to the atmosphere which reduces the amount of fertilizer N available for crop uptake. Surface applications of urea to soil under zero tillage are particularly susceptible to high NH_3 losses as hydrolysis may proceed on the residue-enriched surface prior to urea moving into the soil (Byrnes and Freney 1995). Malhi et al. (1996) reported poor uptake of N by barley when urea was broadcast under zero tillage relative to other methods of placement. Surface-applied urea ammonium nitrate is also susceptible to NH_3 volatilization although generally at a lower magnitude than that of surface-applied urea (Hargrove 1988).

Amendment of urea with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) can reduce NH_3 loss from surface applications of urea (Grant et al. 1996b; Watson et al. 1994a) and UAN (Fox and Piekielek 1993) in the field by delaying urea

hydrolysis. This delay decreases the rate of NH_3 formation and increases the probability of incident rain moving urea into the soil. Use of NBPT shows most promise for reducing NH_3 volatilization under conditions conducive to high NH_3 volatilization (Watson et al. 1994b) and NH_4^+ immobilization such as surface application of urea to a zero tillage system soil (Al-Kanani and Mackenzie 1992) or to a moist soil subject to evaporation or drying (Clay et al. 1990). However, for NBPT to be economically viable, the conserved N must be available to plants to increase plant N content and yield. Crop response to NBPT application will only occur when conditions are conducive to large volatilization or immobilization losses and when N is limiting to crop production (Murphy and Ferguson 1997).

Crop response to improved efficiency of urea application with use of NBPT has predominantly been studied with corn and has been shown to depend on the overall capacity of the crop to benefit from the increased quantity of available N. Results from 78 trials with corn conducted over a five year period across the United States showed NBPT increased grain yields by an average of 4.3 bu acre^{-1} and 1.6 bu acre^{-1} when applied with urea and UAN, respectively. Corn yield in a ridge till system increased when NBPT was used with urea (5.6 bu acre^{-1} increase) in only one year of a 3 year field study where it was concluded that soil and weather conditions were not conducive to NH_3 loss, or nitrogen was not limiting to yield in the other years (Murphy and Ferguson 1997).

Limited information is available on the effectiveness of NBPT-amended urea to improve plant availability of N in the soils of Western Canada (Grant and Bailey 1997; Xiaobin et al. 1995). Field studies were conducted in Manitoba in 1996 and 1997 with zero-till wheat to assess the influence of NBPT on plant yield, N accumulation in plant tissue, and spatial distribution of NO_3^- and NH_4^+ in soil when surface-applied with urea

and UAN under varying soil texture and temperature.

5.3 Materials and Methods

Field experiments were conducted in May and July in 1996 and 1997 (Table 5.1) on Orthic Black Chernozemic soils of differing physical and chemical properties (Table 5.2) (Goh et al. 1993; Hendershot et al. 1993ab; Janzen 1993). Soil moisture contents determined at seeding in May from a directly adjacent study were 33% and 22% for the Newdale CL and Stockton FSL soil, respectively in 1996, and 34% and 18% for the Newdale CL and Stockton FSL soil, respectively in 1997. In the May studies, Katepwa wheat (*Triticum aestivum* L.) was direct-seeded into existing stubble and residue from the previous year's crop, simulating zero-tillage management. For the July studies, Katepwa wheat was hand seeded between rows seeded in May, mowed to a height of 2.5 cm and cleared of fresh residue just prior to seeding in July. Daily air temperature and soil temperature at 5 and 30 cm were recorded throughout each trial period (Table 5.3).

Table 5.1 Study periods for the 1996 and 1997 studies.

	May		July	
	Start	End	Start	End
Newdale CL soil				
1996	May 21	July 03	July 16	August 26
1997	May 20	July 10	July 13	September 13
Stockton FSL soil				
1996	May 28	July 02	July 16	August 26
1997	May 06	June 25	July 11	September 13

Table 5.2 Selected chemical and physical characteristics of soils used^z.

Soil Name	Sand %	Silt %	Clay %	FC %	BD g cm ⁻³	CEC cmol kg ⁻¹	OC %	CaCO ₃ %	pH	EC μ S/cm
Newdale (1996)	32.2	36.3	31.5	30	1.17	49.8	4.3	1.6	8.0	896
Stockton (1996)	76.0	11.8	12.2	23	1.15	23.1	2.7	0.3	7.6	1092
Newdale (1997)	35.8	32.2	32.0	32	1.31	46.7	4.9	3.6	8.2	740
Stockton (1997)	75.5	11.4	13.1	19	1.34	23.2	2.1	1.4	8.2	756

^z All determinations made using 0-15 cm depth composite samples.^y FC = field capacity; BD = bulk density; CEC = cation exchange capacity; OC = organic carbon; pH in water; EC = electrical conductivity saturated paste method.

Table 5.3 Meteorological data collected during each study period.

	Clay Loam Soil				Fine Sandy Loam Soil			
	May		July		May		July	
	1996	1997	1996	1997 ^z	1996	1997	1996	1997
Precipitation (mm)	76	188	118	1	67	185	67	103
Air Temp (°C)								
Mean	16.7	17.7	18.2	20.1	15.8	16.2	18.0	16.7
Low	9.4	11.6	11.3	13.6	7.8	8.8	10.2	9.0
High	24.8	24.2	26.0	27.4	23.1	23.6	26.3	25.1
Mean Soil Temp 5 cm (°C)	16.3	19.5	19.4	21.8	18.4	19.0	20.4	19.4
Mean Soil Temp 30 cm (°C)	14.5	15.5	19.1	19.9	18.0	17.7	22.5	19.6

^z Data available from July 13 to July 29 only due to equipment failure.

White polyvinyl chloride (PVC) cylinders, 20 cm in length by 15 cm diameter, were inserted in the soil to a depth of 5 cm within the seed row with minimal soil disturbance. Prior to treatment application, excess residue was removed from within each

cylinder to maintain similar percent residue coverage among treatments, and all residue was cleared from the immediate area of fertilizer placement. Filter paper was placed on the soil surface in each cylinder and 150 mL distilled water added 24 hrs prior to fertilizer addition to attain equivalent soil surface moisture content within all lysimeters at a site. Fertilizer treatments were dispensed on the soil surface within a 2 cm diameter area at the centre of each cylinder. Clear plexiglass sheets were positioned atop four corner-placed reinforcing bars approximately 30 cm above the cylinders in each block for the first 2 weeks of the study to accommodate irrigation treatments and were then removed to allow incident rainfall to reach the soil.

Each individual study was arranged as a split-plot design with completely randomized blocks. Irrigation was the main plot unit and was randomized within each replicate while the sub-plot consisted of the fertilizer treatments randomly assigned within each irrigation plot. The treatments were an irrigated and a non-irrigated control (no fertilizer or NBPT), 60 kg N ha⁻¹ as urea with and without NBPT (0.14% w/w) both with and without irrigation, and 60 kg N ha⁻¹ as urea ammonium nitrate (UAN) with and without NBPT (0.14% w/w) both with and without irrigation. Irrigation consisted of adding the equivalent of 2 cm of deionized water at 2 and 8 days after fertilization (DAF) with additional watering periods at 26 and 33 DAF for the Stockton FSL May trial in 1997 in an attempt to alleviate moisture stress.

Plants within the lysimeters were harvested at boot, air-dried, weighed, ground with a stainless steel Wiley mill to pass through a 1 mm screen, and analysed for total N (Isaac and Johnson 1976). The number of plants harvested per lysimeter ranged from 0 to 8. This extreme variation was due to uneven emergence and death of plants caused by heat and moisture stress. After plant removal, all soil at the 0-5 cm and 5-10 cm depths

was removed, and three soil cores (2.5 cm diameter) taken from each lysimeter at 10-20, 20-30 and 30-60 cm depths, composited by depth. Multiple heavy rainfalls (97 mm) followed crop removal on the Stockton FSL soil in May 1997, delaying soil removal for 15 days, although the soil was covered with plastic during this period. Field moist soil samples were extracted and analysed for exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (Maynard and Kalra 1993). Technical difficulties rendered $\text{NH}_4\text{-N}$ data in 1996 below 0.25 mg kg^{-1} as unreliable. Values below this limit are reported as "nd".

Statistical analyses were conducted using the MIXED models procedure of the SAS Institute, Inc. (Littell et al. 1998). There was no treatment by irrigation interaction for plant biomass and N data (Table 5.4) and for soil N data (data not shown); therefore data from the two irrigation regimes was combined to show the overall effect of each fertilizer treatment. Contrast analysis probabilities and least squares means standard error are reported for plant N and biomass and log-transformed (Little and Hills 1978) soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ data for each study. Soil data for depths 10-20, 20-30 and 30-60 cm were combined because there were no significant differences among these depths for the various fertilizer treatments. Statistical analyses of $\text{NH}_4\text{-N}$ data were not possible where insufficient data were available in the 1996 studies due to technical difficulties.

Table 5.4 Probability values and standard errors of effect of treatment, irrigation, temperature and soil on total plant N and biomass of wheat.

Source	1996		1997	
	Biomass	Total N	Biomass	Total N
Irrigation	ns	ns	ns	ns
Treatment	ns	ns	**	**
Irrigation*Treatment	ns	ns	ns	ns
Soil	ns	ns	ξ	**
Irrigation*Soil	ns	ns	ns	ns
Treatment*Soil	ns	ns	***	***
Irrigation*Treat*Soil	ns	ns	ns	ns
Temperature ^z	*	**	ξ	ξ
Irrigation*Temperature	**	*	ns	ns
Treatment*Temperature	ns	ns	ns	**
Irrigation*Treat*Temp	ns	ns	ns	ns
Soil*Temperature	ns	ns	ξ	ξ
Irrigation*Soil*Temp	ns	ns	*	*
Treatment*Soil*Temp	ns	ns	ns	ns
Irrigation*Treat*Soil*Temp	ns	ns	ns	ns
LS Means Std Error ^y	57.5	1.3	34.2	0.6

*, **, ***, ξ = significant at p = 0.05, 0.01, 0.001 and 0.0001 levels; ns = not significant at p < 0.05 level.

^z Temperature = May and July study periods

^y Least squares means standard error using Block*Irrigation as the error term.

5.4 Results and Discussion

5.4.1 Plant Biomass and N Accumulation

Treatment effects on plant biomass and N accumulation were only evident in the 1997 studies (Table 5.4) where biomass and total plant N uptake were markedly greater

for the Newdale CL soil in May than other study periods (Tables 5.5 and 5.6). The timing and quantity of precipitation during this study (188 mm) was not limiting to plant growth as in the other trial periods. Although the Stockton FSL site received a similar quantity of precipitation (185 mm), the plants had been harvested immediately before the site received 97 mm, at the end of a prominent dry period which severely hampered crop performance. Uneven germination in the cylinders also contributed to high treatment standard errors, restricting the number of significant treatment effects. In addition, poor crop growth likely restricted plant uptake of nitrogen so that fertilizer N at 60 kg N ha^{-1} plus residual and recently mineralized soil N likely provided sufficient N for plant growth, even if a proportion of the urea fertilizer was volatilized as NH_3 .

There were no differences in plant biomass and N accumulation between urea and UAN fertilizers. On average, amendment of urea with NBPT increased plant biomass and plant N accumulation from 257.2 to 326.6 g m^{-2} and from 5.7 to 7.0 g N m^{-2} , respectively. However, the response was only significant for the 1997 May study on the Newdale CL soil where biomass and total plant N uptake increased from 315.8 to 670.8 g m^{-2} and from 6.1 to 12.3 g N m^{-2} , respectively. Overall, amendment of UAN with NBPT slightly decreased or did not alter plant biomass and N accumulation. On the Stockton FSL soil in July 1997, total plant N uptake decreased from 5.3 to 2.4 g N m^{-2} when UAN was amended with NBPT.

Table 5.5 Plant biomass (g m^{-2}), contrast analysis values and LS means standard error for wheat.

Treatment	Newdale Clay Loam Soil				Stockton Fine Sandy Loam Soil			
	May		July		May		July	
	1996	1997	1996	1997	1996	1997	1996	1997
NI Urea	232.9	245.0	442.3	79.9	317.7	196.3	518.0	168.3
I Urea	238.3	386.6	270.1	122.9	329.7	186.0	184.3	196.4
NI Urea+NBPT	303.3	648.3	361.1	151.5	310.5	199.7	321.8	238.4
I Urea+NBPT	317.5	693.4	381.8	241.4	351.8	262.3	323.5	117.1
NI Control	272.1	725.6	246.7	148.6	188.3	256.4	310.3	135.1
I Control	187.3	328.6	221.0	171.4	283.5	222.1	204.3	137.5
NI UAN	293.0	578.5	404.6	155.4	291.1	178.5	432.4	267.7
I UAN	293.9	610.9	437.3	175.8	237.9	242.8	213.4	93.6
NI UAN+NBPT	319.0	741.3	417.7	115.4	253.3	150.7	379.7	102.6
I UAN+NBPT	335.6	620.7	317.1	125.8	346.7	150.0	227.8	61.0
<u>Contrast</u>								
Treatment vs Control	ns	ns	*	ns	ns	ns	ns	ns
Urea vs UAN	ns	ns	ns	ns	ns	ns	ns	ns
Urea vs NBPT+Urea	ns	**	ns	ns	ns	ns	ns	ns
UAN vs NBPT+UAN	ns	ns	ns	ns	ns	*	ns	ns
LS Means Std Error	40.4	80	155.1	34.7	46.7	20.3	73.7	33.1

*, **, *** = significant at $p = 0.05$, 0.01 and 0.001 levels, respectively; ns = not significant at $p < 0.05$ level; NI = non-irrigated; I = irrigated.

Table 5.6 Plant N accumulation (g N m⁻²), contrast analysis values and LS means standard error for wheat.

<u>Treatment</u>	<u>Newdale Clay Loam Soil</u>				<u>Stockton Fine Sandy Loam Soil</u>			
	<u>May</u>		<u>July</u>		<u>May</u>		<u>July</u>	
	<u>1996</u>	<u>1997</u>	<u>1996</u>	<u>1997</u>	<u>1996</u>	<u>1997</u>	<u>1996</u>	<u>1997</u>
NI Urea	4.9	5.3	8.6	1.0	6.0	5.8	12.8	4.3
I Urea	5.7	6.8	6.2	2.2	6.9	5.2	4.3	5.4
NI Urea+NBPT	6.8	11.7	6.3	2.5	6.5	5.7	8.5	6.6
I Urea+NBPT	6.9	12.8	7.9	3.5	7.3	7.4	8.3	3.2
NI Control	5.6	12.1	5.5	2.6	3.9	7.9	8.0	6.7
I Control	3.9	5.9	5.3	2.5	5.3	6.5	5.5	3.6
NI UAN	5.9	10.9	8.5	2.2	6.1	5.1	11.4	6.2
I UAN	6.6	9.0	9.4	2.7	5.3	7.1	5.7	4.4
NI UAN+NBPT	6.4	13.2	8.0	1.8	5.2	5.9	8.9	2.6
I UAN+NBPT	8.0	11.8	7.5	1.8	8.2	4.8	6.3	2.2
<u>Contrast</u>								
Treatment vs Control	ns	ns	ns	ns	*	*	ns	ns
Urea vs UAN	ns	ns	ns	ns	ns	ns	ns	ns
Urea vs NBPT+Urea	ns	**	ns	ns	ns	ns	ns	ns
UAN vs NBPT+UAN	ns	ns	ns	ns	ns	ns	ns	**
LS Means Std Error	1.1	1.3	3.5	0.5	0.9	0.6	1.8	0.8

*, **, *** = significant at p = 0.05, 0.01 and 0.001 levels, respectively; ns = not significant at p < 0.05 level; NI = non-irrigated; I = irrigated.

Other researchers have observed similar responses in plant N and yield with NBPT-amended urea. In a 3 year study in Western Manitoba, NBPT consistently increased grain yield of barley under zero tillage when surface broadcast with urea (Grant and Bailey 1997). In a growth chamber experiment, vegetative yield and plant nitrogen accumulation of wheat increased with increased rates of NBPT from 0 to 0.25% w/w surface-applied with urea, indicating transference of N conserved from volatilization to

plant growth (Xiaobin et al. 1995). In field experiments, surface applications of urea with NBPT to perennial ryegrass showed N conserved from NH_3 volatilization reduction through use of NBPT was utilized by the plant and translated to dry matter yield (Watson et al. 1994a).

5.4.2 Soil Mineral N

Soil mineral N was lower in 1996 than in 1997 (Tables 5.7 to 5.10), coinciding with lower total precipitation (Table 5.3). The majority of total soil N measured was derived from residual mineral soil N and organic N mineralization and nitrification, as indicated by the high soil N present in the unfertilized check treatments. Nitrification of mineralized and fertilizer N was greater in July when temperatures were slightly higher than in May, as indicated by a lower ratio of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ in July than in May. Overall, total N content in soil and in plant matter was greater on the Stockton FSL soil than the Newdale CL soil, coinciding with greater soil-derived N (greater amounts in control treatments). Lower soil N and plant N accumulation was anticipated on the fine sandy loam soil where low soil moisture should have been more restricting to microbial activity, plant growth and uptake of N in the transpiration stream. However, the Stockton FSL soil may have supported a more labile pool of organic substrate which was readily degraded when the soil was periodically moistened by irrigation or precipitation, resulting in higher N recovery.

Table 5.7 Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Newdale clay loam soil, 1996.

<u>Newdale Clay Loam Soil May</u>											
Irrigation Fertilizer	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.28	0.14	0.26	0.20	0.18	0.02	0.15	0.17	0.15	0.06	1.18
5-10 cm	0.20	0.14	0.18	0.11	0.14	0.02	0.06	0.06	0.16	0.06	1.18
10-20 cm	0.20	0.20	0.29	0.29	0.25	0.05	0.13	0.15	0.00	0.25	1.32
20-30 cm	0.10	0.21	0.26	0.25	0.21	0.05	0.15	0.15	0.00	0.21	1.37
30-60 cm	0.60	0.44	1.05	1.21	0.60	0.28	0.60	0.16	0.40	0.28	1.34
Total	1.38	1.12	2.03	2.06	1.37	0.44	1.10	0.69	0.71	0.87	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.48	0.31	0.31	0.42	0.23	0.21	0.45	0.27	0.35	0.39	1.18
5-10 cm	0.06	0.12	0.11	0.10	0.04	0.09	0.11	0.05	0.11	0.17	1.18
10-20 cm	0.04	0.13	0.04	0.03	0.05	0.00	0.01	0.02	0.12	0.09	1.32
20-30 cm	0.09	0.15	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.09	1.37
30-60 cm	0.06	0.48	0.04	0.00	0.38	0.00	0.00	0.02	0.00	0.28	1.34
Total	0.74	1.20	0.55	0.56	0.71	0.30	0.56	0.36	0.58	1.01	
<u>Newdale Clay Loam Soil July</u>											
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	nd	nd	0.20	nd	nd	nd	nd	0.13	0.47	nd	1.18
5-10 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.18
10-20 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.32
20-30 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.37
30-60 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.34
Total	-	-	0.20	-	-	-	-	0.13	0.47	-	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.37	0.50	0.19	0.47	0.20	0.25	0.34	1.10	0.33	0.51	1.18
5-10 cm	0.08	0.19	0.06	0.14	0.08	0.11	0.10	0.34	0.10	0.21	1.18
10-20 cm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.32
20-30 cm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.37
30-60 cm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.34
Total	0.45	0.69	0.25	0.61	0.28	0.37	0.44	1.44	0.43	0.71	

Table 5.8 Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Stockton fine sandy loam soil, 1996.

Stockton Fine Sandy Loam Soil May											
Irrigation Fertilizer	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
Depth	$\text{NH}_4\text{-N}$ (g N m^{-2})										
0-5 cm	0.26	0.60	0.20	0.46	0.51	0.26	0.32	0.60	0.71	0.40	1.15
5-10 cm	0.12	0.23	0.10	0.18	0.16	0.14	0.16	0.22	0.37	0.53	1.15
10-20 cm	0.27	0.22	0.17	0.22	0.17	0.22	0.35	0.27	0.40	0.48	1.21
20-30 cm	0.14	0.14	0.19	0.23	0.14	0.28	0.39	0.23	0.48	0.55	1.29
30-60 cm	0.29	0.75	0.46	0.62	0.29	1.08	1.82	1.04	0.91	1.53	1.38
Total	1.08	1.93	1.12	1.72	1.27	1.98	3.04	2.36	2.86	3.50	
Depth	$\text{NO}_3\text{-N}$ (g N m^{-2})										
0-5 cm	0.09	0.16	0.12	0.41	0.12	0.09	0.09	0.15	0.15	0.14	1.15
5-10 cm	0.03	0.06	0.04	0.05	0.05	0.03	0.04	0.05	0.05	0.06	1.15
10-20 cm	0.01	0.04	0.07	0.00	0.01	0.00	0.00	0.07	0.00	0.00	1.21
20-30 cm	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.05	0.00	0.00	1.29
30-60 cm	0.06	0.25	0.17	0.26	0.12	0.00	0.24	0.38	0.02	0.02	1.38
Total	0.20	0.50	0.47	0.73	0.29	0.13	0.37	0.69	0.22	0.22	
Stockton Fine Sandy Loam Soil July											
Depth	$\text{NH}_4\text{-N}$ (g N m^{-2})										
0-5 cm	0.24	0.20	0.12	0.58	0.14	0.00	0.26	0.95	0.22	1.20	1.15
5-10 cm	0.10	0.08	0.04	0.10	0.08	0.06	0.14	0.22	0.02	0.20	1.15
10-20 cm	0.05	0.08	nd	nd	nd	nd	nd	0.13	nd	nd	1.21
20-30 cm	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.29
30-60 cm	nd	nd	nd	nd	nd	nd	nd	0.50	nd	nd	1.38
Total	0.39	0.37	0.16	0.68	0.22	0.06	0.40	1.81	0.24	1.40	
Depth	$\text{NO}_3\text{-N}$ (g N m^{-2})										
0-5 cm	0.32	1.07	0.72	1.20	0.26	0.33	0.49	1.42	0.19	1.66	1.15
5-10 cm	0.11	0.21	0.16	0.20	0.14	0.12	0.16	0.23	0.12	0.27	1.15
10-20 cm	0.00	0.25	0.00	0.13	0.10	0.09	0.04	0.18	0.01	0.36	1.21
20-30 cm	0.09	0.19	0.00	0.14	0.12	0.16	0.10	0.28	0.00	0.48	1.29
30-60 cm	0.29	0.26	0.16	0.39	0.12	0.91	0.19	0.82	0.00	0.82	1.38
Total	0.81	1.98	1.04	2.06	0.75	1.62	0.97	2.92	0.32	3.59	

Table 5.9 Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Newdale clay loam soil, 1997.

<u>Newdale Clay Loam Soil May</u>											
Irrigation	Non-Irrig.	Irrigated	Non-Irrig.	Irrigated	Non-Irrig.	Irrigated	Non-Irrig.	Irrigated	Non-Irrig.	Irrigated	Bulk Density
Fertilizer	Urea	Urea	Urea+NBPT	Urea+NBPT	Control	Control	UAN	UAN	UAN+NBPT	UAN+NBPT	g cm^{-3}
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.18	0.16	0.11	0.09	0.12	0.11	0.19	0.18	0.18	0.17	1.22
5-10 cm	0.16	0.15	0.12	0.13	0.12	0.15	0.16	0.17	0.20	0.15	1.22
10-20 cm	0.31	0.26	0.29	0.23	0.25	0.15	0.30	0.31	0.25	0.29	1.27
20-30 cm	0.26	0.27	0.30	0.22	0.25	0.16	0.35	0.37	0.31	0.22	1.30
30-60 cm	1.08	0.66	0.75	0.86	0.54	0.61	0.74	1.19	1.20	0.97	1.54
Total	1.99	1.50	1.56	1.54	1.28	1.19	1.74	2.22	2.14	1.80	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.32	0.24	0.33	0.16	0.23	0.18	0.20	0.15	0.26	0.17	1.22
5-10 cm	0.16	0.13	0.13	0.29	0.09	0.13	0.06	0.09	0.08	0.15	1.22
10-20 cm	0.16	0.33	0.37	0.40	0.14	0.09	0.46	0.13	0.28	0.32	1.27
20-30 cm	0.10	0.10	0.09	0.11	0.07	0.06	0.02	0.01	0.04	0.06	1.30
30-60 cm	0.73	0.65	0.53	0.91	0.42	0.31	0.12	0.26	0.25	0.29	1.54
Total	1.47	1.45	1.44	1.88	0.95	0.77	0.86	0.64	0.90	0.99	
<u>Newdale Clay Loam Soil July</u>											
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.17	0.06	0.16	0.12	0.13	0.10	0.14	0.11	0.13	0.05	1.22
5-10 cm	0.12	0.07	0.08	0.08	0.11	0.09	0.11	0.08	0.10	0.07	1.22
10-20 cm	0.20	0.14	0.19	0.19	0.30	0.22	0.27	0.15	0.15	0.21	1.27
20-30 cm	0.21	0.17	0.30	0.26	0.20	0.24	0.13	0.22	0.15	0.24	1.30
30-60 cm	0.82	0.55	0.68	0.89	0.77	0.73	0.60	0.75	0.61	0.54	1.54
Total	1.52	1.01	1.40	1.54	1.51	1.38	1.25	1.32	1.14	1.11	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.54	0.19	0.81	0.32	0.40	0.36	0.73	0.25	1.10	0.20	1.22
5-10 cm	0.11	0.05	0.13	0.15	0.24	0.16	0.08	0.08	0.21	0.06	1.22
10-20 cm	0.11	0.12	0.10	0.17	0.21	0.18	0.05	0.02	0.05	0.08	1.27
20-30 cm	0.08	0.05	0.10	0.16	0.13	0.17	0.00	0.02	0.03	0.06	1.30
30-60 cm	0.97	0.50	0.53	0.55	0.75	0.89	0.20	0.36	0.33	0.55	1.54
Total	1.81	0.92	1.66	1.35	1.73	1.77	1.07	0.73	1.72	0.94	

Table 5.10 Soil exchangeable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (g N m^{-2}) with depth for the Stockton fine sandy loam soil, 1997.

<u>Stockton Fine Sandy Loam Soil May</u>											
Irrigation Fertilizer	Non-Irrig. Urea	Irrigated Urea	Non-Irrig. Urea+NBPT	Irrigated Urea+NBPT	Non-Irrig. Control	Irrigated Control	Non-Irrig. UAN	Irrigated UAN	Non-Irrig. UAN+NBPT	Irrigated UAN+NBPT	Bulk Density g cm^{-3}
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.15	0.12	0.13	0.15	0.15	0.15	0.19	0.14	0.21	0.20	1.34
5-10 cm	0.14	0.12	0.17	0.14	0.14	0.19	0.22	0.25	0.19	0.18	1.34
10-20 cm	0.30	0.29	0.30	0.32	0.26	0.41	0.40	0.51	0.32	0.38	1.33
20-30 cm	0.25	0.22	0.28	0.25	0.33	0.35	0.38	0.42	0.26	0.27	1.27
30-60 cm	0.43	0.39	0.63	0.73	0.80	0.73	0.94	1.04	0.75	0.92	1.38
Total	1.26	1.14	1.52	1.59	1.67	1.83	2.12	2.34	1.73	1.95	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.34	0.29	0.35	0.24	0.39	0.36	0.29	0.32	0.69	0.33	1.34
5-10 cm	0.20	0.18	0.20	0.23	0.35	0.28	0.34	0.22	0.35	0.25	1.34
10-20 cm	0.48	0.28	0.37	0.33	0.38	0.40	0.45	0.56	0.48	0.52	1.33
20-30 cm	0.31	0.20	0.25	0.23	0.29	0.28	0.53	0.32	0.32	0.35	1.27
30-60 cm	1.72	1.03	1.29	0.86	1.29	1.06	1.37	1.77	1.45	1.27	1.38
Total	3.05	1.98	2.47	1.89	2.69	2.39	2.98	3.19	3.29	2.72	
<u>Stockton Fine Sandy Loam Soil July</u>											
Depth	$\text{NH}_4\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	0.19	0.07	0.38	0.06	0.08	0.10	0.26	0.14	0.30	0.11	1.34
5-10 cm	0.07	0.07	0.10	0.08	0.09	0.08	0.10	0.13	0.13	0.14	1.34
10-20 cm	0.16	0.12	0.17	0.13	0.17	0.18	0.25	0.18	0.22	0.20	1.33
20-30 cm	0.21	0.07	0.17	0.20	0.16	0.15	0.19	0.15	0.16	0.22	1.27
30-60 cm	0.39	0.30	0.36	0.59	0.44	0.57	0.63	0.63	0.63	0.86	1.38
Total	1.01	0.64	1.19	1.06	0.95	1.07	1.43	1.23	1.44	1.51	
Depth	$\text{NO}_3\text{-N (g N m}^{-2}\text{)}$										
0-5 cm	1.09	0.25	1.52	0.29	0.35	0.21	0.76	0.63	1.25	0.37	1.34
5-10 cm	0.26	0.13	0.39	0.20	0.20	0.17	0.37	0.22	0.38	0.20	1.34
10-20 cm	0.51	0.13	0.58	0.69	0.24	0.10	1.14	0.49	0.83	0.46	1.33
20-30 cm	0.27	0.09	0.17	0.19	0.27	0.13	0.68	0.13	0.28	0.19	1.27
30-60 cm	1.30	2.13	1.71	0.96	2.77	1.64	1.93	1.53	1.25	1.64	1.38
Total	3.43	2.73	4.37	2.33	3.84	2.25	4.87	2.99	4.00	2.86	

Nitrate and exchangeable NH_4^+ content of control treatments were frequently not significantly different from N fertilizer treatments, particularly in 1996 due to the presence of residual soil N or recently mineralized N and plant uptake of N (Tables 5.11 and 5.12). Treatment effects likely would have been more pronounced if more N-deficient soils were used in these studies to induce a fertilizer response. In addition, high standard errors for some studies may have masked some treatment effects.

Fertilizer source had a greater impact on soil exchangeable NH_4^+ and NO_3^- content with depth than use of NBPT (Tables 5.11 and 5.12). Measured soil N was greater with UAN than with urea on the Stockton FSL at all depths, but not for the Newdale CL soil in May where recovery was greater from urea than UAN treatments. Since plant N was not significantly different for the two N sources, loss of N via NH_3 volatilization was likely greater for urea than UAN, as observed in a concurrently conducted experiment.

Use of NBPT did not affect total soil mineral N measured. Amendment of urea and UAN with NBPT did not consistently affect soil exchangeable NH_4^+ and NO_3^- content (Tables 5.11 and 5.12). Similarly, Watson et al. (1994a) found no significant effect on NBPT of ^{15}N recovery in soil at 5 cm increments to 15 cm after a 6 week period. N-(n-butyl) thiophosphoric triamide only delays urea conversion and there was likely sufficient time over the study duration for hydrolysis products from all N fertilizer treatments to react and redistribute in the soil. The minimal differences between treatments, N form and N distribution in soil with depth likely resulted from the combination of the lengthy period from time of application to soil analysis and the presence of residual or recently mineralized N.

Table 5.11 Statistical analyses for log-transformed soil NO₃-N and exchangeable NH₄-N data, and NO₃-N as percent of total soil N for 1996.

Newdale Clay Loam Soil																		
Source	Depth 0-5 cm						Depth 5-10 cm						Depth 10-60 cm					
	May			July			May			July			May			July		
	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N
Treatment	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	nd	nd	*	**	*	nd	nd	nd
Depth	-	-	-	-	-	-	-	-	-	-	nd	nd	ns	ns	ns	nd	nd	nd
Treatment*Depth	-	-	-	-	-	-	-	-	-	-	nd	nd	ns	ns	ns	nd	nd	nd
LS Means Std Error ²	0.18	0.33	0.13	0.26	0.28	0.08	0.13	0.32	0.20	0.19	nd	nd	0.08	0.23	0.26	nd	nd	nd
Contrast																		
Treat vs Control	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	nd	nd	ns	ns	ns	nd	nd	nd
Urea vs UAN	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	nd	nd	ns	***	**	nd	nd	nd
Urea vs Urea+NBPT	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	nd	nd	*	ns	ns	nd	nd	nd
UAN vs UAN+NBPT	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	nd	nd	*	ns	ns	nd	nd	nd
Stockton Fine Sandy Loam Soil																		
Source	Depth 0-5 cm						Depth 5-10 cm						Depth 10-60 cm					
	May			July			May			July			May			July		
	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N
Treatment	ns	ns	ns	ns	*	ns	ns	**	ns	ns	ns	**	*	***	*	ns	ns	ns
Depth	-	-	-	-	-	-	-	-	-	-	-	-	*	ns	*	ns	ns	ns
Treatment*Depth	-	-	-	-	-	-	-	-	-	-	-	-	ns	ns	ns	ns	ns	ns
LS Means Std Error ²	0.19	0.24	0.06	0.28	0.35	0.10	0.16	0.18	0.10	0.08	0.28	0.14	0.07	0.12	0.05	0.21	0.50	0.23
Contrast																		
Treat vs Control	ns	ns	ns	*	**	*	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	ns
Urea vs UAN	ns	ns	ns	ns	*	ns	ns	**	ns	ns	*	**	ns	***	*	ns	ns	ns
Urea vs Urea+NBPT	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
UAN vs UAN+NBPT	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	**	ns	*	ns	*	ns

*, **, *** = significant at p = 0.05, 0.01 and 0.001 levels, respectively; ns = not significant at p < 0.05 level; nd = non-determinable; - = not available.

² Least squares means standard error.

Table 5.12 Statistical analyses for log-transformed soil NO₃-N and exchangeable NH₄-N data, and NO₃-N as percent of total soil N for 1997.

Source	Newdale Clay Loam Soil																	
	Depth 0-5 cm						Depth 5-10 cm						Depth 10-60 cm					
	May			July			May			July			May			July		
	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N
Treatment	ns	***	*	ns	ns	ns	**	ns	**	ns	ns	**	***	***	***	***	*	ns
Depth	-	-	-	-	-	-	-	-	-	-	-	-	***	ns	***	***	ns	***
Treatment*Depth	-	-	-	-	-	-	-	-	-	-	-	-	*	ns	ns	ns	ns	ns
LS Means Std Error ^z	0.11	0.10	0.04	0.23	0.23	0.10	0.10	0.13	0.05	0.17	0.28	0.19	0.07	0.14	0.05	0.13	0.26	0.19
<u>Contrast</u>																		
Treat vs Control	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	***	ns	**	*	ns
Urea vs UAN	ns	**	**	ns	ns	ns	***	ns	***	ns	ns	ns	***	ns	***	***	ns	ns
Urea vs Urea+NBPT	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	***	ns	ns	ns	ns	ns	ns
UAN vs UAN+NBPT	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns
Source	Stockton Fine Sandy Loam Soil																	
	Depth 0-5 cm						Depth 5-10 cm						Depth 10-60 cm					
	May			July			May			July			May			July		
	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N	NO ₃ -N	NH ₄ -N	%NO ₃ -N
Treatment	ns	ns	ns	ns	ns	ns	*	*	ns	ns	*	ns	***	***	ns	ns	***	ns
Depth	-	-	-	-	-	-	-	-	-	-	-	-	***	***	***	***	ns	***
Treatment*Depth	-	-	-	-	-	-	-	-	-	-	-	-	ns	ns	ns	ns	ns	ns
LS Means Std Error ^z	0.11	0.10	0.04	0.24	0.18	0.03	0.11	0.14	0.05	0.14	0.11	0.04	0.09	0.10	0.04	0.12	0.09	0.04
<u>Contrast</u>																		
Treat vs Control	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Urea vs UAN	ns	ns	ns	ns	ns	ns	**	**	ns	ns	**	ns	***	***	ns	*	***	ns
Urea vs Urea+NBPT	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns
UAN vs UAN+NBPT	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	ns

*, **, *** = significant at p = 0.05, 0.01 and 0.001 levels, respectively; ns = not significant at p < 0.05 level; nd = non-determinable; - = not available.

^z Least squares means standard error.

5.5 Conclusions

In general, use of NBPT with urea usually tended to increase plant biomass and N accumulation, but somewhat decreased both when applied with UAN. Nitrogen source, irrigation, or NBPT amendment did not consistently alter N form and distribution with depth in soil, although N source had a greater effect than use of NBPT. Plant removal of soil N, contribution of native or residual soil N and the time elapsed from fertilizer application to soil sampling was likely sufficient to overcome any initial impact of NBPT on N form and distribution in soil. The yield and plant N accumulation increases with NBPT-amended urea likely would have been more pronounced if growing conditions were not compromised by use of lysimeters and if native soil N availability for plant growth was limiting as was intended.

6. GENERAL DISCUSSION

Ammonia volatilization from surface-applied urea fertilizers reduces the amount of fertilizer N available to the growing crop. Increasing the rate of urea fertilizer to account for potential NH_3 losses is a management approach to compensate for this inefficiency. However, significant NH_3 loss will not occur every year and the excess fertilizer N can accumulate in the soil, or can be lost from the soil-plant system via denitrification or leaching. Excessive NH_3 emissions to the atmosphere from urea fertilizers can also contribute to formation of the greenhouse gas nitrous oxide (N_2O), acidification of soil and surface waters, toxicity of aquatic organisms and plants, or can stimulate nutrient competition or exclusion in plants (Janzen 1999; McGinn and Janzen 1998; McGinn et al. 1997).

Indirect promotion of N_2O formation and nitrate leaching to groundwater from over fertilization have environmental and health implications, rendering this practice environmentally irresponsible over time. Nitrous oxide is very stable in the troposphere, with a mean lifetime of 150 years (Schlesinger 1991), and is a formidable greenhouse gas with approximately 310 times the warming potential of CO_2 (Agriculture and Agri-Food Canada, Environment Bureau 1999). The gas is transported to the stratosphere where it photodissociates to nitric oxide (Schlesinger 1991), which contributes directly to stratospheric ozone depletion (Janzen 1999). The maximum acceptable concentration of nitrate in drinking water is 45 mg L^{-1} , equivalent to 10 mg N L^{-1} (Anonymous 1993).

Elevated nitrate content in drinking water may cause methemoglobinemia in infants, also known as blue baby syndrome, and may increase the incidence of stomach cancer (Manitoba Agriculture 1999).

Our research indicates a more environmentally sound approach than increasing the fertilizer rate may be to restrict NH_3 volatilization from surface-applied urea fertilizers via amendment with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT). To serve as a practical alternative N source for surface applications, the inhibitor must restrict the rate and total extent of NH_3 volatilization under a wide range of soil, weather and management conditions. In our studies, NBPT markedly reduced NH_3 volatilization and delayed periods of peak loss from urea and UAN fertilizers for the range of soil temperatures and textures present in the field, providing effective control at all rates evaluated (0.05 to 0.15%). The greatest reduction in NH_3 loss occurred during the first week after application, and coincided with periods of maximum loss from unamended urea, which occurred sooner after fertilization in July than in May and were more pronounced on the Stockton FSL soil than on the Newdale CL soil. Total NH_3 losses were reduced even further where the combination of NBPT and irrigation restricted NH_3 volatilization and moved unhydrolyzed urea into the soil, respectively.

According to these modified field studies, an appreciable quantity of NH_3 can volatilize even when conditions are not generally thought to be conducive to loss, such as on cool and moist fine textured soils, making regular use of NBPT a more viable option. However, the study design restricted drying of the surface soil layer because the moist polyfoam discs both prohibited air movement and elevated the humidity of the confined air while still removing volatilized NH_3 to maintain a gradient for volatilization for a longer period than may occur in the field. Under actual field conditions wind movement

would typically dry the surface layer of soil to create a barrier between the moist NH_3 -enriched soil and the atmospheric air to decrease the diffusion gradient and the duration of NH_3 volatilization (Bouwmeester et al. 1985). Consequently, under field conditions the duration and magnitude of NH_3 loss would likely be lower on a fine textured soil where lower soil water flux, greater water retention and higher CEC would restrict NH_3 diffusion to the atmosphere once the surface layer of soil dried, relative to a coarse textured soil. Ferguson and Kissel (1986) observed transport of urea from depth to the surface with evaporating water on a very fine sandy loam soil while Bouwmeester et al. (1985) found reduced NH_3 loss with drying of a soil with a clay content of 470 mg kg^{-1} at wind speeds approximating those present in the field.

To be economically viable, the N conserved from use of NBPT must be translated to increased soil N for crop consumption to ultimately increase crop yield and total N uptake relative to unamended urea. These studies showed the proportion of total N (as NO_3^- , urea and exchangeable NH_4^+ in the soil plus as NH_3 in the air) present as soil N was greatest when urea and UAN were treated with NBPT, corresponding to treatments with the lowest NH_3 loss. At the conclusion of the two and three week studies, the increased soil N was concentrated within the surface 10 cm of soil predominantly as NO_3^- and exchangeable NH_4^+ and therefore was available to plants. Estimated fertilizer N recovery, calculated as total N minus N in control treatments, was generally less than the amount applied. However, as irrigation predominantly transported NO_3^- within the surface 20 cm, leaching below the root zone was not likely the mode of fertilizer N loss. The fertilizer N that was unaccounted for was likely temporarily immobilized or fixed. The effect of NBPT on N form and distribution in soil is temporary (Zhengping et al 1996; Christianson et al. 1993). For the six to eight week studies where plants were grown, soil

N content to 60 cm was not significantly different for the various treatments. The lower total N measured (soil N plus plant N) in these studies relative to the two and three week studies (soil N plus NH_3 in air) is likely due to unaccounted for NH_3 volatilization in addition to immobilization, NH_4^+ fixation or lateral movement of N from the sample area.

To achieve a relative yield increase with NBPT use, NH_3 loss from unamended urea must create a nitrogen deficiency detrimental to crop performance. If soil N status prior to fertilization, or capacity of the soil to supply N during the growing season are sufficient to compensate for urea fertilizer loss as NH_3 , and crop N requirements are met, use of NBPT is less likely to invoke a comparative yield response and thus will not be economically beneficial. Similarly, use of NBPT will also not be advantageous if adverse growing conditions hinder crop performance. Wheat biomass content or total N uptake did not significantly increase with use of NBPT in our plant response experiment because yield variability was high and soil N was not limiting to plant growth and development. Mineralization and/or residual soil N compensated for N lost from unamended urea via NH_3 volatilization, and modified growing conditions impeded crop growth by inducing severe heat and moisture stress to reduce crop N requirements. However, zero till field experiments conducted in the same geographical locations on like textured soils showed significantly increased grain yield of barley with broadcast NBPT-amended urea versus unamended urea (Grant and Bailey 1997) indicating yield benefits are achievable under Western Manitoba field conditions.

7. SUMMARY AND CONCLUSIONS

The field research showed use of NBPT, both with and without irrigation, improved the efficiency of urea and UAN surface applications by reducing NH_3 volatilization and increasing fertilizer-derived N in soil relative to unamended urea and UAN applications for both soil textures and both temperature regimes investigated. Reductions in NH_3 volatilization were slightly greater and of longer duration at the 0.10 and 0.15% w/w rates of NBPT than at the 0.05% rate. The combination of NBPT and irrigation provided the best control of NH_3 volatilization by delaying the onset of urea hydrolysis and moving the unhydrolyzed urea away from the soil surface, respectively, to minimize both early and later NH_3 losses. Total NH_3 loss was lower for UAN than for urea, likely because UAN is only 50% urea-N and the reaction zone of NH_4NO_3 is acidic which limits the pH increase of urea hydrolysis and hence NH_3 formation.

The persistence of NBPT activity was shortest in July on the Stockton FSL soil where warm temperatures and coarse texture of the soil provided an ideal environment for rapid hydrolysis and inhibitor degradation, therefore resulting in higher NH_3 loss and lower recovery of N in soil. Patterns of NH_3 loss were similar for both soils in May because cool soil temperatures likely slowed the rate of urea hydrolysis and upward diffusion of NH_3 to limit the gradient for NH_3 loss to the atmosphere. Ammonia-N conserved through use of NBPT was recovered as soil N, which was localized in the upper 10 cm of soil.

A significant crop response to NBPT use with urea and UAN was not observed, although generally biomass and total N uptake were greater for NBPT-amended than for unamended urea. Similarly, field research conducted on like soils in the same geographical locations showed increased grain yield of barley with broadcast NBPT-amended urea on zero till (Grant and Bailey 1997).

N-(n-butyl) thiophosphoric triamide may not provide benefits every year since NBPT performance is highly dependent on short term environmental conditions surrounding the period of fertilizer application and on soil N supplying power. The lack of response with the plants grown in these studies due to poor growing conditions, and high residual or recently mineralized soil N supports this conclusion. However, when soil and environmental conditions are conducive to high NH_3 volatilization where a nitrogen deficiency would result, and when other conditions are not limiting to growth and development, crop yield potential can be increased through the use of NBPT. Thus, NBPT affords an alternative to the practice of over fertilization to compensate for N lost via volatilization, while concurrently alleviating the negative environmental impact which may accompany frequent over-fertilization, to provide long-term economic benefits to crop production.

Additional research is required to evaluate crop response to surface-applied urea and UAN amended with varying rates of NBPT in the field under variable soil, weather and management conditions representative of Western Manitoba. The recommended rate of urea treatment is 0.14% NBPT w/w. Our preliminary research indicates significant reductions in NH_3 loss from urea at levels as low as 0.05% NBPT w/w. If NBPT-amended urea at lower rates can induce a crop yield response comparable to performance at the recommended rate, use of this product would be more economical, making NBPT-

treated urea an attractive alternative N source for use in Manitoba and other similar soil and climatic areas.

8. CONTRIBUTION TO KNOWLEDGE

The soil, environmental and management factors controlling ammonia volatilization from surface-applied urea fertilizers are numerous and complex. When the combination of conditions are favourable for significant ammonia loss, N availability to the growing crop may be limiting, negatively affecting crop yield potential. While urea efficiency is increased with subsurface placement, soil disturbance problems occur when urea is placed below the soil surface in reduced or zero tillage, perennial or forage crops, or in-crop N fertilization. Our research demonstrated that, in systems where N surface applications are preferred such as in zero tillage, treating urea with the urease inhibitor NBPT may significantly restrict the magnitude and duration of NH_3 volatilization to improve the efficiency of urea fertilization. N-(n-butyl) thiophosphoric triamide successfully delayed the onset of NH_3 volatilization and decreased the total magnitude of NH_3 loss from surface applications of urea and UAN fertilizers under two broad soil texture groups, coarse (Stockton fine sandy loam) and moderately fine (Newdale clay loam) and two broad soil temperature regimes (cool and warm) common to Western Manitoba, when applied with irrigation and without irrigation. The field studies identified weather conditions surrounding the time of fertilizer application as the most important criteria for determining the magnitude of NH_3 loss that could occur. Soil factors related to texture established the extent of NH_3 volatilization that could occur under weather conditions ideal for NH_3 loss.

Our findings indicated the effect of NBPT on soil N form and distribution in soil is only temporary, but that N conserved from NH_3 volatilization via use of NBPT was translated to increased soil N content relative to unamended urea and UAN fertilizers. Unfortunately, shortcomings in experimental design precluded the occurrence of any significant response in plant N uptake and yield response to NBPT-amended urea relative to unamended urea. However, research conducted at similar geographical locations on like soils showed yield response with barley to NBPT use with broadcast urea (Grant and Bailey 1997).

Overall our research demonstrated NBPT is suitable for use under field conditions representative of the Black Soil Zone of Western Manitoba. Use of NBPT is a means of decreasing NH_3 emissions to the atmosphere to reduce agricultural contributions to atmospheric pollution. Benefits of NBPT are likely to be more frequently observed with urea than with UAN which is only 50% urea-N. N-(n-butyl) thiophosphoric triamide is registered for use in Canada and is commercially available as Agrotain, marketed by IMC-Global. Ultimately the economics will depend on the cost of the product versus the frequency of observable yield advantages and money savings by the farmer, and if farmers are willing to make the long term investment, as a response may not be observed every year. The potential to apply NBPT at a rate below the recommended rate of 0.14% may make the product a more affordable and attractive alternative.

9. REFERENCES

- Agriculture and Agri-Food Canada. April, 1999.** Canadian Fertilizer Consumption, Shipment and Trade 1997/1998. Online. Available: <http://www.agr.ca/policy/cdnfert/text.html#tables1-5>.
- Agriculture and Agri-Food Canada. 1998.** Environment Bureau - Addressing Climate Change. Climate change: Greenhouse gases nitrous oxide. Online. Available: http://www.agr.ca/policy/enviroenmen...stewardship/climate_changen2o.html.
- Al-Kanani, T., MacKenzie, A. F. and Barthakur, N. N. 1991.** Soil water and ammonia volatilization relationships with surface-applied nitrogen fertilizer solutions. *Soil Sci. Soc. Am. J.* **55**: 1761-1766.
- Al-Kanani, T. and MacKenzie, A. F. 1992.** Effect of tillage practices and hay straw on ammonia volatilization from nitrogen fertilizer solutions. *Can. J. Soil Sci.* **72**: 145-157.
- Andrews, R. K., Blakeley, R. L. and Zerner, B. 1984.** Urea and urease. Pages 245-283 in G.L. Eichhorn and L. G. Marzilli (Eds.). *Advances in Inorganic Biochemistry*. Volume 6. Elsevier Science Publishing Company, Inc., New York, NY.
- Anonymous. 1993.** Guidelines for Canadian drinking water quality. 5th edition. Canada Communication Group Publishing, Ottawa, Canada. 24 pp.
- Anonymous. 1996.** IMC-Agrico Agrotain Urease Inhibitor Product Information Guidebook. 32 pp.
- Baligar, V. C., Staley, T. E. and Wright, R. J. 1991.** Enzyme activities in Appalachian soils: 2. Urease. *Commun. in Soil Sci. Plant Anal.* **22**: 315-322.
- Beyrouthy, C. A., Sommers, L. E. and Nelson, D. W. 1988.** Ammonia volatilization from surface-applied urea as affected by several phosphoroamide compounds. *Soil Sci. Soc. Am. J.* **52**: 1173-1178.
- Black, A. S., Sherlock, R. R. and Smith, N. P. 1987.** Effect of timing of simulated rainfall on ammonia volatilization from urea, applied to soil of varying moisture content. *J. Soil Sci.* **38**: 679-687.

- Bouwmeester, R. J. B., Vlek, P. L. G. and Stumpe, J. M. 1985.** Effect of environmental factors on ammonia volatilization from a urea-fertilized soil. *Soil Sci. Soc. Am. J.* **49**: 376-381.
- Bremner, J. M. 1982.** Nitrogen-urea. Pages 699-709 in A. L. Page, R. H. Miller and D. R. Keeney (Eds.). *Methods of Soil Analysis. II. Chemical and Microbiological Properties*. 2nd edition. ASA, CSSA, SSSA. Madison, Wisconsin.
- Bremner, J. M. 1995.** Recent research on problems in the use of urea as a nitrogen fertilizer. *Fert. Res.* **42**: 321-329.
- Bremner, J. M. and Chai, H. S. 1989.** Effects of phosphoroamides on ammonia volatilization and nitrite accumulation in soils treated with urea. *Biol. Fertil. Soils.* **8**: 227-230.
- Bremner, J. M. and Krogmeier, M. J. 1988.** Elimination of the adverse effects of urea fertilizer on seed germination, seedling growth, and early plant growth in soil. *Proc. Natl. Acad. Sci. USA.* **85**: 4601-4604.
- Bremner, J. M., McCarty, G. W. and Higuchi, T. 1991.** Persistence of the inhibitory effects of phosphoroamides on urea hydrolysis in soils. *Commun. Soil. Sci. Plant Anal.* **22**: 1519-1526.
- Bremner, J. M. and Mulvaney, R. L. 1978.** Urease activity in soils. Pages 149-196 in R. G. Burns (Ed.). *Soil Enzymes*. Academic Press, London.
- Bremner, J. M. and Zantua, M. I. 1975.** Enzyme activity in soils at subzero temperatures. *Soil Biol. Biochem.* **7**: 383-387.
- Burns, R. G. 1977.** Soil enzymology. *Sci. Prof. Oxf.* **64**: 275-285.
- Byrnes, B. H. and Freney, J. R. 1995.** Recent developments on the use of urease inhibitors in the tropics. *Fert. Res.* **42**: 251-259.
- Carmona, G., Christianson, C. B. and Byrnes, B. H. 1990.** Temperature and low concentration effects of the urease inhibitor N-(n-butyl) thiophosphoric triamide (nBTPT) on ammonia volatilization from urea. *Soil Biol. Biochem.* **22**: 933-937.
- Chai, H. S. and Bremner, J. M. 1987.** Evaluation of some phosphoroamides as soil urease inhibitors. *Biol. Fertil. Soils.* **3**: 189-194.
- Christianson, C. B., Byrnes, B. H. and Carmona, G. 1990.** A comparison of the sulfur and oxygen analogs of phosphoric triamide urease inhibitors in reducing urea hydrolysis and ammonia volatilization. *Fert. Res.* **26**: 21-27.

- Christianson, C. B., Baethgen, W. E., Carmona, G. and Howard, R. G. 1993.** Microsite reactions of urea-nBTPT fertilizer on the soil surface. *Soil Biol. Biochem.* **25**: 1107-1117.
- Christianson, C. B. and Howard, R. G. 1994.** Use of soil thin-layer chromatography to assess the mobility of the phosphoric triamide urease inhibitors and urea in soil. *Soil Biol. Biochem.* **26**: 1161-1164.
- Clay, D. E., Maltzer, G. L. and Anderson, J. L. 1990.** Ammonia volatilization from urea as influenced by soil temperature, soil water content, and nitrification and hydrolysis inhibitors. *Soil Sci. Soc. Am. J.* **54**: 263-266.
- Cotton and Wilkinson. 1962.** *Advanced Inorganic Chemistry. A Comprehensive Text.* Interscience Publishers. pp. 247-249.
- Creason, G. L., Schmitt, M. R., Douglass, E. A., and Hendrickson, L. L. 1990.** Urease inhibitory activity associated with N-(n-butyl) thiophosphoric triamide is due to formation of its oxon analog. *Soil Biol. Biochem.* **22**: 209-211.
- Dick, W. A. 1984.** Influence of long-term tillage and crop rotation combinations on soil enzyme activities. *Soil Sci. Soc. A. J.* **48**: 569-574.
- Evangelou, V. P. 1990.** Regulation mechanisms and field implications of ammonia bonding with various crystalline salts. *Soil Sci. Soc. Am. J.* **54**: 394-398.
- Fairlie, T. E. and Goos, R. J. 1986.** Urea hydrolysis and ammonia volatilization characteristics of liquid fertilizer mixtures II. Studies under modified field conditions. *J. Fert. Iss.* **3**: 86-90.
- Fan, M. X. and Mackenzie, A. F. 1993.** Urea and phosphate interactions in fertilizer microsites: Ammonia volatilization and pH changes. *Soil Sci. Soc. Am. J.* **57**: 839-845.
- Fenn, L. B. and Miyamoto, S. 1981.** Ammonia loss and associated reactions of urea in calcareous soils. *Soil Sci. Soc. Am. J.* **45**: 537-540.
- Ferguson, R. B. and Kissel, D. E. 1986.** Effects of soil drying on ammonia volatilization from surface-applied urea. *Soil Sci. Soc. Am. J.* **50**: 485-490.
- Fox, R. H. and Piekielek, W. P. 1993.** Management and urease inhibitor effects on nitrogen use efficiency in no-till corn. *J. Prod. Agric.* **6**: 195-200.
- Gezgin, S. and Bayrakll, F. 1995.** Ammonia volatilization from ammonium sulphate, ammonium nitrate, and urea surface applied to winter wheat on a calcareous soil. *J. Plant. Nutr.* **18**: 2483-2494.

Gianfreda, L., Rao, M. R. and Violante, A. 1992. Adsorption, activity and kinetic properties of urease on montmorillonite, aluminum hydroxide and $\text{Al}(\text{OH})_x$ -montmorillonite complexes. *Soil Biol. Biochem.* **24**: 51-58.

Goh, T. B., St. Arnaud, R. J. and Mermut, A. R. 1993. Carbonates. Pages 177-185 in M. R. Carter (Ed.). *Soil Sampling and Methods of Analysis*. CSSS, CRC Press, Boca Raton, Florida.

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

Grant, C. A., Ferguson, R., Lamond, R., Schlegel, A. and Thomas, W. 1996a. Use of urease inhibitors in the Great Plains. Pages 318-329 in J. L. Havlin (Ed.). *Great Plains Soil Fertility Conference Proceedings*. Volume 6. Denver, Colorado. March 4-6, 1996. Kansas State University, Manhattan Kansas.

Grant, C. A., Jia, S., Brown, K. R. and Bailey, L. D. 1996b. Volatile losses of NH_3 from surface-applied urea and urea ammonium nitrate with and without the urease inhibitors NBPT or ammonium thiosulphate. *Can. J. Soil Sci.* **76**: 417-419.

Grant, C. A. and Bailey, L. D. 1997. Effectiveness of urease inhibitors on the Canadian Prairies. Pages 191-200 in *Papers Presented at the 40th Annual Manitoba Society of Soil Science Proceedings*.

Grant, C. and Flaten, D. 1998. Fertilizing for protein content in wheat. Pages 151-168 in D. B. Fowler, W. E. Geddes, A. M. Johnston and K. R. Preston. (Eds.). *Wheat production and marketing: proceedings of the wheat protein symposium* March 9 and 10, 1998 Saskatoon, Saskatchewan, Canada. Printcrafters Inc., Winnipeg, Manitoba.

Harre, E. A. and Bridges, J. D. 1988. Importance of urea fertilizers in B. R. Bock and D. E. Kissel (Eds.). *Ammonia Volatilization from Urea Fertilizers*. National Fertilizer Development Center, Muscle Shoals, Alabama.

Hargrove, W. L. 1988. Soil, environmental, and management factors influencing ammonia volatilization under field conditions. Pages 17-36 in B. R. Bock and D. E. Kissel (Eds.). *Ammonia Volatilization from Urea Fertilizers*. National Fertilizer Development Center, Muscle Shoals, Alabama.

Hendershot, W. H., Lalande, H. and Duquette, M. 1993. Soil reaction and exchangeable acidity. Pages 141-145 in M. R. Carter (Ed.). *Soil Sampling and Methods of Analysis*. CSSS, CRC Press, Boca Raton, Florida.

Hendershot, W. H., Lalande, H. and Duquette, M. 1993. Ion exchange and exchangeable cations. Pages 167-176 in M. R. Carter (Ed.). *Soil Sampling and Methods of Analysis*. CSSS, CRC Press, Boca Raton, Florida.

- Hendrickson, L. L. 1992.** Corn yield response to the urease inhibitor NBPT: Five-year summary. *J. Prod. Agric.* **5**: 131-137.
- Hendrickson, L. L. and Douglass, E. A. 1993.** Metabolism of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) in soils. *Soil Biol. Biochem.* **25**: 1613-1618.
- International Fertilizer Industry Association. (No Date).** Nitrogen, Phosphorus and Potash Statistics. Online. Available: <http://www.fertilizer.org/IFADATA/netline.htm>.
- Isaac, R. A. and Johnson, W. C. 1976.** Determination of total nitrogen in plant tissue. *J. Assoc. Off. Anal. Chem.* **59**: 98-100.
- Isermann, K. 1994.** Agriculture's share in the emission of trace gases affecting the climate and some cause-oriented proposals for sufficiently reducing this share. *Environ. Pollut.* **83**: 95-111.
- Janzen, H. H. 1993.** Soluble salts. Pages 161-166 in M. R. Carter (Ed.). *Soil Sampling and Methods of Analysis*. CSSS, CRC Press, Boca Raton, Florida.
- Janzen, H. H. 1999.** The Health of Our Air: Toward Sustainable Agriculture in Canada. Agriculture and Agri-Food Canada, Research Branch, Ottawa. 98 pp.
- Keerthisinghe, D. G. and Freney, J. R. 1994.** Inhibition of urease activity in flooded soils: Effect of thiophosphoric triamides and phosphoric triamides. *Soil Biol. Biochem.* **26**: 1527-1533.
- Keerthisinghe, D. G. and Blakeley, R. L. 1995.** Inhibition of jack bean urease by phosphoric- and thiophosphoric triamides. *Soil Biol. Biochem.* **27**: 739-742.
- Killham, K. 1994.** *Soil Ecology*. Cambridge University Press, Great Britain. 242 pp.
- Kissel, D. E. and Cabrera, M. L. 1988.** Factors affecting urea hydrolysis. Pages 53-66 in B. R. Bock and D. E. Kissel (Eds.). *Ammonia Volatilization from Urea Fertilizers*. National Fertilizer Development Center, Muscle Shoals, Alabama.
- Kissel, D. E., Cabrera, M. L. and Ferguson, R. B. 1988.** Reactions of ammonia and urea hydrolysis products with soil. *Soil Soc. Am. J.* **52**: 1793-1796.
- Koelliker, J. K. and Kissel, D. E. 1988.** Chemical equilibria affecting ammonia volatilization. Pages 37-52 in B. R. Bock and D. E. Kissel (Eds.). *Ammonia Volatilization from Urea Fertilizers*. National Fertilizer Development Center, Muscle Shoals, Alabama.
- Krogmeier, M. J., McCarty, G. W. and Bremner, J. M. 1989.** Phytotoxicity of foliar-applied urea. *Proc. Natl. Acad. Sci. USA.* **86**: 8189-8191.

- Kolodziej, A. F. 1994.** The chemistry of nickel-containing enzymes. *Progress in Inorganic Chemistry*. **41**: 493-598.
- Lai, C. M. and Tabatabai, M. A. 1992.** Kinetic parameters of immobilized urease. *Soil Biol. Biochem.* **24**: 225-228.
- Littell, R. C., Milliken, G. A., Stroup, W. W. and Wolfinger, R. D. 1998.** SAS System for Mixed Models. SAS Institute. Inc., Cary, NC. 656 pp.
- Little, T. M. and Hills, F. J. 1978.** *Agricultural Experimentation: Design and Analysis*. John Wiley and Sons, New York. 350 pp.
- Malhi, S. S., Nyborg, M. and Solberg, E. D. 1996.** Influence of source, method of placement and simulated rainfall on the recovery of ^{15}N -labelled fertilizers under zero tillage. *Can J. Soil. Sci.* **76**: 93-100.
- Mamo, M., Taylor, R. W. and Shuford, J. W. 1993.** Ammonium fixation by soil and pure clay minerals. *Commun. Soil Sci. Pl. Anal.* **24**: 1115-1126.
- Manitoba Agriculture. (1999).** Health Concerns of Nitrate. Online. Available: <http://www.gov.mb.ca/agriculture/soil/fbd01s03.html>.
- Maynard, D. G. and Kalra, Y. P. 1993.** Nitrate and exchangeable ammonium nitrogen. Pages 25-38 in M. R. Carter (Ed.). *Soil Sampling and Methods of Analysis*. CSSS, CRC Press, Boca Raton, Florida.
- McCarty, G. W., Bremner, J. M. and Chai, H. S. 1989.** Effect of N-(n-butyl) thiophosphoric triamide on hydrolysis of urea by plant, microbial, and soil urease. *Biol Fertil. Soils.* **8**: 123-127.
- McGinn, S. M. and Janzen, H. H. 1998.** Ammonia sources in agriculture and their measurement. *Can. J. Soil Sci.* **78**: 139-148.
- McGinn, S., Paul, J. and Grant, C. 1997.** Ammonia emissions and impact in agriculture. Problem formulation for ammonia in the aquatic environment. Agricultural nitrogen air emissions in Canada: an overview. Record of Meeting, Friday, May 30, 1997. Ottawa, Canada.
- McInnes, K. J., Ferguson, R. B., Kissel, D. E. and Kanemasu, E. T. 1986.** Field measurements of ammonia loss from surface applications of urea solution to bare soil. *Soil Sci. Soc. Am. J.* **78**: 192-196.
- Medina, R. and Radel, R. J. 1988.** Mechanisms of urease inhibition. Pages 137-174 in B. R. Bock and D. E. Kissel (Eds.). *Ammonia Volatilization from Urea Fertilizers*. National Fertilizer Development Center, Muscle Shoals, Alabama.

- Mobley, H. L. T. and Hausinger, R. P. 1989.** Microbial ureases: Significance, regulation and molecular characterization. *Microbiological Reviews*. **53**: 85-108.
- Moulin, A.P. and Beckie, H.J. 1994.** Predicting crop residue decomposition in cropping systems. Pages 7-14 *in* Proceedings Soils and Crops Workshop, Soil & Crops '94, University of Saskatchewan, Saskatoon, Sask., 24-25 February.
- Moyo, C. C., Kissel, D. E. and Cabrera, M. L. 1989.** Temperature effects on soil urease activity. *Soil Biol. Biochem.* **21**: 935-938.
- Mulvaney, R. L. and Bremner, J. M. 1981.** Control of urea transformations in soils. Pages 153-196 *in* E. A. Paul and J. N. Ladd (Eds.). *Soil Biochemistry*. Volume 5. Marcel Dekker, Inc. New York, NY.
- Murphy, T. L. and Ferguson, R. B. 1997.** Ridge-till corn and urea hydrolysis response to NBPT. *J. Prod. Agric.* **10**: 271-282.
- Nelson, D. W. 1982.** Gaseous losses of nitrogen other than through denitrification. Pages 327-163 *in* F. J. Stevenson (Ed.). *Nitrogen in Agricultural Soils*. ASA, CSSA, SSSA. Madison, Wisconsin.
- Nommik, H. 1973.** The effect of pellet size on the ammonia loss from urea applied to forest soil. *Plant and Soil*. **39**: 309-318.
- O'Deen, W. A. and Follett, R. F. 1992.** Ammonia emission from soybean-amended calcareous soil with various soil temperature and moisture levels. *Soil Sci. Soc. Am. J.* **84**: 893-896.
- Paulson, K. N. and Kurtz, L. T. 1969.** Locus of urease activity in soil. *Soil Sci. Soc. Am. Proc.* **33**: 897-901.
- Pettit, N. M., Smith, R. J., Freedman, R. B. and Burns, R. G. 1976.** Soil urease: activity, stability and kinetic properties. *Soil. Biol. Biochem.* **8**: 479-484.
- Reynolds, C. M., Wolf, D. C. and Armbruster, J. A. 1985.** Factors related to urea hydrolysis in soils. *Soil Sci. Soc. Am. J.* **49**: 104-108.
- Reynolds, C. M. and Wolf, D. C. 1987.** Effect of soil moisture and air relative humidity on ammonia volatilization from surface-applied urea. *Soil Sci.* **143**: 144-152.
- Schlesinger, W. H. 1991.** *Biogeochemistry: An Analysis of Global Change*. Academic Press Inc., San Diego, California. 443 pp.
- Schmidt, E. L. 1982.** Nitrification in soil. Pages 253-288 *in* F. J. Stevenson (Ed.). *Nitrogen in Agricultural Soils*. ASA, CSSA, SSSA. Madison, Wisconsin.

- Sherlock, R. R. and Goh, K. M. 1985.** Dynamics of ammonia volatilization from simulated urine patches and aqueous urea applied to pasture. II. Theoretical derivation of a simplified model. *Fert. Res.* **6**: 3-22.
- Singh, R. and Nye, P. H. 1984.** The effect of soil pH and high urea concentrations on urease activity in soil. *J. Soil Sci.* **35**: 519-527.
- Singh, Y. and Beauchamp, E. G. 1988.** Nitrogen transformations near urea in soil with different water potentials. *Can. J. Soil Sci.* **68**: 569-576.
- Skujins, J. 1978.** History of abiotic soil enzyme research. Pages 1-33 in R. G. Burns (Ed.). *Soil Enzymes*. Academic Press, London.
- Smith, J. L., Papendick, R. I., Bezdicek, D. E. and Lynch, J. M. 1993.** Soil organic matter dynamics and residue management. Pages 65-94 in F. B. Metting, Jr. (Ed.). *Soil Microbial Ecology*. Marcel Dekker, Inc. New York.
- Sokal, R. R. and Rohlf, F. J. 1981.** *Biometry: The Principles and Practice of Statistics in Biological Research*. 2nd edition. W. H. Freeman and Company, San Francisco. 859 pp.
- Steel, R. G. D., Torrie, J. H. and Dickey, D. A. 1997.** *Principles and Procedures of Statistics a Biometrical Approach*. 3rd edition. McGraw-Hill, Boston, Massachusetts. 666 pp.
- Tabatabai, M. A. and Bremner, J. M. 1972.** Assay of urease activity in soils. *Soil Biol. Biochem.* **4**: 479-487.
- Technicon Industrial Systems. 1977.** Individual/simultaneous determination of N and/or P in BD acid digests. Industrial method no. 334-74 W/B+. Technicon Industrial Systems, Tarrytown, NY.
- Technicon Industrial Systems. 1980.** Industrial method number 600-80a. Urea in soil extracts. Technicon Industrial Systems, Tarrytown, NY.
- Tisdale, S. J., Nelson, W. L., Beaton, J. D. and Havlin, J. L. 1993.** Soil and fertilizer nitrogen. Pages 109-175 in P. F. Corey (Ed.). *Soil Fertility and Fertilizers*. 5th edition. Macmillan Publishing Company, New York, New York.
- Toews, W. H. 1971.** Comparison of Urea and Ammonium Nitrate as Determined by Yield Data, Nitrogen Uptake and Ammonia Volatilization in Field, Greenhouse and Laboratory Experiments. Master of Science Thesis, Department of Soil Science, University of Manitoba, Winnipeg, MB.
- Toews, W. H. and Soper, R. J. 1978.** Effects of nitrogen source, method of placement and soil type on seedling emergence and barley crop yields. *Can. J. Soil Sci.* **58**: 311-320.

Vittori Antisari, L., Marzadori, C. and Gioacchini, P. 1996. Effects of the urease inhibitor N-(n-butyl) thiophosphoric triamide in low concentrations on ammonia volatilization and evolution of mineral nitrogen. *Biol. Fertil. Soils.* **22**: 196-201.

Watson, C. J., Poland, P., Miller, H., Allen, M. B. D., Garrett, M. K. and Christianson, C. B. 1994a. Agronomic assessment and ^{15}N recovery of urea amended with the urease inhibitor nBTPT (N-(n-butyl) thiophosphoric triamide) for temperate grassland. *Plant and Soil.* **161**: 167-177.

Watson, C. J., Miller, H., Poland, P., Kilpatrick, D. J., Allen, M. D. B., Garrett, M. K. and Christianson, C. B. 1994b. Soil properties and the ability of the urease inhibitor N-(n-butyl) thiophosphoric triamide (nBTPT) to reduce ammonia volatilization from surface-applied urea. *Soil Biol. Biochem.* **26**: 1165-1171.

Xiaobin, W., Jingfeng, X., Grant, C. A. and Bailey, L. D. 1995. Effects of placement of urea with a urease inhibitor on seedling emergence, N uptake and dry matter yield of wheat. *Can. J. Plant Sci.* **75**: 449-452.

Xu, J. G., Heeraman, D. A. and Wang, W. 1993. Fertilizer and temperature effects on urea hydrolysis in undisturbed soil. *Biol. Fertil. Soils.* **16**: 63-65.

Yeomans, J. C. 1991. Inhibition of nitrogen transformations in soil: Potentials and limitations for agriculture. *Trends in Soil Science.* **1**:127-158.

Zantua, M. I., Demenil, L. C. and Bremner, J. M. 1977. Relationships between soil urease activity and other soil properties. *Soil Sci. Soc. Am. J.* **41**: 350-352.

Zhengping, W., Van Cleemput, O. and Baert, L. 1996. Movement of urea and its hydrolysis products as influenced by moisture content and urease inhibitors. *Biol. Fertil. Soils.* **22**: 101-108.

10. APPENDICES

Appendix Ia. Daily meteorological data for the May study on the Newdale clay loam soil, 1996.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Precip. mm
05/23	1	10.7	18.8	5.3	9.3	0
05/24	2 (I)	9.9	17.2	4.2	8.4	0
05/25	3	11.7	19.0	3.7	9.5	0
05/26	4	13.8	23.4	4.8	11.7	0
05/27	5	14.8	25.9	2.6	13.2	0
05/28	6	16.7	26.4	4.0	14.1	0
05/29	7	17.8	28.9	6.2	15.3	0
05/30	8 (I)	17.4	26.8	5.8	13.5	0
05/31	9	14.5	22.9	10.1	13.0	16
06/01	10	13.8	16.1	10.2	14.3	3
06/02	11	15.5	25.4	8.1	10.5	2
06/03	12	8.9	11.8	6.1	14.2	1

Appendix Ib. Daily meteorological data for the July study on the Newdale clay loam soil, 1996.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Precip. mm
07/18	1	21.2	27.0	17.4	22.0	0
07/19	2 (I)	20.3	25.2	17.8	21.4	9
07/20	3	19.1	23.1	17.0	20.1	26
07/21	4	19.5	23.7	15.4	20.5	23
07/22	5	16.8	21.7	13.2	18.6	0
07/23	6	16.4	21.3	12.1	17.5	0
07/24	7	16.3	20.6	12.9	17.4	0
07/25	8 (I)	17.2	22.8	13.1	18.0	0
07/26	9	17.4	24.6	11.6	19.5	0
07/27	10	15.9	19.3	13.0	17.9	0
07/28	11	16.4	21.6	12.9	18.8	0
07/29	12	15.5	20.0	12.7	17.2	10

Appendix Ic. Daily meteorological data for the May study on the Stockton fine sandy loam soil, 1996.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Precip. mm
05/30	1	18.4	29.1	6.7	16.4	0
05/31	2 (I)	15.3	21.7	11.2	14.6	20
06/01	3	14.5	19.9	11.2	14.1	2
06/02	4	16.1	23.7	10.1	15.2	0
06/03	5	10.8	14.8	8.0	11.9	0
06/04	6	16.0	27.2	5.9	15.6	0
06/04	7	15.8	22.7	9.52	14.7	0
06/05	8 (I)	15.8	22.7	9.5	13.1	14
06/06	9	12.7	17.0	9.0	16.3	0
06/07	10	16.5	24.2	8.8	17.9	0
06/08	11	18.8	28.3	9.9	20.9	0
06/09	12	22.8	33.1	13.7	23.1	2

Appendix Id. Daily meteorological data for the July study on the Stockton fine sandy loam soil, 1996.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Precip. mm
07/18	1	22.0	30.6	14.6	24.1	0
07/19	2 (I)	24.9	33.4	18.1	22.6	3
07/20	3	22.8	29.6	19.2	21.4	3
07/21	4	21.8	28.6	18.2	22.0	29
07/22	5	21.4	27.4	16.5	20.6	0
07/23	6	18.9	26.1	13.1	20.3	0
07/24	7	18.8	26.8	11.7	19.5	1
07/25	8 (I)	17.9	24.5	13.9	19.4	0
07/26	9	18.7	26.6	13.3	20.4	0
07/27	10	19.9	31.0	11.9	18.9	1
07/28	11	18.2	24.2	14.7	18.9	0
07/29	12	18.4	24.7	14.1	18.1	5

Appendix Ie. Daily meteorological data for the May study on the Newdale clay loam soil, 1997.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Soil 30 cm °C	Precip. mm
05/28	7	15.4	24.1	5.1	13.2	8.7	0
05/29	8 (I)	17.1	25.5	8.7	14.3	9.7	0
05/30	9	19.4	26.9	11.4	15.2	10.5	0
05/31	10	19.4	28.2	12.9	15.6	11.4	0
06/01	11	21.7	31.4	14.3	16.9	11.9	1
06/02	12	20.8	29.1	14.2	17.8	12.9	0
06/03	13	21.1	28.1	13.3	18.2	13.7	0
06/04	14	19.9	27.4	12.7	18.3	14.3	0
06/05	15	18.1	25.5	11.1	18.2	14.7	0
06/06	16	17.8	25.2	9.2	18.0	14.8	0
06/07	17	20.0	28.8	8.2	18.3	15.0	0
06/08	18	21.3	29.4	12.8	19.3	15.5	0
06/09	19	23.5	31.3	14.1	20.2	16.1	0
06/10	20	22.5	30.1	15.2	16.4	16.7	0
06/11	21	21.1	29.9	11.6	23.4	17.1	0

Appendix If. Daily meteorological data for the July study on the Newdale clay loam soil, 1997.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Soil 30 cm °C	Precip. mm
07/24	1	22.5	31.0	15.6	23.1	19.8	0
07/25	2 (I)	22.6	29.3	16.4	22.7	20.2	0
07/26	3	20.4	26.3	15.7	22.7	20.7	0
07/27	4	18.1	26.0	10.9	21.3	20.8	0
07/28	5	16.5	22.2	9.9	19.6	20.2	0
07/29	6	18.3	27.2	9.6	20.3	19.6	0
07/30	7	19.4	26.4	10.6	20.8	19.8	0
07/31	8 (I)	21.6	30.5	15.3	21.9	19.9	0
08/01	9	21.3	31.2	10.6	22.0	20.0	0

No weather data after August 1 because of equipment failure.

Appendix Ig. Daily meteorological data for the May study on the Stockton fine sandy loam soil, 1997.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Soil 30 cm °C	Precip. mm
05/10	3	13.5	24.2	2.9	14.1	10.1	0
05/11	4	8.1	14.7	3.1	12.2	10.5	2
05/12	5	5.8	12.8	0.2	11.2	10.0	0
05/13	6	5.5	10.9	1.0	9.3	9.7	0
05/14	7	2.4	9.0	-5.2	8.4	8.3	0
05/15	8 (I)	3.3	15.1	-8.8	7.3	7.8	0
05/16	9	11.1	22.6	-1.3	11.9	8.3	0
05/17	10	7.3	16.5	-0.6	11.2	9.9	1
05/18	11	2.0	3.9	-1.2	6.9	9.4	0
05/19	12	5.2	10.4	2.1	7.3	7.6	0
05/20	13	4.3	9.4	-4.7	7.9	7.4	0
05/21	14	5.5	12.0	-2.7	7.2	7.4	5
05/22	15	9.2	14.9	4.8	9.5	7.4	0
05/23	16	9.8	17.9	4.6	11.4	8.5	0
05/24	17	9.8	16.8	4.9	12.0	10.1	0
05/25	18	10.8	17.8	4.5	12.8	10.8	0
05/26	19	12.5	20.4	3.8	14.4	11.7	0
05/27	20	14.5	23.5	3.3	16.4	12.8	0
05/28	21	14.8	24.3	2.6	19.7	14.2	0

Appendix Ih. Daily meteorological data for the July study on the Stockton fine sandy loam soil, 1997.

Date Month/Day	DAF	Air Mean °C	Air High °C	Air Low °C	Soil 1 cm °C	Soil 30 cm °C	Precip. mm
07/24	1	22.4	33.6	14.7	23.9	22.7	4
07/25	2 (I)	22.6	32.1	13.4	25.5	22.9	1
07/26	3	20.3	26.5	15.7	26.0	23.4	0
07/27	4	18.1	26.7	10.2	24.8	23.2	10
07/28	5	16.4	25.5	7.6	23.4	22.7	0
07/29	6	18.7	29.3	7.2	23.8	22.2	5
07/31	8 (I)	22.7	32.7	15.5	24.8	23.3	1
08/01	9	21.3	33.0	9.9	24.8	23.5	0
08/02	10	18.1	27.2	9.2	23.0	23.5	0
08/03	11	19.8	30.8	11.4	24.1	22.5	0
08/04	12	19.8	30.1	9.3	24.2	22.5	0
08/05	13	20.2	28.9	12.5	24.8	22.7	1
08/06	14	21.6	32.0	10.3	25.4	22.7	1
08/07	15	25.1	36.0	13.9	26.9	23.4	0
08/08	16	23.5	33.5	15.8	26.3	24.5	1
08/09	17	12.4	16.1	8.4	18.1	23.3	0
08/10	18	14.4	22.4	8.3	17.7	20.2	2
08/11	19	16.0	26.5	7.1	18.6	19.8	0
08/12	20	12.7	21.4	3.8	18.3	19.8	0
08/13	21	14.9	25.6	1.2	19.1	19.2	4

Appendix IIa. Cumulative $\text{NH}_3\text{-N}$ loss (% of applied N) minus control for 1996 (Manuscript 3)

Treatment	Days After Fertilization				
	1	2	5	8	12
Newdale Clay Loam Soil: May					
NI Urea	0.09	0.58	7.22	14.44	16.93
I Urea	0.16	0.39	4.50	7.90	8.39
NI U+NBPT	0.00	0.07	0.96	2.23	4.11
I Urea+NBPT	0.01	0.05	0.45	1.28	1.56
NI UAN	0.12	0.49	2.57	6.22	7.16
I UAN	0.33	0.85	2.06	3.16	3.49
NI UAN+NBPT	0.08	0.23	0.75	1.66	2.39
I UAN+NBPT	0.01	0.13	0.40	0.81	1.06
Newdale Clay Loam Soil: July					
NI Urea	3.01	16.87	26.04	27.48	28.13
I Urea	4.09	15.76	20.81	21.82	22.03
NI U+NBPT	0.55	1.84	6.94	11.52	14.23
I Urea+NBPT	0.60	1.54	2.64	3.27	3.92
NI UAN	4.98	10.43	15.87	16.59	17.05
I UAN	3.84	8.98	11.73	12.15	12.31
NI UAN+NBPT	0.77	1.69	3.94	5.30	6.71
I UAN+NBPT	1.02	4.53	5.68	6.58	7.14
Stockton Fine Sandy Loam Soil: May					
NI Urea	0.07	0.77	24.31	29.83	32.29
I Urea	0.08	0.60	15.77	19.83	21.26
NI U+NBPT	0.02	0.10	0.61	2.06	7.21
I Urea+NBPT	0.04	0.09	0.36	1.00	2.16
NI UAN	0.07	0.17	1.40	3.59	7.49
I UAN	0.11	0.25	0.45	2.74	3.71
NI UAN+NBPT	0.04	0.08	0.43	1.24	3.34
I UAN+NBPT	0.02	0.07	0.19	0.34	0.64
Stockton Fine Sandy Loam Soil: July					
NI Urea	5.09	16.15	25.80	28.17	29.46
I Urea	2.74	13.42	22.01	23.65	24.14
NI U+NBPT	0.45	1.40	8.93	18.65	23.48
I Urea+NBPT	1.09	2.33	8.55	13.10	14.86
NI UAN	1.60	4.78	12.60	15.95	16.89
I UAN	1.20	4.13	11.19	12.71	13.18
NI UAN+NBPT	0.47	0.91	2.69	5.25	9.06
I UAN+NBPT	0.29	0.80	2.04	3.43	4.58

Appendix IIb. Cumulative $\text{NH}_3\text{-N}$ loss (% of applied N) minus control for 1997 (Manuscript 3).

Treatment	Days After Fertilization							
	1	2	5	8	12	15	19	21
Newdale Clay Loam Soil: May								
NI Urea	0.07	0.22	4.09	15.88	20.97	21.93	22.76	22.97
I Urea	0.04	0.23	2.30	4.17	4.45	4.49	4.50	4.53
NI U+NBPT	0.01	0.13	0.55	0.91	1.55	2.02	2.50	2.73
I Urea+NBPT	0.01	0.07	0.14	0.21	0.24	0.26	0.28	0.32
NI UAN	0.14	0.44	3.58	8.45	11.14	11.92	12.64	12.97
I UAN	0.13	0.40	1.36	2.89	3.10	3.18	3.20	3.22
NI UAN+NBPT	0.16	0.36	1.48	2.63	3.60	4.13	4.77	5.03
I UAN+NBPT	0.10	0.30	0.45	0.65	0.72	0.74	0.75	0.76
Newdale Clay Loam Soil: July								
NI Urea	0.05	1.05	15.84	17.49	18.91	19.30	19.62	19.70
I Urea	0.06	0.89	12.79	13.08	13.13	13.32	13.44	13.51
NI U+NBPT	0.01	0.10	1.03	2.09	4.99	6.22	7.08	7.73
I Urea+NBPT	0.00	0.11	0.96	1.39	1.88	2.05	2.98	3.06
NI UAN	0.08	0.69	6.09	6.41	7.55	7.77	7.99	8.05
I UAN	0.09	0.54	3.40	3.67	3.86	3.88	4.35	4.36
NI UAN+NBPT	0.19	0.56	2.84	3.74	4.49	4.84	4.91	4.94
I UAN+NBPT	0.03	0.16	0.95	1.13	1.28	1.28	1.28	1.28
Stockton Fine Sandy Loam Soil: May								
NI Urea	0.00	0.26	6.89	15.93	18.90	19.63	20.62	21.10
I Urea	0.00	0.23	0.76	1.01	1.05	1.05	1.11	1.12
NI U+NBPT	0.01	0.07	0.31	0.50	0.84	1.07	1.80	2.28
I Urea+NBPT	0.00	0.04	0.07	0.13	0.17	0.17	0.20	0.24
NI UAN	0.49	0.81	4.48	8.97	12.78	14.05	14.96	15.40
I UAN	0.68	1.15	3.96	6.28	6.74	6.88	7.13	7.23
NI UAN+NBPT	0.40	0.82	1.54	2.00	2.84	3.24	4.22	4.83
I UAN+NBPT	0.38	0.72	1.00	1.14	1.23	1.23	1.30	1.33
Stockton Fine Sandy Loam Soil: July								
NI Urea	0.77	3.51	26.18	30.31	33.65	34.92	35.78	36.18
I Urea	0.39	2.30	15.30	16.50	17.01	17.11	17.17	17.21
NI U+NBPT	0.11	0.29	3.17	9.13	17.84	21.83	26.04	27.10
I Urea+NBPT	0.09	0.25	1.76	2.81	3.53	3.81	4.12	4.20
NI UAN	1.28	3.31	23.97	27.50	29.84	30.69	31.27	31.49
I UAN	0.63	2.82	10.38	11.17	11.50	11.67	11.72	11.76
NI UAN+NBPT	0.42	1.03	7.21	10.53	17.06	19.56	21.47	22.11
I UAN+NBPT	0.44	0.97	5.75	8.27	8.93	9.19	9.28	9.32

Appendix IIIa. Variable NBPT Rate Study $\text{NH}_3\text{-N}$ (% of applied N) minus control in 1996
(Manuscript 4).

Newdale Clay Loam Soil: May					
Days After Fertilization					
Treatment	1	2	5	8	12
Urea (0.00% NBPT)	0.03	0.43	5.86	11.93	5.66
Urea (0.05% NBPT)	0.12	0.11	0.92	2.55	0.84
Urea (0.10% NBPT)	0.05	0.09	0.39	1.08	1.17
Urea (0.15% NBPT)	0.05	0.01	0.32	0.92	1.56
Newdale Clay Loam Soil: July					
Treatment	1	2	5	8	12
Urea (0.00% NBPT)	1.66	9.44	10.18	2.03	0.75
Urea (0.05% NBPT)	0.32	0.86	2.91	2.50	1.88
Urea (0.10% NBPT)	0.28	0.76	2.57	2.49	2.20
Urea (0.15% NBPT)	0.26	0.57	2.67	2.81	2.24
Stockton Fine Sandy Loam Soil: May					
Treatment	1	2	5	8	12
Urea (0.00% NBPT)	0.13	0.71	14.67	5.65	3.03
Urea (0.05% NBPT)	0.01	0.17	0.85	2.78	6.83
Urea (0.10% NBPT)	0.01	0.13	0.62	1.38	2.76
Urea (0.15% NBPT)	0.00	0.08	0.61	1.95	3.29
Stockton Fine Sandy Loam Soil: July					
Treatment	1	2	5	8	12
Urea (0.00% NBPT)	2.56	7.70	12.67	1.93	0.92
Urea (0.05% NBPT)	0.22	0.44	4.08	6.19	5.68
Urea (0.10% NBPT)	0.21	0.59	4.63	5.24	2.50
Urea (0.15% NBPT)	0.09	0.46	4.15	6.42	5.02

Appendix IIIb. Variable NBPT Rate Study $\text{NH}_3\text{-N}$ (% of applied N) minus control in 1997
(Manuscript 4).

Newdale Clay Loam Soil: May								
Treatment	Days After Fertilization							
	1	2	5	8	12	15	19	21
Urea (0.00% NBPT)	0.04	0.21	4.53	10.84	4.36	1.12	0.70	0.19
Urea (0.05% NBPT)	0.07	0.10	0.64	0.92	1.37	1.03	1.23	0.49
Urea (0.10% NBPT)	0.03	0.10	0.63	0.62	1.41	0.47	0.84	0.39
Urea (0.15% NBPT)	0.02	0.06	0.34	0.39	1.07	0.97	0.96	0.36
Newdale Clay Loam Soil: July								
Treatment	1	2	5	8	12	15	19	21
Urea (0.00% NBPT)	0.09	1.70	18.30	3.03	1.91	0.55	0.44	0.12
Urea (0.05% NBPT)	0.01	0.12	2.11	1.37	2.56	0.35	0.47	0.06
Urea (0.10% NBPT)	0.01	0.09	1.19	0.76	0.93	0.62	0.65	0.32
Urea (0.15% NBPT)	0.01	0.07	1.04	0.83	0.93	0.49	0.46	0.15
Stockton Fine Sandy Loam Soil: May								
Treatment	1	2	5	8	12	15	19	21
Urea (0.00% NBPT)	0.07	0.22	6.86	7.53	3.00	0.75	1.23	0.58
Urea (0.05% NBPT)	0.04	0.21	0.34	0.40	0.91	0.69	1.73	0.92
Urea (0.10% NBPT)	0.03	0.05	0.28	0.24	0.74	0.39	1.24	0.72
Urea (0.15% NBPT)	0.09	0.09	0.21	0.15	0.42	0.25	0.79	0.53
Stockton Fine Sandy Loam Soil: July								
Treatment	1	2	5	8	12	15	19	21
Urea (0.00% NBPT)	0.70	2.70	33.21	4.55	6.64	1.14	0.84	0.25
Urea (0.05% NBPT)	0.15	0.42	8.63	8.77	11.05	3.70	2.46	0.50
Urea (0.10% NBPT)	0.09	0.18	6.31	5.38	8.12	3.81	4.62	1.00
Urea (0.15% NBPT)	0.09	0.19	5.21	5.51	9.70	4.08	5.49	1.50

Appendix IV. LSMeans total N as NO_3^- , exchangeable NH_4^+ and plant N (g N m^{-2}) for the 1996 and 1997 studies (Manuscript 5).

Newdale Clay Loam Soil 1996								
Treatment	May				July			
	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N
NI Urea	0.74	1.38	4.90	7.02	0.45	-	8.60	9.05
I Urea	1.20	1.12	5.70	8.02	0.69	-	6.20	6.89
NI U+NBPT	0.55	2.03	6.80	9.38	0.25	0.20	6.30	6.75
I U+NBPT	0.56	2.06	6.90	9.52	0.61	-	7.90	8.51
NI Control	0.71	1.37	5.60	7.68	0.28	-	5.50	5.78
I Control	0.30	0.44	3.90	4.64	0.37	-	5.30	5.67
NI UAN	0.56	1.10	5.90	7.56	0.44	-	8.50	8.94
I UAN	0.36	0.69	6.60	7.65	1.44	0.13	9.40	10.97
NI UAN+NBPT	0.58	0.71	6.40	7.69	0.43	0.47	8.00	8.90
I UAN+NBPT	1.01	0.87	8.00	9.88	0.71	-	7.50	8.21

Newdale Clay Loam Soil 1997								
Treatment	May				July			
	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N
NI Urea	1.47	1.99	5.30	8.76	1.81	1.52	1.00	4.33
I Urea	1.45	1.50	6.80	9.75	0.92	1.01	2.20	4.13
NI U+NBPT	1.44	1.56	11.70	14.70	1.66	1.40	2.50	5.56
I U+NBPT	1.88	1.54	12.80	16.22	1.35	1.54	3.50	6.39
NI Control	0.95	1.28	12.10	14.33	1.73	1.51	2.60	5.84
I Control	0.77	1.19	5.90	7.86	1.77	1.38	2.50	5.65
NI UAN	0.86	1.74	10.90	13.50	1.07	1.25	2.20	4.52
I UAN	0.64	2.22	9.00	11.86	0.73	1.32	2.70	4.75
NI UAN+NBPT	0.90	2.14	13.20	16.24	1.72	1.14	1.80	4.66
I UAN+NBPT	0.99	1.80	11.80	14.59	0.94	1.11	1.80	3.85

Stockton Fine Sandy Loam Soil 1996								
Treatment	May				July			
	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N
NI Urea	0.20	1.08	6.00	7.28	0.81	0.39	12.80	14.00
I Urea	0.50	1.93	6.90	9.33	1.98	0.37	4.30	6.65
NI U+NBPT	0.47	1.12	6.50	8.09	1.04	0.16	8.50	9.70
I U+NBPT	0.73	1.72	7.30	9.75	2.06	0.68	8.30	11.04
NI Control	0.29	1.27	3.90	5.46	0.75	0.22	8.00	8.97
I Control	0.13	1.98	5.30	7.41	1.62	0.06	5.50	7.18
NI UAN	0.37	3.04	6.10	9.51	0.97	0.40	11.40	12.77
I UAN	0.69	2.36	5.30	8.35	2.92	1.81	5.70	10.43
NI UAN+NBPT	0.22	2.86	5.20	8.28	0.32	0.24	8.90	9.46
I UAN+NBPT	0.22	3.50	8.20	11.92	3.59	1.40	6.30	11.29

Stockton Fine Sandy Loam Soil 1997								
Treatment	May				July			
	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Plant-N	Total N
NI Urea	3.05	1.26	5.80	10.11	3.43	1.01	4.30	8.74
I Urea	1.98	1.14	5.20	8.32	2.73	0.64	5.40	8.77
NI U+NBPT	2.47	1.52	5.70	9.69	4.37	1.19	6.60	12.16
I U+NBPT	1.89	1.59	7.40	10.88	2.33	1.06	3.20	6.59
NI Control	2.69	1.67	7.90	12.26	3.84	0.95	6.70	11.49
I Control	2.39	1.83	6.50	10.72	2.25	1.07	3.60	6.92
NI UAN	2.98	2.12	5.10	10.20	4.87	1.43	6.20	12.50
I UAN	3.19	2.34	7.10	12.63	2.99	1.34	4.40	8.73
NI UAN+NBPT	3.29	1.73	5.90	10.92	4.00	1.44	2.60	8.04
I UAN+NBPT	2.72	1.95	4.80	9.47	2.86	1.51	2.20	6.57