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Products of Urea Hydrolysis in Soil Alter the Solubility, Plant Uptake, and Transport of Elements

by

Danial John Heaney ©

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

in

Soil Science

Department of Renewable Resources

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DJ Heaney

10615 43 Street
Edmonton, Alberta
Canada, T6H 4V2

December 1, 2000

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *Products of Urea Hydrolysis in Soil Alter the Solubility, Plant Uptake, and Transport of Elements* in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Soil Science.

Dr. Geza Racz (External Examiner)

M. J. Dudas

Dr. Marvin Dudas (Supervisor)

Dr. William McGill

Dr. Gregory Taylor

Y. Feng

Dr. Yongsheng Feng

J. A. Robertson

Dr. James Robertson

November 29, 2000

This thesis is dedicated to my father,
John Joseph Heaney
You could pay me no finer complement than
to call me my father's son.

ABSTRACT

Adding urea to soil creates a fertilizer reaction zone (FRZ) in which hydrolysis produces NH_3 and subsequently NH_4^+, raising pH. Oxidation to NO_3^- follows reducing pH. Although urea reaction products impact pH, one of the master variables in soil, little is known about how this affects pH sensitive nutrient and non-nutrient elements. Two experiments examining soil solution during the urea hydrolysis phase showed that soluble organic carbon (SOC), Al, Fe, Cu, Mn, Zn, B, and P concentrations were two to three order of magnitude higher in urea treatments compared to controls. Complexation with SOC and possibly NH_3 was the major mechanism responsible for increased concentrations. In greenhouse and field experiments, concentration and total accumulation in barley of several soil-derived nutrients, most consistently Mn, were greater when urea rather than calcium nitrate was the nitrogen source. Manganese uptake by barley and DTPA extractable Mn in soil were increased when urea was applied to soils pre-incubated with $MnSO_4$. Copper uptake and DTPA extractable Cu in soil pre-incubated with $CuSO_4$ were unaffected by urea application. Nesting urea with Cu-fertilizer enhanced early season Cu uptake from Cu-EDTA, but not from CuO or $CuSO_4$. Addition of Cu-EDTA also increased uptake of Mn. The crop uptake data suggests that urea hydrolysis products increase plant availability of the more weakly complexed and pH sensitive elements such as Mn, and have little or no effect on strongly complexed pH insensitive elements such as Cu. In a rainfall simulation experiment, runoff losses of SOC, P, Al, Fe, and Cu were from two-fold to two orders of magnitude larger in soils fertilized with urea and Cu compared to soils fertilized with Cu alone. Filtration of samples to selectively remove organics suggested that up to 30% of the soluble Cu in runoff was complexed with low molecular weight SOC. Twice as much sediment was transported from the urea treated soils relative to the unfertilized controls. Losses of sediment adsorbed nutrient elements were estimated at two orders of magnitude higher than solution losses. Overall the results suggest that urea hydrolysis products significantly alter the solubility, availability, and mobility of biologically important elements in soil.

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LIST OF ABBREVIATIONS

AS	Ammonium sulphate
AN	Ammonium nitrate
ANOVA	Analysis of variance
BBCH	Name of plant growth stage scale, not an abbreviation.
BDL	Below detection limit
CEC	Cation exchange capacity
CN	Calcium nitrate
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DTPA	Diethylenetriaminepentaacetic acid
EC	Electrical conductivity
EDTA	Ethylenediaminetetraacetic acid
FA	Fulvic acid
FRZ	Fertilizer reaction zone
HA	Humic acid
I	Ionic Strength
IC	Ion chromatography
ICP	Inductively coupled plasma emission spectroscopy
LOD	Limit of detection
LOQ	Limit of quantitation
SOC	Soluble organic carbon
SOM	Soil organic matter
UAN	Urea-ammonium nitrate

CHAPTER 1

INTRODUCTION

Whether in bands, nests, seedrows, or broadcast; whether solid, liquid, or gas; fertilizer reacts with soil to create a unique microsite in soil. Hauck (1984) called this microsite the fertilizer reaction zone (FRZ). He hypothesized that the chemical nature of the fertilizer, rather than the soil, controls such master variables as pH and ionic strength in the FRZ. Thus, the solution and surface chemistry within the FRZ can differ markedly from the surrounding soil, and the microsites formed by different fertilizers, even those supplying the same nutrient, can differ substantially. It is axiomatic that what happens in the microsite of a fertilizer will govern how that fertilizer affects soils, plants, and the larger environment. This thesis focuses on urea as the fertilizer. It examines the effects of urea hydrolysis products on soil solution, on plant uptake of elements derived from soil and fertilizer, and finally on transport of FRZ reaction products from soil into the larger environment.

Urea in Soil

More than a million tonnes of granular urea is sold in Western Canada each year accounting for approximately 40% of the nitrogen applied to prairie soils (Korol and Rattray 2000). As a proportion of total fertilizer N, urea use has increased over the past decade, in large part because of its compatibility with single pass seeding systems. Although exact data are not available on amounts and areas, farmer surveys have indicated that concentrated fertilizer placement, as bands or in the seedrow, is three times more common than broadcast placement (AAFC 1999). Whether concentrated or not, a urea granule has an almost instantaneous effect on the surrounding soil. This could be likened to the ripples created by a pebble dropped into a three-dimensional pool, but in a pool, the passing of the ripples doesn't change the water. The ripples created by urea significantly alter soil solution. These changes can be summarized as follows:

The surface of the granule rests on soil aggregates. The area in contact is not great, likely less than half the surface area of the granule. Driven by the potential difference, dry fertilizer moist soil, H_2O *molecules diffuse onto the urea creating a surface film of moisture. Simultaneously with liquid movement, vapor condenses, adding to the water film on the granule surface. Within seconds, the granule starts to dissolve and urea diffuses through the water film and into the soil. At this early stage, the path away from the granule is tortuous, following the water film along the margin of pores. Close to the granule face, dissolution exceeds diffusion and the water film rapidly saturates with urea. Further dissolution is controlled by the diffusion rate.*

On the diffusion front, urea molecules contact urease molecules, likely stabilized on a soil colloid. The first reaction zone products, NH_3 *and* CO_2*, start to appear and diffuse away from the catalytic surface. They start to hydrolyze the surrounding water, creating* NH_4^+, OH^-, *and* HCO_3^-.

As NH_4^+ *accumulates along clay surfaces, Ca and Mg are displaced from exchange sites into the soil solution. New reactions occur,* Ca^{2+} *reacts with* CO_3^{2-} *to form* $CaCO_3^{\circ}$*. As* *more NH_4^+ displaces Ca^{2+} into solution, the concentration of $CaCO_3^\circ$ increases to the point where it begins to precipitate out of solution. At the colloidal surface, the forces holding the colloids together are under attack. The ion layer is now dominated by NH_4^+. Dispersion starts to force individual clay platelets apart. Colloidal fragments, both organic and mineral, become suspended in the soil solution.*

At the soil water-air interface, rising pH drives NH_3 into the soil air. It diffuses outward until re-adsorbed in water films, where it reacts, forming NH_4^+ and raising pH. Nitrosomonas starts to produce NO_2^-, which in turn drives NO_3^- production by Nitrobacter. Nitrate starts to accumulate, but then stops as rising pH soon inhibits nitrifying bacteria. Rising osmotic potential makes it difficult for all organisms to imbibe water. Ammonia levels continue to rise disrupting cell membranes. Biological activity ceases. The diffusing front of urea continues outward leaving a near sterile zone behind it.

The preceding synthesis is supported in part by experimental work on urea reported in the literature. Other parts have been inferred from work with other nitrogen fertilizers particularly anhydrous ammonia (NH_3). Rachhpal-Singh and Nye (1984b) concluded, based on measurements of diffusion rates, that soil solution near the granule was saturated and that observed dissolution rates could be explained in terms of significant water vapor movement to the granule. Several authors have reported that rising urea concentrations inhibit urease activity, but the inhibiting concentrations reported vary widely. Working with a tropical soil, Rachhpal-Singh and Nye (1984a) found optimum urease activity at pH 6.5, but within the pH range 5-8, activity was depressed when urea-N concentration exceeded 10 mol L^{-1} regardless of pH. Substrate inhibition has been measured at much lower urea-N concentrations, near 5 mmol L^{-1}, in Gray Luvisolic soils (Monreal *et al.* 1986). The latter authors also found that when urea was localized in a nest, nitrifying bacteria in the surrounding soil were killed. This confirmed early work by Wetselaar *et al.* (1972) that suggested high osmotic potential, high pH, and high NH_4^+ concentrations near urea bands created an environment hostile to nitrifying bacteria. In terms of more general effects on microbial life, a number of authors have measured reductions in microbial numbers and/or activity near NH_3 bands (Eno and Blue 1954, Eno *et al.* 1955, and Parr 1969).

Fenn *et al.* (1981), in formulating their general theory of ammonia loss from nitrogen fertilized soils, suggested that precipitation of Ca displaced from the cation exchange complex by NH_4^+ occurs once urea hydrolysis raises soil pH above 7. Later Kissel *et al.* (1988) obtained results suggesting that $CaCO_3$ precipitation was significant, accounting for 15-20 % of C added as urea, only when pH rose above 8. They also suggested that precipitation of $CaCO_3$, and to a lesser extent $MgCO_3$, caused conversion of HCO_3^- to CO_3^{2-}, and that the accompanying release of H^+ kept pH from rising above 9.

Although there are little data available on the effects of urea on soil mineral colloids, a number of NH_3 and NH_4^+ based compounds are known to reduce soil structure in the short-term (Fox *et al.* 1952, Gifford and Strickling 1958, Epshteyn and Agafonov 1977). Soil degradation concerns led to a number of studies on the effects of NH_3 and ammonium hydroxide (NH_4OH) on soil organic matter (SOM). Tomasiewicz and Henry (1985) found that soluble organic carbon (SOC) increased up to four-fold following NH_3 application to undisturbed cores from ten Chernozemic soils. The amount of carbon solubilized varied with the amount of NH_3 applied, distance from the injection site, and the water content of the soil. Norman et al. (1987) reported similar results on Indiana soils. Myers and Thien (1988) treated a soil with combinations of NH_4OH and two acidic phosphate salts and then leached the soil with water. They found that all three compounds increased SOC levels compared to untreated soil and the amount of SOC extracted was positively correlated with the pH of the leachate. Earlier Nemec and Vopenka (1971) had reported that addition of NH_3 and NH_4OH increased extractions of humic substances from soils to a greater extent than did ammonium sulphate (AS) or ammonium nitrate (AN).

The characteristics and fate of this SOC brought into solution by N fertilizer are poorly understood. Homann and Grigal (1992) measured the molecular weight of SOC in leachate following urea addition to a forest site. Their results showed that a high proportion of the SOC was composed of molecules with molecular weights greater than 14,000 daltons. This molecular weight range and solubility under basic conditions suggested that the SOC in their system was predominantly humic acid (HA). Urea and NH_3 both increase soil pH initially but a pH decrease accompanies subsequent NH_4^+ oxidation (Hauck 1984). Humic acids tend to coagulate and precipitate under acidic conditions. This process is enhanced at higher ionic strengths and higher HA concentrations in soil solution (Ghosh and Schnitzer 1980). Tomasiewicz and Henry (1985) and Norman *et al.* (1987) suggested that SOC brought into solution by NH_3 would decrease through polymerization, flocculation, and conversion to insoluble acidic forms as NH_4^+ oxidized. On the other hand, Norman *et al.* (1988) found that SOC brought into solution by NH_3 did not persist beyond 40 to 50 days, nor was it significantly reduced by acidifying the soil to pH 4.5 with H_3PO_4. In their study, disappearance of SOC was accompanied by release of CO_2 leading them to the conclusion that microbial transformations were the primary mechanism for removal of SOC from the soil solution.

Although little has been done on the short-term effects of urea on soil solution, longer-term effects on soil properties have been examined in a range of soils. Intrawech *et al.* (1982) compared physical and chemical characteristics of soil after ten years of application of NH_3, urea, ammonium nitrate (AN), and urea ammonium nitrate (UAN) to four Kansas soils. Although there were no discernible differences in physical properties, they found that all N sources had reduced soil pH relative to the control. Ammonium and NO_3^- levels were increased but there were no significant effects on available P or exchangeable Ca, Mg, K, or Na. All N sources did, however, increase available Mn and decrease available Zn. Similar decreases in pH were reported for a Black Chernozemic soil after six years of surface application of various granular N fertilizers (Goh *et al.* 1987). These researchers found that exchangeable Ca and Mg had declined by 35 and 50% respectively in the 0-5 cm depth of the urea treatments compared to the control. The displacement of Ca and Mg in the urea treatments was less than in AS or AN treatments. Interestingly, measurement of water dispersible clay indicated that after six years, soil stability was higher in the urea treatments compared to the control, AN, and AS treatments. A ten year comparison of banded urea and NH_3 on a Brown Chernozem showed that pH was gradually reduced 0.2 to 0.8 units (Ukrainetz *et al.* 1995). The reduction was proportional to N rate, was greater when NH_3 was the N source, and was greater at the application depth (10 cm) than above or below (Bouman *et al.* 1995).

Biederbeck *et al.* (1996) measured microbial population in treatments from this experiment. They reported that bacterial and fungal numbers increased with N rate and were greater in NH_3-treated relative to urea-treated soil. Nitrifying bacteria populations were increased at rates below 100 kg N ha^{-1} but were not different from the controls at higher rates. Actinomycete populations declined with N rate. The reduction was greater when NH_3 was the N source.

Effects of pH, Ionic Strength, and Organic Matter on Soil Solution

Urea induces significant changes in soil. In the short-term, these changes are related to the pH increase accompanying urea hydrolysis. Over the long-term, changes appear to be attributable to the net reduction in pH brought about by nitrification. Soil pH is an index of acid-base equilibrium in soils, and whether viewed in the short- or long-term, disruption of this equilibrium sets off a web of reactions that alter the physical, chemical, biochemical and biological attributes of the soil. One of the important subsets of reactions within this web (important in that they control mobility and plant availability) are those controlling distribution of elements among solid and solution phases. In the FRZ created by urea, element distribution, or more correctly re-distribution, will be governed by changes in the stability of inorganic and organic complexes and the solubility of minerals. The equilibria of the reactions involved tend to be strongly affected by pH and, to a lesser extent, by ionic strength (*I*). Formation and dissociation of inorganic complexes and the precipitation and dissolution of minerals are also strongly influenced by organic ligands in solution and binding sites on solid phase organics. Although these processes have not been studied specifically in the FRZ of urea, they have been widely studied in unfertilized soils using a variety of approaches.

Relating ion activities to the solubility of different minerals and predicting speciation via solubility and stability constants has met with some success with major elements (McBride 1994, Chapter 4). Lindsay (1980) used thermodynamic data to show that Ca and Mg minerals tend to be too soluble to persist in acid soils, but calcite or calcite-dolomite will precipitate once pH rises above 7. He concluded that $Ca^{2+}$and Mg^{2+} activities are controlled by exchange equilibria below pH 7 and solubility of the carbonates above pH 7. Hasset and Jurinak (1971) had earlier shown that a higher activity of Ca^{2+} and Mg^{2+} was supported in soil solution as the Ca to Mg ratio decreased. The solution activities of Al^{3+} and Fe^{3+} tend to decrease with increasing pH, but declines in total concentration can be offset by formation of soluble complexes at alkaline pH's (Lindsay 1980). Well-aerated soils contain a number of different Fe oxides, each with a different solubility, and solution Fe is likely controlled by the most soluble form (Schwertmann and Taylor 1989). Iron(III) forms a number of hydrolysis species as well as complexing with a range of inorganic ligands. The activities of these complexes decline as pH increases. The exception is $Fe(OH)_4^-$, which becomes the dominant inorganic Fe species in solution above pH 8.5 (Norvell and Lindsay 1982). As a result, total concentration of inorganic species of Fe(III) in solution declines five orders of magnitude between pH 3 and 7.5, are lowest between pH 7.5 and 8.5, and start to increase above pH 8.5 (Lindsay 1991). Aluminum(III) behaves similarly, forming $Al(OH)_4^-$, but the solubility minimum occurs between pH 6 and 7 (McBride 1994, Chapter 5).

Co-precipitation and adsorption reactions can reduce the solubility of trace metals in soil to well below that predicted from the solubility of pure mineral forms (McBride 1994, Chapter 4). Schwab and Lindsay (1983) found that in a well-aerated calcareous soil, Mn-carbonates controlled Mn^{2+} activity in soil solution. In neutral to acid and/or poorly drained soils, Mn^{2+} is likely under control of Mn-oxides (Lindsay 1991). Sims (1986) found that raising the pH of four soils shifted Mn from the exchangeable to the oxide adsorbed fractions. Lindsay (1991) calculated the speciation of solution Mn over a pH range of 4 to 9. His solubility diagrams suggest that complexes are relatively unimportant and Mn^{2+} dominates solution Mn unless ligands, for example SO_4^{2-} or Cl^-, are added or CO_2 level is raised above that normally found in soils. The solubility of Mn can be reduced in soils high in labile-P, such as those receiving P fertilizer additions, through precipitation of Mn-P minerals (Boyle and Lindsay 1986, Lindsay and Brennan 1987). The activity of Cu^{2+} declines in well-aerated soils as pH rises to 7. At pH's above 7, $Cu(OH)_2^{\circ}$ and/or $CuCO_3^{\circ}$ help maintain, but will not increase total Cu concentration in soil (Jeffrey and Uren 1983, Lindsay 1991). Results from several studies suggest that Zn^{2+} activity declines approximately two orders of magnitude for each unit increase in pH (Norvell *et al.* 1987, Ma and Lindsay 1990). Above pH 7.7, $ZnOH^+$ replaces Zn^{2+} as the dominant solution species (Lindsay 1991).

Summarizing the effects of urea on inorganic metal species, soluble Ca, Mg, Mn and Zn in the FRZ should decline during the initial high pH phase. Soluble Cu is likely to decrease in soils with initial pH below 7, but stay the same in neutral and alkaline soils. Soluble Al and Fe may form negatively charged species. Whether or not this results in a net increase in solution Al and Fe depends on the initial pH value relative to their respective solubility minima. Total soluble Mo would be expected to increase regardless of initial pH as solubility of soil-Mo generally increases an order of magnitude for each unit increase in pH (Vlek and Lindsay 1977). Once the urea hydrolysis products are neutralized, further conversion of NH_4^+ to NO_3^- would tend to acidify the soil and increase the proportion of free metal cations.

The inorganic chemistry does not occur in isolation from SOM, which can have a profound effect on the soil solution. Soil organic matter is rich in acid functional groups and consequently the availability of metal reactive sites tends to go up with pH (Stevenson and Fitch 1986). Whether or not this increases metal solubility depends on the distribution of SOM between solid and solution phases. A large number of studies (e.g. Boyle and Fuller 1987, McGrath *et al.* 1988, Dunnivant *et al.* 1992) have shown that increasing the SOC increases the metal concentration in solution. Fractionation studies have shown that Cu complexed to solid phase SOM is largely unaffected by changing pH, but the proportion of Mn held in SOM increases substantially with pH (Sims 1986, Shuman 1986).

The affinity of metals for SOC varies with the nature of the metal, the ligand, soil type and pH (Stevenson 1991). Hodgson *et al.* (1966) found 5 to 90% of Zn in organic complexes compared to 76 to 99% of Cu in the same set of soils. Fuji *et al.* (1982) found an order of magnitude difference in total solution concentration between metals (Zn>Cu>Fe). The majority of soluble Zn (63%) and virtually all the Cu and Fe (99%) were complexed in their sludge amended soils. Conversely, Sanders (1983) determined that nearly all the Zn in water extracts from five English soils was present as Zn^{2+}. His findings were similar for Mn^{2+} and Co^{2+}.

Aluminum toxicity is an important limitation on plant growth under acidic conditions (Foy *et al.* 1965) and has been related specifically to Al^{3+} activity (Blamey *et al.* 1983). Detoxification by additions of organic acids such as citrate and oxalate suggests that Al complexes strongly with ligands containing multiple carboxyl groups even at low pH (Hue *et al.* 1986, Kerven *et al.* 1991). Kerven *et al.* (1995) used ^{27}Al NMR to show that the major proportion of Al was ligand bound at pH's as low as 3.1, in systems rich in organic acids. Complexes with soluble humic materials are also important in maintaining soil solution concentrations of Al (Schnitzer and Kodama 1977, Kodama and Schnitzer 1980). The proportion of Al complexed with soluble organic carbon tended to rise with pH when compared in acidic field soils, (Driscoll *et al.* 1985). However, the average charge on soluble Al species is zero at neutral pH ($Al(OH)_3^0$) and approaches -1 at pH 9 ($Al(OH)_4^-$) (Marion *et al.* 1976). So even if complexing sites are available, they may have an affinity for cationic species of elements other than Al at the pH levels found in the FRZ.

Several researchers have found that total metal concentrations in soil solution increase when ionic strength (*I*) increases. Alva and Sumner (1990) used $CaCl_2$ in ten-fold increments from 0.1 to 100 mmol L^{-1} to increase *I* in three highly weathered acid subsoils. They found that total soluble Al increased an order of magnitude for each order of magnitude increase in *I*. Fotovat and Naidu (1998) varied *I* from 0 to 0.02 mol L^{-1}, using Na^+, K^+, Ca^{2+}, or Mg^{2+} as the indexing cation, in two acidic and two alkaline sodic soils. The trend in DOC, Cu, and Zn varied depending on soil type. Increasing *I* tended to decrease DOC concentrations, more so in alkaline than in acid soils. It decreased soluble Cu in all soils and soluble Zn in the alkaline soils. It had the opposite effect, increasing soluble Zn four to twenty-fold in the acidic soil. Similar reports of increased Zn solubility in relation to additions of basic cations (Shukla *et al.* 1980, Stahl and James 1991, Winistorfer 1995) suggest that increasing *I* displaces Zn from cation exchange sites in acid to neutral soils. Studies on Cu enriched soils have found that increasing *I* reduces soluble Cu (Shukla *et al.* 1980, Xie and McKenzie 1990, Stahl and James 1991, Zhu and Alva 1993, Winistorfer 1995). In a study at indigenous Cu levels, McLaren *et al.* (1981) found that increasing *I* increased Cu adsorption by montmorillonite about two-fold, but had only minor effects on adsorption by humic acid.

The major elements forming oxyanions in soil are C, N, and S. Concentration of carbonic acid in soil is regulated by $CO_{2(g)}$ concentration in soil air, while speciation into HCO_3^- and CO_3^{2-} is controlled by pH (McBride 1994, Chapter 8). In the FRZ, urea produces CO_2 as a reaction product, and high CO_2 along with high pH likely leads to elevated CO_3^{2-} activity, at least initially. Precipitation of $CaCO_3$ and $MgCO_3$ may reduce CO_3^{2-} activity once NH_4^+ displaces Ca^{2+} from cation exchange sites (Kissel *et al.* 1988). Nitrate forms complexes with a number of metals but does not form precipitates in soil. Sulphate is similar, except it can precipitate as $CaSO_4{\bullet}2H_2O$. Soil organic matter is a reservoir of both N and S and solution levels in non-saline soils are in large part controlled by biological cycling rather than adsorption or precipitation reactions.

Phosphorus also exists as an acid oxyanion (H_3PO_4) in soil solution and consequently its speciation is highly pH dependent. At pH's above 8, HPO_4^{2-} would be the dominant species; PO_4^{3-} doesn't start to appear in quantity until pH exceeds 12 (Bohn *et al.* 1979, Chapter 10). Phosphate concentrations in soil solution are controlled by mineralization (McGill and Cole 1981), precipitation (Mansell *et al.* 1985, Cho 1991), and adsorption (Sawhney 1977, Mansell *et al.* 1985, Eghball *et al.* 1990). The latter two processes are strongly influenced by pH and to a lesser extent by *I* (Muljadi *et al.* 1966, Hingston *et al.* 1972, Bar-Josef *et al.* 1988). The high pH in the FRZ of urea, along with elevated Ca^{2+} activity would tend to increase precipitation of Ca-P, reducing P concentration in solution. However, in prairie soils a large portion, half or more according to McGill and Cole (1981), of labile-P is associated with SOM. Perturbations that dissolve SOM are likely to increase total soluble-P.

From Soil Solution to Plant Availability and Mobility

Plants take up a range of elements from soil. Some are essential, some merely beneficial. Most can be toxic at high levels and some at relatively low levels. Soils have a potential to provide elements to plants, which is generally referred to as an element's availability. Sposito (1989, Chapter 13) defined an element as available, "*if it is present as, or can be transformed readily to the free ion species, if it can move to the plant root on a time scale that is relevant to plant growth and development, and if once absorbed by the root, it affects the life cycle of the plant.*" The classic view of soil fertility holds that plants take up specific ionic forms of the essential elements from the soil solution. These ions move to the root surface through diffusion and/or mass flow where they are taken into the plant and the depleted solution is recharged through a variety of processes depending on the element.

Sposito (1984) suggested that plant availability is controlled by the ion activity of the species required. A number of studies examining plant uptake as a function of ion activity support this view both for essential and toxic elements (e.g. Pavan *et al.* 1982, Bingham *et al.* 1983, Schwab and Lindsay 1983). More recently, Bell *et al.* (1991) found that increasing total concentration of metals in solution while maintaining activity of the metal ions constant increased availability to barley.

Studies of elements like Fe show that the activity of metals in soil solution is in some cases far below the minimum threshold for plant growth determined in simple nutrient solutions (Schwab and Lindsay 1983). Plants still grow implying that plants are not passive recipients of what the soil solution has to offer. In fact, plants use a number of strategies to influence element availability in soil solution. For metal micronutrients, this can include manipulating acidity, redox potential and chelation in the rhizosphere (Manthey *et al.* 1994). Plants also increase availability of essential elements bound to carbon through the release of exo-cellular enzymes, for example phosphatase (Juma and Tabatabai 1988). Uptake of a number of elements, for example P and Zn, is enhanced through the symbiotic relationships with mycorrhiza (George *et al.* 1994). All of the above processes still fall within Sposito's definition of availability. Karpukhin *et al.* (1984) showed direct uptake of organically chelated Mn opening the possibility that some essential elements can move from soil into plants without changing to inorganic ion forms.

Passioura *et al.* (1972) showed that roots do not grow into nitrogen fertilizer bands but tend to proliferate along the margins. This suggests that the margins of the FRZ intersect with the rhizosphere and that changes in element form or amount in soil solution within the FRZ can affect availability and plant uptake. For example, Petrie and Jackson (1984a,b) showed that the acidification caused by banded ammonium sulphate increased Mn in solution and uptake by barley and oats. Unlike ammonium sulphate, urea initially raises soil pH. It is also quite likely to cause dissolution of SOM in a manner similar to anhydrous NH_3. It seems probable, based on the idea that soil solution is significantly altered within the FRZ, that urea will significantly alter the availability and uptake of a number of elements by plants.

Transport of elements to plants through the soil solution involves movement on the scale of a few millimeters, while transport from soil into the larger environment can involve movement on scales ranging from meters to kilometers. None-the-less, several of the same factors that alter plant availability may also affect mobility on this larger scale. Soluble organic carbon can act, through complexation reactions, as a carrier of metals through soil and into surface and groundwater (Zunino and Martin 1977). Non-metal elements can also be transported by SOC. For example, dissolved organic phosphorus makes up a significant portion of the P carried from agricultural lands in both surface and drainage waters (Heathwaite 1997, Brookes *et al.* 1997). Speciation of metals into neutral and negatively charged species is another process through which mobility could be altered, as is displacement of ions from cation exchange sites by NH_4^+. Consistent with this latter idea, Otchere-Boateng and Ballard (1978) found that urea enhanced the leaching of Ca and Mg displaced from cation exchange sites once nitrification had acidified the soil. Analogous to the argument made for plant availability, it seems probable that urea perturbs soil in ways that would significantly alter transport of elements through runoff and leaching.

Research

My interest in the effects of fertilizer on soil solution stemmed from earlier work comparing the effects of placement methods on nitrification of N derived from urea *versus* AS (Heaney *et al.* 1987). The results showed that when granular N was concentrated, the soil near the band could not buffer against significant pH changes. Apparent recovery of fertilizer-N, calculated as treatment minus control for mineral N extracted with KCl, was significantly greater than 100% and was greatest in the more concentrated placements. This result suggested that fertilizer-N enhanced conversion of soil-N to plant available forms. Similar observations of the priming effect of NH_4^+-salts had been reported in the literature over a period of four decades. Jansson and Persson (1982) attributed it to increased mineralization of biomass-N as soil microflora shifted towards more acid tolerant species. On the other hand, Nommik and Vahtras (1982) attributed it to release of fixed NH_4^+ from clay lattices as pH declined.

After some thought two ideas emerged. The first was that if fertilizer-N changed the availability of soil-N, might it also be affecting the availability of other nutrients. The second was that nutrients strongly affected by pH were the ones most likely to be affected by fertilizer-N. Further soil analysis showed that AS, but not urea, had increased Miller-Axley extractable-P and $CaCl_2$ extractable-Mn (D.J. Heaney, unpublished data). Urea with its power to raise pH during the hydrolysis stage was of more interest than AS or AN which are strictly acidifying. I was curious to examine solution concentrations of nutrient elements within the FRZ of urea. What I expected was that increased pH in the

FRZ would decrease the solution concentration of ions and complexes of Fe, Cu, Mn, Zn and P, and increase those of Al and Mo. Although I did not have capability to measure activities of individual species, I could use inductively coupled plasma emission spectroscopy (ICP) to simultaneously measure total concentrations for a range of metals and non-metals in soil solution.

From the above, I developed the experiment reported in Chapter 2 which was in essence a reconnaissance of soil solution within the FRZ of urea. The results were not what I expected. Total concentrations of elements in solution increased in some cases two to three orders of magnitude following urea addition. It was apparent that inorganic chemistry involving OH^- and CO_3^{2-} was not controlling metal concentrations, and metals and other elements from the solid phase were entering solution. Thermodynamic considerations indicated that free metal ions and hydroxide or carbonate complexes were not responsible. Organic matter seemed a likely alternative. Although there was nothing specific on short-term effects of urea on SOM, a number of researchers had reported that NH_3 solubilized SOM (Tomasiewicz and Henry 1985, Norman *et al.* 1988). The second experiment, reported in Chapter 3, examined total element concentrations in soil solution in relation to SOC concentrations over a wider range of soils. It also compared solution from the FRZ of urea to the FRZ of AS.

The results showed that urea did in fact solubilize SOM and that high solution concentrations of a number of elements were reasonably well correlated with SOC. At this point, the results raised a number of questions:

- How does total soluble metal and SOC in the FRZ vary among soils and among fertilizer products?
- What is the source of the metals entering the total soluble pool in the FRZ - the solid organic phase or the solid mineral phase or both?
- Does fertilizer mobilize metal contaminants in polluted soils?
- What are the chemical characteristics of the SOC solubilized by urea?
- What functional groups are involved in metal complexing?
- How does the FRZ change over time and how long does it persist in reduced tillage systems?
- Are the metals and SOC brought into solution in the FRZ transported out of the FRZ?
- Are organic contaminants carried with the SOC?
- What is the fate of SOC and metals transported down the profile into acidic, basic or neutral subsurface horizons?
- Does metal solubilization in the FRZ lead to increased or reduced availability in the rooting zone?
- What is the fate of SOC in the rhizosphere?
- How do urea and other fertilizers interact when they are placed together in a band or nest?

While all of the above were valid questions, the overriding question that needed answering was one of agricultural and environmental significance. Further characterization of the FRZ would not be particularly rewarding unless there were impacts at a scale larger than a few millimeters from a urea granule. Thus determining whether or not urea altered plant uptake and mobility of nutrient elements from the FRZ shaped the remaining experiments. For soil derived essential elements, the intensity factor or nutrient available for immediate uptake is usually associated with the activity of the free ion in the soil solution (Sposito 1989, Chapter 13). The capacity factor is associated with those mineral and organic phases that are capable of replenishing the soil solution within the time frame of a growing season. If high pH in the FRZ was reducing solution activity, then it may have decreased intensity of a number of essential elements as well. Conversely, increases in total solubility may have brought previously occluded nutrients into contact with the soil solution, and increased the capacity factor. The effects of urea on uptake by barley of soil derived and fertilizer elements were examined in the three experiments found in Chapters 4 and 5. Higher soluble concentrations even if not plant available might be mobile. The effects of urea on mass flow transport of various elements were examined in the last experiment reported in Chapter 6.

Methodology

Various techniques have been developed for removing solution from the soil without significantly altering its composition. Parker (1921) compared miscible column displacement against a high volume water:soil method. Interestingly, his review of the contemporary literature indicates that all major techniques –high volume extracts, column displacement, centrifugation, pressure extrusion, and suction– had all been tried by his contemporaries. Progress during the subsequent eighty years has largely been through refinement of these early approaches. Adams *et al.* (1980) compared column displacement to centrifugation with and without immiscible liquid. Their solution data suggested that the three methods were essentially the same, but the centrifugation techniques were more convenient and required less technical skill. Immiscible displacement techniques rely on relatively dense, usually organic, liquids including carbon tetrachloride, fluorocarbon, 1,1,1-trichlororethane, ethyl benzoylacetate, and tetrachloroethylene (Mubarak and Olsen 1976, Whelan and Barrow 1980, Kittrick 1983, Elkhatib *et al.* 1986). Variations in toxicity, volatility, and cost make them more or less convenient to use. Centrifuge techniques that do not use displacing fluids have the advantage of being non-destructive, but tend to yield small quantities of solution unless large soil volumes are extracted (Adams *et al.* 1980). Elkhatib *et al.* (1987) developed a rapid method of centrifugation that yielded reasonable solution volumes based on a 25 g soil sample. However, their method required modified centrifuge tubes. Thibault and Shepard (1992) developed a comparable system using inexpensive disposable syringes and centrifuge tubes. Soil solutions displaced using their system were not different from solutions obtained using immiscible displacement (Shepard *et al.* 1992).

A number of researchers, including Alzubaida and Webster (1983), Miller *et al.* (1989), and Heck and Mermut (1992), have characterized the composition and speciation of soil solutions using saturated paste extractions as a proxy for soil solution. Studies directly comparing extracts to displaced soil solution have reached different conclusions. Comparison in relatively ion rich saline and sodic soils have shown extracts to be a poor proxy for soil solution (Carter *et al.* 1979, Janzen and Chang 1988, Kohut and Dudas 1994). Extracts more accurately estimate soil solution in highly weathered soils with low ion concentrations (Gillman and Bell 1978). Fotovat *et al.* (1997) showed that Cu and Zn concentration decreased with increasingly higher volumes of extracting water, but concentrations at field capacity could be predicted using a Langmuir relationship. Since the relationship needs to be determined for each soil, the usefulness of this approach is likely confined to repeated experiments with the same or a small group of soils.

For examining soil solution in the FRZ, the choice was between centrifugation displacement or more convenient saturated paste extraction. The latter was rejected based on its tendency to alter solution characteristics in ion rich environments (such as an FRZ). Preliminary work on field moist soils showed that the centrifugation method of Thibault and Shepard (1992) was reasonably convenient and reproducible. It was however not effective in extracting solution from high clay soils once they had been treated with urea. This was overcome by choosing clay loam or coarser textured soils for the experiments.

There are a variety of techniques available for determining concentration of elements in soil solution. Methods for directly measuring activity of ions are less numerous. Electrochemical approaches include anodic stripping voltammetry and ion specific electrodes (Mota and Correia dos Santos 1995). Non-electrochemical techniques based on resins, chelate equilibrium, spectroscopy, and size separation have also been used for a number of cation and anion species (Apte and Batley 1995). For the most part, direct ion activity techniques have been applied to a single species or to speciate a single element (e.g. Webb *et al.* 1993, Sauve *et al.* 1998).

A third technique for estimating speciation in soil solution is use of thermodynamically based equilibrium models. These offer an advantage in that they can use total solution concentrations as input for speciation, speciate numerous elements simultaneously, and provide insight in solution-dissolution reactions (Mattingood and Zachara 1995). The disadvantages include need for large sets of accessory data characterizing the soil solution, including accurate formation constants, and the assumption of equilibrium conditions.

For the purposes of this study, the approach was to use total solution concentrations to estimate gross changes in soil solution for a range of elements. The soil solution model GEOCHEM was used to examine complexation and solubility reactions, but only as a tool to help in synthesis of concepts in the final chapter.

The effects of the FRZ on plant availability of nutrient and toxic elements was determined by growing plants in contact with the FRZ and measuring element uptake (Chapter 4 and 5). Plants provide a direct measure of availability, and while it is intuitively pleasing to use plants to measure availability, there is a major drawback. Change in any factor that increases plant growth, for example raising availability of N, can cause dilution of other non-limiting nutrients (Prevot and Ollagnier 1961). Jarrel and Beverly (1981) developed a technique based on comparative yield, tissue concentration, and total uptake for distinguishing dilution of nutrients from effects induced by experimental factors. While this helps in interpretation, it does not solve the problem entirely as dilution effects can mask real treatment effects. Changes in plant availability of nutrients other than N would be most easily interpreted if yields were the same in all treatments. Since agricultural soils in Alberta are generally N limited, experiments were designed to equalize N availability among urea and comparative treatments. Calcium nitrate (CN) was used for this purpose. Based on its chemistry, a neutral salt source of oxidized N with the most common labile soil cation as the associate ion, CN was assumed to be the least perturbing alternative N source. The Ca^{2+} from CN can precipitate with CO_3^{2-} resulting in release of H^+ from HCO_3^-; however, the effect of this reaction on pH is slight compared to acidification associated with ammonium based fertilizers. Comparison of long-term effects in a Black Chernozemic soil support the assumption that CN additions have less of an effect on soil chemistry than urea (Goh *et al.* 1987).

In the greenhouse experiments, plants were grown to maturity. In the field experiment, plants were harvested at early heading and again at maturity. Constraints on greenhouse space and numbers of samples limited the number of treatments that could be included in experiments. The decision was made to harvest greenhouse plants at maturity, integrating fertilizer effects over all growth stages, rather than harvesting at several stages. The justification for this approach was that a wider range of soils could be used if sampling times were reduced.

In the greenhouse experiment reported in Chapter 5, a method was required to evaluate the availability of Fe, Cu, Mn, and Zn in the FRZ after harvest. Successive extraction procedures have been used by researchers to assess availability of elements in various soil fractions –soluble, exchangeable, organic, oxide bound, etc. (Sims 1986, Liang *et al.* 1991). These techniques differ considerably based on the element. For example, Shuman (1991) lists 17 different procedures for the micronutrients. An alternative was the simple multi-element DTPA test. DTPA extraction was initially found to correlate well with plant metal content by Brown *et al.* (1971) and Randall *et al.* (1976). Later it was refined and calibrated for assessing micronutrient deficiencies on neutral and calcareous soils (Lindsay and Norvell 1978). DTPA forms soluble metal-chelate complexes, which reduce free metal ion activity. Ion activity is replenished from solid labile phases. This simulates plant uptake (Sims and Johnson 1991) and when indexed to crop growth reflects both the intensity and capacity aspects of availability (Viets and Lindsay 1973). For the soil analysis in Chapter 5, the DTPA test was chosen rather than more complicated procedures.

Column and lysimeter techniques have been used by a number of researchers to study leaching of fertilizer nutrients and reaction products (e.g. Otchere-Boateng and Ballard 1978, Rubeiz *et al.* 1992, Clay *et al.* 1995). Movement of fertilizer nutrients and reaction products with surface runoff has been measured using techniques at various scales including watersheds (Hubbard *et al.* 1991), field plots (Goss *et al.* 1993, Gascho *et al.* 1998), and microplots (Hubbard *et al.* 1989). For experiments conducted at the latter two scales, rainfall simulation techniques have become increasingly popular. Rainfall simulation was originally developed as a tool for measuring erosion (Miller 1987). It has been adapted for measuring nutrient and herbicide movement under a variety of fertilizer, tillage and manure treatments on field soils (e.g. Hubbard *et al.* 1989, Shreve *et al.* 1995, Gascho *et al.* 1998, Torbert *et al.* 1999). Rainfall simulation offers researchers the advantage of controlling parameters; such as rainfall intensity, antecedent soil moisture, slope, and time; that are uncontrollable at field scale (Burgoa *et al.* 1993, Bowman *et al.* 1994). One disadvantage is that simulations are usually at relatively high rainfall intensities. This worse case approach tends to estimate losses higher than those measured in watershed experiments (Wauchope and Burgoa 1993). Consequently, care must be taken if results are scaled up and scaling techniques are not fully developed.

Despite some limitations, rainfall simulation techniques are extremely useful in making relative comparisons between treatments or soils under standard conditions. As part of a project examining P export from manured soils, my research group developed a rainfall simulator for use in the laboratory. This simulator is similar in terms of rainfall delivery to that used by Shreve *et al.* (1995) in field studies. It differs in that it allows collection of leachate as well as runoff and can apply rainfall to four treatments simultaneously. Technical details of nozzles, flow rates, and dimensions are given in Chapter 6. Under standard operating conditions it delivers a rainfall intensity of 65 mm h^{-1} at approximately 90% of the kinetic energy of natural raindrops (Ralph Wright, personal communication).

A word on terminology is required. Carbon in soil solution is referred to in older literature as soluble organic carbon (SOC). Most recent literature refers to dissolved organic carbon (DOC). The latter is operationally defined as the organic C passing through a filter of 0.45 µm pore size (Moore 1997). In the experiments reported in Chapters 2 and 3, samples were filtered through 8 µm fiberglass slivers as part of the centrifugation. As the samples were small and clear, they were not filtered further prior to total element analysis. In the rainfall simulation experiment in Chapter 6, runoff and leachate experiments were cloudy and were filtered through 0.45 µm pore filters prior to analysis. In this thesis, I have used soluble as a more general term to refer to total element in solution. Dissolved has been used only when the result reported has been obtained from analysis of 0.45 µm pore filtered solutions.

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CHAPTER 2

SHORT-TERM CHANGES IN THE FERTILIZER REACTION ZONE OF UREA GRANULES APPLIED TO TWO AGRICULTURAL SOILS

Introduction

When a fertilizer granule is added to soil a fertilizer reaction zone (FRZ) forms in which solid and solution phase chemistry is dominated by the chemistry of the fertilizer (Hauck 1984). The changes in soil chemistry that define the FRZ can be envisioned as a series of reactions occurring at and behind a diffusion front spreading out from the granule. For urea, the reaction sequence begins when pellets contact soil particles and their solution films. Urea dissolves and diffuses outward from the pellet surface. Water diffuses towards the pellet. The interaction between these three processes determines the concentration of aqueous urea at the pellet surface and thus the magnitude of the gradient driving diffusion. If the dissolution rate exceeds the diffusion rate then a saturated solution will form at the pellet surface. Rachhpal-Singh and Nye (1984) found that a saturated urea solution may be as concentrated as 10 M and that movement of water vapor plays a significant role in dissolution of solid phase urea.

As aqueous urea diffuses into the soil, it makes contact with urease and is hydrolyzed:

$$OC(NH_2)_2 + H_2O \overset{\text{urease}}{\rightleftharpoons} 2NH_3 + CO_2 \qquad \text{Eq. 2.1}$$

Monreal *et al.* (1986) found that urease activity was inhibited at urea concentrations greater than 5 mM in a Gray Luvisolic soil. They also found that when urea was localized in a nest, nitrifying bacteria were killed in the surrounding soil. The inhibition of nitrification may be a result of high osmotic potential and/or fluctuating pH in the soil affected by the fertilizer (Wetselaar *et al.* 1972). Likely urea hydrolysis and nitrification occur at an outward moving diffusion front where urea levels are relatively low.

The NH_3 released during urea hydrolysis reacts with water to form NH_4^+ and OH^-, thereby increasing solution pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{Eq. 2.2}$$

The high pH environment increases the activity of CO_3^{2-}. Kissel *et al.* (1988) found that Ca^{2+} displaced from cation exchange sites by NH_4^+ reacts with HCO_3^- and CO_3^{2-} to form $CaCO_3$. Displacement of Ca^{2+} from exchange sites may also increase precipitation of Ca-P compounds. Transition metals such as Fe, Cu, Mn and Zn would also be expected to precipitate as hydroxide and carbonate minerals (Knezek and Ellis 1980).

Ammonium is converted to NO_2^- and then NO_3^- by ammonium oxidizing and nitrite oxidizing bacteria respectively. Hydronium ion formed during the oxidation reaction neutralizes OH^- generated by NH_3 hydrolysis. Solution pH is reduced. Depending on the magnitude of the pH reduction, solids come into solution. Solids brought into solution by a drop in solution pH may include Ca-P as well as compounds containing Fe, Cu, Mn, and Zn (Faurie and Fardeau 1990, Lindsay 1981, Miller *et al.* 1970.

The long-term effect of urea application is soil acidification. In a well-buffered Black Chernozemic soil, urea broadcast at 336 kg ha^{-1} y^{-1} reduced pH approximately one unit over six years (Goh *et al.* 1987). Urea application also resulted in migration of basic cations down the profile. Similarly in a Brown Chernozem, pH was reduced approximately half a unit in the zone of application after 10 years of banding urea at 180 kg ha^{-1} y^{-1} (Biederbeck *et al.* 1996). Intrawech *et al.* (1982) found that 10 years of urea application had no effect on physical properties but decreased extractable Zn and increased extractable Mn. The above effects arise from reactions occurring within the FRZ. Although they involve the solid phase, the soil solution is the medium through which change takes place. Little is known about the short-term effects adding urea has on the composition of the soil solution and in particular the quantities of elements in solution. In order to characterize the changes in soil solution in the FRZ of urea, an incubation experiment was performed. The objective of the experiment was to measure short-term changes in solution pH; ionic strength, and soluble nutrient elements in the FRZ. The approach was to create a soil environment similar to that found in fertilizer bands by adding granular urea at two rates. Changes in these treatments were compared to soil outside the band represented by controls incubated without urea.

Materials and Methods

Soils and Fertilizers

Bulk surface samples weighing 15-20 kg were collected from two Alberta Agriculture research sites one in central and the other in southern Alberta. These bulk samples were partially dried in the laboratory, large aggregates were broken up by hand and the sample mixed in a large tray. Sub-samples for characterization were taken at this point by collecting and mixing portions from 15 to 20 places in the tray, air drying and grinding to pass 2.0 mm. The processed bulk sample was stored in sealed plastic pails at 3°C until the start of the experiments.

Granular fertilizer grade urea was passed through a 2 mm screen and then a 1.7 mm screen. Prills retained on the 1.7 mm screen were used in the experiment. Sub-samples of the urea were dissolved in deionized water and analyzed over a range of urea concentrations to determine the quantity of contaminant elements in the urea.

Incubation Experiments

The incubation experiment was a 3 X 2 X 5 factorial with three urea treatments, two soils, and five sampling times. Each soil/treatment/time sub-unit was replicated three times in a randomized complete block. In order to match the size of the experiment to the capacity of solution extracting procedures, blocks were run sequentially. The time elapsed between the start of the first block and the completion of the third block was ninety days. The experimental design partitions error arising from changes in the soil during storage or differences in incubation conditions into the block term of the ANOVA.

To prepare each experimental block a representative sub-sample of approximately 2.5 kg of each soil was removed from storage, thoroughly mixed, and placed in sealed 5 L plastic pails. The pails were placed in a closed cabinet at room temperature for three days. Duplicate sub-samples from each soil were dried at 105°C for 24 hours and the soil water content calculated. After three days, the soils were removed from the incubation room. Each experimental sub-unit was set up by weighing the equivalent of 125 g of soil oven dry basis into a plastic tray and adding zero, 1.00 g or 10.00 g of urea. The 1-g and 10-g urea treatments gave mean center to center distances between pellets of approximately 7 and 3.5 mm respectively. Soil and fertilizer were mixed and then deionized water was added as a fine spray to bring the soil water content to 75% of saturation. The soil-fertilizer mixture was transferred to a 250 mL plastic pot, with a diameter of 8 cm. Each pot was placed in a 2 L plastic container. In order to capture volatilized NH_3, a 100 mL beaker containing 10 mL of 6.47 mM boric acid was added to the container. Containers were sealed and incubated in a closed cabinet at 21 ± 3°C.

Three extra control treatments were prepared and extracted the same day. The data from these samples were used to calculate the time zero concentrations of elements in soil solution.

At each sampling time, all containers were opened and the beaker containing boric acid replaced. The removed beakers were covered with parafilm until they could be titrated. One of each soil/fertilizer subunit, six containers in total, was removed from the cabinet for solution extraction and chemical analysis.

Extraction Procedures

In both experiments, soil solution was extracted using the centrifugation procedures described in detail by Thibault and Shepard (1992). Disposable polypropylene syringes (30 mL) were cut off at the 30 mL mark. Fibreglass slivers (8 μm in diameter) were placed in the bottom of the syringe barrel. Soil from the incubation pots (30.00 g wet weight) was weighed into the disposable syringe barrels. Four barrels were prepared from each incubation pot. Each barrel was placed in a 50 mL polycarbonate centrifuge tubes containing a 20 mm high piece of acrylic tubing at the bottom to create a space for displaced soil solution. The soil was centrifuged for 20 minutes at 5000 rpm in a Sorval, RC-5 Superspeed Refrigerated Centrifuge (Dupont Instruments, Newtown, Conneticut).

The extracted soil solution from the four tubes was combined into one sample. Solution samples were stored at 3°C in sealed polypropylene bottles until they could be further analyzed. Storage times ranged from one to four days.

Chemical Analysis

Soil characteristics were determined using standard methods. Soil pH was measured in a 2:1 water to soil suspension using a combined electrode and Fisher Acumet Model 50 pH meter (Fisher Scientific, Nepean, Ontario, Canada). Electrical conductivity (EC) was measured on the same suspension using an electrical conductivity bridge on a Radiometer Model CDM 83 conductivity meter (Bach-Simpson Ltd., London, Ontario, Canada). Soil organic matter (SOM) was determined by loss on ignition at 1100°C. Clay content was determined by the hydrometer method with pre-treatment to remove SOM as described by Sheldrick and Wang (1993). Saturated water content was estimated from bulk density measurements of the ground soil. Trace metals were extracted by the DTPA method as described by Liang and Karamanos (1993). Extracts were analyzed using the ICP described below for soil solution analysis. Exchangeable cations and cation exchange capacity (CEC) were determined using the ammonium acetate method described by Hendershot *et al.* (1993). In the analytical step, ICP was used to measure Ca, Mg, K, and Na for exchangeable cations and NH_4^+ concentration was measured by autoanalyzer (Technicon Instrument Corporation 1973).

The boric acid solution from each incubation container was titrated to a pH endpoint of 5.8 with 5.00 mM H_2SO_4. Solution pH and EC were measured on the day of extraction using the equipment described for soil analysis. Ionic strengths were calculated from electrical conductivity data using the equations of Griffin and Jurinak (1973).

$$I = 0.013\text{EC} \qquad \text{Eq. 2.3}$$

Where I is ionic strength in mol L^{-1} and EC is given in dS m^{-1}.

Total elements in the soil solution were measured using a Jobin-Yvon model JY70PLUS Inductively Coupled Plasma Spectrophotometer (ATS Scientific Ltd., Oakville, Ontario, Canada). Operating limits of detection (LOD) and limits of quantitation (LOQ) were determined for each element using the method of Keith *et al.* (1983). The instrument was calibrated before each run using Seignory Chemical Product certified standards (SCP Scientific Ltd., St. Laurent, Quebec, Canada) diluted to appropriate ranges for each element. Analytical values less than the LOD were recorded as below detection limit (BDL), and were treated as zero values in the statistical analysis.

Ammonium in soil solution was measured on a Technicon II Autoanalyzer (Technicon Instrument Corporation, Tarrytown, New York, USA) using the indophenol blue procedure (Technicon Instrument Corporation, 1973).

Anions (NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}) in soil solution were measured using a Dionex Ion Chromatograph (IC) equipped with a conductivity detector (Dionex Corporation, Sunnyvale, California, USA). Prior to IC analysis, samples were filtered to remove organic molecules from solution using a SEP-PAC® C18 cartridge filter (Waters Corporation, Milford, Massachusetts, USA).

Statistical Analysis

Analysis of variance was performed using SAS-PC. A separate ANOVA was performed for each analyte following the model below:

ANOVA Eq. 2.4

Source	n	df
(R) Blocks	3	2 (r-1)
(A)Treatments	3	2 (a-1)
(B) Soils	2	1 (b-1)
(C) Time	5	4 (c-1)
(AB)Treatments X Soils		2 (a-1)(b-1)
(AC)Treatment X Time		8 (a-1)(b-1)
(BC) Soils X Time		4 (b-1)(c-1)
(ABC)Treatment X Soils X Time		8 (a-1)(b-1)(c-1)
Error		58 (r-1)(abc-1)
Total	90	89 (rabc-1)

The ANOVA was performed on each data set for days 4 through 20. The time zero values were not included in the ANOVA as the data were collected from control samples only. The time zero data are included in figures to provide a reference point for variables prior to urea addition. Effects were taken as significant if the probability of obtaining F by chance was less than 1% ($p<0.01$). Significant differences among main effect means were determined using Tukey's studentized range test in cases where interaction terms were not significant. Tukey's studentized range test controls Type I error but tends to increase the Type II error rate. When combined with $p < 0.01$, the determination of significant differences among means is conservative. Interactions were significant for a number of analytes. In these cases, contrasts of interest suggested by the data were made following the procedures outlined by Steel *et al.* (1997, Chapter 15).

Results

Soil and Fertilizer

Soil 1 contains more soil organic matter (SOM) than Soil 2, but they are similar in clay content (Table 2.1). They are similar in pH but differ in EC. As EC is linearly related to salt content, Soil 2 contains approximately five times the soluble salt content of Soil 1. Soil 1 has a higher CEC, which is consistent with its higher SOM content. The cation exchange complex is strongly base saturated in both soils and dominated by exchangeable Ca. However, Soil 2 contains proportionally more exchangeable Mg than Soil 1. Soil 1 has a higher saturated water content, which is consistent with higher SOM.

Analysis of contaminant elements in urea showed that the elements, Ca, K, Al, Fe and Mn were not present in the urea in detectable amounts (Table 2.1). Phosphorus at 1.16 mmol kg^{-1} was the most abundant contaminant in urea. Magnesium, Na, P, Cu, and Zn were also present in detectable quantities.

Statistical Analysis

Contrasts of soils within treatments and treatments within soils were performed for cases where the soil*treatment term was significant (Tables 2.2, 2.3). These contrasts are for data pooled across all sampling times. Probabilities of F for the treatment contrasts within soils are presented with the main ANOVA's. Data for soil comparisons within treatments are not shown in tabular form but are reported qualitatively within the appropriate section of the text.

Solution pH and Ionic Strength

Solution pH in the urea treatments rose during the first four days and then remained relatively constant near 9 for the remainder of the experiment (Figure 2.1a,b). By Day 20, the solution pH in the control soils had declined to 5.1 and 5.7 for Soil 1 and Soil 2 respectively. All main effects and interactions were statistically significant for solution pH except for the experimental block term (Table 2.2). Within Soil 1, differences among treatments were significant at the $p<0.01$ level. The urea treatments were different from the control but not from each other in Soil 2.

Ionic strength was elevated in response to urea treatments in both soils (Figure 2.1c,d). Only the treatment and soil*treatment interaction effects were significant (Table 2.2). Comparisons across soils within treatments showed that only the 10-g treatment was significantly different between soils. Within soils, all three treatments were statistically different.

Nitrogen

Ammonia volatilization initially increased in the two urea treatments compared to the control and then declined (Figure 2.2a,b). All effects were significant with respect to NH_3 volatilized except for the soil*time interaction (Table 2.2). Ammonia volatilized from the 10-g treatment was significantly greater than from the 1-g treatment in Soil 1 but the difference was not significant in Soil 2.

Solution NH_4^+ concentrations initially rose and then leveled off and remained relatively constant. (Figure 2.3a,b). Time and the time interaction effects were not significant for solution NH_4^+ (Table 2.2). The 1-g treatments behaved the same in the two soils, whereas the 10-g treatment behaved differently. Within soils, the 1-g and 10-g treatments were significantly different from each other and the control.

Solution NO_3^- declined over the first four days in the controls then remained relatively constant through to Day 20 (Figure 2.3c,d). Soil, treatment and soil*treatment interaction terms were significant. Between soils, F was significant for the 1-g and 10-g treatments. Solution NO_3^- was higher in Soil 2 for both treatments. Within Soil 1, the 10-g treatment was significantly different from the control, but not the 1-g treatment. All treatments were different from each other within Soil 2.

Additions of urea increased NO_2^- levels relative to the controls (Figure 2.3e,f). Only the treatment effect was significant. Separation of the treatment means – 0 (BDL), 0.43, and 0.25 mmol L^{-1} respectively for the control, 1-g and 10-g treatments – using Tukey's Studentized Range Test showed that the two urea treatments were different from the controls but not from each other.

Phosphorus and Sulphur

Phosphate concentrations in soil solution were variable. For most samples, no PO_4^{3-} peak was detectable. Three samples were obviously contaminated with PO_4^{3-}. This contamination had not been evident in earlier analysis of total P in the same solutions. All ion chromatography data from these samples were rejected. The PO_4^{3-} data were not pursued further.

Total P concentrations in solution tended to increase as the incubation progressed (Figure 2.4a,b). Increases were greatest during the first eight days of incubation in the urea treatments. In the controls, total P concentrations rose consistently throughout the incubation. Soil*treatment and soil*time interactions were significant (Table 2.2). Contrast of treatments within soil showed that all differences among treatments were significant within Soil 1. Treatment ranking of total P in solution was 10-g > 1-g > control. Only the 10-g > control difference was significant in Soil 2.

Total S in soils solution gradually increased during the incubation in the urea treatments in Soil 1 (Figure 2.4c). Total S in Soil 2 stayed constant in all treatments from Day 4 to Day 20 (Figure 2.4d). Contrasts showed significant differences in total S in soil solution among all three treatments in Soil 1 (Table 2.2). Within Soil 2, the 10-g treatment differed from the control but the 1-g did not.

Sulphate-S concentration in the 10-g urea treatment of Soil 1 increased between T_0 and Day 12 (Figure 2.4e). In Soil 2, the SO_4^{2-}-S concentrations were relatively constant between Day 4 and Day 20 (Figure 2.4e). Sulphate-S was markedly less than total-S in Soil 1, but was similar to total S in Soil 2. Sulphate-S levels differed significantly with treatment and with soil, but interactions were not significant. Separation of treatment means showed that SO_4^{2-}-S was significantly higher in the 10-g than in the control and 1-g treatment but the latter were not different from each other.

Total Calcium, Magnesium, Potassium and Sodium in Solution

Solution Ca concentrations tended to be lower in the urea treatments than in the control in both soils from Day 8 onward in Soil 1 and Day 4 onward in Soil 2 (Figure 2.5a,b). All terms of the ANOVA were significant except for the block effect and the soil*time interaction (Table 2.3). Treatment contrasts across soils showed that soluble Ca in controls and 10-g urea treatments differed between soils. In the comparison of 1-g treatments, F was not significant suggesting that solution Ca responded similarly to the 1-g urea treatment in both soils. When treatments were compared within Soil 1, solution Ca in the 1-g urea treatment was significantly less than in the control and in the 10-g treatment. Solution Ca concentrations in the two urea treatments were not significantly different in Soil 2, but both were significantly lower the control.

Trends in solution Mg concentration appeared similar to those for Ca particularly for Soil 2 (Figure 2.5c,d). In Soil 1, contrast of treatment within soil shows that the 1-g urea treatment was less than the control (Table 2.3). The 10-g urea treatment was not different from the control. Concentrations were significantly different among all treatments in Soil 2.

There were no significant main effects or interaction terms generated within the ANOVA for Na concentration in soil solution (Table 2.3). The mean Na concentrations across times and treatments were 3.0 mmol L^{-1} in Soil1 and 3.9 mmol L^{-1} in Soil 2.

Unlike Ca and Mg concentrations, solution K was elevated in the urea treatments compared to the controls (Figure 2.5e,f). In Soil 1, K concentrations in the 10-g urea treatment exceeded that in the 1-g urea treatment. The opposite trend occurred in Soil 2. The soil and treatment main effects were significant in the K concentration ANOVA (Table 2.3). However the soil*treatment interaction was also significant and treatment and soil differences had to be explored within the context of the interaction. Within treatments between soils, the controls were not significantly different, nor were the 1-g treatments. Solution concentration of K in the 10-g treatments was higher in Soil 1. Within each soil, all three treatments were different from each other.

Total Aluminum, Iron, Copper, Manganese and Zinc in Soil Solution

The effects of urea on total Al in soil solution differed between the two soils (Figure 2.6a,b). Soluble Al in soil 1 increased two orders of magnitude when urea was added to the soil and concentrations were maintained over the 20 days of the experiment. Aluminum concentration in Soil 2 varied inconsistently from time to time. In the Al ANOVA, the soil*treatment and treatment*time interactions were significant (Table 2.3). When F values were calculated within treatments, the control was not significantly different in the two soils. Both the urea treatments were significantly greater in Soil 1 than their counterpart in Soil 2. Within Soil 1, all treatments were different from each other. In Soil 2, none of the treatments were statistically different.

Trends for soluble Fe were similar to those for Al (Figure 2.6c,d). Soil 1 released considerably more Fe into the soil solution when urea was added than did Soil 2. All terms of the main ANOVA were significant. Comparisons within treatments showed that the controls were not significantly different between the two soils. Soluble Fe concentrations in the urea treatments of Soil 1 were both significantly higher than their counterparts in Soil 2. Within soils, Fe concentration differed significantly among all treatments in Soil 1. There were no significant treatment differences in Soil 2.

Solution Cu response to urea additions was generally similar to Al and Fe in Soil 1 but differed in Soil 2 (Figure 2.6e.f). All main and interaction effects were significant when the Cu concentration data were subjected to ANOVA (Table 2.3). Contrasts within treatments showed that differences between soils were significant for the urea treatments, but not the controls. Within soils, F was significant for all comparisons among treatments in Soil1. In Soil 2, Cu concentrations in the control were not significantly different from the 1-g urea treatment, but concentrations in the 10-g urea treatment were significantly greater than the control and 1-g treatment.

Trends in solution Mn were dissimilar from those of the other transition metals and Al (Figure 2.7a,b). All the main effects were significant in the ANOVA. Of the interaction terms, only soil*treatment was significant. Within treatments, all contrasts were significant. Solution manganese concentrations in the control treatments were lower in Soil 1 than in Soil 2. For the urea treatments, Mn concentrations were higher in Soil 1 than in Soil 2. Within Soil 1, the control and 1-g treatments were not different, but soluble Mn in the 10-g treatment was significantly higher than both. The concentrations in the control were significantly higher than both other treatments in Soil 2.

Trends in solution Zn levels were similar to Al, Fe, and Cu in that the effects of urea were more pronounced in Soil 1 than in Soil 2 (Figure 2.7c,d). Within treatments, the controls were the same in both soils while the 1-g and 10-g treatments behaved differently between soils. Within Soil 1, Zn concentrations in the 10-g treatment were significantly greater than both the control and the 1-g treatments. F values calculated for treatment comparisons were not significant in Soil 2.

Discussion

The original hypothesis for this experiment was that the initial increase in pH brought about by urea hydrolysis would reduce the concentration of alkaline earth and transition metals in the soil solution as well as non-metals such as P. This would be followed by a rise in concentration as NH_4^+ was converted to NO_3^- and the pH of the soil solution declined. Several lines of evidence show that urea hydrolysis has occurred. The increased pH in urea treatments compared to the controls (Figure 2.1a,b), the volatilization of NH_3 (Figure 2.2), and the accumulations of NH_4^+ in soil solution (Figure 2.3a,b) are all indicators of urea hydrolysis.

The data are more difficult to interpret with respect to nitrification. Based on the pH data, nitrification has not proceeded to the point where solution pH has started to decline in either soil. Nitrification would have to produce sufficient acid to neutralize the $CaCO_3$

formed during hydrolysis before pH declined. Wetselaar *et al.* (1972) found that nitrification was inhibited in ammonium based fertilizer bands. This would suggest that in soils in the field, nitrification would likely start on the edge of the FRZ and proceed inwards. Events that perturb the FRZ – rainfall, root growth, tillage – would accelerate nitrification. In the system set up for this experiment, the entire soil volume is likely FRZ and based on the pH data not conducive to nitrification.

The NO_2^- data suggest that ammonium oxidation was occurring at least initially. Nitrite was not detectable in solution samples from the control treatments but was in the urea treatments (Figure 2.3e,f). Generally, NO_2^- does not accumulate in soil. However, ammonium oxidizing bacteria tend to be more tolerant of alkaline pH than do nitrite oxidizing bacteria (Alexander, 1981). It is consistent with this pH sensitivity of ammonium oxidizing versus nitrifying bacteria that some NO_2^- should accumulate as the pH increases in the urea treatment.

The NO_3^- pool was apparently active, in the sense that reactions consuming NO_3^- were taking place, in the controls during the first four days of the experiment (Figure 2.3c,d). This activity could be attributed to either denitrification (water was added to the soils at time zero) or immobilization. In the urea treatments, net changes in the NO_3^- pool were small from Day 4 to Day 20. Overall, the nitrogen data support the idea that biologically mediated reactions were not occurring in the urea treated soils after Day 4.

Raising pH tends to precipitate metals in soil solution. The formation and dissolution of metal precipitates takes the general form:

$$aM^{z+}_{(aq)} + bL^{y-}_{(aq)} \rightleftarrows M_aL_{b(s)} \qquad \text{Eq. 2.5}$$

where M^{z+} is the metal and L^{y-} the ligand. The dissolution reaction is described by the solubility product (K_{sp}), where the quantities for M and L are activities rather than concentrations:

$$K_{sp} = (M^{z+})^a (L^{y-})^b \qquad \text{Eq. 2.6}$$

Substituting OH^- for L^-, increasing pH reduces the ion activity of metals forming relatively insoluble hydroxides. Similarly, increased (CO_2^{2-}) would tend to reduce the activity, and concentration, of metals forming low solubility carbonate salts.

Basic cations displaced from exchange sites, as NH_4^+ concentration increased in the experimental system, would first enter the soil solution. Whether they remained in solution, and were detectable as an increase in solution concentration, or precipitated out depended largely on the solubility of their hydroxide and carbonate salts. The hydroxides of alkali and alkaline earth metals are highly soluble. Potassium and Na also form highly soluble carbonate salts. Total K concentrations increased in the urea treatments compared to the control (Figure 2.5). In both soils, Ca and Mg levels in the urea treatments tended to be equal to or less than those in the controls. Kissel *et al.* (1988) found that Ca^{2+} displaced by NH_4^+ following addition of urea to two Kansas soils was precipitated as $CaCO_3$. They suggested urea hydrolysis provided the CO_3^{2-}. The Ca and Mg concentrations in the urea treatments relative to the controls suggest that both elements were precipitating out of solution (Figure 2.5).

The data show that total concentrations of Al plus the transition metals Fe, Cu, Zn, and Mn increased over time in response to urea additions in Soil 1 (Figures 2.6,2.7). In Soil 2, the response to added urea was less consistent. Only Cu levels increased. Total Al, Fe and Zn concentrations were not statistically different from concentrations in the controls. Solution Mn levels remained unchanged in the urea treatments but were considerably below those in the control.

One potential source of metals is contaminants in the urea. The level of contamination was calculated for the 10-g urea treatment as if the entire amount of contaminant were dissolved in the soil solution at 75% saturation (Table 2.1). The contaminant levels calculated were generally one to two orders of magnitude less than the concentrations actually measured in solutions from the the urea treatments. Contaminants in the urea were not a major factor affecting the results.

As solution pH increases in soil, activity of the ions Fe^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} decreases exponentially (Lindsay, 1981). Total metal concentrations in solutions extracted from the urea treatments were one to three orders of magnitude higher than concentrations in the controls. Several mechanisms could have increased total metal concentrations in soil solution within the FRZ. These include increased ionic strength; complex formation with added inorganic ligands, and addition of organically complexed metals.

Ionic strength (I) is the sum of concentration (c) times valence (z) as follows:

$$I = \tfrac{1}{2} \Sigma c_i z_i^2 \qquad \text{Eq. 2.7}$$

In this experiment, I was estimated from EC values using Eq. 2.3. The effect of changing ionic strength on ion activity can be estimated by first using the extended Debye-Huckel equation (Eq. 2.9) to estimate the activity coefficient (γ):

$$\log \gamma_i = -0.5091 z_i^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \qquad \text{Eq. 2.8}$$

Where B has a value of 0.33 and a is the approximate size of the hydrated ion. The value of γ can be used with c to calculate activity (a):

$$a = \gamma c \qquad \text{Eq. 2.9}$$

From the above, activity becomes a smaller proportion of concentration as ionic strength increases. For a metal ion in equilibrium with a solid mineral or complexed organic phase, an increase in ionic strength by addition of an electrolyte would initially decrease the metal ion activity. The return to equilibrium activity through dissolution or desorption of the metal from the solid phase would increase metal ion concentration. Activity coefficients were estimated for Fe^{3+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} in the controls and urea treatments. For Soil 1, γ was reduced by 26 to 41% by the increase in ionic strength induced by urea addition. In Soil 2, the reduction in γ was 10 to 25% in the urea treatments compared to the controls. This would suggest that the ionic strengths measured in the urea treatment would support ion concentrations from 1.2 to 2 times higher than in the controls depending on the particular urea treatment and valence of the metal. At least it would if the increase in ionic strength was due to the addition of a neutral salt as an electrolyte. In Soil 1, the change in ionic strength in the 10-g treatment was accompanied by a change in solution pH from 7.8 to 8.9. The effect of pH on activity of a transition metal cation in equilibrium with a solid hydroxide form $M(OH)_z$ is

$$K_{sp} = (M^{z+})(OH^-)^z \qquad \text{Eq. 2.10}$$

The decrease in (M^{z+}) at equilibrium would be approximately two orders of magnitude for a bivalent metal cation and three orders for a trivalent metal cation when the pH changed from 7.8 to 8.9. Increasing pH has a similar effect on metal ion complexation with organic acids and soil humates, shifting the reaction toward the complexed form and away from the free metal ion (Stevenson 1991). The role of increased ionic strength is negligible in the context of the observed pH changes and the actual magnitude of the increases in metal concentrations.

The idea that complex formation is bringing the transition metals into solution has to be explored in the context of ligand additions to the soil solution. Hydrolysis of urea increases the activity of OH^- and CO_3^{2-}, which can form complexes with metal ions.

$$Cu^{2+}_{aq} + 2OH^-_{aq} \rightleftharpoons Cu(OH)_2{}^\circ_{aq} \qquad \text{Eq. 2.11}$$

$$Cu^{2+}_{aq} + CO_3{}^{2-}_{aq} \rightleftharpoons CuCO_3{}^\circ_{aq} \qquad \text{Eq. 2.12}$$

Using Cu^{2+} as an example,

The activity of $Cu(OH)_2{}^\circ$ is maintained at about 10^{-5} µmol L^{-1} at pH's 7 through 9 (Lindsay 1981, Norvell and Lindsay 1969). The activity of $CuCO_3{}^\circ$ is similar in soil solution, but is responsive to changing pCO_2. Data compiled by Lindsay (1991) suggest that even at 1000 times atmospheric pCO_2, $CuCO_3{}^\circ$ would only reach 10^{-2} µmol L^{-1}, four orders of magnitude below values observed in the urea treatments. Similar arguments can be made for Zn and Mn; however, Fe and Al can speciate at pH above 7 to form $Fe(OH)_4^-$ and $Al(OH)_4^-$. Calculations by Lindsay (1991) suggest that for $Fe(OH)_4^-$ in equilibrium with a solid phase at pH 9 –the solution pH for the 10-g treatment in Soil 1 where soluble Fe concentrations were largest– activity would be approximately 10^{-9}. This corresponds to an $Fe(OH)_4^-$ concentration of approximately 0.002 µmol L^{-1} at the ionic strengths measured in the 10-g treatment of Soil 1. Similar estimates based on McBride (1994, Chapter 5) give approximate $Al(OH)_4^-$ concentrations of 6 µmol L^{-1}. Comparing these approximations to measured soluble Al and Fe suggests that formation of hydroxy anions may have played a significant role in increasing soluble Al, but not Fe, in urea treatments. A third inorganic ligand that increases as a result of urea hydrolysis is NH_3. Ammonia complexes with Cu^{2+} and Zn^{2+} to form highly stable complex ions such as,

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \qquad K_f = 1.1 \times 10^{13} \qquad \text{Eq. 2.13}$$

$$Zn^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Zn(NH_3)_4]^{2+}_{(aq)} \qquad K_f = 7.8 \times 10^{8} \qquad \text{Eq. 2.14}$$

The formation of these complexes can increase the total concentration of a metal in soil solution even in cases where a solid of low solubility or a complex of low dissociation controls the activity of the metal ion. For example, using a soil solution in equilibrium with Cu $(OH)_2$, Eq. 2.13 could be combined with Eq. 2.15 to give Eq. 2.16.

$$Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad K_{sp} = 4.8 \times 10^{-20} \qquad \text{Eq. 2.15}$$

$$Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4{}^{2+}{}_{(aq)} + 2OH^-_{(aq)} \qquad K_c = 5.3 \times 10^{-7} \qquad \text{Eq.. 2.16}$$

K_c, the product of K_{sp} and K_f, relates to the ion activities in Eq. 2.16 as follows:

$$Kc = \frac{(Cu(NH_3)_4{}^{2+})(OH^-)^2}{(NH_3)^4} \qquad \text{Eq. 2.17}$$

After rearrangement the equation can be solved for $([Cu(NH_3)_4]^{2+})$ if (NH_3) and (OH^-) are known.

This was done after using the Ka value associated with Eq. 2.18, average pH for Days 4 to 20, and average $[NH_4^+]$ to estimate (NH_3) using Eq. 2.19.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H^+ \qquad K_a = 5.7 \times 10^{-10} \qquad \text{Eq.. 2.18}$$

$$(NH_3) = \frac{K_a[NH_4]\gamma}{10^{-pH}} \qquad \text{Eq. 2.19}$$

The estimates of equilibrium $(Cu(NH_3)_4{}^{2+})$, under the average conditions of the various treatments, were then converted to concentration using γ calculated using Eq. 2.9. The same approach was used for Zn.

Estimates of $Cu(NH_3)_4{}^{2+}$ and $Zn(NH_3)_4{}^{2+}$ concentrations are shown for soil solution in equilibrium with the metal hydroxide (Table 2.4). Both $Cu(OH)_2$ and $Zn(OH)_2$ are too soluble to persist in soil (Lindsay 1981). Norvell and Lindsay (1969,1972) estimated K° for a Soil-Cu and Soil-Zn solid phase in equilibrium with Cu^{2+} and Zn^{2+} in soil solution. When their K° values are used in the calculation of metal-ammonia ion activity, the concentration of metal that would be supported in solution declines 3 to 7 orders of magnitude compared to $Cu(OH)_2$ or $Zn(OH)_2$. Based on these calculations, speciation with NH_3 in the FRZ could significantly enhance soluble Cu and Zn concentrations in soils containing solid phases 1 to 3 orders of magnitude more soluble than the Soil-Cu or

Soil-Zn reported by Norvell and Lindsay (1969,1972). Results by Ma and Lindsay (1990) show a range of Zn activities approaching two orders of magnitude in soils equilibrated at the same pH. Certainly in soils where Cu or Zn fertilizer and urea were added together speciation with NH_3 could maintain significant amounts of the metal in soluble form.

The formation of complex ions would not account for increases in all transition metals. Iron, for example, does not speciate strongly with NH_3. Nor could it account for the increased concentrations of non-metals such as P and S. It therefore seems likely that some other mechanism was also increasing concentrations of solution elements in the urea treatments. Several authors have shown that anhydrous ammonia solubilizes SOM (Nemec and Vopenka 1971, Norman *et al.* 1987, Tomasiewicz and Henry 1985). Both urea and anhydrous ammonia initially increase pH and disperse soil colloids. Since, the stability of metal-organo complexes generally increases with pH (Stevenson 1991), any increase in total solution metals brought about by SOM dissolution would have been due to increases in complexed rather than free ion forms. In short, SOM shifted from the solid to the solution phase and brought attached metals with them. A similar case could be made for non-metals such as P and S, SOM came into solution bringing adsorbed and/or ester bonded P and ester or carbon bonded S with it.

Conclusions

Soil solution concentrations of metal and non-metal elements increased in the FRZ of urea. There were sufficient differences between the two soils to suggest that reactions within the FRZ may differ substantially among soil types. Increased ionic strength following urea hydrolysis could not account for the increases in concentrations. Speciation with NH_3 was thermodynamically predicted for some metals, such as Cu and Zn but could not account for increases in all elements. Further research will be required to elucidate the role of soluble SOM in the FRZ. Other questions of interest arising from this research include the plant availability and uptake of elements brought into soil solution within the FRZ and the mobility of these elements in the soil profile.

Table 2.1. Soil and fertilizer analysis for incubation experiment plus detection limits for ICP analysis of total element concentration.

Soil Analysis

Soil No.	Class	Soil Organic Matter	Clay	Saturated water Content	pH	EC	CEC (+)	Exchangeable Cations			
								Ca	Mg	Na	K
			kg kg^{-1}			*dS m^{-1}*			*mmol kg^{-1}*		
Soil 1	Dark Gray Luvisol	0.070	0.31	0.50	5.9	0.30	185	74	11	0.02	5.2
Soil 2	Orthic Brown Chernozem	0.028	0.31	0.42	6.2	1.5	152	42	18	0.6	5.6

Urea Analysis

	Ca	Mg	K	Na	P	S	Al	Fe	Cu	Mn	Zn
			mmol kg^{-1}						*µmol kg^{-1}*		
Urea[x]	BDL	0.014	BDL	0.067	1.16	0.56	BDL	BDL	17	BDL	5
			mmol L^{-1}						*µmol L^{-1}*		
Soil 1[y]	–	–	–	0.014	0.25	0.12	–	–	3.6	–	1.1
Soil 2	–	–	–	0.020	0.35	0.17	–	–	5.0	–	1.5

Detection Limits ICP[z]

	Ca	Mg	K	Na	P	S	Al	Fe	Cu	Mn	Zn
	0.005	0.004	0.01	0.01	0.002	0.003	0.001	0.1	0.05	0.02	0.1

[x] Values reported mean of three replicates.

[y] Amount of contaminant element added to soil solution in 10-g urea treatment if all contaminant element dissolved.

[z] Detection Limits for ICP analysis determined following Keith et al. 1982.

Table 2.2. Analysis of variance for NH_3 volatilized and various solution analytes.

Source	NH_3	pH	EC	NH_4^+	NO_3^-	NO_2^-	Total P	SO_4^{2-}	Total S
					P[x]				
Block	ns[y]	ns	ns	0.0001	0.0001	ns	0.0001	0.0003	ns
Soil	*0.0001*	*0.006*	*ns*	0.0001	0.0001	ns	0.0001	0.002	0.0001
Treatment	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Time	0.0001	0.0001	ns	ns	ns	ns	0.0001	ns	0.0001
Soil*Treat	0.0001	0.0001	0.0001	0.0001	0.0001	ns	0.0001	ns	0.0001
Soil*Time	ns	0.006	ns	ns	ns	ns	0.0003	ns	ns
Treat*Time	0.0001	0.0001	ns	ns	ns	ns	ns	ns	ns
Soil*Treat*Time	0.0005	0.004	ns	0.007	ns	ns	ns	ns	ns
					Treatment contrasts within Soil 1				
Control – 1-g urea	**	**	**	**	ns	–	**	–	**
Control – 10-g urea	**	**	**	**	**	–	**	–	**
1-g urea – 10-g urea	**	**	**	**	ns	–	**	–	**
					Treatment contrasts within Soil 2				
Control – 1-g urea	**	**	**	**	**	–	ns	–	ns
Control – 10-g urea	**	**	**	**	**	–	**	–	**
1-g urea – 10-g urea	ns	ns	**	**	**	–	ns	–	**

[x] Probability of obtaining F by chance in ANOVA analysis. Values greater than 0.01 are reported as non-significant (ns).

** F calculated for contrast was highly significant (p = 0.01).

Table 2.3. Analysis of variance for various metals and Al in soil solution.

Source	Ca	Mg	Na	K	Al	Fe	Cu	Mn	Zn
					P[x]				
Block	ns	0.007	ns	0.0004	ns	0.003	0.0003	ns	ns
Soil	0.001	0.0001	ns	0.0001	0.0001	0.0001	0.0001	0.002	0.0001
Treatment	0.0001	0.0001	ns	0.0001	0.0001	0.0001	0.0001	0.009	0.0001
Time	0.0001	0.0003	ns	ns	0.002	0.0001	0.0001	0.002	0.0001
Soil*Treatment	0.0001	0.0001	ns	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Soil*Time	ns	ns	ns	ns	ns	0.0001	0.0001	ns	0.0005
Treat*Time	0.0001	0.0004	ns	ns	0.008	0.0003	0.0006	ns	ns
Soil*Treatment*Time	0.0007	ns	ns	ns	ns	0.0002	0.004	ns	ns
					Treatment contrasts within Soil 1				
Control – 1-g urea	**	**	–	**	**	**	**	ns	ns
Control – 10-g urea	ns	ns	–	**	**	**	**	**	**
1-g urea – 10-g urea	**	**	–	**	**	**	**	**	ns
					Treatment contrasts within Soil 2				
Control – 1-g urea	**	**	–	**	ns	ns	ns	**	ns
Control – 10-g urea	**	**	–	**	ns	ns	**	**	ns
1-g urea – 10-g urea	ns	**	–	**	ns	ns	**	ns	ns

[x] Probability of obtaining F by chance in ANOVA analysis. Values greater than 0.01 are reported as non-significant (ns).

** F calculated for contrast was highly significant (p = 0.01).

Table 2.4. Calculated equilibrium concentration of complex Cu and Zn ions in soil solution compared to measured total concentrations averaged Day 4 to Day 20.

	Solution Species	Equilibrium Solid	Treatment		
			Control	1-g	10-g
				μmol L^{-1}	
Soil 1	$Cu(NH_3)_4^{2+}$	$Cu(OH)_2$	$8 X 10^{-11}$	$7 X 10^{3}$	$1.7 X 10^{6}$
	$Cu(NH_3)_4^{2+}$	Soil-Cu[x]	$1 X 10^{-16}$	$1 X 10^{-4}$	2.2
	Total Cu[y]		<0.05[z]	10	40
	$Zn(NH_3)_4^{2+}$	$Zn(OH)_2$	$4 X 10^{-11}$	$3 X 10^{3}$	$7 X 10^{5}$
	$Zn(NH_3)_4^{2+}$	Soil-Zn	$1 X 10^{-20}$	$9 X 10^{-5}$	0.02
	Total Zn		6	9	30
Soil 2	$Cu(NH_3)_4^{2+}$	$Cu(OH)_2$	$4 X 10^{-6}$	$8 X 10^{3}$	$4 X 10^{4}$
	$Cu(NH_3)_4^{2+}$	Soil-Cu	$5 X 10^{-12}$	0.01	0.05
	Total Cu		<0.05[z]	2	10
	$Zn(NH_3)_4^{2+}$	$Zn(OH)_2$	$2 X 10^{-6}$	$4 X 10^{3}$	$2 X 10^{4}$
	$Zn(NH_3)_4^{2+}$	Soil-Zn	$5 X 10^{-14}$	$1 X 10^{-4}$	$5 X 10^{-4}$
	Total Zn		4	3	3

[x] Soil-Cu and Soil-Zn as described by Norvell and Lindsay (1969, 1972).

[y] Total Cu measured in soil solution averaged Day 4 to Day 20.

[z] Value was below detection limit for Cu by ICP.

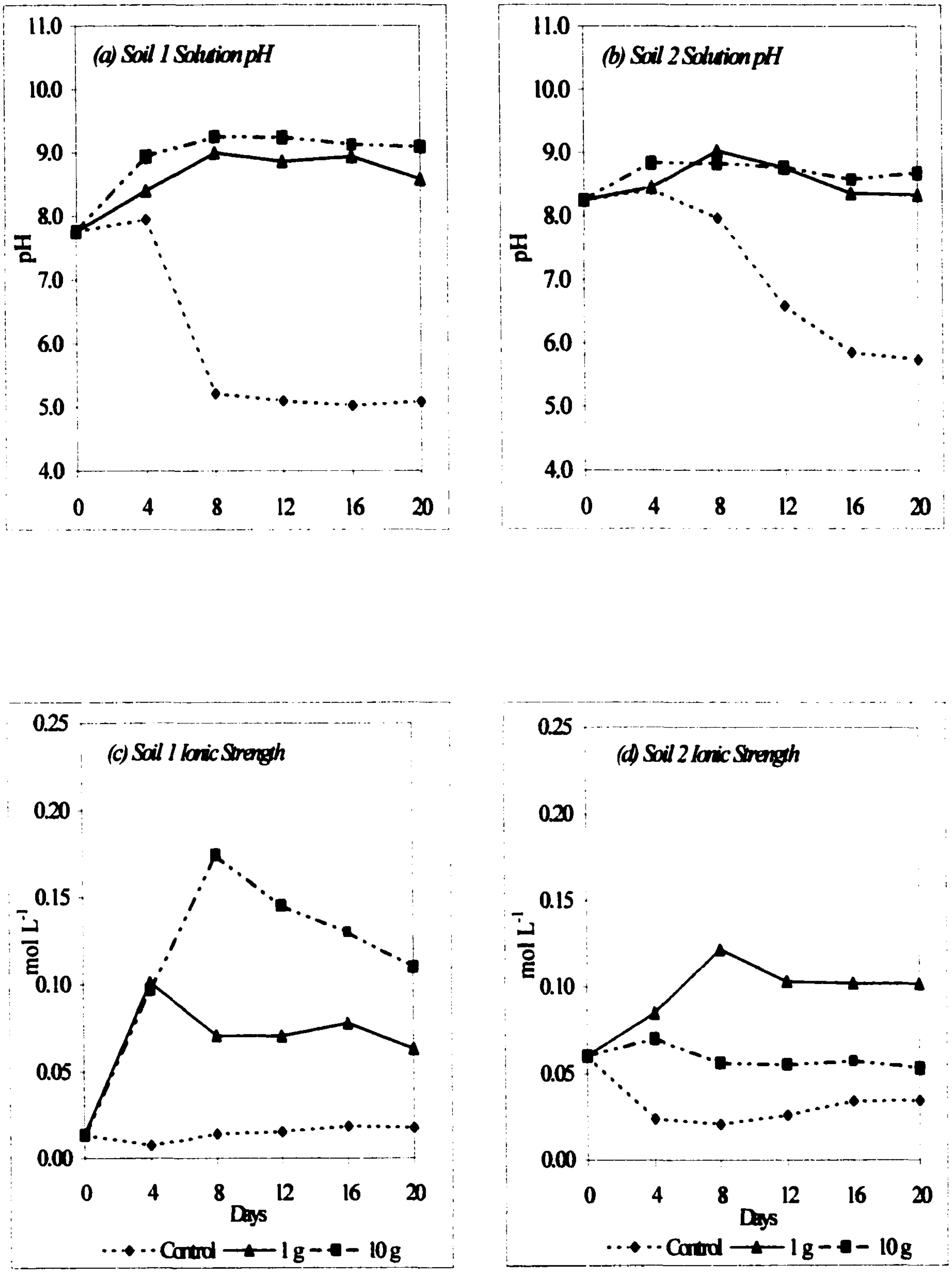

Figure 2.1. Soil solution pH and ionic strength following addition of urea to two soils.

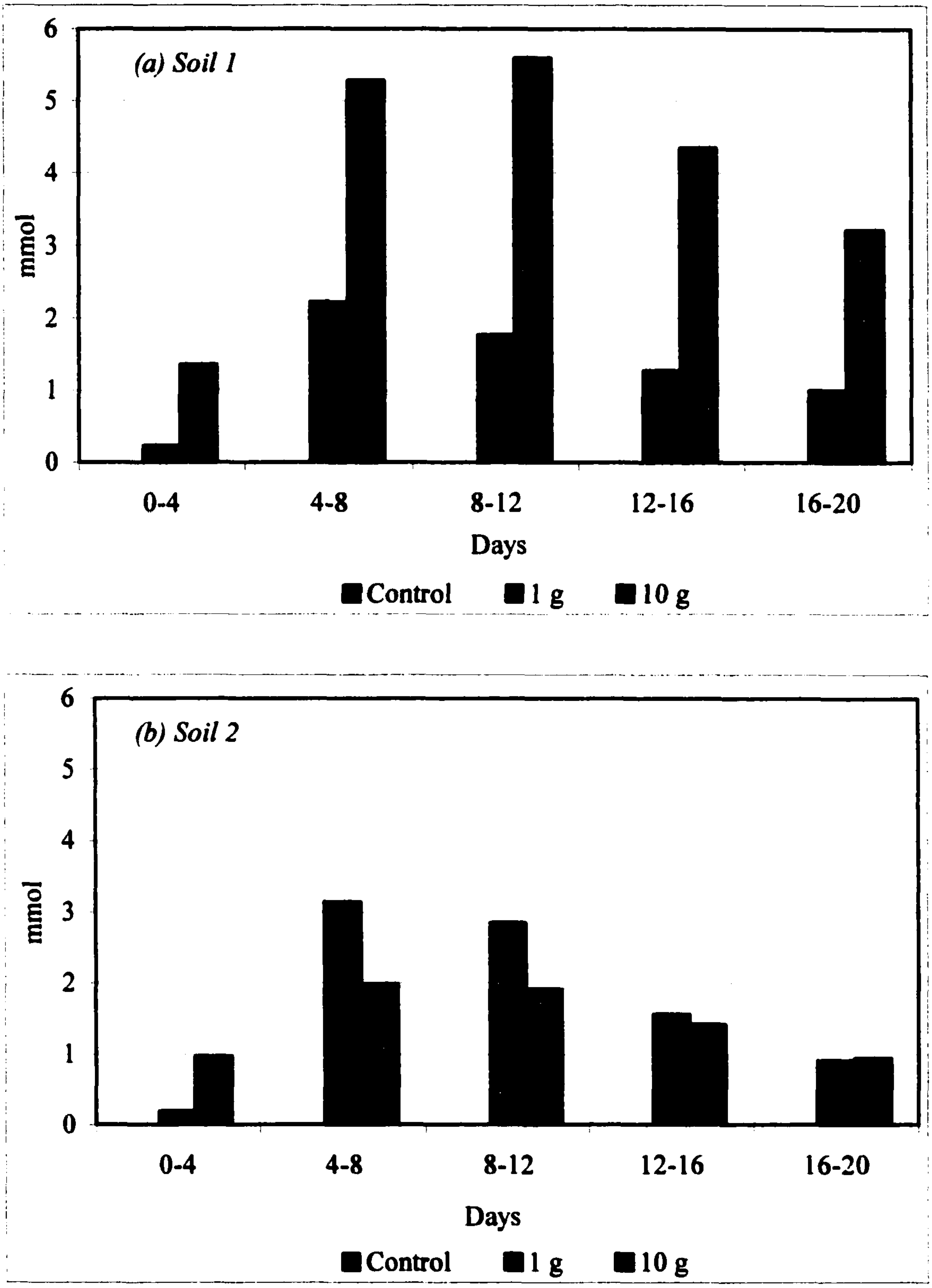

Figure 2.2. Ammonia volatilization from two soils during successive four day periods following urea addition.

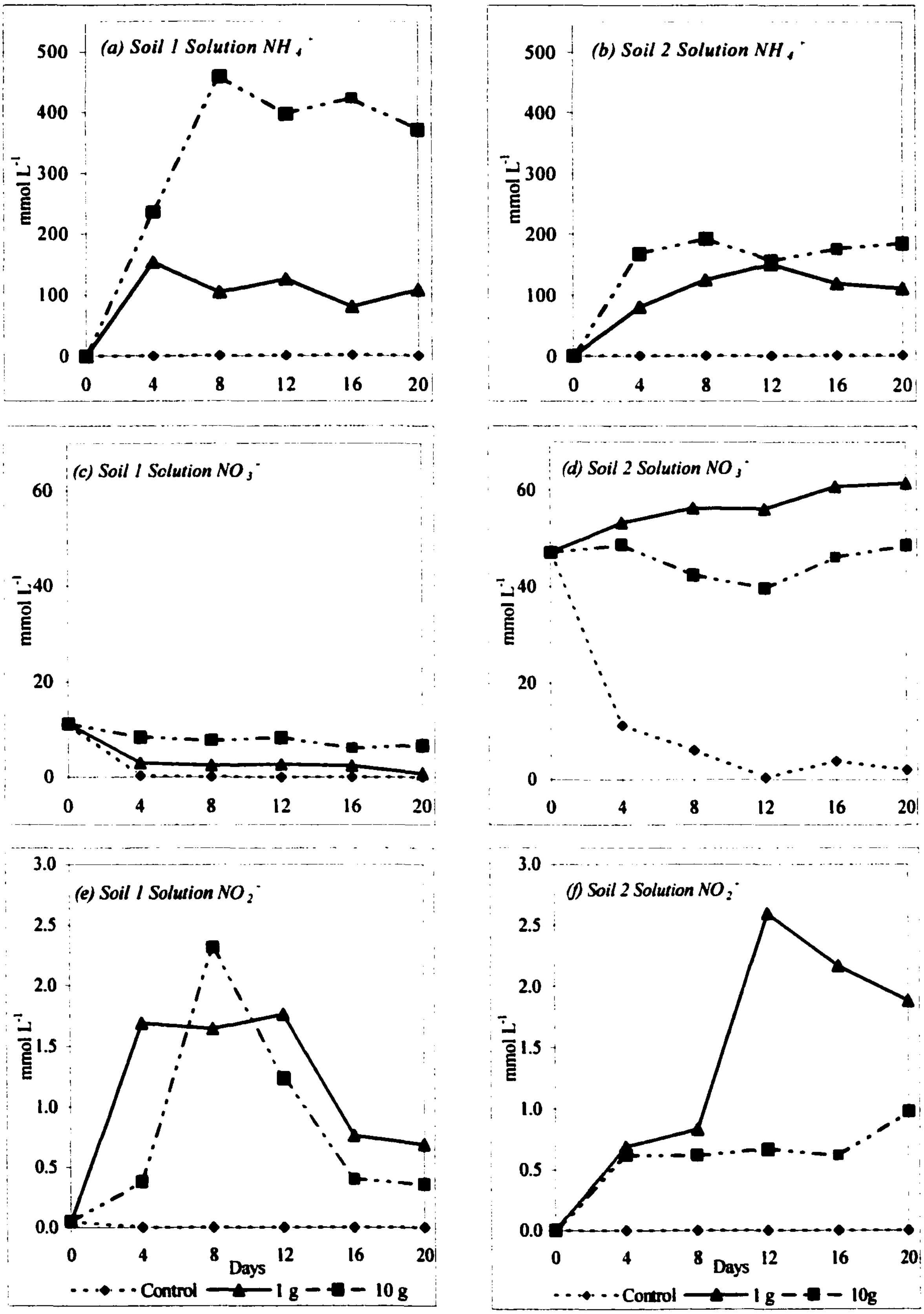

Figure 2.3. Soil solution NH_4^+, NO_3^-, and NO_2^- following addition of urea to two soils.

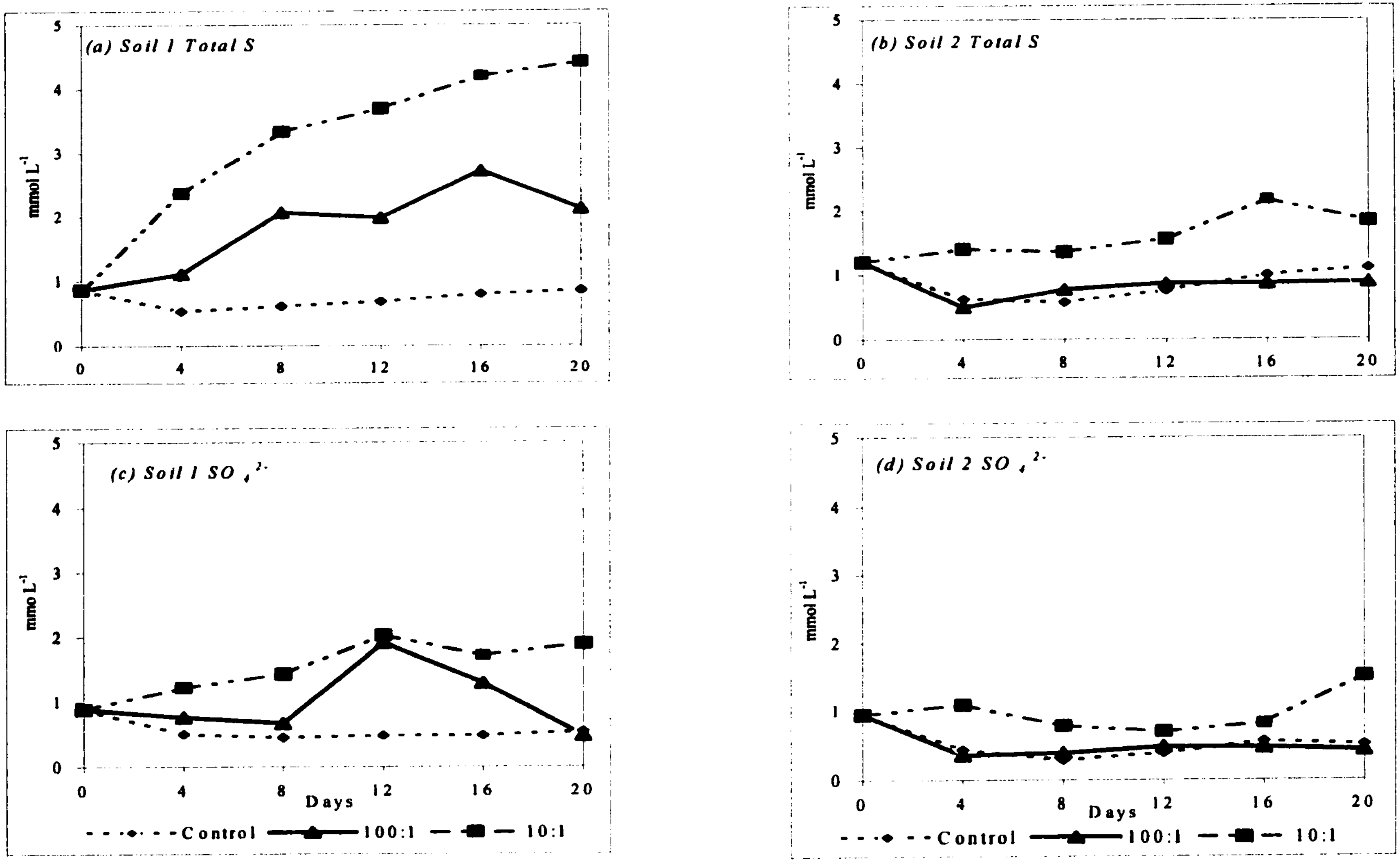

Figure 2.4. Total S and SO_4^{2-} in soil solution following addition of urea to two soils.

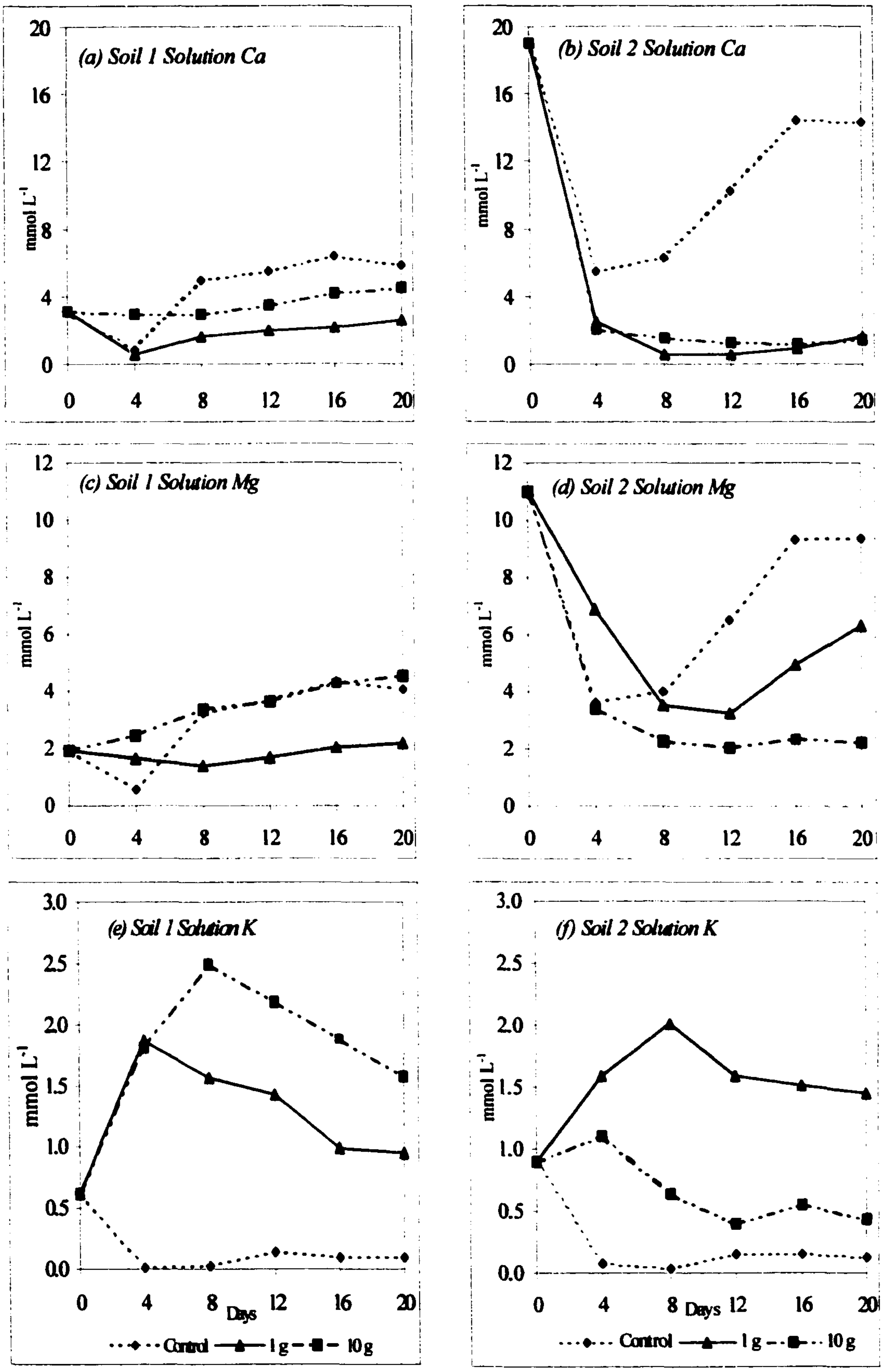

Figure 2.5. Total Ca, Mg and K in soil solution following addition of urea to two soils.

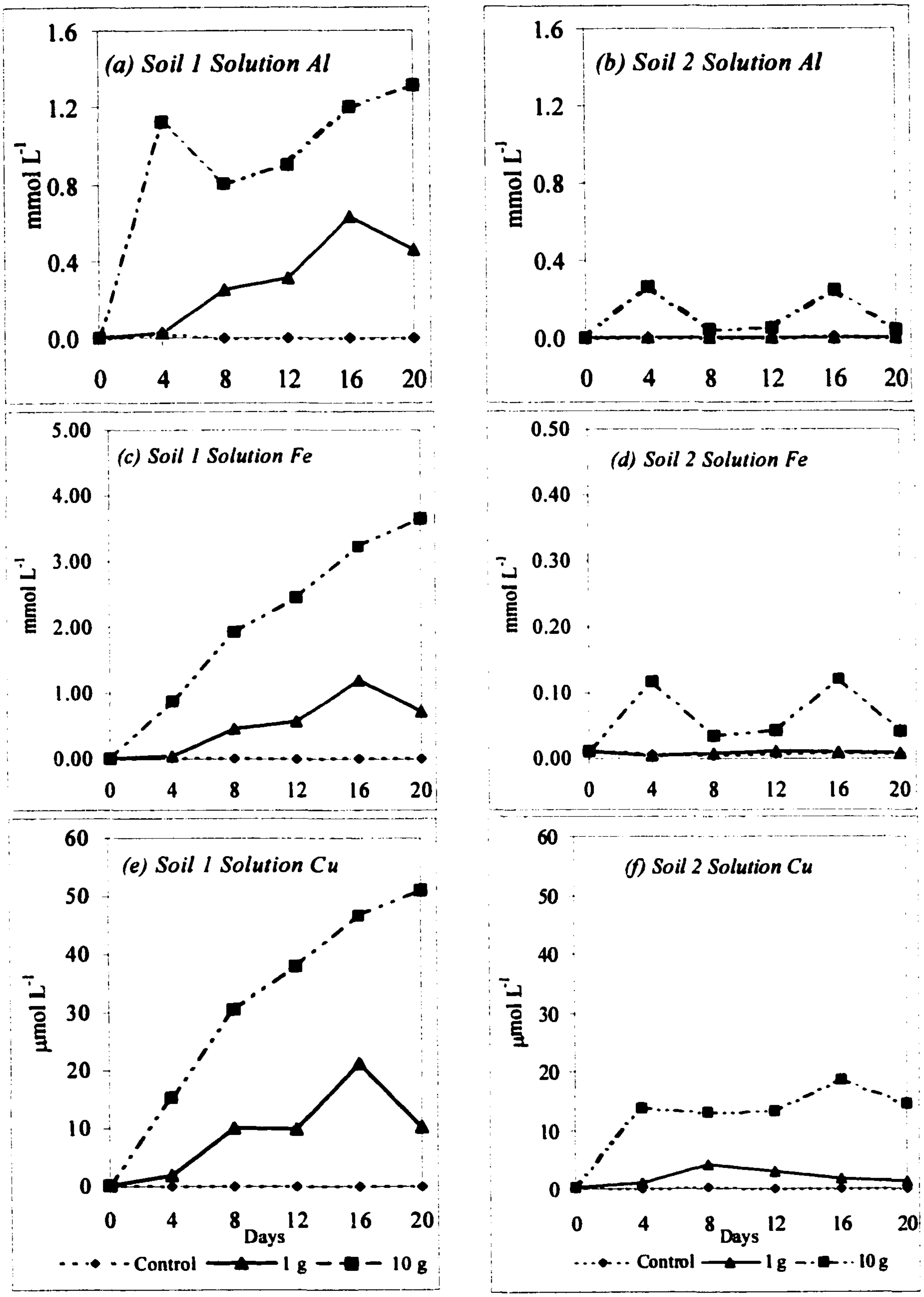

Figure 2.6. Soil solution Al, Fe, and Cu following addition of urea to two soils.

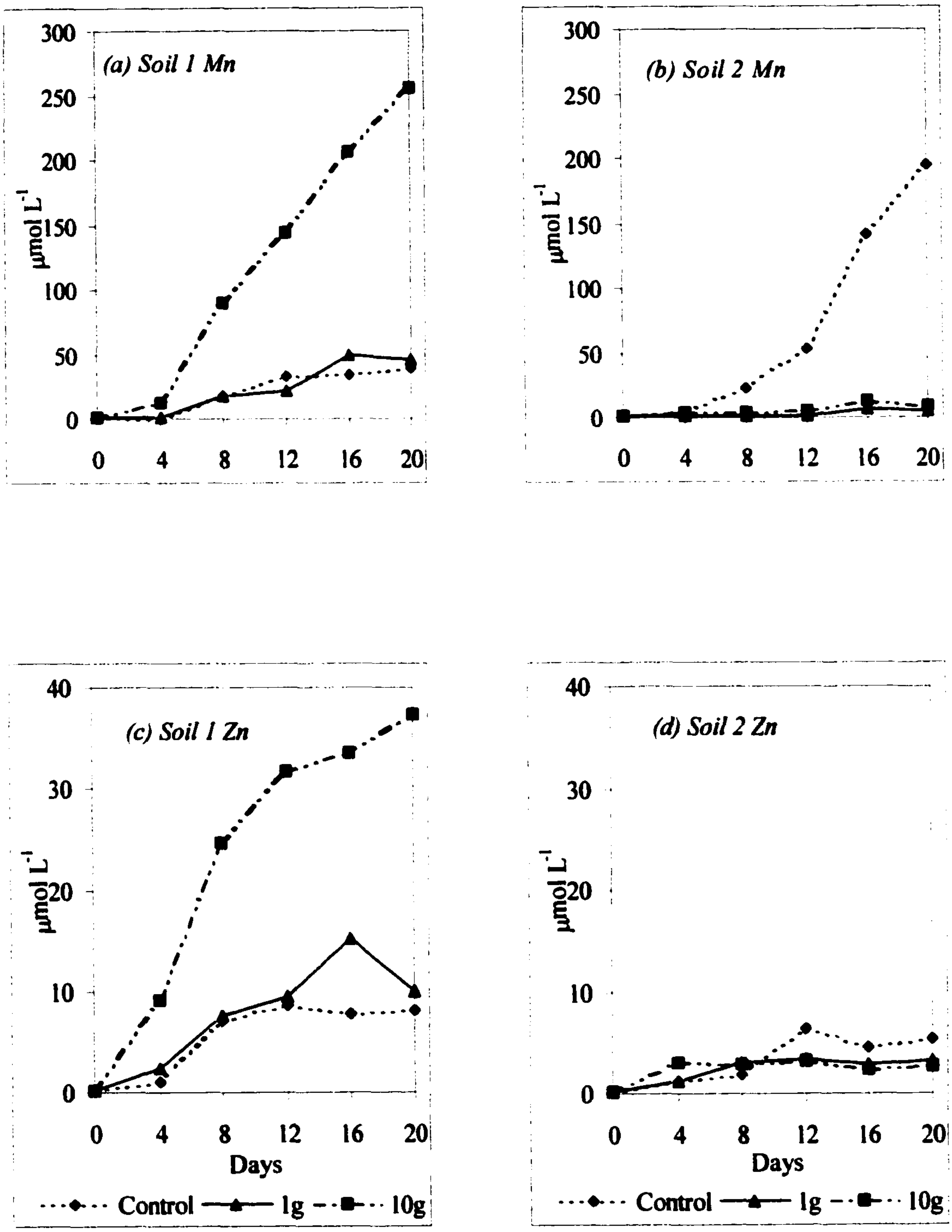

Figure 2.7. Total Mn and Zn in soil solution following addition of urea to two soils.

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CHAPTER 3

SOLUBILIZATION OF CARBON, METALS, AND NON METALS IN PRAIRIE SOILS TREATED WITH UREA AND AMMONIUM SULPHATE

Introduction

The experiment reported in Chapter 2 showed that addition of urea granules significantly altered solution in the surrounding soil. Solution pH was higher in the fertilizer reaction zone (FRZ) as was ionic strength (*I*). The solution concentration of some elements, for example Ca, tended to decrease. Although pH was higher in the FRZ compared to the control, solution concentrations of several transition metals, including Fe and Cu, increased. Solution concentrations of the non-metals P and S also increased.

If all urea-N applied is first hydrolyzed and is then converted to NO_3^-, two moles of OH^- and four moles of H^+ are produced per mole of urea. The overall reaction of urea in soil is acidic. The pH data from Chapter 1 suggested that the changes observed over 20 days were occurring during the initial alkaline phase of urea transformation. Conversion to NO_3^- had not proceeded to the point where solution pH began to decline. Within this alkaline environment, thermodynamic considerations suggested that complexation reactions were responsible for increased metal concentrations. Of particular interest was complexation with soil organic matter (SOM) brought into solution by the higher pH.

Short-term effects of nitrogen fertilizer on SOM have been reported in the literature. Tomasiewicz and Henry (1985) measured changes in soluble organic carbon (SOC) following anhydrous ammonia (NH_3) application in undisturbed cores from the Ap horizon of ten Chernozemic soils. They found that SOC increased in all soils following treatment. The amount of carbon solubilized varied with the amount of NH_3 applied, distance from the injection site (<2.5, 2.5-5.0, 5.0-7.5 cm), and the water content of the soil (field capacity or wilting point). Similar results were reported by Norman *et al.* (1987) working with soils in Illinois. Myers and Thien (1988) treated a soil with NH_4OH and two acidic phosphate salts singly and in combination and then leached the soil with water. All three compounds increased SOC levels compared to untreated soils when applied individually. The amount of SOC extracted was positively correlated with the pH of the leachate. Earlier Nemec and Vopenka (1971) had reported that addition of NH_3, ammonium sulphate (AS), ammonium hydroxide, and ammonium nitrate (AN) all increased extraction of humic substances from soil.

Does adding urea solubilize SOM as well as increasing total concentrations of metals and non-metals in solution? In order to address this question, an incubation experiment was performed. The objectives were to see if trends in soluble elements observed in Experiment 1 occurred over a wider range of soil types and to compare SOC levels in the FRZ of urea to ammonium sulphate (AS) and untreated soil.

Materials and Methods

Soils and Fertilizers

Bulk soil samples consisting of four 20 L pails were collected from the 0-5 cm depth of nineteen Alberta Agriculture research sites in central and southern Alberta. Soils were collected in late October or early November, after crop removal but before the soils had frozen. Each sample was collected from an area of approximately 10 m^2. Three 20 mm diameter cores were taken from each pail, mixed, dried at room temperature, and ground to pass 2.0 mm. These sub-samples were used for characteristic analysis. Bulk samples were spread in 1.5 by 3 m trays and partially dried. Large aggregates were broken by passing them through a screen with 6 mm openings and the sample mixed. Sub-samples of approximately 5 kg for the incubation experiment referred to in this chapter were taken at this point by collecting and mixing portions from 30 places in the tray. The processed bulk sample was stored in sealed plastic pails at 4°C until the commencement of the experiment.

Granular fertilizer grade urea and AS were used in these experiments. Passing the fertilizer through a 2 mm screen and then a 1.7 mm screen reduced the range of prill diameters. Prills retained on the 1.7 mm screen were used in the experiment.

Incubation Experiments

Experiment 2 was a factorial design with eight soils, and three treatments replicated three times in a randomized complete block design. Blocks were run sequentially with a two-day delay between the start of each. To prepare each experimental block a representative sub-sample of approximately 0.5 kg of each soil was removed from storage, thoroughly mixed and placed in a covered 5 L plastic pail. The pails were placed in a closed cabinet at room temperature for three days. Duplicate sub-samples from each soil were dried at 105°C for 24 hours and the soil water content calculated.

After three days, the soils were removed from the incubation room. Each experimental sub-unit was set up by weighing the equivalent of 125 g of soil oven dry basis into a plastic tray and adding zero, 1.00 g urea, or 1.40 g AS. The fertilizer rates provided equivalent number of granules and the same average distance between granules. More N was added in the urea treatments (0.46 g) than in the AS treatments (0.29 g). Soil and fertilizer were mixed and then deionized water was added as a fine spray to bring the soil water content to 75% of saturation. The soil-fertilizer mixture was transferred to a 250 mL plastic pot, with a diameter of 8 cm. Soil depth within the pot ranged from 12 to 17 mm depending on soil bulk density. Each pot was placed in a 2 L plastic container. Containers were sealed and incubated in a growth chamber at 25±2°C for 14 days. Every two days the containers were opened to permit air exchange.

Analytical Procedures

Soil solution was extracted using the centrifugation procedures developed by Thibault and Shepard (1992) and described in detail in Chapter 2. Solution pH and EC were measured on the day of extraction using a combined electrode and Fisher Acumet Model 50 pH meter (Fisher Scientific, Nepean, Ontario, Canada) and an electrical conductivity bridge on a Radiometer Model CDM 83 conductivity meter (Bach-Simpson Ltd., London, Ontario, Canada). Electrical conductivity was not measured on small samples. Soluble organic carbon was measured by ultra-violet promoted persulphate oxidation using an Astro 2001 System 2 Soluble Carbon Analyser (Astro International Corporation, League City, Texas). Soluble inorganic carbon was measured on the same instrument following acidification of the samples with 10% H_3PO_4. Urea in solution was measured following the diacetylmonoxime method describe by Bremner (1982) with minor modifications. Specifically a 1 mL aliquot of soil solution replaced the 2 M KCl extract used in the original method. Total elements in the soil solution were measured using a Jobin-Yvon model JY70PLUS Inductively Coupled Plasma Spectrophotometer (ATS Scientific Ltd., Oakville, Ontario, Canada). Operating limits of detection (LOD) and limits of quantitation (LOQ) were determined for each element using the method of Keith *et al.* (1982). The instrument was calibrated before each run using Seignory Chemical Product certified standards (SCP Scientific Ltd., St. Laurent, Quebec, Canada). Analytical values less than the LOD were recorded as below detection limit (BDL) and were treated as zero values in the statistical analysis.

Statistical Analysis

Analysis of variance was performed using SAS-PC. A separate ANOVA was performed for each analyte (Eq. 3.1). Main effects were taken as significant if the probability of obtaining F by chance was less than 5% ($p < 0.05$). Significant differences among main effect means were determined using Tukey's studentized range test (MSD) where applicable. When the interaction term of the ANOVA was significant ($p < 0.05$), treatment means could not be compared across all soils. Interaction means (treatments within soils) were first plotted to examine the nature of the interaction. Comparison of treatment means within soils was performed using the LSMEANS program in SAS. This approach calculates the probability of t for all possible mean comparisons among the interaction means. It does not maintain the protection level associated with the original experimental model unless it is restricted to pre-planned comparisons (R.C. Yang, personal communication). To protect against error, only treatments within each soil were compared and only if the main effect was significant at $p < 0.05$. Treatment differences within soils were accepted as significant if $p < 0.05$.

ANOVA Eq. 3.1

Source	n	df
(R) Blocks	3	2
(A)Treatments	3	2
(B) Soils	8	7
(AB)Treatments X Soils		14 (a-1)(b-1)
Error		56 (r-1)(ab-1)
Total	72	71 (rab-1)

Total solution concentrations of elements were correlated with SOC concentrations. The correlation coefficient (r) and coefficient of determination (r^2) were calculated using the CORREL function in EXCEL. In cases where $r > 0.60$, the significance of r was tested at $p < 0.01$.

Results

Soil Characteristics

Soils used in this study were selected to give a range of characteristics. Soil organic matter (SOM) ranged from 0.021 to 0.081 kg kg^{-1} (Table 3.1). While Soils 11 and 13 were relatively low in SOM within the context of Canadian prairie soils, they would be considered relatively high SOM soils in much of the world. Clay content ranged from 0.09 to 0.36 kg kg^{-1}. Extractable Fe and Mn tended to be higher in the low pH soils. Soil

15, which was relatively high in Cu, Zn and Mn compared to the other alkaline soils, had received 120 Mg ha^{-1} of feedlot manure in October of the previous year. In Soils 11, 13 and 15, the sum of positive charge arising from basic cations exceeds the CEC if Ca and Mg are considered divalent. These discrepancies may be due to speciation, trace amounts of sparingly soluble salts such as gypsum, or the hysteresis effect associated with replacing a divalent with a monovalent cation, in this case NH_4^+ (van Bladel and Laudelout, 1967). In the acid soils, base cations are less than 100% of the CEC.

Alkali and Alkaline Earth Metals

The interaction term of the ANOVA was not significant for total Ca and Na in soil solution (Table 3.2). This allows estimation of treatment differences across all soils. Mean solution Ca was highest in the AS treatment. Concentrations in the urea and control treatments were not significantly different. Differences in Na means among all three treatments were significant. Solution Na was highest in the urea treated soils and lowest in the control.

Mg concentrations in the controls were not different from the urea treatments. Concentrations of Mg in AS treatments were significantly higher than both the control and the urea treatments within all soils. Ammonium sulphate addition also increased solution concentrations of K, but the magnitude of the change varied with soil. The increases were significant in the AS treatments compared to the control and urea treatments in Soils 11, 13, 15, 16 and 25. There were significant treatment*soil (AB) interactions for both Mg and K. The significant interaction was caused by differences in the magnitude of the effect AS had on solution Mg. The nature of the interaction was similar for K.

Transition Metals and Boron

For Fe, Cu, Mn, and Zn, interpretation of treatment effects was confounded by significant treatment*soil interactions (Table 3.3). Separation of treatment means within soils showed a similar pattern for Fe and Cu. With the exception of Soil 15, solution concentrations were higher in the urea treatments compared to the controls. The control and AS means were not significantly different. In seven soils, Zn concentrations were significantly higher in the urea treatments than in the controls or AS treatments. In the most acidic soil, Soil 28, soluble Zn was highest in the AS treatment. The Mn data were variable. Variability tended to be highest among replicates in the AS treatments. Total Mn levels were significantly higher in the AS treatments compared to the controls in Soils 28 and 29. No other differences among treatment means were significant.

Treatment, soil, and interaction terms were significant for B, Co, and Mo (Table 3.4). The concentrations of all three elements were significantly higher in the urea treatments compared to the controls. The differences were one to two orders of magnitude for Co and Mo. Molybdenum concentrations in the AS treatments were significantly less than in the urea treatments, but not different from the controls. Solution concentrations of Co in AS treatments followed a similar trend except in Soil 28. Differences in total B concentrations were smaller, ranging from two to four-fold. Boron concentration in the AS treatment was less than in the urea treatment in all soils. The difference was significant in Soils 11, 13, 15, 23, and 25.

Major Non-Metal Elements

Results for Al and P show that urea had an effect on solution levels compared to the control, whereas AS did not (Table 3.5). Since the interaction terms were significant, treatment means were separated within soils. The results were consistent qualitatively in that Al and P concentrations were always significantly higher in the urea treatments compared to the control and AS treatments. This suggests that the treatment interaction with soil was arising from differences in the magnitude of the response to urea. Total S concentrations in the AS treatments were significantly higher than in the other two treatments. Mean comparisons between the control and urea treatments showed no significant differences with the exception of Soil 16, where S was reduced in the urea treatment.

Solution pH, Ionic Strength, and Soluble Organic Carbon

The data shown in Table 3.6 are for variables that may be useful in understanding changes in the solution elements measured by ICP. Analysis of variance for solution pH showed a significant block effect. The treatment effect was also significant, whereas the soil and interaction effects were not. Examination of the block means (data not shown) showed that pH in the last block incubated was lower than the other two. Comparison of the treatment means across all soils shows that urea did not have a significant effect on pH compared to the control, whereas AS did reduce solution pH significantly. The average reduction was equivalent to an order of magnitude increase in H^+ activity.

Small sample size precluded measurement of EC and calculation of ionic strength (*I*) on a number of solutions. Analysis of variance was not performed on the *I* data due to the large number of missing values. The data available suggest that AS increased *I* more than did urea.

Total soluble organic carbon measurements were corrected for urea in solution prior to statistical analysis. Corrected values are reported as SOC (Table 3.6). Urea concentrations in soil solution extracted from the urea treatments ranged from below detection limit to 11 mmol L^{-1}. The interaction term of the ANOVA was significant for SOC. Separation of treatment means within soils showed that AS had no significant effect on SOC compared to the control. Soluble organic carbon in the urea treatments on the other hand were two to three orders of magnitude higher than in the control or AS treatments. Inorganic carbon accounted for 25 to 50% of the total soluble carbon in soil solutions from the control and AS treatments (data not shown). In the urea treatments, inorganic carbon was 10 to 20% of total soluble carbon concentrations, proportionally less than in the control and AS treatments but an order of magnitude higher in absolute concentration.

Correlation was used to estimate the strength of the relationship between total elemental concentrations in solution and SOC levels (Table 3.7). The r-values exceeded 0.60 for Al, Fe, Cu, Zn, Co, Mo, and P. In all cases in which r exceeded 0.60, r was significant at $p < 0.01$. Correlation of SOC was less than 0.60 with B and Mn.

Discussion

The reduced pH in the urea treatments of the third block suggested that after 14 days, acid production from nitrification has overcome base production from urea hydrolysis.

Blocks 1 and 2 had not apparently proceeded to that stage after 14 days. The block effect complicates the use of pH data in explaining trends in other solution elements. In the urea treatment, pH depression would only commence after any $CaCO_3$ or $MgCO_3$ precipitated during the initial hydrolysis phase had been dissolved and neutralized. In the experiment reported in the previous chapter, solution pH in the controls started near pH 8, but declined to below pH 6 in both soils after 14 days. The decline was attributed to microbial respiration increasing pCO_2. In the current experiment, solution pH's in the controls of all eight soils were near pH 8. A reason for this high pH in the controls may be that the soils were sufficiently wet to allow reduction reactions to proceed. Reduction reactions tend to consume H^+ and prevent pH depression (Lindsay 1979).

Concentrations of SOC in solution increased following ure addition. This is consistent with the dispersion of fulvic and humic acids at high pH reported by Schnitzer (1978). Myers and Thien (1988) found a strong correlation between pH and dissolved organic matter (DOM) following additions of ammonium hydroxide and/or ammoniated phosphates. Tomasiewicz and Henry (1985) correlated SOC with NH_4^+ concentrations following NH_3 addition. Both suggested that pH alone was not the cause of SOM dissolution and that the dispersive properties of NH_4^+ likely played a role. The data reported here suggest that a shift to higher pH alone, as in the control samples, does not dissolve SOM. Nor would it appear that increased NH_4^+ concentration alone, as in the AS treatments, causes any significant dissolution.

Solution Ca and Mg concentrations in urea treatments did not increase relative to the controls. In the AS treatment, Ca and Mg accumulated in soil solution compared to the controls. Ammonium would have displaced Ca and Mg from cation exchange sites in both urea and AS treatments. The data suggest that Ca and Mg were precipitated as carbonates following displacement in the urea treatments. In the AS treatments, there was no enhanced source of CO_3^{2-} to drive precipitation of displaced Ca and Mg. In addition, the reduction in pH as NH_4^+ nitrifies would tend to support a higher solution concentration of Ca and Mg in soils in equilibrium with atmospheric CO_2. Precipitation of Ca and Mg in urea treatments was previously reported by Kissel *et al.* (1988).

Increased K and Na concentrations in solutions suggest that AS displaced K^+ and Na^+ from cation exchange sites. The K increases were significant in soils with relatively high levels of exchangeable K. In soil 11, the quantity of K in solution was approximately double the amount originally measured as exchangeable. Ammonium sulphate may have displaced inter-lattice K in this soil. Ammonium derived from urea hydrolysis appears to have displaced Na^+ and K^+ from cation exchange sites. The trend is statistically significant for Na but not for K.

Overall, the data for basic cation forming metals while not explicit are consistent with displacement of exchangeable cations from the CEC by NH_4^+, and in the case of urea, precipitation of divalent forms as carbonates.

Solution concentrations of Al, Fe, Cu and Zn increased with urea addition. All were significantly correlated with SOC levels. These elements form relatively strong complexes with SOM through a variety of mechanisms (Stevenson and Fitch 1986, Schnitzer 1986). The two most important appear to be linkages between the metal cation and adjacent phenolic OH and COOH groups or between the metal and two adjacent carboxyl groups (Gamble *et al.* 1970, Schnitzer 1969, Boyd *et al.* 1981). Cobalt and Mn on the other hand, tend to form weak associations with SOM. Data from McBride (1978, 1982) suggest that for Mn the strength of the complexes formed increases as pH rises. Total solution Mn was not significantly correlated with SOC. Total Co on the other hand was correlated. Interestingly when the three largest outliers were removed r for Mn increased to 0.75.

Of the elements normally present in soil solution as oxyanions, solution concentrations of all except S increased in response to added urea. The concentrations of Mo and P were highly correlated with SOC. Solution B levels were not well correlated, SOC only accounting for 29% of the variation in B. Although solution B concentrations increased in the urea treatments, the increase was proportionally small compared to increases in other elements.

The small increase in B compared to the relatively large increases for elements like Fe and Cu illustrates the complexity of the urea perturbed system. If the effect of urea was straight forward, i.e. –SOM dissolves and brings into solution attached metals and non-metal elements, then the increase in SOC would more closely match the increase in total element concentration. This was not the case. Correlation shows that there is some proportionality between SOC and several of the elements measured, but the proportion is not one to one. The ratio of SOC in urea to control treatments within a soil ranged from 27 to 81. The ratio for total B in solution ranged from 1.8 to 4.1. For Cu and Fe, which forms strong complexes with SOM and SOC, the ratios ranged from 39 to 620 and 10 to 1050, respectively. Some of this variation is inherent, particularly for strongly complexing metals. It reflects differences among soils in both the element's concentration in the solid organic phase and the density of complexing sites in SOM. It may also reflect differences among soils with respect to the fate of organic molecules and associated metals in the FRZ. Dispersion or dissolution of SOM may expose new reaction sites to the soil solution that are capable of further complexing solution ions. On the other hand, conversion of SOM to DOM may expose physically occluded nutrient elements, such as P, to mineralization as the FRZ ameliorates over time and is repopulated by soil organisms. In both these scenarios, there may be significant effects on biological availability and/or mobility of the elements within the soil system.

Conclusions

Urea hydrolysis products dissolve SOM and increases SOC concentrations in soil solution. Increases in solution concentrations of a number of transition metals and non-metals such as B and P occur concurrently with the dissolution of SOM. The eight soils used in this study represented a range of soil characteristics found in the agricultural soils of Western Canada. The trends in SOC and element concentrations within the FRZ of urea as described here would apply to most of the soils of Western Canada. At the same time, there were significant differences among soils in terms of amounts of SOC and elements found in soil solution. This may not only reflect the inherent variability among soils, but also differences in the fate of FRZ products.

Table 3.1. Soil classification and some chemical and physical characteristics of soils used in incubation experiment.

Soil No.	Soil Subgroup	Organic Matter	Total N	Total P	Clay	Saturated Water Content
				$kg\ kg^{-1}$		
11	Orthic Brown Chernozem	0.024	0.0011	0.0007	0.09	0.26
13	Calcareous Brown Chernozem	0.021	0.0010	0.0004	0.15	0.34
15	Dark Brown Solodized Solonetz	0.062	0.0027	0.0008	0.32	0.56
16	Orthic Dark Brown Chernozem	0.037	0.0015	0.0008	0.23	0.41
23	Eluviated Black Chernozem	0.081	0.0036	0.0004	0.26	0.60
25	Dark Gray Luvisol	0.074	0.0033	0.0006	0.30	0.51
28	Gleyed Dark Gray Luvisol	0.050	0.0020	0.0004	0.36	0.54
29	Dark Gray Solodized Solonetz	0.062	0.0023	0.0005	0.22	0.58

Table 3.1. Continued.

Soil No.	pH	DTPA Extractable Metals				Exchangeable Cations				CEC
		Fe	Cu	Zn	Mn	Ca	Mg	Na	K	
		µmol kg^{-1}				*mmol kg^{-1}*				*mmol(+) kg^{-1}*
11	7.1	109	4.4	29	74	48	5.6	2.0	7.0	80
13	7.5	75	7.4	22	78	56	13.8	3.0	11.1	120
15	7.6	135	26.5	73	126	109	25.3	4.3	28.2	235
16	6.8	194	13.2	15	171	48	11.0	1.7	9.6	172
23	6.8	1360	7.7	33	321	140	25.8	1.6	3.6	367
25	5.6	2370	7.1	171	497	88	15.5	1.0	10.5	283
28	4.6	2440	14.3	8	340	61	12.1	1.8	4.1	277
29	5.5	2560	6.9	89	407	70	8.4	0.8	2.7	227

Table 3.2. Total calcium, magnesium, potassium, and sodium in soil solution following incubation with urea and ammonium sulphate.

Soil Number	Ca			Mg			K			Na		
	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS
	mmol L^{-1}											
11	7.2	5.5	21.5	1.0a[x]	1.3a	7.9b	2.0a	6.2b	23.0c	2.9	5.0	3.7
13	4.4	1.5	14.2	0.9a	1.2a	13.2b	1.4a	3.8a	16.4b	6.2	8.3	8.8
15	6.0	1.8	20.8	1.3a	0.7a	7.7b	3.5a	5.5a	12.7b	7.8	8.4	6.1
16	7.2	1.6	15.8	2.4a	0.9a	9.8b	4.3a	2.8a	12.0b	4.1	5.4	4.9
23	1.8	4.1	12.5	0.4a	1.0a	5.9b	0.1a	0.7a	0.9a	3.6	8.4	6.6
25	6.0	5.6	11.5	1.0a	1.0a	7.5b	0.9a	2.6a	8.6b	3.6	7.4	4.8
28	0.5	2.6	10.5	0.1a	0.6a	8.0b	0.2a	0.7a	1.9a	3.6	5.6	5.5
29	0.7	6.8	10.9	0.2a	1.1a	6.4b	0.1a	1.0a	1.9a	3.0	4.1	4.5
Mean	4.2a[y]	3.7a	14.6b							4.4a	6.5b	5.6c
ANOVA	*F*		*p*[z]	*F*		*p*	*F*		*p*	*F*		*p*
Block	0.35		0.7033	0.04		0.9561	0.19		0.8311	2.5		0.0944
Treat (A)	48		0.0001	189		0.0001	88		0.0001	14		0.0001
Soil (B)	2.2		0.0520	3.2		0.0077	23		0.0001	9.0		0.0001
AB	1.3		0.2237	2.2		0.0205	8.6		0.0001	1.3		0.2708

[x] Treatment means for each element within each soil are different if followed by a different letter, $p < 0.05$.

[y] Treatment means for each element across all soils are different if followed by a different letter, $p < 0.05$.

[z] Probability of obtaining a larger F by chance.

Table 3.3. Total iron, copper, zinc, and manganese in soil solution following incubation with urea and ammonium sulphate.

Soil Number	Fe			Cu			Zn			Mn		
	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS
	$\mu mol\ L^{-1}$											
11	4.1a[x]	980b	12a	0.40a	57b	1.1a	0.34a	30b	1.5a	4.2a	460a	4.5a
13	8.3a	930b	8.6a	0.27a	22b	0.92a	0.25a	9.0b	1.0a	0.34a	171a	41a
15	1.8a	220a	2.8a	0.62a	24b	0.70a	0.21a	10b	0.54a	0.78a	89a	6.7a
16	3.0a	510b	4.1a	0.35a	29b	0.58a	0.10a	6.5b	0.90a	3.1a	200a	8.2a
23	23a	860b	5.7a	0.07a	10b	0.33a	0.27a	6.7b	0.97a	0.65a	74a	4.4a
25	1.4a	1500b	10a	0.04a	22b	0.34a	0.22a	16b	2.4a	0.41a	55a	47a
28	110a	1000b	42a	0.39a	72b	0.57a	3.6a	5.2a	11b	6.3a	69a	1600b
29	140a	6100b	32a	0.33a	60b	0.68a	1.0a	18b	5.3a	13a	540ab	680b

<u>ANOVA</u>	*F*	*p*[y]	*F*	*p*	*F*	*p*	*F*	*p*
Block	2.3	0.1148	0.32	0.7258	0.99	0.3792	0.26	0.7752
Treat (A)	264	0.0001	464	0.0001	95	0.0001	3.5	0.0378
Soil (B)	56	0.0001	22	0.0001	7.7	0.0001	2.4	0.0376
AB	52	0.0001	22	0.0001	8.9	0.0001	2.3	0.0155

[x] Treatment means for each element within each soil are different if followed by a different letter, $p < 0.05$.

[y] Probability of obtaining a larger F by chance.

Table 3.4. Total boron, cobalt, and molybdenum in soil solution following incubation with urea and ammonium sulphate.

Soil Number	B			Co			Mo		
	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS
					$\mu mol\ L^{-1}$				
11	114a[x]	343b	152a	0.53a	35b	1.2a	0.69a	4.7b	1.2a
13	178a	454b	294a	0.22a	18b	1.6a	0.50a	4.0b	1.4a
15	225a	570b	190a	0.55a	14b	1.2a	0.67a	4.6b	1.1a
16	156a	423b	283ab	0.53a	16b	1.2a	0.50a	3.1b	1.2a
23	181a	743b	393c	0.07a	5.4b	0.76a	0.31a	3.7b	0.76a
25	166a	621b	326c	0.22a	4.8b	0.92a	0.38a	3.7b	0.99a
28	208a	364b	318ab	0.17a	4.3b	6.4b	0.32a	10b	1.1a
29	163a	320b	285ab	0.31a	9.1b	3.4a	0.44a	5.7b	1.1a

ANOVA	*F*	p^y	*F*	*p*	*F*	*p*
Block	4.8	0.0126	0.06	0.9380	1.4	0.2485
Treatment (A)	75	0.0001	237	0.0001	246	0.0001
Soil (B)	6.0	0.0001	19	0.0001	8.8	0.0001
AB	2.3	0.0045	23	0.0001	9.0	0.0001

[x] Treatment means for each element within each soil are different if followed by a different letter, $p < 0.05$.

[y] Probability of obtaining a larger F by chance.

Table 3.5. Total aluminum, phosphorus, and sulphur in soil solution following incubation with urea and ammonium sulphate.

Soil Number	Al			P			S		
	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS
					mmol L^{-1}				
11	0.02a[x]	1.88b	0.03a	0.04a	2.21b	0.36a	1.22a	7.46a	86.41b
13	0.03a	2.35b	0.03a	0.03a	0.66b	0.09a	3.90a	3.55a	86.44b
15	0.01a	0.19a	0.01a	0.08a	0.84b	0.17a	3.07a	5.24a	55.05b
16	0.01a	0.92b	0.01a	0.06a	0.75b	0.13a	19.02a	2.84b	79.16c
23	0.07a	0.80b	0.01a	0.01a	0.46b	0.04a	1.03a	3.11a	83.67b
25	0.01a	0.78b	0.01a	0.02a	1.22b	0.06a	1.71a	5.57a	90.84b
28	0.35a	1.38b	0.37a	0.01a	0.87b	0.09a	1.23a	4.71a	88.63b
29	0.47a	3.81b	0.18a	0.02a	1.26b	0.07a	0.83a	3.58a	86.44b

<u>ANOVA</u>	*F*	*p*[y]	*F*	*p*	*F*	*p*
Block	0.94	0.3989	0.56	0.5731	3.9	0.0271
Treatment (A)	239	0.0001	254	0.0001	807	0.0001
Soil (B)	27	0.0001	14	0.0001	2.3	0.0436
AB	17	0.0001	9.0	0.0001	3.1	0.0017

[x] Treatment means for each element within each soil are different if followed by a different letter, $p < 0.05$.

[y] Probability of obtaining a larger F by chance.

Table 3.6. Soil solution pH, ionic strength, and soluble organic carbon following incubation with urea and ammonium sulphate.

Soil Number	pH			Ionic Strength			SOC		
	Control	Urea	AS	Control	Urea	AS	Control	Urea	AS
					mol L^{-1}			*mmol L^{-1}*	
11	8.52	7.95	7.31	0.023	0.055	0.53	11a[x]	635b	24a
13	7.85	8.15	7.40	0.018	0.073	0.38	8a	237b	14a
15	8.12	8.07	7.42	0.024	mv	0.22	13a	352b	17a
16	8.83	8.31	7.28	0.012	0.053	0.27	8a	331b	13a
23	8.97	8.30	7.59	0.008	0.043	0.13	11a	306b	14a
25	8.36	8.25	7.24	0.021	0.062	0.22	8a	635b	15a
28	8.31	8.15	6.46	0.005	0.060	0.20	13a	475b	10a
29	8.42	8.19	6.49	0.004	0.061	0.21	13a	627b	10a
Mean	8.42a[y]	8.17a	7.15b						
<u>ANOVA</u>	*F*		*p*[z]				*F*		*p*
Block	33		0.0001				0.44		0.6440
Treat (A)	31		0.0001				1140		0.0001
Soil (B)	1.2		0.3182				21		0.0001
AB	0.81		0.6542				20		0.0001

[x] Treatment means within each soil are different if followed by a different letter, $p < 0.05$.

[y] Treatment means across all soil are different if followed by different letters.

[z] Probability of obtaining a larger F by chance.

Table 3.7. Correlation of various total soluble elements with soluble organic carbon.

	Al	Fe	Cu	Zn	Mn	Co	Mo	B	P
r	0.73	0.68	0.85	0.79	0.09	0.66	0.78	0.54	0.89
r^2	0.53	0.46	0.73	0.62	0.01	0.44	0.61	0.29	0.80
	**	**	**	**	ns	**	**	ns	**

** – r is significant at $p < 0.01$.

ns – non-significant.

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CHAPTER 4

UPTAKE OF NUTRIENT AND NON-NUTRIENT ELEMENTS BY BARLEY GROWN IN CONTACT WITH THE FERTILIZER REACTION ZONE OF UREA

Introduction

In the first two experiments, solution elements within the fertilizer reaction zone (FRZ) of urea were measured. Those measurements showed that relative to control soils the concentrations of a number of elements were substantially different in solution from the FRZ. Solution concentrations of some elements, for example Ca and Mg, decreased but increases were more common. These included cation forming transition metals (Fe, Cu, Mn, Zn and Co), an anion forming metal (Mo), and non-metals (Al, S, P and B). Soluble organic carbon (SOC) concentrations also increased. Although the data suggested that SOC complexes played a role in increased solution concentrations, transition metals forming ion pairs with NH_3 could also have driven dissolution or desorption reactions. A number of researchers have found that other pH raising fertilizers, such as anhydrous ammonia or ammonium hydroxide, increase the solubility of humic substances (Nemec and Vopenka 1971, Tomasiewicz and Henry 1985, Norman *et al.* 1987, Myers and Thien 1988). Furthermore, metal-humic complexes, particularly with fulvic acid (FA), play a key role in maintaining metals in soil solution (Stevenson and Fitch 1986). Thus, complexes with SOC, while not necessarily the only mechanism responsible, were likely important in increasing solution concentrations of elements within the FRZ.

One of the questions raised by the earlier experiments was how the increase in the total soluble concentration of nutrient elements affected their availability and uptake by plants. A number of researchers have shown that organo-metal complexes maintain plant availability by preventing precipitation of metals such as Cu and Zn (McLaren and Crawford 1973, Murthy 1982, Mandal and Mandal 1986). In the FRZ of urea, however, soluble does not necessarily mean more plant available. The alteration of conditions that lead to dissolution of the solid humates, such as the increase in OH^- from NH_3 hydrolysis, would tend to increase the stability of complexed metals. The main mechanism increasing stability is an increase in dissociation of acidic functional groups, which results in an increase in binding sites (Stevenson 1991). Rising pH would also tend to increase ion pairing, converting readily available free metal ions to less available species.

Thus, the increased solution metal concentrations within the FRZ could result in decreased plant availability. This may also vary considerably among the different metals depending on the nature of the metal and the complexing agent. Coombes *et al.* (1977) found that Cu uptake by barley was inversely related to the negative charge on the complexing ligand. A number of additional studies, for example Dragun *et al.* (1976) and Harrison *et al.* (1984) have demonstrated that increasing the concentration of chelating agent in the nutrient medium increases the solubility of Cu, but decreases its uptake by plants. Chelation of Mn may or may not increase availability. Sardzhveladadze and Shuvalov (1984) found that EDTA increased uptake of Mn by cotton and tea seedlings; whereas, complexes with FA have been shown to decrease Mn adsorption by plants (Karpukhin *et al.* 1984). Chelation involving siderophores plays an important role in the

Fe nutrition of plants, but whether plants take up the metal-siderophore complexes intact has not been determined (Laurie and Manthey 1994).

The uptake of essential and non-essential elements by plants varies with the element, plant type, and environmental conditions. At any given time, the concentration of a soil derived element in a plant occurs through the interaction of many processes in the soil-plant system. Despite this complexity, elemental concentration in plants generally reflects availability in soil (Jones 1991, Kabata-Pendias and Pendias 1992). Nutrient elements must be in an available chemical form before plants will take them up. Passioura and Wetselaar (1972) found that wheat roots were excluded from fertilizer bands. Elements can be in a chemically available form but be spatially unavailable for plant uptake.

Plant uptake of metal and nutrient elements brought into solution following urea addition was examined in a greenhouse experiment using six different soils and barley as the test crop. The hypothesis was that uptake of nutrient elements from plants grown in soil containing a urea band would differ from plants grown in a similar volume of soil without a band and that differences in uptake would be evidence of differences of element availability in soil. The experimental approach was to create a FRZ by placing a layer of urea treated soil within the rooting zone of barley and comparing tissue concentration and uptake of selected elements to a control. This method compares overall availability but does not distinguishing between chemical and spatial components.

It was assumed that urea fertilized plants would yield substantially more than the controls unless an N source was provided. The yield difference would make interpretation of results difficult, particularly for micronutrient elements, due to dilution/concentration effects. The controls needed to be fertilized as well, but in a way that would increase available N with minimal disturbance to other solution variables. Since the variable of greatest concern was solution pH, a neutral salt source of N, calcium nitrate (CN), was chosen. Earlier work on a Dark Brown Chernozemic soil by Goh *et al.* (1987) showed that over six years of N application, CN had relatively little impact on soil chemical and physical properties compared to urea, ammonium nitrate and ammonium sulphate. To further reduce the impact on soil solution, it was decided to provide the CN in four increments rather than as one application at the beginning of the experiment.

Materials and Methods

Soils and Fertilizers

Soil samples for use in the greenhouse were collected from the 0-10 cm depth at six Alberta Agriculture research sites in central and southern Alberta. For the sake of brevity, the soil materials used have been designated by a two-digit number in the text. The classification of the pedons sampled was, for Soils 11, 13, 14, 22, 28, and 29 respectively, Orthic Brown Chernozem, Calcareous Brown Chernozem, Dark Brown Solodized Solonetz, Orthic Black Chernozem, Gleyed Dark Gray Luvisol, and Dark Gray Solodized Solonetz.

Bulk samples were passed through a sieve with 65 mm openings and air dried in large trays. Sub-samples for characterization were taken following sieving by collecting and mixing portions from 15 to 20 places in the tray. These sub-samples were air dried and ground to pass 2.0 mm. The processed bulk sample was stored in sealed plastic pails at 4°C until the start of the experiments.

Granular fertilizer grade urea and certified grade calcium nitrate (CN) were used as N sources. Passing the fertilizer through a 2 mm screen and then a 1.7 mm screen reduced the range of urea prill sizes. Prills retained on the 1.7 mm screen were used in the experiment. Reagent grade $CaHPO_4$ and K_2SO_4 were used as P, K and S sources.

Greenhouse Experiment

The experimental design compared six soils and two fertilizer treatments. Each soil/treatment sub-unit was replicated four times in complete blocks. The first treatment was granular urea applied at a rate of 1.00 g N pot^{-1} to create an FRZ. The 1-g rate gave slightly different concentrations in each soil due to bulk density differences, but was approximately 450 mg N kg^{-1} soil.

To start each urea treatment, a 10 mm layer of fine washed sand was added to the bottom of a 2.8 L self-watering pot. A layer of soil was added on top of the sand and packed to give a final thickness of 20 mm. Urea granules were spread on the surface of the second layer. Soil for the third 50 mm thick layer was weighed into a 4 L pail. Fertilizer solution containing 0.125, 0.125 and 0.042 g pot^{-1} of P, K, and S respectively was mixed into the soil in the pail. The third layer was spread over the urea granules and packed by tapping. Twelve barley seeds (*Hordeum vulgare* cv. Tukawa) were placed on top of the soil surface and covered with a final 20 mm layer of soil. The pot was then placed on a balance and deionized water added to bring the soil to field capacity.

The CN treatments were prepared by creating the four layers as described above; however, no nitrogen was added to the surface of the second layer. Instead, CN was added in solution to the water well at the bottom of the pots in four 0.25 g N increments. The first increment was added during the initial wetting of the soil. The remaining increments were added on days 25, 36 and 46 respectively.

Pots were loosely covered with dark plastic in the greenhouse until seedlings had emerged. Thereafter they were exposed to a 16 hours light, 8 hours dark regime. Supplemental lighting was provided from 0400 to 0900 hours and from 1700 to 2000 hours every day. Lights were kept on during the 0900 to 1700 hours period if the chamber temperature stayed below 30°C. Each block of twelve pots was centered under a bank of three lights and was re-randomized every second day following emergence.

Watering was performed initially every second day by placing each pot on a balance and adding deionized water until the soil field capacity weight was regained. Towards the end of the experiment, the pots were watered daily.

Plants were harvested after 63 days. BBCH growth stage at harvest ranged from 83, early dough, to 85, soft dough depending on soil, block, and treatment. Shoots were cut off approximately 5 mm above the soil surface. They were then cut into 50 mm lengths and placed in a pre-weighed paper bag. Bags were placed in an oven at 60°C for 48 hours and then weighed. Dried samples were ground in a Wiley mill and then sealed in plastic vials until they could be analyzed. A 2 g ground sub-sample was dried at 135°C for 2 hours to determine moisture. The water content was later used to correct yield and concentration values to a dry matter basis.

Soil Analysis

Soils were characterized using standard methods. Soil pH was measured in a 2:1 water to soil suspension using a combined electrode and Fisher Acumet Model 50 pH meter (Fisher Scientific, Nepean, Ontario, Canada). Organic matter was determined by loss on ignition at 1100°C. Total N and P were determined on micro-Kjeldahl digests (McGill and Figueiredo 1993). Digests were analyzed on a Technicon Autoanalyzer II® (Technicon Instrument Corporation, Tarrytown, NY, USA) using the indophenol blue procedure for N and the ammonium molybdate-ascorbic acid procedure for P (Technicon Instrument Corporation, 1973a,b). Sand, silt and clay were determined by the hydrometer method with pre-treatment to remove SOM as described by Sheldrick and Wang (1993).

Field capacity was determined by first filling a plexiglas column (5 cm ID by 30 cm height) with soil ground to pass 2 mm. The columns were hinged lengthwise and capped on the lower end with a removable 100 μm mesh screen. Deionized water (200 mL) was added from the top and allowed to infiltrate. Following infiltration, the columns were covered, but not sealed tightly, with parafilm and allowed to equilibrate in a vertical position for 48 hours. The columns were then split and a 15 cm subsample removed from the middle of the wetted portion. This subsample was weighed, dried at 105°C for 24 hours and re-weighed.

Trace metals were extracted by the DTPA method as described by Liang and Karamanos (1993). Extracts were analyzed using the inductively coupled plasma emission spectrophotometer (ICP) described below for plant analysis. Exchangeable cations and cation exchange capacity (CEC) were determined using the ammonium acetate method described by Hendershot *et al.* (1993). In the analytical step, the ICP was used to measure Ca, Mg, K, and Na for exchangeable cations and NH_4^+ concentration was measured by autoanalyzer (Technicon Instrument Corporation 1973a).

Plant Analysis

Analysis of total N, P and Ca in samples started with digestion of 1 g samples using Association of Official Analytical Chemists (AOAC) method 976.06, standard semi-micro Kjeldahl technique (AOAC 1990a). Analytes in the digest were determined colorimetrically on an Autoanalyzer II (Technicon Instrument Corporation, Tarrytown, NY, USA). Total N was determined using the indophenol blue method, total P using the ammonium molybdate/ammonium metavanadate method, and Ca using the cresolphthalein method (Technicon Instrument Corporation 1977). Quality control (QC) was maintained by analyzing a standard sample of ground alfalfa with each block of twenty samples and comparing the values obtained to pre-set acceptance limits.

For the remaining elements, 1 g samples were first digested using the standard nitric-perchloric method (AOAC 1990b). Elemental analysis of the digests was performed on a Jobin-Yvon model JY70PLUS Inductively Coupled Plasma Spectrophotometer (ATS Scientific Ltd., Oakville, Ontario, Canada). Operating limits were determined by repeatedly analyzing blank digests and determining the standard deviation (s) for each element in the blanks (Keith *et al.* 1983). The limits of detection (LOD) and limits of quantitation (LOQ) were set at 3s and 10s respectively. Analytical values less than the LOD were recorded as below detection limit (BDL), and were treated as zero values in the statistical analysis. The instrument was calibrated using Seignory Chemical Product certified standards (SCP Scientific Ltd., St. Laurent, Quebec, Canada) diluted to appropriate ranges for each element. For QC purposes, a standard alfalfa sample and a digestion blank were included with each set of twenty digests.

Statistical Analysis

Analysis of variance was performed using SAS-PC. A separate ANOVA, as shown in Eq. 4.1 was performed for each analyte:

ANOVA Eq. 4.1

Source	n	df
(R) Blocks	4	3
(A) Soil	6	5
(B)Treatment	2	1
(AB)Soil*Treatment		5 (a-1)(b-1)
Error		33 (r-1)(ab-1)
Total	48	47 (rab-1)

A probability of Type I error of less than 5% ($p < 0.05$) was used as the separation between significant and non-significant *F* values from ANOVA. For significant treatment effects without the confounding influence of a significant interaction term, a significant *F* also indicated a significant difference between treatment means. Significant soil*treatment interactions were examined following the procedures outlined by Steel *et al.* (1997, Chapter 15) for *F* based contrasts within interactions using a single degree of freedom. For treatment within soil, contrast also served as an evaluation of the significance of mean difference as there were only two treatments. When required, differences among soil and soil*treatment means were evaluated for significance using the LSMEANS program in SAS-PC. A probability of Type I error of less than 5% ($p < 0.05$) was used as the separation between significant and non-significant *t* values from LSMEANS.

Systematic interpretation of results was performed using the protocol devised by Jarrell and Beverly (1981). This system uses qualitative differences (increase, decrease, or no change) in yield, element accumulation, and element concentration to interpret the effects of experimental factors on element availability. Qualitative difference was based on the mean of the urea treatment relative to the mean of the CN treatment within each soil. Only significantly different means ($p < 0.05$) were assigned to the increase or decrease classes. The system was applied to ten elements. Data for Al were excluded since there was no evidence of treatment effects.

Results

Soils

The soils used in this experiment covered a range of pH's from 4.6 to 7.5 (Table 4.1). Soils 11, 13 and 14 were all slightly alkaline, whereas Soils 22, 28, and 29, were slightly to strongly acidic. DTPA extractable Fe and Mn concentrations were greater in the lower pH soils. In the alkaline soils, Ca and Mg occupied a larger proportion of the exchange complex. The soils ranged in texture from loamy sand to silty clay loam. Clay, expressed as a proportion of the mineral fraction, ranged from 90 to 360 g kg $^{-1}$. Soil organic matter ranged from 21 to 76 g kg^{-1} soil. The lower pH soils tended to have higher soil organic matter.

Yield

Yields tended to be higher in the CN treatments compared to the urea treatments (Table 4.2). Both soil and treatment effects were significant in the ANOVA, but interpretation of the simple effects was confounded by the significant interaction term. Contrast of treatment means within soils showed that CN produced significantly higher yields than urea in Soils 11, 13, 14 and 22. Yields were not significantly different in Soils 28 and 29.

Concentration of Major Elements in Barley

Treatment had no significant effect on Ca concentration (Table 4.3). The soil effect was significant, but interpretation was confounded by the significant interaction term. Soil and interaction terms were significant whereas treatment was not. This suggests that Ca concentration varied by soil within one treatment, but not within the other. The range of means in CN compared to urea suggests that the significant variation likely occurred within the CN treatment. This was verified by contrast; F was significant for soil within the CN treatment but not within the urea treatment.

The soil and treatment effects were significant for the Mg concentration data. Since the interaction term was also significant, F was calculated for treatments within soils. Magnesium concentrations in plants fertilized with CN were significantly higher in Soils 28 and 29 compared to those fertilized with urea.

The soil and treatment effects for K concentration were significant. Since the interaction term was not significant, treatment means were compared across all soils. Potassium concentration was consistently higher in the urea treatment.

Analysis of variance for Na concentration showed that main effects were confounded by a significant interaction between soils and treatments. Contrasts of treatment within soils divided the response of Na to N source into three groups. In Soils 11, 14, 22, and 28, Na concentration in barley did not vary significantly with N source. In Soil 13, tissue Na was significantly higher when urea was the N source. In Soil 29, Na concentration was lower when urea was used as the N source.

The soil, treatment, and interaction effects were all highly significant for P concentration. Contrasts of treatments within soil showed that P concentrations were significantly higher in the urea treatments except for Soil 28.

For S concentration, contrasts showed significant or highly significant treatment effects within Soils 11, 13, 14 and 29. There was no significant treatment effect within Soils 22 or 28. The tissue concentrations of S were higher in the plants grown using urea in Soils 11, 13, and 14. The reverse was found in Soil 29.

Uptake of Major Elements by Barley

The block term was not significant for any of the major elements for which plant uptake was calculated and analyzed by ANOVA (Table 4.4). The main effects were significant and the interaction term non-significant for uptake of Ca, Mg, and S. This allows straight forward analysis of the treatment and soil effects. Accumulation of Ca, Mg, and S by barley grown using CN as the N source was significantly higher than by barley grown using urea.

Contrast of K uptake by treatment within soil showed that uptake was significantly higher by plants grown using CN in Soils 11, 13, 14 and 22. There was no significant treatment effect on K uptake for Soils 28 and 29. Application of the treatment within soil contrast to P uptake data showed no difference in Soils 11, 22, and 28. Phosphorus uptake was higher by plants using CN in Soils 13 and 14. It was lower in Soil 29. Comparison of Na accumulation within soils led to acceptance of the null hypothesis of no difference for all soils except Soil 29. Barley extracted more Na from Soil 29 when it was grown using CN as the N source.

Concentration of Trace Elements in Barley

Analysis of variance for the six elements listed in Table 4.5 showed that the block effect was non-significant in all cases. The soil term was significant for all elements except Fe. The treatment term was significant for B, Fe, Cu, and Mn. Significant interactions disallowed direct interpretation of the simple effects for B, Fe, Cu, and Mn. Contrast of treatments within soil was used to aid in interpretation of treatment effects for these elements. Boron concentrations were significantly higher in plants grown with urea in Soils 13, 22 and 29. B concentrations in plants grown on the remaining soils did not differ with treatment. Fe concentrations were higher in the urea treatment for plants grown in Soils 11 and 13, but did not vary significantly in the remaining soils. Concentrations of Mn were higher in plants grown on urea in Soils 11, 22, 28, and 29, but there were no differences in Soils 13 and 14. Variation of copper concentration by treatment within soil was unlike the other elements. Concentrations were higher in plants grown on urea in Soils 11, 13, and 22. They were not significantly different in plants grown on Soils 14 and 29. Copper concentration was highest in the CN treatment plants for Soil 28, the soil with the lowest pH.

Uptake of Trace Elements by Barley

Analysis of Variance on data generated for uptake of trace elements showed the effects of blocking were not significant (Table 4.6). The soil*treatment interaction term was not significant for Al, Fe, and Zn. In the case of Al, the soil effect was significant but the treatment effect was not. Accumulations of Fe and Zn were higher for plants grown using CN as the N source. Averaged across all soils the difference was 27% for Fe and 31% for Zn.

Contrasts of treatment within soil for B showed no significant treatment effect for plants grown on Soil 28. Plants grown using CN extracted more B in Soils 11, 13, and 14. For plants grown in Soils 22 and 29, more B was taken up from the urea treatment.

The pattern was similar for Mn uptake. The null hypothesis was accepted for treatments within Soil 11, but rejected for all other soils. The data suggest that Mn uptake increased with CN as the N source for plants grown in Soils 13 and 14, but was significantly less in Soils 28 and 29.

Systematic Data Interpretation

Plant data could not be interpreted with respect to availability of the element in soil in 26 of 60 cases (Table 4.7). In seventeen cases, relative increases in elemental concentration in plants grown using urea compared to CN were accompanied by reduced yield and reduced accumulation. This combination was interpreted as a concentration effect. Nine cases could be interpreted as treatment having had no effect on availability. Availability was affected by treatment in eight cases. These included five cases where increased concentration was accompanied by increased accumulation, interpreted as synergy or increased availability. There were also two cases that were interpreted as antagonism or decreased availability.

Discussion

Examining the concentration data with respect to the original hypothesis, the treatment effect was significant for most elements. Superficially, the data support rejection of the original hypothesis. Changes in element solubility in the FRZ of urea did affect availability and crop uptake. Several factors confound this simple interpretation of the data. In the final analysis, the original hypothesis can be rejected, but the influence of these confounding factors must be incorporated into that conclusion.

The first of these factors is the significant interaction between soil and treatment for most elements. Either the magnitude or the direction of the treatment response differed among soils. The difference in magnitude was expected. The concept that nutrient availability varies among soils with a range of chemical and physical attributes is universally accepted. The difference in direction of response (for example compare S concentration in Soils 11, 13, and 14 to Soil 29) is more interesting. It suggests that the relative importance of processes controlling availability differed among soils. Controlling processes were not measured directly in this experiment. Some insight into possible processes can be obtained by comparing the results with the experiments reported in earlier chapters and in the literature.

The second factor was the treatment effect on yield. Yields from urea treatments were significantly lower than those from CN treatments in four out of six soils. Symptoms observed in the greenhouse suggested that seedling damage by NH_3 was the cause of this reduction. Yield differences among soils were most likely caused by differences in soil properties, since the threshold rate at which urea causes damage in Alberta soils varies inversely with clay, soil organic matter, and soil moisture (D.C. Penney, unpublished data). Yields were similar between treatments in the two most acidic soils where the ratio of NH_3 to NH_4^+ was likely the lowest. Yield differences complicated interpretation of treatment effects on availability, particularly since the yield differences were relatively large in a number of soils.

The original premise for using plant concentration data was that concentration in plants reflects availability in soil. This relationship is the foundation for using tissue tests as a diagnostic tool. However, the relationship is modified by the diluting effects of yield on concentration Increased plant growth due to removal of a nutrient limitation or other growth factor, for example addition of an N fertilizer, can result in dilution of other non-limiting elements in the plant (Jarrell and Beverly 1981). Conversely, factors that reduce plant growth can result in increased elemental concentration in plants, the concentration effect. For the barley data, observations suggested that urea reduced yield, concentrating elements, rather than CN induced yield increases diluting elements.

Concentration/dilution effects make it difficult to ascribe differences in concentration to treatment induced changes in availability of non-limiting nutrients. The solution is to adjust limiting nutrients into the positive response or luxury feeding range. This equalizes yields and allows straightforward interpretation of concentration data. The decision to use CN, an N source that perturbs soils to a much lesser extent than urea, as the comparative treatment, rather than an unfertilized control, was based on this requirement for equal yields. The first exception to this requirement, when both yield and concentration increase, did not apply to any of the data sets. The second exception when yield decreases but concentration and accumulation increase was observed in two data sets. As CN treatments out yielded urea treatments in four out of six soils, the interpretation of the data with respect to the original hypothesis was difficult except in Soils 28 and 29. In these two soils, interpretation was straightforward. Yields were not significantly different. Therefore, differences in concentration were attributable to differences in availability. Non-interpretable data sets could be broken into two groups. The first group contained data sets that could not really occur. For example, accumulation or yield did not change, but concentration did. These arose because only statistically significant mean differences were assigned to the increase or decrease classes. Assignment of non-significant differences, particularly for the accumulation values, to the no difference class confounded the interpretation in these cases. The second group of non-interpretable data was composed of possible combinations –for example, decreased accumulation and decreased yield with no concentration change– from which no insight into availability could be extracted.

In the interpretable data sets, urea addition decreased Mg and Cu availability in Soil 28. The decrease in Mg availability was consistent with the formation of $MgCO_3$ in the FRZ of urea as reported by Kissel *et al.* (1988). It was also consistent with the reduction in solution Mg found in the soil solution experiments reported in Chapter 2 and 3. With respect to Cu, Soil 28 had the lowest initial pH and would thus have had the greatest pH change in the FRZ zone. Increased complexation with soil organic matter due to increased pH could account for reduced availability, but so could ion pairing with NH_3 or OH^- and/or $CuCO_3$ precipitation.

In barley grown on Soils 22 and 29, the data suggest that the availability of B increased when urea was the N source. Although B normally occurs as an anion or non-dissociated H_3BO_3 in soil solution, it may complex with cis-hydroxyl groups on organic matter (Gupta *et al.* 1985, Evans 1987). Alternatively, organically bound B may also be released into the soil solution during turnover of microbial biomass (Gupta *et al.* 1985). The results presented in Chapter 3 showed that urea increased B concentration in the soil solution relative to the control, but relative to other elements or SOC the increases were small.

Availability of Mn increased in the urea treatments of Soils 22, 28 and 29. This may be linked to increased SOC levels during the urea hydrolysis phase as reported in Chapter 3 or, as reported by Petrie and Jackson (1984a,b), the acidifying effects of nitrification on Mn availability and uptake. The barley data reflect uptake over the whole season and thus gives no indication of how urea induced an increase in Mn availability. However, consider the following. The increase in soil pH caused by urea hydrolysis would have increased the formation of Mn-organic matter complexes. These complexes would be mobile as the organic matter was in solution. Diffusion and/or mass flow to the roots would tend to move these Mn-complexes out of the FRZ. Once in the rhizosphere or regions of the FRZ where nitrification had acidified soil solution, complexes would tend to dissociate releasing available Mn^{2+}.

Conclusions

Yield differences between the urea and CN treatments confounded interpretation of most of the data from this experiment. Growing barley in contact with a urea band did induce changes in plant availability of several elements in individual soils but no general trend emerged. The most consistent of these changes was the increase in Mn availability in the three acidic soils. The changes in availability as experienced by the plants were not of the magnitude observed in soil solution from earlier experiments with many of these same soils. Based on what was observed in this experiment, changes in availability may be detectable at a statistically significant level, but availability did not appear to be altered in ways that would be considered agronomically significant.

Table 4.1. Chemical and physical characteristics of soils used in greenhouse experiment.

Soil No.	pH	Organic Matter	Total N	Total P	Sand	Silt	Clay	Field Capacity	Saturation
			$g\ kg^{-1}$			$g\ kg^{-1}$		$kg\ kg^{-1}$	
11	7.1	24	1.1	0.7	810	100	90	0.152	0.261
13	7.5	21	1.0	0.4	650	200	150	0.187	0.343
14	7.5	47	2.1	0.6	270	400	330	0.262	0.502
22	6.2	76	3.1	0.6	380	370	250	0.302	0.495
28	4.6	50	2.0	0.4	190	450	360	0.343	0.544
29	5.5	62	2.3	0.5	240	540	220	0.308	0.578

	Extractable Trace Metals				Exchangeable Cations				
	Fe	Cu	Zn	Mn	Ca	Mg	Na	K	CEC (+)
		$\mu mol\ kg^{-1}$					$mmol\ kg^{-1}$		
11	110	4.4	29	74	48.4	5.6	2.0	7.0	80
13	75	7.4	22	78	55.6	13.8	3.0	11.1	120
14	98	21	12	108	123.7	20.6	3.0	15.2	196
22	785	15	46	418	63.4	11.8	1.8	12.8	311
28	2400	14	8	340	60.6	12.1	1.8	4.1	277
29	2600	6.9	89	407	70.0	8.4	0.8	2.7	227

Table 4.2. Dry matter yield of barley grown with urea or calcium nitrate as the nitrogen source.

Soil No.	Barley Shoots		
	Urea	Calcium Nitrate	Mean Difference[x]
	g pot^{-1}		*P*
11	8.6	14.3	0.0005
13	7.3	17.0	0.0001
14	13.7	21.9	0.0001
22	16.0	25.2	0.0001
28	11.4	13.1	ns
29	11.8	9.3	ns

Source	ANOVA
	P[y]
Block	ns
Soil(A)	0.0001
Treat(B)	0.0001
AB	0.0003

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[x] Probability of Type I error based on LSMEANS (paired t-test) in SAS. Value of t was deemed non-significant (ns) if $p > 0.05$.

[y] Probability of Type I error based on F from ANOVA. F was deemed non-significant (ns), if $p > 0.05$.

Table 4.3. Concentration of major elements in barley grown using urea or calcium nitrate as the N source.

Soil No.	Concentration in Barley Shoots[x]																	
	Ca			Mg			K			Na			P			S		
	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN
	mmol kg^{-1}																	
11	129		153	53		63	646		572	6		4	120	**	80	25	*	18
13	169		112	94		77	450		425	21		8	89	**	64	36	**	22
14	164		136	78		84	549		510	17		10	87	**	67	28	*	21
22	168		121	70		70	592		514	4		3	110	**	78	31		28
28	161		182	86	*	114	353		322	27		26	76		82	24		23
29	173		242	76	**	126	246		221	11		28	75	**	48	28	**	46
Treat Mean							473	**	427									

Source	ANOVA					
	P^y					
Block	ns	ns	ns	ns	ns	ns
Soil A	0.0259	0.0001	0.0001	0.0001	0.0001	0.0001
Treat B	ns	0.023	0.0001	ns	0.0001	0.026
AB	0.0416	0.015	ns	0.0003	0.0001	0.0001

[x] Treatment means and treatment means within soils for each element are different at $p < 0.05$ or $p < 0.01$ if separated by * or ** respectively. Means compared using LSMEANS (paired t-test) in SAS.

[y] Probability of Type I error based on F from ANOVA. F. F was deemed non-significant (ns), if $p > 0.05$.

Table 4.4. Uptake of major elements in barley grown using urea or calcium nitrate as the N source.

Soil No.	Accumulation in Barley Shoots[x]																	
	Ca			Mg			K			Na			P			S		
	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN
	mmol pot⁻¹																	
11	1.09		2.18	0.45		0.90	5.45	**	8.17	0.05		0.05	1.06		1.14	0.21		0.26
13	1.18		1.92	0.66		1.32	3.26	**	7.25	0.14		0.13	0.65	**	1.09	0.26		0.37
14	2.13		2.98	1.02		1.83	7.41	**	11.2	0.22		0.21	1.18		1.46	0.38		0.46
22	2.68		3.02	1.12		1.76	9.48	**	12.9	0.06		0.09	1.80		1.94	0.49		0.71
28	1.83		2.39	0.98		1.49	4.02		4.20	0.31		0.34	0.86		1.07	0.28		0.30
29	2.04		2.25	0.90		1.17	2.87		2.05	0.13	**	0.22	0.87	**	0.34	0.33		0.43
Treat Mean	1.83	**	2.45	0.86	**	1.41										0.32	**	0.42
Source	ANOVA																	
	p[y]																	
Block	ns			ns			ns			ns			ns			ns		
Soil A	0.0001			0.0001			0.0001			0.0001			0.0001			0.0001		
Treat B	0.0001			0.0001			0.0001			0.0164			0.0094			0.0001		
AB	ns			ns			0.0001			0.0055			0.0019			ns		

[x] Treatment means and treatment means within soils for each element are different at $p < 0.05$ or $p < 0.01$ if separated by * or ** respectively. Means compared using LSMEANS (paired t-test) in SAS.

[y] Probability of Type I error based on F from ANOVA. F. F was deemed non-significant (ns), if $p > 0.05$.

Table 4.5. Concentration of trace elements in barley grown using urea or calcium nitrate as the N source.

Soil No.	Concentration in Barley Shoots[x]																
	Al		B			Fe			Cu			Zn			Mn		
	Urea	CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN
	$\mu mol\ kg^{-1}$																
11	762	798	622		525	856	**	547	37	**	26	452		319	750	**	393
13	816	485	887	*	725	1057	**	587	48	*	42	436	*	276	619		461
14	1320	1300	703		728	759		705	56		53	192		158	526		641
22	706	654	1260	**	685	663		587	44	**	31	381		360	1620	**	411
28	1040	704	1010		889	784		721	34	**	53	326		461	2167	**	1510
29	530	673	1110	**	858	641		800	27		22	472		550	1355	**	334

	Critical Tissue Concentration Ranges[y]					
	Al	B	Fe	Cu	Zn	Mn
Deficient		500-1000	<900	30-80	150-300	270-450
Sufficient		1000-2000	2000-9000	80-480	400-2200	360-5400
Toxic	>4000	>4500	>9000	320-1600	1500-6000	5400-9000

Source	ANOVA					
	P^{z}					
Block	ns	ns	ns	ns	ns	ns
Soil A	0.0108	0.0001	ns	0.0001	0.0002	0.0001
Treat B	ns	0.0001	0.0075	0.0179	ns	0.0001
AB	ns	0.0003	0.0234	0.0001	ns	0.0001

[x] Treatment means and treatment means within soils for each element are different at $p < 0.05$ or $p < 0.01$ if separated by * or ** respectively. Means compared using LSMEANS (paired t-test) in SAS.

[y] Critical values assembled from Jones (1991), Kabata-Pendias and Pendias (1992), and Alberta Agriculture, Food and Rural Development data (unpublished).

[z] Probability of Type I error based on F from ANOVA. F was deemed non-significant (ns), if $p > 0.05$.

Table 4.6. Uptake of trace elements in barley grown using urea or calcium nitrate as the N source.

Soil No.	Accumulation in Barley Shoots[x]																	
	Al			B			Fe			Cu			Zn			Mn		
	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN	Urea		CN
	µmol pot^{-1}																	
11	6.5		11.4	5.3	*	7.5	7.2		7.8	0.31		0.37	3.8		4.5	6.3		5.6
13	6.3		8.4	6.5	**	12.3	7.4		10.2	0.35	**	0.72	3.3		4.7	4.6	*	7.9
14	17.2		28.5	9.5	**	15.9	10.2		15.5	0.76	**	1.17	2.6		3.4	7.2	**	14.0
22	11.3		16.5	20.2	*	17.2	10.6		14.8	0.71		0.79	6.1		9.1	25.9	**	10.3
28	11.8		9.2	11.5		11.6	9.0		9.4	0.39	**	0.70	3.7		6.0	24.7	**	19.8
29	6.0		6.2	13.0	*	8.0	7.5		7.4	0.31		0.21	5.6		5.1	15.9	**	3.3
Treat Mean							8.6	*	10.9				4.2	**	5.5			

Source	ANOVA					
	P^{y}					
Block	ns	ns	ns	ns	ns	ns
Soil A	0.0140	0.0001	0.0022	0.0001	0.0001	0.0001
Treat B	ns	0.0765	0.0347	0.0001	0.0003	0.0001
AB	ns	0.0003	ns	0.0073	ns	0.0001

[x] Treatment means and treatment means within soils for each element are different at $p < 0.05$ or $p < 0.01$ if separated by * or ** respectively. Means compared using LSMEANS (paired t-test) in SAS.

[y] Probability of Type I error based on F from ANOVA. F was deemed non-significant (ns), if $p > 0.05$.

Table 4.7. Interpretation of elemental availability based on accumulation, yield, and concentration for barley grown in the greenhouse, urea relative to CN treatment.

Major Elements

Soil	Ca				Mg				K				P				S			
	Ac[x]	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int
11	↓[y]	↓	0	X[z]	↓	↓	0	X	↓	↓	↑	C	0	↓	↑	C	0	↓	↑	C
13	↓	↓	↑	C	↓	↓	0	X	↓	↓	0	X	↓	↓	↑	C	0	↓	↑	C
14	↓	↓	0	X	↓	↓	0	X	↓	↓	0	X	↓	↓	↑	C	0	↓	↑	C
22	0	↓	0	X	↓	↓	0	X	↓	↓	↑	C	0	↓	↑	C	↓	↓	0	X
28	↓	0	0	X	↓	0	↓	A-	0	0	0	N	0	0	0	N	0	0	0	N
29	0	0	↓	X	0	0	↓	X	0	0	0	N	↑	0	↑	A+	0	0	↓	X

Trace Elements

	B				Fe				Cu				Zn				Mn			
	Ac	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int	Ac	Yld	Con	Int
11	↓	↓	0	X	0	↓	↑	C	0	↓	↑	C	0	↓	0	X	0	↓	↑	X
13	↓	↓	↑	C	0	↓	↑	C	↓	↓	↑	C	↓	↓	↑	C	↓	↓	0	X
14	↓	↓	0	X	↓	↓	0	X	↓	↓	0	X	0	↓	0	X	↓	↓	0	X
22	↑	↓	↑	A+	↓	↓	0	X	0	↓	↑	C	↓	↓	0	X	↑	↓	↑	A+
28	0	0	0	N	0	0	0	N	↓	0	↓	A-	↓	0	0	X	↑	0	↑	A+
29	↑	0	↑	A+	0	0	0	N	0	0	0	N	0	0	0	N	↑	0	↑	A+

[x] Sub-column heading abbreviations are accumulation (Ac), yield (Yld), concentration (Con), and interpretation (Int).

[y] Relative comparison symbols used in body of table are decrease (↓), increase (↑), and no difference (0).

[z] Symbols are not interpretable (X), concentration effect (C), no effect (N), increased availability (A+), decreased availability (A-).

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CHAPTER 5

UPTAKE OF COPPER AND MANGANESE FERTILIZERS BY BARLEY GROWN USING UREA AS THE NITROGEN SOURCE

Introduction

In Western Canada, urea is the most commonly used nitrogen fertilizer (Korol and Rattray 2000). In addition to use as a sole source of N, it is widely used as an N source in dry bulk blends and liquid formulations. Part of its popularity is due to its compatibility with direct seeding systems. Use of micronutrient fertilizers has risen on the prairies in recent years. Of particular note, has been the increase in Cu application following recognition of Cu deficiency in prairie soils (Kruger *et al.* 1985, Solberg *et al.* 1993). Manganese use is not as common as Cu. Manganese deficiency has most commonly associated with oat production, but affects a wider range of crops particularly on organic soils (Karamanos *et al.* 1984,1985, Reid 1982).

The experiments described in chapter 2 and 3 showed that soil solution within the fertilizer reaction zone (FRZ) formed by urea granules differed chemically from solution in control soils. Solution concentrations of a number of elements, including Cu and Mn, were considerably higher inside the FRZ. Other important changes included increased pH and higher concentrations of soluble organic carbon (SOC). In chapter 4, elemental concentrations were measured in barley grown in contact with a urea FRZ and compared to concentrations in barley fertilized with calcium nitrate (CN) solution. Nitrogen source had a significant effect on elemental concentration for a variety of macro- and micronutrient elements. The results suggested that in some soils these changes within the FRZ of urea affected the plant availability of Cu and Mn.

Changes in pH affect Cu and Mn differently. Sims (1986) reported that increasing soil pH shifted Mn from exchangeable to organically bound and MnO forms but did not alter Cu distribution. Shuman (1986) reported that organically bound Mn was increased and Cu decreased slightly by increasing lime additions. Both researchers found that crop uptake correlated with soil pH for Mn but not for Cu. Liang *et al.* (1991) measured copper fractions in twenty-seven Saskatchewan soils. They found that soil pH was correlated (r = 0.43*) with acid extractable Cu, but not with any of the other fractions measured. McLaren *et al.* (1973, 1981) found that at high Cu levels, increasing pH increased adsorption of Cu in oxide fractions, but had little effect when Cu levels were low.

Shuman (1988) measured Cu and Mn distribution in four soils following addition of wheat straw. He found that Mn converted from less soluble oxide forms to more soluble and potentially available exchangeable and organic forms while Cu distribution was not affected. He attributed this change in part to Mn reduction accompanying organic matter degradation. McGrath *et al.* (1988) found that total concentration of Cu and Mn in soil solution was not greatly affected, but Cu^{2+} activity decreased and SOC increased as peat was added to a mineral soil. Additions of soluble humic materials to nutrient solutions have been shown to reduce plant uptake of both Cu and Mn (de Kreij and Basar 1995). The reduced uptake was accompanied by reduced solution concentrations of Mn, but Cu concentrations did not change.

Whether fertilizing with urea alters availability and plant uptake of Cu and Mn fertilizers has not been examined specifically. In a two-year study, Soon *et al.* (1997) reported that Cu concentration in wheat increased with N rate. The N source was coincidentally urea. Darusman *et al.* (1991) found that after 20 years of application, urea additions increased DTPA extractable Cu and Mn compared to the unfertilized control but not compared to other fertilizer N sources. They attributed the differences to soil acidification brought about by nitrification of NH_4^+.

Fertilizer sources of Cu and Mn include soluble sulfate and chloride salts, sparingly soluble oxides, and a wide array of chelated formulations (Martens and Westermann 1991). The fate of these different fertilizer forms in soils differs considerably. Liang *et al.* (1991) found that one-week after addition to seven soils, 5 mg Cu kg^{-1} added as $CuSO_4$ had been largely redistributed into oxide and organic matter fractions. The amounts redistributed into the more available exchangeable and specifically adsorbed fractions were relatively minor. Conversely, Miller *et al.* (1987) reported that when $CuSO_4$ was added at a rate of 48 mg Cu kg^{-1}, a high proportion was found in exchangeable and specifically adsorbed forms after 29 days. Karamanos *et al.* (1986) compared CuO, $CuSO_4$, and Cu-chelate sources for correcting deficiencies in cereal and oilseed crops in prairie soils. They found that CuO did not correct deficiency in the year of application but did the following year, suggesting that it is relatively slow to redistribute into available fractions.

Although, urea use is widespread and micronutrient use is increasing, the interaction of urea with micronutrient fertilizer has not been specifically investigated in prairie soils. Two experiments were performed to determine if urea interacted with micronutrient fertilizers in ways that altered plant availability and uptake of the micronutrients. In a greenhouse experiment, Cu and Mn were added to soil as soluble salts and incubated for thirty days. Granular urea was then added to create a FRZ and the soil cropped to barley. Concentration of Cu and Mn in harvested plants was compared to concentrations in control treatments in which calcium nitrate (CN) added in solution was the nitrogen source. The specific hypothesis was that urea addition to soil had no effect on the availability of previously applied Cu and Mn as measured by plant uptake. The second experiment was performed in the field on an Eluviated Black Chernozem. Copper fertilizer in the form of a soluble salt, an insoluble oxide, and a soluble synthetic chelate was added in a concentrated placement with urea. Concentration of Cu in barley at heading and at maturity was used as the indicator of availability. Treatments with no copper, CN as the N source, or no nitrogen were included for comparative purposes. The specific hypothesis of this second experiment was that adding different forms of Cu fertilizer has no effect on Cu availability in the FRZ of urea.

In addition to measuring plant concentrations of macro- and micronutrient elements specifically added as fertilizer, concentrations of a number of other elements were also measured. Thus, a secondary objective for both experiments was to further examine the plant availability of a range of soil derived, as opposed to fertilizer derived, elements in the FRZ of urea.

Materials and Methods

Greenhouse Experiment

Bulk surface samples, 60 L by volume, were collected after harvest from two Alberta Agriculture research sites one in central Alberta near Barrhead (Dark Gray Luvisol) and the other in southern Alberta near High River (Eluviated Black Chernozem). These samples were air dried in 1.5 by 2.5 m trays. Large aggregates were broken by passing the soil through a 5 mm screen. Following sample mixing, sub-samples for characterization were taken by collecting and mixing soil from 15 to 20 places in the tray and grinding to pass 2.0 mm. The processed bulk sample was sealed in 20 L plastic pails and stored at 3°C until the start of the experiments.

The experiment was set up using a split-split plot design in four replicates. The two soils were main plots. Three micronutrient fertilizer treatments were compared as sub-plots within the main plots. Two sources of nitrogen, urea and calcium nitrate, were compared at the sub-subplot level.

The sub-plots were set up by first mixing three 20 L pails of each soil in a rotating soil mixer. Thirty-six 1500 g (oven dry basis) sub-samples were weighed into 4 L plastic pails. The 4 L pails were split in three groups of twelve. Copper sulphate was added in 10 mL of solution at a rate of 400 μmol Cu kg^{-1} soil (25 mg kg^{-1} soil) to one group of pails. Manganese sulphate was added at 450 μmol Mn kg^{-1} (25 mg kg^{-1}) soil to the second group. The third group received 10 mL of deionized water. Each pail was mixed thoroughly and then the soil adjusted to field capacity water content with deionized water. These sub-treatments were randomized and incubated in the dark for thirty days at room temperature (18-22°C). Lids were removed every two days to allow air exchange. Soils within the pails were mixed on day 10 and day 20 and the sub-treatments re-randomized. On day 30, the lids were removed and the soils dried to the point where they were easy to handle.

Dividing each subplot of twelve pails into three groups of four set up sub-subplots. One group of four was set aside as the control. Urea pellets equivalent to 200 mg N kg^{-1} soil was added to the pails of the second group and mixed. Calcium nitrate was added in 10 mL solution at a rate of 200 mg N kg^{-1} soil to the third group. All groups then received P, K, and S in 10 mL solution at rates of 50, 50, and 20 mg kg^{-1} soil respectively. Soils within pails were then mixed to evenly distribute the fertilizer.

Seeding each of the sub-subplots was performed by first adding 600 g fine washed sand to the bottom of a 2.5 L self-watering pot. The soil from a sub-subplot pail was then added on top of the sand. A 1 cm layer of untreated soil was added by weight on top and twelve barley (*Hordeum vulgare* cv. Tukawa) seeds placed on the soil surface. The seeds were covered with a second 1 cm layer, added by weight, of untreated soil. Total weight for pot and soil at field capacity water was calculated. Pots were adjusted to field capacity by adding distilled water until the appropriate weight was reached. Treatment-soil combinations were assigned to blocks at this point.

Pots were placed in a greenhouse and covered loosely with dark plastic until emergence. There after they were grown in a 16 h light, 8 h dark environment. Supplemental lighting was provided throughout the light period, 0400 hours to 2000 hours. Chamber temperature was maintained between 25 and 30°C during the light period and between 20 and 25°C during the dark period. Each block of 12 pots was centered under a bank of lights. Pots within each block were re-randomized every second day. Pots were watered by placing the pot on a balance and adding sufficient distilled water to the self-watering well to bring the soil back to field capacity. Pots were watered every second day initially. As the plants grew, the regime was changed to daily watering.

Plants were harvested 74 days after seeding at BBCH growth stage 87, the hard dough stage. Plants from each pot were cut off approximately 5 mm above the soil surface. They were then cut into 50 mm lengths and placed in a pre-weighed paper bag. Bags were placed in an oven at 60°C for 48 hours and then weighed. Dried samples were ground in a Wiley mill and then sealed in plastic vials until they could be analyzed. A ground sub-sample was dried at 105°C for 24 h and later used to correct yield and analyte measurements to a dry matter basis. The soils within the pots were allowed to air dry. The soil from the layer receiving N fertilizer was separated from the sand layer below and the surface layer above, ground to pass 2 mm, and stored in plastic bags until analysis could be performed.

Field Experiment

The field experiment was a 3 X 4 factorial using a randomized complete block in four replicates. It was performed on an Eluviated Black Chernozem at the University of Alberta's Ellerslie farm. Three nitrogen sources (no-nitrogen, urea, and calcium nitrate) and four copper sources (no Cu, $CuSO_4 \cdot 5H_2O$, CuO, and Cu-ETDA) were combined to give twelve treatment plots per block.

Fertilizers were blended in the laboratory and then placed as nests within the treatment plots, ten nests to a plot. For those plots requiring Cu treatments, the appropriate amount of product to provide 0.300 g Cu was mixed with 150 g finely ground oven dried soil in a 4 L pail. Ten 10 g portions of the soil-copper mix were weighed into coin envelopes. To those treatments requiring nitrogen, urea (1.00 g) or CN (2.70 g) was weighed out and transferred into the coin envelopes. The envelopes were shaken to mix the contents and then stored in sealed plastic bags to prevent deliquescence prior to use. Final rates were 0 or 4.6 g N plot^{-1} and 0 or 0.2 g Cu plot^{-1}. This is equivalent to 115 kg N ha^{-1} and 5 kg Cu ha^{-1} based on a paired row arrangement with fertilier placed in rows 0.4 m apart.

The day of plot establishment, P, K, and S were broadcast across the plot area at rates of 30, 50, and 20 kg ha^{-1} respectively. The plot area was then rototilled to a depth of approximately 0.10 m and packed with coil packers to provide a firm seedbed. The plot area was divided into four quadrants to form replicates. Twelve 1.4 m by 0.6 m plots separated by 1.2 m borders were marked out in each replicate. The twelve fertilizer combinations were then assigned randomly within each block.

Fertilizer was applied along a 1 m line of ten nests centered within the plot. Nests were centered at a horizontal spacing of 100 mm. A wooden template was used to insure uniform spacing of nests and seed-rows. Each nest was created by removing a 25 mm diameter soil core to a depth of 100 mm through the template. The appropriate fertilizer treatment was added from the prepared envelopes through a funnel. The soil core was returned to the hole and packed lightly. Two rows of barley (*Hordeum vulgare cv.* Tukawa) 1 m long were planted 100 mm to either side of the row of fertilizer nests.

Planting depth was 25 mm. Seeding rate was based on a target density of 250 plants m^{-2}. Seed for each row had been counted into envelopes beforehand to insure the same number of seeds were planted in each plot. Seedrows were packed following seeding by placing a 1.2 m long plank over the row and walking up and down the plank.

Blocks 1 and 4 were fertilized and seeded on May 29. Rain during the afternoon of May 29 delayed seeding of Blocks 2 and 3 until May 31. The borders were seeded to barley on May 31 using a 1.2 m double disk drill with on row packing. Seeding depth was 20 mm and row spacing 0.2 m.

One 1 m row from each plot was harvested on July 29. BBCH growth stages at harvest ranged from 47, flag leaf sheath opening, to 51, tip of inflorescence emerging from sheath, depending on block and treatment. Plants were harvested by cutting stems 5-10 mm above the soil surface. Plants were placed in plastic bags and stored in coolers over night. The following days plants were washed with distilled water to remove any soil particles, placed in pre-weighed paper bags and dried at 50°C until stable weights were obtained. Plants were then ground in a Wiley mill and stored in plastic vials until analyzed. Sample moistures for correction of yield and concentration measurements to a dry matter basis were determined by drying 2 g sub-samples in a 135°C oven for two hours.

The second row from each plot was harvested on September 5. BBCH growth stage at harvest ranged from 87 to 89, hard dough to fully ripe. Plants were cut at 15-20 mm above the soil surface, washed with distilled water, and placed in cloth bags. The samples were dried in the bags at 50°C until stable weights were obtained and then threshed to determine grain and straw yield. Grain samples were ground in a cyclone mill and straw samples in a Wiley mill. Ground samples were stored in plastic vials until analysis. Sample moisture for correction of yield and concentration measurements to a dry matter basis was determined as described earlier.

Soil Analysis

Soils characteristics (Table 5.1) were determined using standard methods. Soil pH was measured in a 2:1 water to soil suspension using a combined electrode and Fisher Acumet Model 50 pH meter (Fisher Scientific, Nepean, Ontario, Canada). Organic matter was determined by loss on ignition at 1100°C. Total N and P were determined on micro-Kjeldahl digests (McGill and Figueiredo 1993). Digests were analyzed on a Technicon Autoanalyzer II® (Technicon Instrument Corporation, Tarrytown, NY, USA) using the indophenol blue procedure for N and the ammonium molybdate-ascorbic acid procedure for P (Technicon Instrument Corporation, 1973a,b). Sand, silt and clay were determined by the hydrometer method with pre-treatment to remove SOM as described by Sheldrick and Wang (1993).

Field capacity was determined by first filling a Plexiglas column (5 cm ID by 30 cm height) with soil ground to pass 2 mm. The columns were hinged lengthwise and capped on the lower end with a removable 100 μm mesh screen. Deionized water (200 mL) was added from the top and allowed to infiltrate. Following infiltration, the columns were covered, but not sealed tightly, with parafilm and allowed to equilibrate in a vertical position for 48 hours. The columns were then split and a 15 cm subsample removed from the middle of the wetted portion. This subsample was weighed, dried at 105°C for 24 hours and re-weighed.

DTPA extractable Cu, Mn, Fe, and Zn were extracted as described by Liang and Karamanos (1993). Extracts were analyzed using the ICP described below for plant analysis. Exchangeable cations and cation exchange capacity (CEC) were determined using the ammonium acetate method described by Hendershot *et al.* (1993). In the analytical step, ICP was used to measure Ca, Mg, K, and Na for exchangeable cations and NH_4^+ concentration for cation exchange capacity was measured by autoanalyzer (Technicon Instrument Corporation 1973a).

Plant Analysis

Analysis of total N, P and Ca in samples started with digestion of 1 g samples using standard semi-micro Kjeldahl technique (AOAC 1990a). Analytes in the digest were determined colorimetrically on an Autoanalyzer II (Technicon Instrument Corporation, Tarrytown, NY, USA). Total N was determined using the indophenol blue method, total P using the ammonium molybdate/ammonium metavanadate method, and Ca using the cresolphthalein method (Technicon Instrument Corporation 1977).

Other elements were determined by first digesting 1.000 g samples in a standard nitric-perchloric digest (AOAC 1990b). A Jobin-Yvon model JY70PLUS Inductively Coupled Plasma Spectrophotometer (ATS Scientific Ltd., Oakville, Ontario, Canada) was used to analyze the digests. Operating limits of detection (LOD) and limits of quantitation (LOQ) were determined for each element using the method of Keith *et al.* (1982). The instrument was calibrated before each run using Seignory Chemical Product certified standards (SCP Scientific Ltd., St. Laurent, Quebec, Canada) diluted to appropriate ranges for each element. Analytical values less than the LOD were recorded as below detection limit (BDL), and were treated as zero values in the statistical analysis.

Statistical Analysis

Analysis of variance for the greenhouse experiment was performed using SAS-PC. A separate ANOVA was performed for each analyte. The model for the greenhouse experiment was a split-split plot (Eq. 5.1). The field experiment was analyzed as a 3 X 4 factorial in a randomized complete block design of four replicates (Eq. 5.2). In both ANOVA's, main and interaction effects were taken as significant if the probability of Type I error was less than 5% ($p<0.05$). Significant differences among main effect means were determined using Tukey's studentized range test in cases where interaction terms were not significant. Tukey's studentized range test controls Type I error but tends to increase the Type II error rate. For certain analytes, interactions were significant. In these cases, comparisons of interest suggested by the data were made. F was calculated for specific comparisons within the interaction terms following Steel *et al.* (1997, Chapter 15). When required the probability of significant difference between interaction means were separated using the LSMEANS procedure in SAS.

ANOVA Eq. 5.1

Source	n	df
(R) Blocks	4	3 (r-1)
(A)Soils	2	1 (a-1)
Mainplot Error		3 (r-1)(a-1)
(B) Micronutrients	3	2 (b-1)
(AB) Soil*Micronutrients		2 (a-1)(b-1)
Subplot Error		12 a(r-1)(b-1)
(C) Nitrogen	2	1 (c-1)
(AC) Soil*Nitrogen		1 (a-1)(c-1)
(BC) Micronutrients*Nitrogen		2 (b-1)(c-1)
(ABC) Soil*Micronutrients*Nitrogen		2 (a-1)(b-1)(c-1)
Sub-Subplot Error		18 ab(r-1)(c-1)
Total	48	47 (rabc-1)

ANOVA Eq. 5.2

Source	n	df
(R) Blocks	4	3
(A) Copper	4	3
(B) Nitrogen	3	2
(AB) Copper*Nitrogen		6 (a-1)(b-1)
Error		33 (r-1)(ab-1)
Total	48	47 (rab-1)

Results

Greenhouse Experiment

Barley grown on the High River soil significantly out yielded barley grown on the Barrhead soil in all treatments (Figure 5.1a). Yield was higher when urea was the N source. Soil type had a significant effect on yield (Table 5.2). At the subplot level, neither Mn nor Cu addition had a significant effect on yield, but at the sub-subplot level, the nitrogen source effect was highly significant. The F value calculated for the soil effect was highly significant for Mn concentration in barley. The F value for nitrogen was significant. Values of F for all other terms were not significant. Since there are only two soils at the main plot level and two N sources at the sub-subplot level interpretation is straightforward. Manganese concentration was higher, 22% on average, in barley grown on the High River soil compared to the Barrhead soil. This soil difference was evident and consistent when comparing soils within treatments (Figure 5.1b). The nitrogen source effect was less clearly visible when examining the individual treatment (micro*nitrogen) means. The Mn concentration in barley averaged across all urea treatments was 857 μmol kg^{-1} compared to 733 μmol kg^{-1} for CN. Although adding Mn had no effect on Mn uptake, comparing Mn concentrations in the Cu treatments suggests a urea-$CuSO_4$ interaction that was not evident in the ANOVA analysis.

Averaged across all treatments Cu concentration in barley grown on the Barrhead soil was 59 μmol kg^{-1} compared to 41 μmol kg^{-1} for High River. In the ANOVA for Cu concentration, the soil effect was highly significant. The difference due to soil was consistent across all nitrogen-micronutrient combinations and significant for all combinations except CN (Figure 5.1c). At the subplot level, the micronutrient effect was highly significant, whereas the interaction term was not significant. The data show that Cu concentrations were elevated in plants from the sub-plot treatments that received Cu fertilizer (Figure 5.1c). Nitrogen source was not significant with respect to copper concentration.

The soil term was significant in post harvest soil samples for pH, Fe, Cu, Mn, and Zn (Table 5.3). The micronutrient effect was significant in the ANOVA's for Cu and Mn. While the N source effect was significant for pH, Fe, and Mn. Significant interactions prevented straight forward interpretation of the main effects. Soil pH means were significantly higher in the High River soil compared to the Barrhead soil across all treatments (Figure 5.2a), but the difference was small, less than 0.2 units on average. Comparing N source the only significant mean difference in pH was between CN+Cu and urea+Cu. The difference was 0.1 pH unit. Extractable micronutrient levels were higher in the High River than in the Barrhead soil. Extractable Mn was higher in the urea treatment than in the CN treatment when no micronutrient fertilizer was added with the nitrogen; when Mn was added; and when Cu was added (Figure 5.2b). Copper fertilizer increased extractable Cu (Figure 5.2c). Extractable Cu in the treatments fertilized with urea did not change relative to the CN treatments. Extractable Fe and Zn (data not shown) were similar to Mn in that extractable levels were increased in urea treatments relative to CN treatments.

With respect to other nutrient elements in barley, the soil effect was not significant for Fe concentration (Table 5.2). It was significant for of Ca, Mg, K, P, S, B, and Zn. In the latter group, with the exception of B, either the soil*micronutrient (K and S) or soil*nitrogen (Ca, Mg, and Zn) term was also significant. Dealing first with B, mean B concentration in barley grown on the Barrhead soil was 974 μmol B kg^{-1} compared to 486 B μmol kg^{-1} in the High River soil. For K and S, the simple micronutrient effect was not significant suggesting that the added micronutrients affected K and S concentration in barley grown on the two soils differently. Potassium concentration was significantly higher in treatments receiving Mn grown on the Barrhead soil (328 mmol K kg^{-1}) compared to control (306 mmol K kg^{-1}) and Cu amended (307 mmol K kg^{-1}) treatments. Potassium concentration was lower in barley grown on Mn treatments in the High River (399 mmol K kg^{-1}) soil compared to control (436 mmol K kg^{-1}) and Cu amended (421 mmol K kg^{-1}) treatments. Sulphur concentration in barley grown on Mn amended Barrhead soil was 57 mmol S kg^{-1}, significantly higher than the concentrations in the control and Cu amended treatments at 44 and 47 mmol S $kg^{-}1$ respectively. The S concentration in plants grown on High River soil did not differ among micronutrient treatments. Mean concentration across all treatments was 39 mmol S kg^{-1}.

Relative to CN, concentrations of Ca and Mg were significantly higher and K and P significantly lower in barley grown on the Barrhead soil when urea was the N source

(Figure 5.3a). In urea fertilized plants grown on the High River soil, Ca and Mg concentrations were significantly lower, as was Zn concentration (Figure 5.3b). Accumulations of nutrient elements were in all cases significantly higher in barley grown using urea compared to CN on the Barrhead soil. Barley grown on the High River soil accumulated significantly more K, P, S, B, and Fe when urea was the N source. Cu accumulation was also significantly higher for barley grown with urea. The relative value was 168% for Barrhead and 165% for High River. Comparative values for Mn were 192 and 145%.

Field Experiment

The ANOVA's from the field experiment show that the nitrogen source factor (A) was significant for yield and several of the elemental concentration measured (Table 5.4). The copper source factor (B) was significant for Cu concentration in shoots, grain, and straw and for Mn and Zn concentration in straw. The interaction of nitrogen and copper (AB) was not significant except for P concentration in grain and Fe in straw. With the exception of these two variables, interpretation of the main effects was possible without the confounding influence of interactions.

At heading, dry matter production was larger in plots receiving urea or CN compared to plots receiving no N (Figure 5.4a). Averaged across all Cu treatments, the mean yields from urea and CN treatments were greater than the N control (No N) treatment, but were not different from each other. Comparing across all Cu treatments at maturity, grain yields differed significantly among the three N treatments (Figure 5.4b). Straw yield at maturity exhibited a similar trend to shoots at heading (Figure 5.4c). Within Cu treatments for grain, the mean separations suggest an interaction between Cu source and N source that was not detected by the ANOVA. Whether this is a synergistic interaction of $CuSO_4$ and CuO with urea or an antagonistic interaction with CN cannot be determined.

Nitrogen concentration at heading tended to be greater in the plants grown on urea compared to those grown with CN or with No N (Figure 5.5a). The differences among N sources were much smaller in both grain and straw at maturity (Figure 5.5b,c). When averaged across all Cu treatments, N concentration was higher in grain and straw from urea treatments compared to CN treatments. The N concentration in grain and straw did not differ between the urea treatments and the N control when averaged across all Cu treatments.

Compared across all Cu treatments, N source means for Cu concentration differed significantly in grain but not in straw or shoots at heading (Figure 5.6). Copper concentrations in grain were lower in the higher yielding urea and CN treatments compared to the N control treatments, suggesting a dilution effect. The nitrogen*copper interaction was not significant for any of the crop components. The means for shoots, however, suggest a positive interaction between Cu-EDTA and urea (Figure 5.6a).

The ANOVA suggested that the copper factor was significant in shoots, grain, and straw. When the copper means across all N treatments were compared Cu concentrations were always numerically highest when Cu-EDTA was the Cu source. In shoots, the mean Cu concentration across Cu-EDTA treatments was 52 μmol kg $^{-1}$ and was significantly different from CuO, $CuSO_4$, and Cu control (No Cu) at concentrations of 32, 33, and 35 μmol kg^{-1} respectively. In grain, the relative differences among copper means were reduced. The mean ranking was Cu-EDTA, $CuSO_4$, CuO, and Cu control. The means were respectively, 58, 55, 52 and 52 μmol kg^{-1}. The Cu-EDTA mean was significantly different from the CuO and Cu control means, but not from the $CuSO_4$ mean. Only the highest mean concentration, Cu-EDTA at 30 μmol kg^{-1}, and the lowest mean concentration, CuO at 25 μmol kg^{-1}, were significantly different in straw.

The concentrations of the macronutrients K, P and S were significantly affected by N source in barley shoots (Table 5.4). Comparison of N source means showed that K and S concentrations, expressed as a percentage of the CN treatment, were greater in plants grown using urea as the N source (Figure 5.7a). The comparison of means for micronutrients showed that concentrations of Mn and Zn were greater in plants grown using urea as the N source compared to those grown using CN (Figure 5.7b).

A similar comparison shows that concentration of Fe, Mn and Zn in grain was greater when urea, as compared to CN, was the fertilizer (Figure 5.8a). There was a small but statistically significant dilution of P concentration. In straw, the mean concentration of Fe was significantly less for urea as the N source compared to CN. There were no relative differences in the concentrations of Mn and Zn. (Figure 5.8b).

Discussion

Greenhouse Experiment

In the greenhouse experiment, using urea as the N source increased yield. Adding Mn or Cu fertilizer had no effect on yield, but added Cu did increase Cu concentration in barley. Extractable Cu measured prior to the start of the experiment was above the 6 μmol Cu kg^{-1} (0.4 mg kg^{-1}) critical limit suggested for prairie soils by Karamanos *et al.* (1986). Tissue concentrations, however, were in the range (30-80 μmol Cu kg^{-1}) associated with deficiency (Jones 1991, Kabata-Pendias and Pendias 1992). Extractable Mn levels were well above the critical soil test level of 25 μmol kg^{-1} (1.4 mg kg^{-1}) prior to $MnSO_4$ addition (Sims and Johnson 1991). Tissue concentrations of Mn were also above the deficiency range of 270-450 μmol kg^{-1} (Jones 1991, Kabata-Pendias and Pendias 1992). Copper availability appeared to be a limiting factor based on tissue levels, but not when based on the pre-seeding soil test. The lack of yield response suggests that Cu was not limiting. Manganese availability did not appear to be a limiting factor.

Using the criteria of Jarrell and Beverly (1981) for interpreting crop data, the increased yield, accumulation, and concentration suggested that urea had a synergistic effect on Mn availability. Copper accumulation and yield increased when urea was the N source. Copper concentration, however, was the same for both N sources. This ruled out the possibility that urea decreased Cu availability. If availability had decreased, concentration would have decreased as well. The results were less definitive with respect to positive interaction between urea and Cu. Urea increased yield and Cu availability, but dilution masked the effect, or available Cu was sufficient to support the yield increase induced by urea. Based on post-harvest soil analyses, Cu availability was no different between N sources.

Manganese concentrations in barley were greater when urea was the N source, but adding fertilizer Mn did not affect uptake. The synergistic effect of urea on Mn uptake was enhanced by Cu addition. Younts (1964) reported that adding Mn with Cu fertilizer increased Cu uptake. He postulated that Mn competed with Cu in complexing reactions maintaining more Cu in available form. In the current work, Cu and Mn were added separately. Copper, with its tendency to form more stable complexes, may have displaced Mn from complexing sites and as a result increased Mn availability. The dissolution of SOM brought about by urea may have enhanced this effect by increasing the accessibility of complexation sites. Adding Mn, which forms weak complexes, did not increase Cu availability. The increase in Mn availability suggested by the plant data is supported by the soil data. More Mn was DTPA extractable in the urea treatments after harvest than in the CN treatments.

Urea generally causes an increase in soil pH during hydrolysis, followed by a decrease as the NH_4^+ produced nitrifies. Plants were only sampled at a late growth stage; therefore, uptake data do not distinguish between early and late uptake and provide no insight into the specific mechanism by which availability was increased. A number of researchers have shown that Mn availability, based on distribution among different fractions, generally decreases as pH increases (Sims 1986 and Liang *et al.* 1991), but their results were based on systems where pH was not perturbed. Shuman (1985, 1986) found that adding lime caused Mn to redistribute to the plant available exchangeable and organic fractions, but this did not result in increased Mn concentrations in plants. Petrie and Jackson (1884a) found higher yields and Mn concentration in barley fertilized with ammonium sulphate (AS) compared to urea. They attributed the difference to AS reducing and urea increasing pH of the soil solution by -0.7 and +0.3 units respectively (Petrie and Jackson 1984a). Similar results, based on soil solution measurements taken 14 days after fertilizer addition, were obtained in an earlier experiment (Chapter 3, this volume). The results showed that urea increased solution Mn concentrations, but so did AS. Increases in solution Mn brought about by urea were associated with the initial high pH phase and increased SOC, while those brought about by AS were associated with pH decreases.

Soluble may or may not mean plant available. While the literature suggests that soil acidification by fertilizer increases Mn availability (Petrie and Jackson 1984b, Jackson and Carter 1976, Miner *et al.* 1986); these changes were associated with pH differences of 0.7 units or more. Post harvest soil samples from the FRZ in the greenhouse experiment showed little difference in pH. The pH in CN compared to urea treatments was 5.6 versus 5.5 in the Barrhead soil and 6.0 versus 5.8 in the High River soil. It seems unlikely that such small changes in pH would significantly affect Mn availability. In any case, the effect of pH reducing fertilizers on Mn availability does not exclude a different mechanism from increasing Mn availability during the high pH phase associated with urea hydrolysis. The idea that urea increases the concentration of soluble Mn complexed to SOC and that this might lead to greater Mn transport to the root is an intriguing hypothesis for consideration in future research.

Field Experiment

The DTPA extractable Cu levels prior to Cu addition and the tissue concentration of Cu both suggest that Cu was below critical thresholds and may have been limiting crop growth (Karamanos *et al.* 1986, Jones 1991, Kabata-Pendias and Pendias 1992). Yield did not respond to Cu additions regardless of source, but Cu concentration in shoots at heading and grain at maturity was highest when Cu-EDTA was the source. Plants grown on $CuSO_4$ and CuO treatments were no different, with respect to Cu concentration, than those grown without Cu. Apparently, Cu availability was not increased by applying these two Cu products in a concentrated placement. The type of N applied with the Cu did not change this. This is not surprising for CuO, which is only sparingly soluble, and would have become even less soluble as urea increased solution pH. On the other hand, highly soluble $CuSO_4$ was probably redistributed quickly into various fractions, the organic fraction being one of the more important (Liang *et al.* 1991). Based on crop uptake, neither solubilization of SOM nor any subsequent acidification due to nitrification altered Cu availability in the $CuSO_4$-urea treatments.

Urea increased the plant availability of Cu applied as Cu-EDTA up to heading compared to both the control and CN source. By maturity, these differences had disappeared. Crop uptake up to heading would have included uptake during the high pH phase of urea transformation. Unlike $CuSO_4$, Cu-EDTA can persist in soil solution and its persistence increases at higher pH. This is due in part to increasing affinity of EDTA for Cu as pH increases and Fe precipitates (Norvell 1991). A second contributing factor may be reduced adsorption of EDTA by soil as pH increases (Norvell and Lindsay 1969). Furthermore, EDTA does not break down rapidly in soil solution persisting well beyond 15 weeks (Tiedje 1977). Since plant roots tend not to grow into concentrated fertilizer placements (Passioura and Wetselaar 1972), increased availability of Cu-EDTA was likely a result of increased mobility in the urea nests. The results show that using urea as the N source increased the comparative plant availability of Cu applied as Cu-EDTA in the early growth stages of barley. Further research would be required to clarify the mechanism through which this was achieved.

Availability of Other Nutrient Elements

In the greenhouse experiment, concentration varied significantly with N source for Ca, Mg, and K in barley grown on the Barrhead soil and for Ca, Mg, and Zn on the High River soil. Since yields with urea were always significantly higher than CN yields, and total accumulations were as high or higher, all relative decreases in concentration were attributable, at least in part, to dilution. This included K concentration in barley grown on Barrhead soil and Ca, Mg, and Zn in barley grown on High River soil. On the other hand, relative increases in Ca and Mg concentration in barley grown on the Barrhead soil suggested that urea increased availability of these elements. For the remaining elements measured, concentration did not vary with N source, but higher yields when urea was the N source resulted in higher elemental accumulation. Cases such as these are confounded and cannot be interpreted with respect to effects of the experimental factors, in this case N source, on element concentration in the plant (Jarrell and Beverly 1981). Dilution is also a masking effect and may conceal differences due to experimental factors.

Similar results from the field experiment for plants harvested at heading were somewhat easier to interpret. Yield did not differ between the urea and CN treatments; therefore relative differences in tissue concentration of an element reflect differences in availability. Urea increased the availability of K, S, Mn, and Zn relative to CN. There was no difference in relative availability for Ca, Mg, P, Al, Fe, or B. A smaller set of elements was measured in the grain and straw. Urea increased grain yield relative to CN but had no effect on straw yield. Concentration and accumulation of Mn, and Zn were higher in grain from the urea plots compared to the CN plots, but were not different in straw. When the grain and straw results were combined and used to calculate whole plant values, the results were consistent with what was found for shoots harvested at heading; Mn and Zn were more available when urea was the N source. The grain results (increased yield, concentration, and uptake) suggested that urea enhanced Fe availability, while the straw results (no change in yield, decreased concentration and uptake) suggested antagonism between urea and Fe. When combined, whole plant yield was higher in urea compared to CN, Fe concentration was lower, and Fe accumulation was unchanged. Based on the whole plant, differences between urea and CN could be attributed to dilution of Fe between heading and maturity.

Conclusions

The original hypothesis for the greenhouse experiment that urea additions do not alter the availability of previously applied Cu and Mn can be rejected in the case of Mn. The availability of previously applied Mn was higher in urea fertilized soils relative to CN fertilized soils. The results for Cu were less clear. The data suggest with some certainty that availability of previously applied Cu was not reduced in the FRZ of urea, but distinguishing between nil and positive effects was confounded by nitrogen source effects on yield.

The original premise in the field experiment was that concentrating urea and Cu fertilizer together in nests would not alter Cu availability. This was true when the Cu source was CuO or $CuSO_4$, but false when Cu-EDTA was applied. Up to heading, concentrating Cu-EDTA with urea in soil increased uptake of Cu relative to Cu-EDTA placed with CN or by itself, supporting the conclusion that reactions of urea within the nest enhanced availability of Cu applied as Cu-EDTA.

Analysis of other elements in barley suggested that relative to CN, urea perturbed the soil-plant system in ways that altered crop uptake of a number of macronutrient and micronutrient elements. The effects of using urea as the N source, when they were measurable and interpretable, were generally synergistic. Not surprisingly, changes in nutrient availability varied among soils.

Table 5.1. Chemical and physical characteristics of soils used in greenhouse and field experiments.

Soil/Site	pH	Organic Matter	Total N	Total P	Sand	Silt	Clay	Field Capacity	Saturation
			$g\ kg^{-1}$			*$g\ kg^{-1}$*		*$kg\ kg^{-1}$*	
Barrhead	6.3	44	3.3	0.5	440	300	260	0.288	0.471
High River	6.4	49	3.1	0.6	380	370	250	0.302	0.495
Ellerslie	6.3	105	–[x]	–	150	400	450	–	–

	Extractable Trace Metals				Exchangeable Cations				CEC
	Fe	Cu	Zn	Mn	Ca	Mg	Na	K	(+)
		$\mu mol\ kg^{-1}$					*$mmol\ kg^{-1}$*		
Barrhead	1910	13	49	590	84.5	9.0	1.0	BDL	190
High River	1350	23	61	1260	96.0	18.0	1.0	10.0	240
Ellerslie	2780	15	55	620	176	18.9	1.0	4.7	380

[x] Dash (-) signifies analysis was not performed.

Table 5.2. Probabilities of F from analysis of variance for yield and elemental concentrations in barley harvested from greenhouse experiment.

Source	Measured Variable[x]										
	Yield	Ca	Mg	K	P	S	B	Fe	Cu	Mn	Zn
Block	0.01	ns	ns	ns	ns	0.05	ns	ns	ns	ns	ns
Soil(A)	0.01	0.0003	0.0001	0.0007	0.04	0.002	0.0001	ns	0.002	0.001	0.004
Micros(B)	ns	ns	ns	ns	ns	ns	ns	ns	0.0002	ns	ns
AB	ns	ns	ns	0.002	ns	0.005	ns	ns	ns	ns	ns
Nitrogen(C)	0.01	ns	ns	0.002	ns	ns	ns	ns	ns	0.03	0.03
AC	ns	0.03	0.004	ns	ns	ns	ns	ns	ns	ns	0.03
BC	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
ABC	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

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[x] When $p > 0.05$, F was deemed non-significant (ns).

Table 5.3. Probabilities of F from analysis of variance for pH and DTPA extractable metals in soil following harvest of greenhouse experiment.

Source	Measured Variable[x]				
	pH	Fe	Cu	Zn	Mn
			P		
Block	ns	ns	ns	ns	ns
Soil(A)	0.001	0.04	0.008	0.02	0.0001
Micros(B)	ns	ns	0.0001	ns	0.01
AB	ns	ns	0.006	ns	ns
Nitrogen(C)	0.0008	0.0001	ns	ns	0.0001
AC	ns	ns	0.002	ns	0.03
BC	0.005	ns	ns	ns	ns
ABC	ns	ns	0.001	0.04	0.03

[x] When $p > 0.05$, F was deemed non-significant (ns).

Table 5.4. Probabilities of F from analysis of variance for yield and element concentrations in barley harvested from field experiment.

Source	Measured Variable^{x,y}												
	Yield	N	Ca	Mg	K	P	S	B	Al	Fe	Cu	Mn	Zn
						Shoots at Heading							
Blocks	0.02	ns	ns	ns	0.04	0.004	ns	ns	0.004	ns	ns	ns	ns
Nitrogen (A)	0.0001	0.0001	ns	ns	0.0001	0.002	0.002	ns	ns	ns	ns	0.004	0.0001
Copper (B)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	0.04	ns	ns
AB	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
						Grain at Maturity							
Blocks	0.0008	ns	–	–	–	ns	–	–	–	ns	ns	0.03	0.002
Nitrogen (A)	0.0001	0.004	–	–	–	0.0001	–	–	–	0.01	0.002	0.006	0.02
Copper (B)	ns	ns	–	–	–	ns	–	–	–	ns	0.02	ns	ns
AB	ns	ns	–	–	–	0.02	–	–	–	ns	ns	ns	ns
						Straw at Maturity							
Blocks	0.0002	0.002	–	–	–	ns	–	–	–	0.0006	ns	0.003	0.0005
Nitrogen (A)	0.0001	0.01	–	–	–	ns	–	–	–	0.003	ns	ns	ns
Copper (B)	ns	ns	–	–	–	ns	–	–	–	ns	0.03	0.04	0.02
AB	ns	ns	–	–	–	ns	–	–	–	0.01	ns	ns	ns

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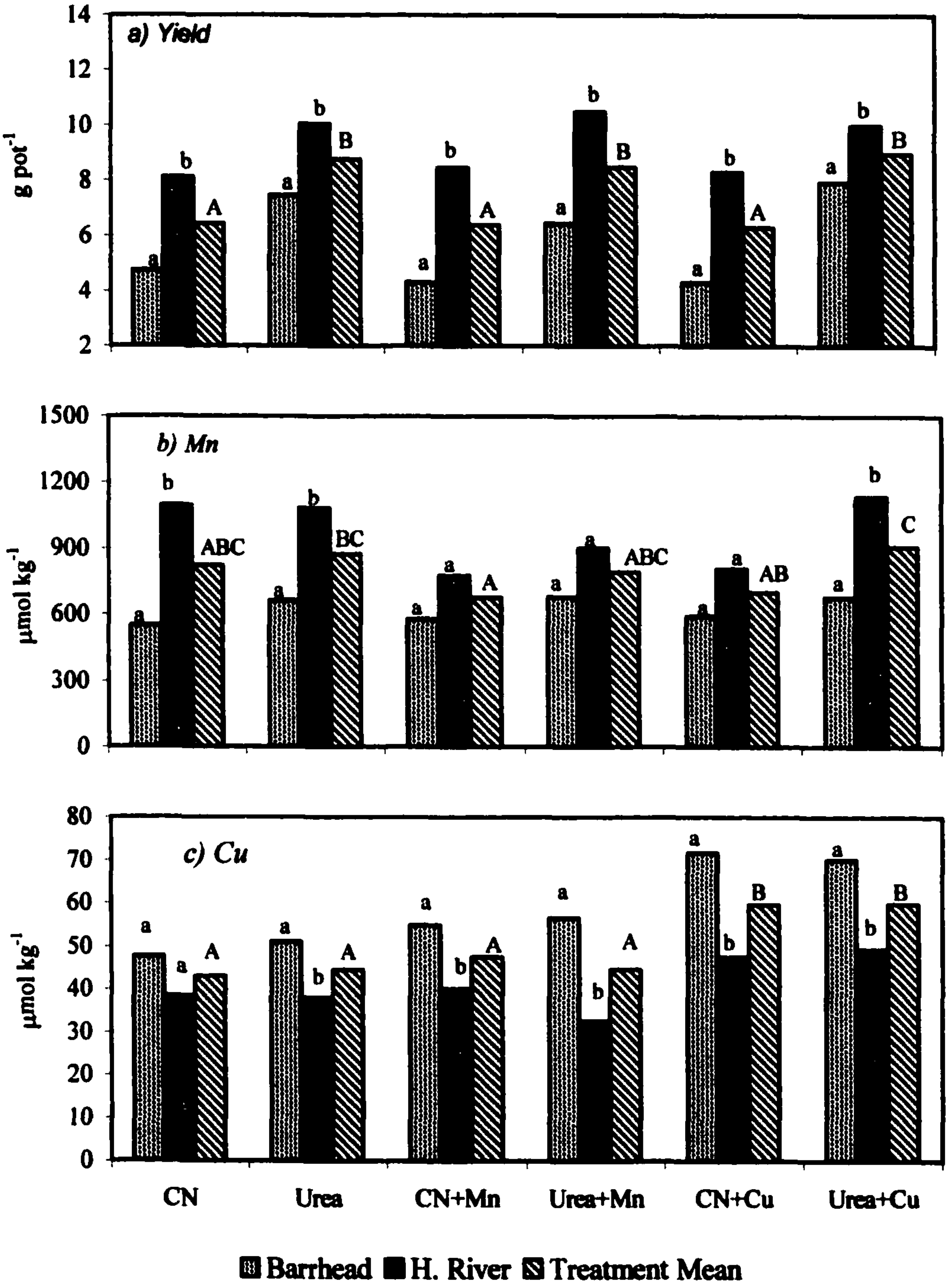
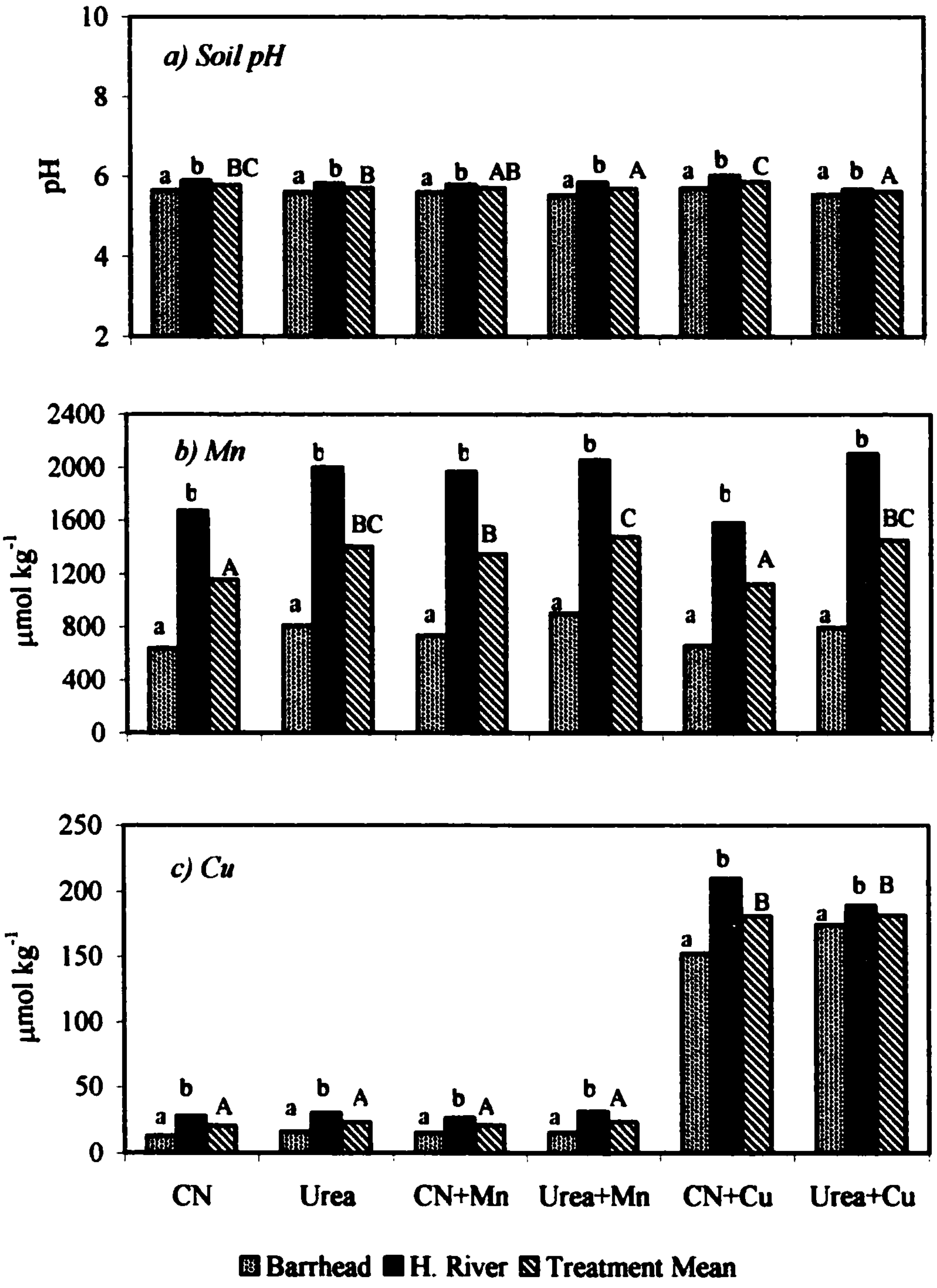
[x] When $p > 0.05$, F was deemed non-significant (ns).

[y] Dash (–) signifies concentration was not determined.



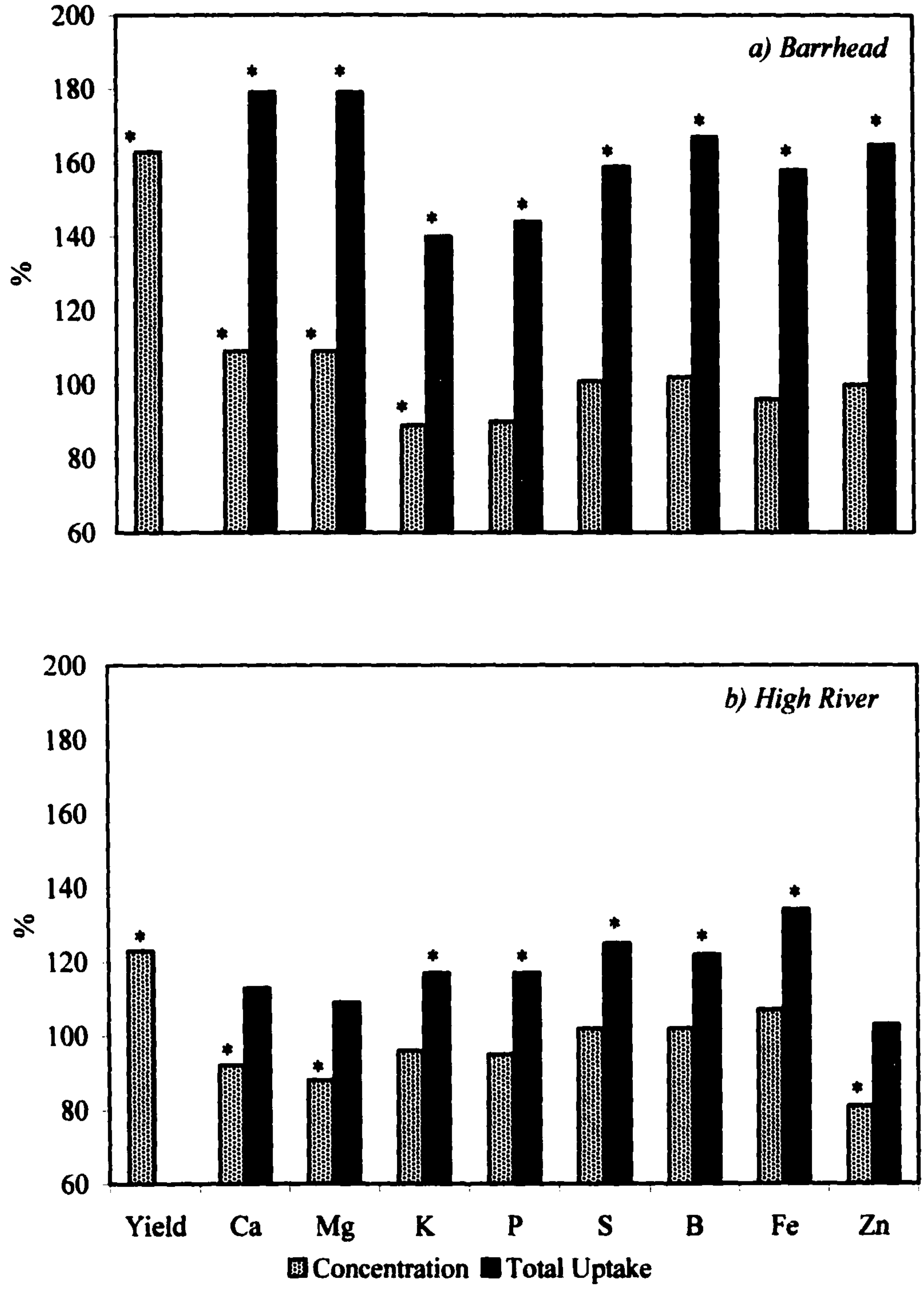
Soil means within treatments were different ($p < 0.05$) if lower case letter on top of adjacent columns differs. Treatment means were different ($p < 0.05$) if upper case letter on top of treatment mean columns differ.

Figure 5.1. Effects of N source and Cu or Mn additions on yield, Mn concentration and Cu concentration in greenhouse barley.



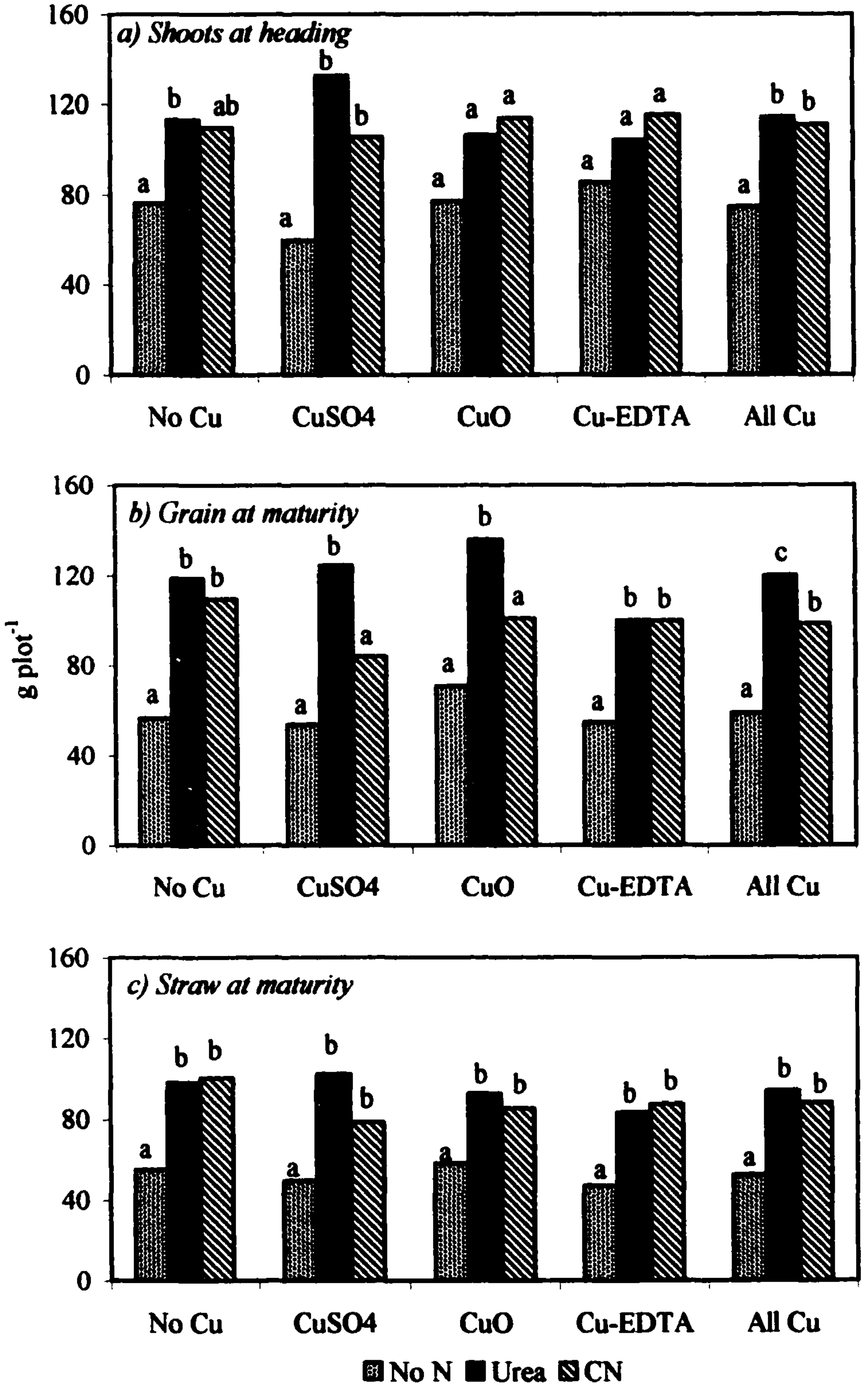
Soil means within treatments were different ($p < 0.05$) if lower case letter on top of adjacent columns differs. Treatment means were different ($p < 0.05$) if upper case letter on top of treatment mean columns differ.

Figure 5.2. Effects of N source and Cu or Mn additions on post-harvest pH and DTPA extractable Mn and Cu in soils from greenhouse experiment.



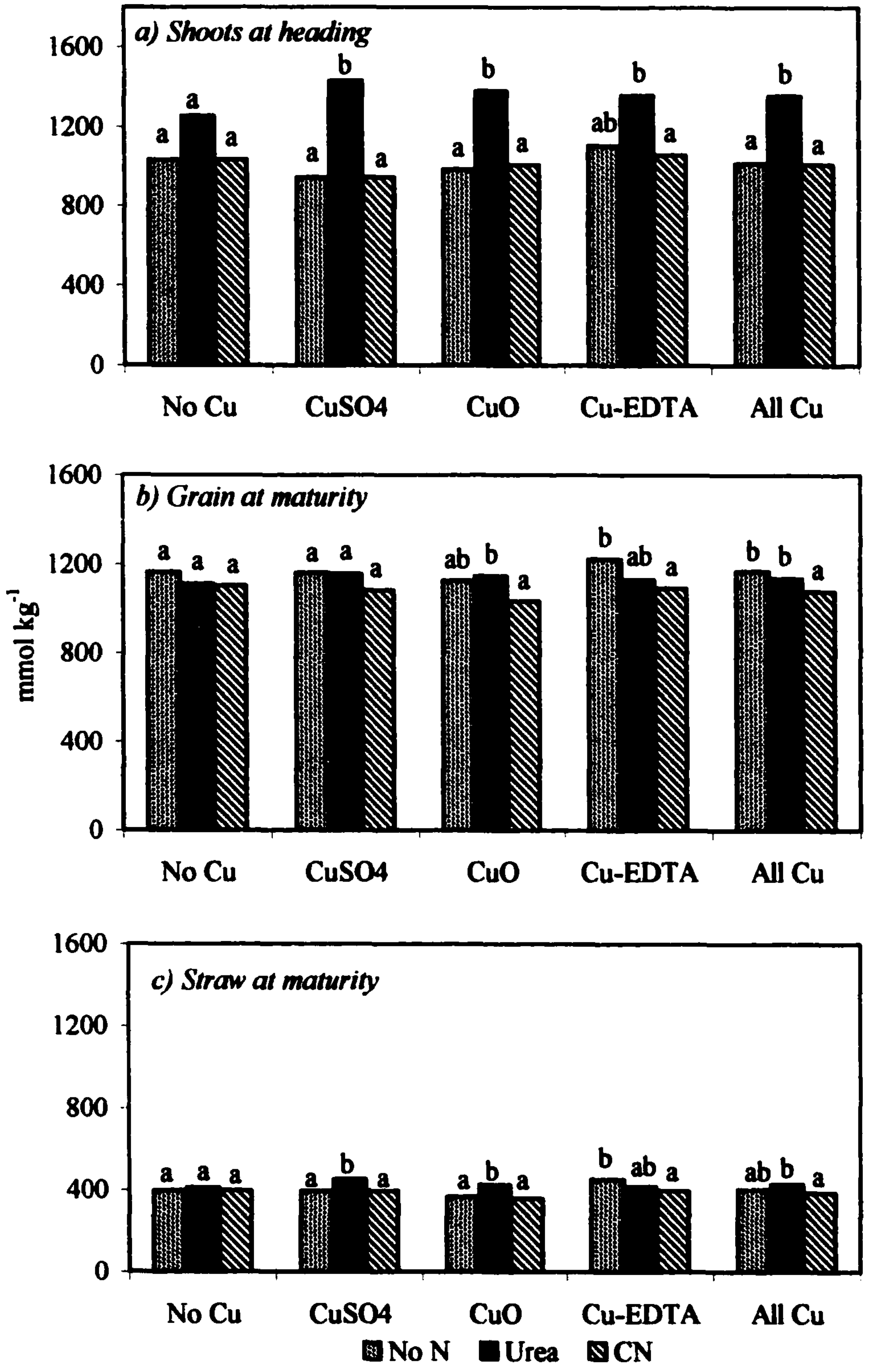
Difference between urea and CN treatment was significant if (*) appears on top of column ($p < 0.05$).

Figure 5.3. Yield, element concentration, and total elemental uptake for barley grown on urea treatments in the greenhouse expressed as a percentage of barley grown on CN treatments.



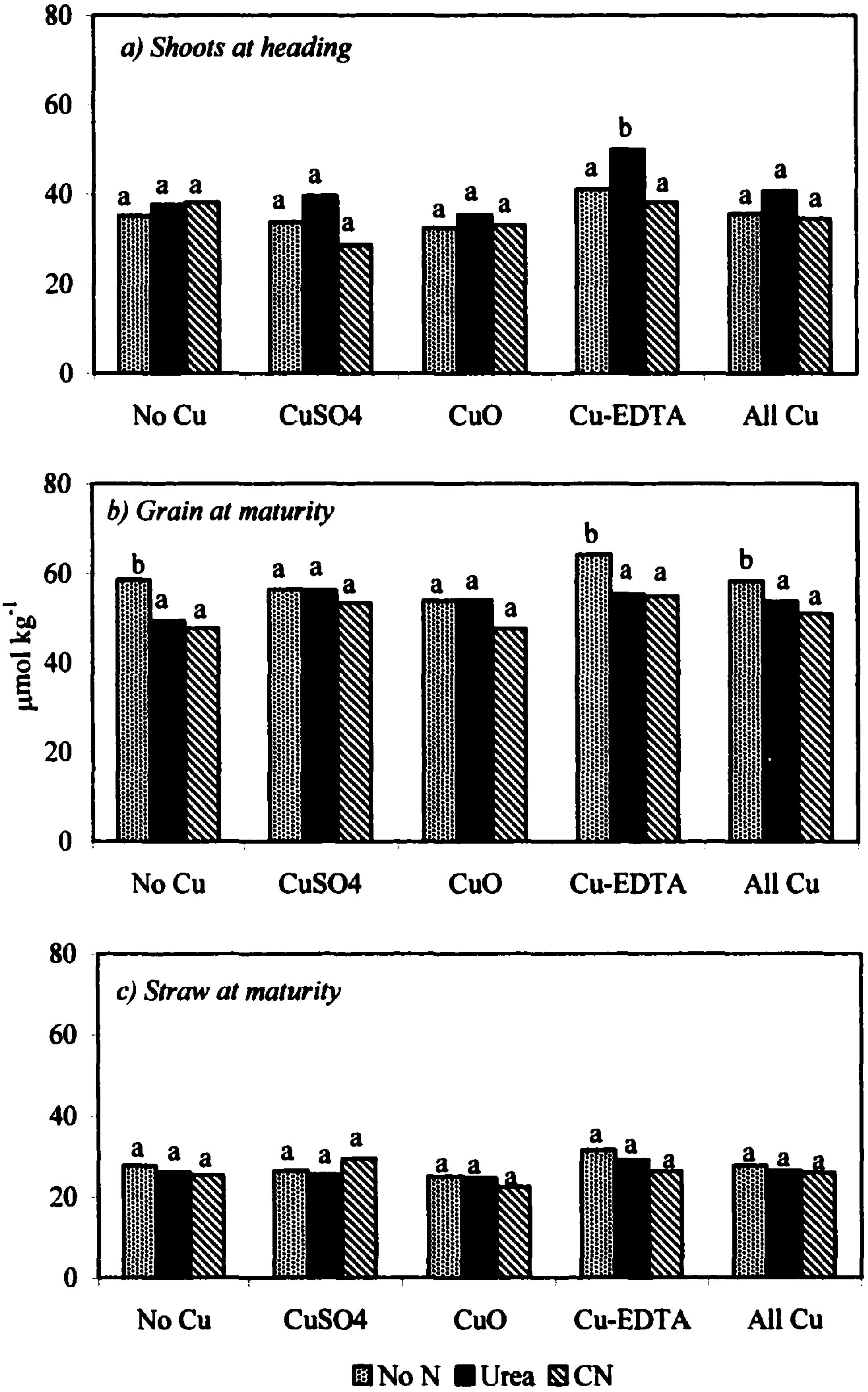
Means within Cu treatments are significantly differ if letters on columns differ ($p < 0.05$)

Figure 5.4. Yield of barley in field experiment as affected by N and Cu.



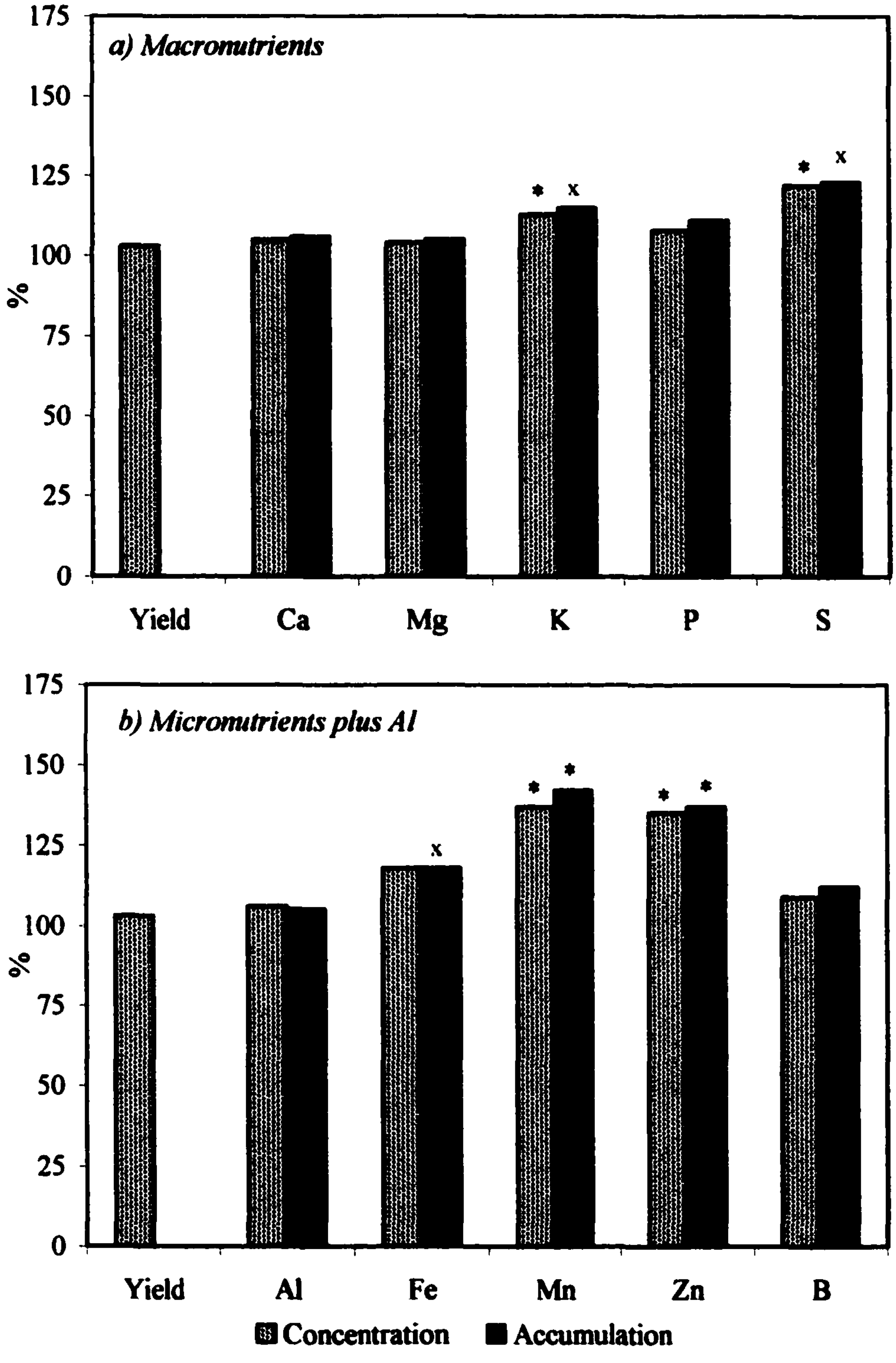
Means within Cu treatments are significantly differ if letters on columns differ ($p < 0.05$)

Figure 5.5. Nitrogen in field-grown barley as affected by N and Cu.



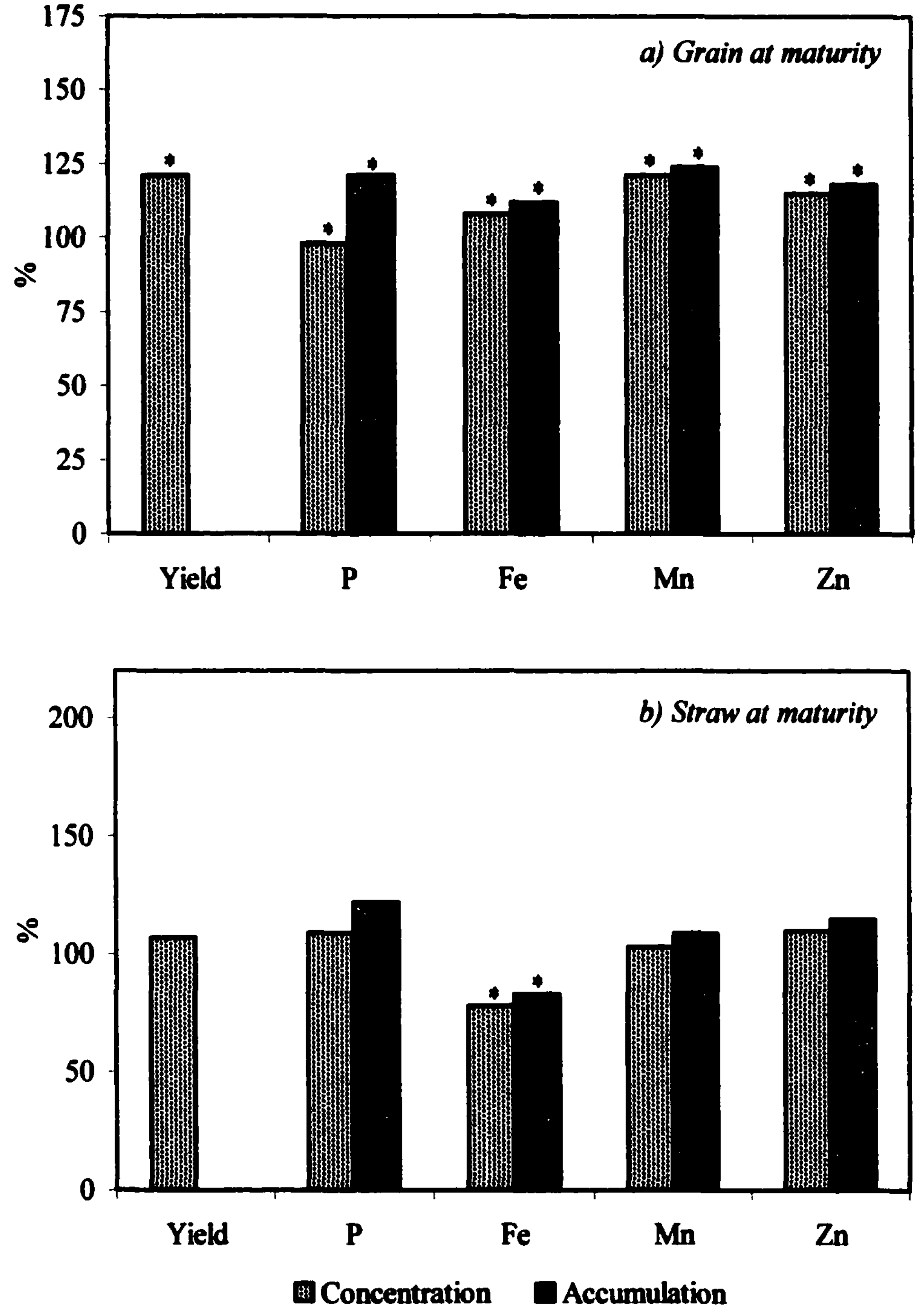
Means within Cu treatments are significantly differ if letters on columns differ ($p < 0.05$)

Figure 5.6. Cu in field-grown barley as affected by N and Cu.



The effect of urea were significantly different from CN at $p < 0.05$ (*) or $p < 0.10$ (x).

Figure 5.7. Yield, element concentration, and element accumulation at heading in barley shoots from urea treatments expressed as a percentage of CN treatments (field experiment).



* The effect of urea was significantly different from CN at $p < 0.05$.

Figure 5.8. Yield, element concentration, and element accumulation at maturity in barley from urea treatments expressed as a percentage of CN treatments (field experiment).

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CHAPTER 6

TRANSPORT OF ELEMENTS FROM THE FERTILIZER REACTIONS ZONE OF GRANULAR UREA UNDER SIMULATED RAINFALL CONDITIONS

Introduction:

Adding granular urea to soil creates a fertilizer reaction zone (FRZ). Hydrolysis of urea increases the pH within the FRZ and dissolves soil organic matter (SOM) to release soluble organic carbon (SOC) into the soil solution. Solution concentrations of a number of nutrient and non-nutrient elements are also increased (Chapters 2 and 3). These elements include Al, Fe, Cu, Mn, Zn, Mo, B, P, and S. This raises the question, is mobility of these FRZ products increased as well?

This is a timely and pertinent question. Transport of FRZ products can potentially reduce the crop availability of fertilizer and non-fertilizer nutrient elements in soil. Movement of FRZ products into surface waters with runoff or ground waters through leaching is potentially damaging to water quality. Products such as SOC, mineral-N, and bioavailable P have the potential to enhance eutrophication of surface waters. Heavy metals, including plant nutrient metals such as Cu and Zn, in water have raised a number of environmental and health concerns.

Mass flow could move products out of the FRZ along two pathways. The first is surface flow or runoff. The second is leaching from the application zone, which can have a shallow horizontal (inter-flow) as well as a vertical component. Solute movement through these pathways can occur at much different velocities. Runoff is capable of moving solutes kilometers in a day while leaching velocities tend to be meters per year for water and considerably less for conservative solutes. Attenuation occurs through a number of complex and interrelated processes such as microbial immobilization, plant uptake, adsorption, and precipitation reactions.

Co-transport of elements from and through soils, particularly Al and Fe with C in forest soils, has been studied in relation to pedogenesis for near 200 years (McKeague *et al.* 1986). More recently, progress has been made in the characterization of low molecular weight organics and their role in dissolution and transport of metal and nutrient elements (Pohlman and McColl 1988, Dosskey and Bertsch, 1997). The effects of chemical amendments including fertilizers on SOC and co-transport phenomena have received less attention. Zhu and Alva (1993) found that $CaSO_4$ and $MgSO_4$ additions decreased and K_2SO_4 increased Cu and Zn leaching. Copper and Zn concentrations in leachate were positively correlated with dissolved organic carbon (DOC). Kudeyarova and Kvaratskheliya (1990) found that fertilizer phosphates increased solubility and transport of metallic cations. More specifically with nitrogen fertilizer, Ogner (1975) showed that urea additions increased the solubility of carbon in humic soil horizons. Using a column technique in the laboratory, Wang and Alva (1999) found that ammonium nitrate increased and isobutylidene diurea reduced SOC leaching in sandy soils. Otchere-Boateng and Ballard (1978) had earlier found in a field study that urea additions to a forest soil reduced Ca and Mg leaching initially, but increased it once nitrification had acidified the application zone.

Simulated rainfall techniques were developed initially for use in erosion studies. They offer the experimenter the opportunity to control the hydrology and perform reproducible experiments. They have been adopted for use in nutrient transport studies, primarily to examine runoff of applied fertilizer and manure N and P under different field application methods (Shreve *et al.* 1995, Gascho *et al.* 1998, Torbert *et al.* 1999). The use of simulated rainfall to examine transport of FRZ products has been limited. Clay et al. (1995) examined transport of soluble carbon following fertilization with anhydrous ammonia. Although they found anhydrous ammonia increased DOC transport, they had configured their system to prevent runoff and confined their observations to DOC in leachate.

In Alberta Agriculture's erosion laboratory, a system has been developed for simultaneously raining on up to four soil treatment combinations. This system permits collection of surface runoff and leachate. It has proven reliable in reproducing rainfall, runoff and leachate volumes across replicates in both time and space. Thus far, it has been used to examine differences in P transport in relation to manure loading rate, soil type, and slope. It would appear to be a promising tool in the examination of the question posed earlier, are FRZ products transported out of the application zone? Towards answering this question, a rainfall simulation experiment was performed comparing urea fertilized to control treatments in two soils. The primary objective of this experiment was to determine the mobility of FRZ products under simulated rainfall conditions. A secondary objective was to determine if urea affected the mobility of added trace metals. To accomplish this second objective, $CuSO_4$ was added to the soils prior to the imposition of the urea treatments. The experimental hypothesis, stated in the null form, was that adding urea to soil would not significantly alter the transport of major or trace elements.

Materials and Methods

Soils and Fertilizers

Approximately 800 L soil samples were collected from the 0-10 cm depth at two Alberta Agriculture, Food and Rural Development research sites near Devon, Alberta. Examination of soil horizons showed that the polypedons sampled were an Eluviated Black Chernozem and a Solonetzic Black Chernozem at the Chamulka and Borys sites respectively. Samples were collected in early November 1999 and stored outside in 200 L barrels at field moisture until March 2000. Each barrel was screened to pass 10 mm, stones and excess straw removed and the soil thoroughly mixed in a large tray. Subsamples for analysis of soil characteristics and initial nutrient status were taken after screening and mixing. Both soils had a fine to medium granular structure following screening. The aggregates in the Chamulka soil were more friable than those in the Borys soil.

Reagent grade $CuSO_4$:$5H_2O$ was used as the Cu source and technical grade granular urea as the urea source. The urea was screened through a 2 mm followed by a 1.7 mm sieve. Granules retained on the 1.7 mm sieve were used in the experiment. A subsample of urea was analyzed for trace elements.

Experimental Design

The experiment was designed as a 2 X 2 factorial with two soils differing in texture and two treatments, urea versus no urea. The surface 2 cm of the soil was amended with Cu in all treatments. The experiment was run as a randomized complete block in three replicates. Blocks were rained on sequentially with five days separation between the completion of one block and the commencement of the next.

Soil Pre-Treatment

Twenty days prior to commencement of rainfall simulation, one barrel of each soil was screened, mixed and six 12 kg subsamples removed. Each subsample was placed in a plastic tray 75 X 50 X 50 cm (l X w X h). Copper (0.5 g) was added to each 12 kg portion by sprinkling 1 L of copper sulphate solution from a watering can while the soil was being mixed. Mixing was continued for 5 minutes following Cu addition. Soils were then adjusted to field capacity by adding distilled water and mixing further. Trays were covered with plastic tops, but were not sealed, and were incubated at approximately 20°C. Covers were removed and the soil mixed within the trays every second day until used in rainfall simulation.

Incubation and Rainfall Simulation

Five days prior to rainfall simulation, a second barrel of each soil was screened, mixed, and sampled. Soil was loaded into stainless steel double bottomed rain-frames 0.95 m long by 0.50 m wide. The inner bottom consisted of steel mesh covered with a 5 mm acrylic plastic sheet containing evenly spaced 25 mm holes. The holes accounted for 10% of the area of the sheet. Soil depth was adjusted to 8 cm with a leveling device. Two frames were prepared for each soil.

Following preparation of the 8 cm soil layer, two of the plastic trays containing the Cu amended soil prepared earlier were selected at random for each soil. Soil within each plastic tray was mixed, sampled separately and assigned to its counterpart in the rain frames. An initial 1 cm layer of the Cu amended soil was added to the soil surface within each frame and leveled. Urea granules (50 g) were applied to the new surface in one frame of each soil type. A further 1 cm layer of the Cu amended soil was added to the surface of all frames followed by final leveling. The frames were covered with plexiglas covers to reduce evaporative loss. Atmospheric exchange over the soil was maintained through the 1 cm runoff collection port. Frames were immediately wet from below by flooding the lower compartment of the rain-frame and allowing water to move upward through capillary rise. The water table was maintained at a depth of 9 cm from the soil surface for approximately 18 hours and then removed. The soils were allowed to drain freely and incubate at approximately 20°C for five days.

Rainfall was applied in a dual chamber rainfall simulator, which is capable of raining on four rain-frames simultaneously. This simulator employed two 50 SQW vee jet® nozzles set at a height of 3.05 m above the surface of the rain-frames. Flow to each nozzle was metered at 214 mL sec^{-1} to deliver rainfall at a target intensity of 65 mm hr^{-1} at the soil surface. Slope was set at 7% by adjusting the angle of the entire rain frame relative to the horizontal plane.

Water used for the simulation was City of Edmonton treated water that had been passed through a K charged resin exchange water softener to reduce the Ca concentration. Water samples were taken before, during, and after each run and analyzed for the same constituents analyzed in runoff and leachate.

Runoff samples were collected starting at initiation of run off (T_0) and 6, 12, 18, 24, 30, 36, 50, 70 and 90 minutes thereafter. The T_0 sampling was terminated when sufficient runoff was collected for analytical purposes and the time from T_0 recorded. Subsequent runoff samples were collected for 1 minute. Leachate was sampled starting at 10, 20, 30, 50 and 85 minutes after T_0. Sampling duration varied, but was long enough to collect sufficient sample for analytical purposes, generally 4-5 minutes. Sample end times were recorded so that flow rates could be calculated.

Runoff and leachate samples were sealed and weighed immediately. Upon completion of the simulation the samples were transferred to the analytical lab where they were allowed to settle for a minimum of 1 hour. After 1 hour, approximately 25 mL of the supernatant was decanted into 50 mL plastic vials for pH and EC analysis. A second portion of the supernatant (approximately 100 mL) was decanted and filtered under vacuum through 0.45 µm Millipore® filters. The filtrate was split into three 25-30 mL samples and stored in vials at 3°C until analysis could be performed. With the exception of urea all analysis was performed within 48 hours. One vial was treated with phenyl mercuric acetate (PMA) to inhibit urease activity until urea concentration could be determined. The residual samples including sediment were stored in the original collection vessels at 3°C until all chemical analyses were complete. The residual samples including quantitative transfer of sediment were passed through Whatman® No. 42 filters. Sediment collected on the filter was dried at 60°C until stable mass was obtained (24-36 hours) and then weighed. Unaccounted for sediment, mainly from the colloidal fraction, following the protocol above has been calculated at less than 2% (Mohamed Amrani, personal communication).

One to two hours following cessation of rainfall, soil samples were collected from the 0-2 cm and 2-10 cm depth of the rainframe. Samples were air dried, ground to pass 2 mm, and stored at room temperature until they could be analyzed.

Chemical Analysis

Soils were characterized using standard methods. Soil pH was measured in a 2:1 water to soil suspension. Organic matter was determined by loss on ignition at 1100°C. Sand, silt and clay were determined by the hydrometer method with pre-treatment to remove SOM as described by Sheldrick and Wang (1993). Trace metals were extracted by the DTPA method as described by Liang and Karamanos (1993). Extracts were analyzed using the ICP described below for elemental analysis of runoff and leachate samples. Exchangeable cations and cation exchange capacity (CEC) were determined using the ammonium acetate method described by Hendershot *et al.* (1993). In the analytical step, ICP was used to measure Ca, Mg, K, and Na for exchangeable cations. Ammonium concentration was measured by autoanalyzer. Soil NH_4^+ and NO_3^- were extracted with 2 M KCl and analyzed using a Technicon II® Autoanalyzer (Maynard and Kalra 1993).

On runoff and inter-flow samples, pH was measured using a combined electrode and Fisher Acumet Model 50 pH meter (Fisher Scientific, Nepean, Ontario, Canada).

Electrical conductivity was measured using Radiometer Model CDM 83 conductivity meter equipped with an immersion conductivity bridge (Bach-Simpson Ltd., London, Ontario, Canada). Dissolved organic carbon (DOC) was measured by ultra-violet promoted persulphate oxidation using an Astro 2001 System 2 Soluble Carbon Analyzer (Astro International Corporation, League City, Texas). Total inorganic carbon (TIC) was measured on the same instrument following conversion of carbonates to CO_2 with 10% H_3PO_4.

Total macro and trace elements in runoff and inter-flow were measured using a Jobin-Yvon model JY70PLUS Inductively Coupled Plasma Spectrophotometer (ATS Scientific Ltd., Oakville, Ontario, Canada). Simultaneous analyses were performed for boron, sodium, magnesium, aluminum, sulphur, phosphorus, potassium, calcium, manganese, iron, cobalt, zinc, copper, and molybdenum. Operating limits of detection (LOD) and limits of quantitation (LOQ) were determined for each element using the method of Keith *et al.* (1982). The ICP was calibrated before each run using Seignory Chemical Product certified standards (SCP Scientific Ltd., St. Laurent, Quebec, Canada). Analytical values less than the LOD were recorded as below detection limit (BDL), and were treated as zero values in the statistical analysis. Concentration and export quantities have been reported as total soluble quantities unless specified otherwise.

Ammonium and NO_3^- were analyzed colorimetrically using a Technicon II® Autoanalyzer (Technicon Instrument Corporation 1971, 1973). Urea in runoff and inter-flow was measured using the modified diacetyl monoxime method as detailed in Bremner (1982). This method was originally developed for analysis of urea in 2 M KCl soil extracts. For the purposes described here, an aliquot (1-5 mL) of either runoff or inter-flow was used instead of the 2 M KCl extract. Urea analysis was performed on the PMA treated runoff and leachate samples from the first replicate. As urea was not present in detectable quantities in the controls, urea determination was limited to one leachate and two runoff samples from the control treatments in each of the second and third replicates.

Statistical Analysis

Means from soil samples taken before urea addition and after rainfall were compared using paired t-tests. Total export was calculated for water, sediment in the case of runoff, and each chemical analyte using an iterative process that first approximates and then integrates the dependent variable as a function of time. Analysis of variance was performed on the total export data using SAS-PC. A separate ANOVA (Eq. 6.1) was performed for each variable measured for runoff and leachate. Main effects (soil or treatment) were deemed significant if F exceeded the critical F value at p = 0.05 and the

Source		N	df	Eq. 6.1
(R) Blocks	(r-1)	3	2	
(A) Soils	(a-1)	2	1	
(B) Treatment	(b-1)	2	1	
(AB) Soil X Treatment	(a-1)(b-1)		1	
Error	(r-1)(ab-1)		6	

interaction term was not significant. Means of the individual soil-treatment combinations were separated using the LSMEANS program in SAS PC. Mean comparisons were only performed in cases where main effects and/or the interaction effects were significant.

Results

Soil, Fertilizer, and Water

The surface soils collected from the Borys and Chamulka sites were similar in soil organic matter but differed substantially in texture (Table 6.1). The textural difference was in the sand and clay fractions. Borys contained almost twice the clay content of Chamulka. The silt fraction was similar in both soils. Both soils were well aggregated following screening, but the Chamulka aggregates were more friable. Cation exchange capacity, and thus ammonium retention capacity, was 35% higher in the Borys soil.

The most notable contaminant in the urea was total inorganic carbon (TIC). This is likely $(NH_4)_2CO_3$ formed as an intermediate product during urea formation. As its dissolution products were the same as those formed by urea hydrolysis, the effects of TIC contained in urea were captured within the urea effects. For the trace elements measured in urea, only Cu was present in detectable quantities.

Total K concentrations were higher than Ca and Mg in the rainfall water (Table 6.1). The mean Na concentration (data not shown) was 0.17 mmol L^{-1}. The mean total inorganic carbon (TIC) concentration suggests that aqueous CO_2 species were the most abundant anions. The pH of the water was 7.8, therefore the TIC was very close to 100% HCO_3^- (Bohn *et al.* 1979, Chapter 4). Total S concentrations suggest that SO_4^{2-} on an equivalency basis was approximately 80% of HCO_3^- concentration.

Low CV's for pH, ionic strength, TIC, K, and S indicate that the water was consistent throughout the experiment with respect to macro-chemistry. In the case of Fe and Cu, the mean values were below the detection limit due to a high number of BDL observations, which were treated as zeros in computing the mean. The non-zero values recorded were less than three times the detection limit. Analytical values within this range typically have high variance (Keith *et al.* 1983).

Before and After Soil Analysis

Soils could not be sampled immediately prior to rainfall simulation without disturbing the soil surface. The comparison of before and after results reflects changes in soil during the five-day incubation as well as those induced by rainfall (Table 6.2). In the control treatments, there was generally little change in concentration of the analytes before and after incubation and rainfall. The exceptions were Mn, Cu, and NO_3^--N. Before and after values suggest that Mn was removed from the DTPA extractable pool in the 2-10 cm depth of the Chamulka soil. The data also suggest removal of NO_3^--N from the 0-2 cm and increase in NO_3^--N concentration in the 2-10 cm depths of both soils. Cu concentration in the DTPA extractable pool of the control treatments declined in the 0-2 cm depth of both soils, but there was no change in the 2-10 cm depth.

Post-rain concentrations of DTPA extractable Fe, Mn, and Cu were significantly less than pre-incubation concentrations in the 0-2 cm depth of the urea treated soils. Zinc concentrations were unchanged. Extractable Fe and Zn concentration did not change significantly during incubation and rainfall in the 2-10 cm depth of the Borys soil.

Manganese and Cu concentrations decreased. In the Chamulka soil, concentrations of Fe, Cu and Mn were significantly lower after rainfall.

The NH_4^+–N concentrations in the 0-2 cm depth of the urea treatments were much higher in the post-rain samples suggesting considerable urea hydrolysis took place during incubation. Consistent with downward migration following rainfall infiltration, NH_4^+-N concentrations were higher in the 2-10 cm depth in the post-rain samples from the urea samples.

Runoff, Leachate, pH, Ionic Strength and Erosion Rate

Discharge rates for runoff increased rapidly during the first 20 minutes of rainfall and then stabilized (Figure 6.1a). Equilibrium discharge rates were reached more rapidly on the Chamulka soil than the Borys soil. Runoff rates from the two soils were within 5% once equilibrium was reached. Treatment did not have a significant effect on runoff volume (Figure 6.1b). The leachate discharge rate declined throughout the rainfall simulation (Figure 6.1c). The decline was greater in the Borys soil. Analysis of variance showed that soil had a significant effect on leachate volume. No other experimental factors were statistically significant. Total leachate volumes from the Borys soil were higher than from the Chamulka soil (Figure 6.1d). Leachate volume was approximately 10 % of runoff volume in the Borys soil and 5% in the Chamulka soil.

The runoff from urea treated soils was significantly more alkaline, by approximately 0.3 pH unit, than that from the control soils (Figure 6.2a). Runoff from urea treatments was also consistently higher than that of rainfall by about 0.3 units. The pH in leachate tended to equilibrate over the course of the rainfall event, stabilizing in the range of 7.0 to 7.2 in all cases (Figure 6.2b).

The ionic strength *(I)* of runoff from the urea treated soils was initially higher than from the control soils (Figure 6.3a). Over the course of the rain event, ionic strength in runoff from both urea and controls declined from initial values in the range of 6.2 to 9.3 mmol L^{-1} to values in the range of 4.2 to 4.4 mmol L^{-1}. These latter values are close to the ionic strength of the rainwater at 4.2 mmol L^{-1}. Conversely, ionic strength rose in leachate from the start to the end of the rainfall event (Figure 6.3b). There was no evidence of a significant treatment effect accompanying this rise. Ionic strength of leachate at the end of the simulation was more than double that of rainwater or runoff.

Erosion rate rose rapidly following initiation of runoff and reached apparent equilibrium between 20 and 30 minutes (Figure 6.4a). Erosion rates were higher from the Chamulka soil than from the Borys soil. Total sediment export was significantly higher in the urea treatments of both soils compared to the controls (Figure 6.4b). The relative difference as a percent of control was larger in the Borys soil (79%) compared to the Chamulka soil (53%). Total sediment removed in runoff was less than 2% of total soil mass in all cases.

Nitrogen in Runoff and Leachate

In run-off, the concentration of NH_4^+–N was two orders of magnitude higher from the urea treatments than from the controls (Figure 6.5a). Ammonium-N concentrations in runoff from the Chamulka soil were higher than from the Borys soil at the initiation of runoff. However, both converged to approximately 5 mmol L^{-1} after 90 minutes. Treatment did not seem to affect NO_3^--N in runoff from the Borys soil (Figure 6.5b). In the Chamulka soil, NO_3^--N concentrations were higher in runoff from the control in the first sample but thereafter concentrations in control and urea treatments were nearly identical. Urea was not detected in samples from the control treatments of the first replicate. It was assumed that urea was not present in detectable quantities in samples from control treatments in subsequent replicates. Urea measurements performed on several runoff and inter-flow sample from the second and third simulations validated this assumption. In the urea treated soils, urea-N concentrations in runoff declined with time, but urea-N was still detectable after 90 minutes (Figure 6.5c).

Total NH_4^+–N export was not significantly different between soils, but was strongly affected by treatment (Table 6.3). Ammonium-N export in leachate was significantly higher from the urea treatments than from the controls, but was two orders of magnitude less than export in runoff. Total export of NO_3^-–N in runoff was significantly higher in the Chamulka soil compared to the Borys soil. Treatment differences were not significant. Urea-N export was higher from the urea treatments in the Borys soil than in the Chamulka soil. Export in leachate did not vary with soil in the mean comparison, but treatments within soils differed.

Total Inorganic and Dissolved Organic Carbon in Runoff and Leachate

Concentrations of TIC in runoff were higher throughout the run in the urea treatments compared to the controls (Figure 6.6a). The pH suggests that for both the urea and control treatments, HCO_3^- rather than CO_3^{2-} was the dominant ionic form of TIC. In the controls, TIC concentrations were constant after 36 minutes. The equilibrium concentrations were very close to the mean concentration in the rainwater. The concentrations of DOC were initially more than four times higher in runoff from the urea compared to the control treatment. (Figure 6.6b). The DOC concentrations declined in both treatments over time, but more so in the urea treatment, narrowing the relative difference considerably after 90 minutes.

Export of TIC was significantly higher in runoff from urea treatments, but there were no significant differences between treatments for leachate (Table 6.3). In the Borys soil, four times more DOC was exported in runoff from urea treatments compared to the controls. The difference between treatments was three-fold in the Chamulka soil. There were no significant treatment differences in DOC export through leachate.

DOC concentrations in samples from the urea treatments were corrected by subtracting urea-C prior to statistical analysis. Urea C concentrations and exports on a molar basis are half those shown for urea-N. Urea-C export in the urea treatments was approximately 5% and 3% of corrected DOC in runoff from the Borys and Chamulka soils respectively.

Ca, Mg, K, P and S in Runoff and Leachate

Calcium concentrations in runoff from the controls were initially higher than from the urea treatments (Figure 6.7a). Concentration declined as the simulation progressed but at 90 minutes, Ca concentrations in runoff from the controls were still double those from the urea treatments. Magnesium behaved in a manner very similar to Ca. Magnesium concentrations in runoff (data not shown) were approximately 20% of those measured for Ca. Runoff transported less Ca and Mg from the urea treated soil in runoff than from the control soil (Table 6.4). Export in leachate was not affected by treatment but did vary with soil for both Ca and Mg.

Potassium concentrations in runoff tended to rise as the rainfall event proceeded (Figure 6.7b). For the respective soils, K concentrations were lower in runoff from the urea treatments compared to the controls. Potassium concentrations in runoff were less than those in the rainwater, suggesting that contact with the soil attenuated K. Attenuation was greater in the urea treated soils than in the controls.

During ICP analysis of the first replicate, problems were encountered with acquisition of signal from the photodetector reading the spectral line for P. There was insufficient sample to rerun the analysis once the problem was corrected. Phosphorus data from the first replicate were discarded. Concentration of P in runoff declined with time in both soils (Figure 6.7c). However, concentration in runoff from the urea treatments remained higher than the controls throughout the rainfall event. Phosphorus export in runoff was doubled on average by addition of urea to the soil, but was not significantly different between soils. Phosphorus export in leachate was not significantly different between treatments or soils (Table 6.4).

Sulphur in runoff declined from an initial concentration of 1.0 mmol L^{-1} (average of all treatments, S concentration curve not shown) to 0.61 mmol L^{-1} at 30 minutes. The mean S concentration in the rainwater was 0.59 mmol L^{-1}. Sulphur concentrations did not change from 30 to 90 minutes. There were no significant effects of treatment on S export through runoff (Table 6.4). Soil and treatment had a significant effect on sulphur export in leachate. Sulphur exports were higher from control treatments than from urea treatments and were higher from the Borys soil.

Aluminum and Trace Metals

Aluminum and Fe concentrations in runoff fluctuated with time (Figure 6.8a,b). Overall, Al and Fe concentrations tended to be higher in runoff from the urea treatments than from the controls. When compared point to point, there is a high degree of correlation between the Fe and Al concentrations in runoff ($r^2 = 0.92$, $p < 0.001$). The correlation between Fe and Al concentrations in leachate (data not shown) was also high ($r^2 = 0.95$, $p < 0.001$). Although Cu was added to the 0-2 cm depth in both controls and urea treatments, it was measured in much higher quantities in runoff from the urea treatments (Figure 6.8c). In the controls, Cu concentrations were below the detection limit (0.05 µmol L^{-1}) in a number of samples. The Cu concentration curves follow the pattern seen earlier for NH_4^+–N and DOC. They were not similar to the Al and Fe curves. Manganese and Zn concentrations in runoff were near or below the detection limits in a large number of samples. Poor replication in this range plus the problems associated with dealing with values below detection in statistical analysis prevented any meaningful interpretation of Mn and Zn concentrations or export in runoff.

Export of Al and Fe in runoff from the urea treatments was more than double that from the controls (Table 6.5). Export of Cu in runoff was the same from both soils. There was a significant treatment effect. Copper exports from urea treatments were an order of magnitude higher than from controls. For export with leachate, treatment effects were not significant at $p \leq 0.05$ for any of the trace elements.

Discussion

The original hypothesis for this experiment was that urea application would not change the transport of elements solubilized in the FRZ. Using simulated rainfall in a laboratory setting allowed testing this hypothesis under conditions that closely approximated surface and near surface hydrological processes found in the field. Initially wetting the soils from below might be construed as a situation that applies only to a limited number of soils in natural environments. This procedure may have brought urea hydrolysis products to the surface. However, evaporation from the soil surface drives mass flow of water towards the surface under natural conditions. Diffusion of urea and urea reaction products through soil solution as well as diffusion of NH_3 through soil air would also lead to intersection of FRZ with the soil surface during the five days separating fertilizer application and rainfall.

Laboratory simulation removed a large part of the hydrological variation inherent in field soils and allowed reasonable replication. The CV for runoff volume during the first 30 minutes was 14%. This includes any treatment and soil effects on runoff volume. For the total runoff volume over 90 minutes, the CV was 6%. The absolute variability for leachate was similar to runoff. Standard deviations were 1.60 and 2.35 L respectively for leachate and runoff. However, the relative variability was higher, CV of 42%, due to the lower leachate volume. This suggests that replication of runoff was good. It also suggests that leachate volume differences were similar in magnitude to the experimental variability in runoff rates.

In this experiment, high fertilizer rates were used primarily to amplify effects. These rates, equivalent to 10 kg Cu ha^{-1} and 460 kg N ha^{-1} if calculated on an aerial basis, were much greater than would normally be applied to these soils in normal crop production. Rates that are more typical for these soils would be 50 to 100 kg N ha^{-1} and 0.5 to 2 kg Cu ha^{-1}. Soils are exposed to similar concentrations, approximately 2000 mg N kg^{-1} and 40 mg Cu ha^{-1}, when fertilizer is banded or seed-placed. For example, placing the same concentrations in the seed-row using an implement with 20% seedbed utilization, the rates used in this experiment were 92 kg N ha^{-1} and 2 kg Cu ha^{-1}. In this context, the rain-frames can be considered as an approximation of the surface of a seed-row or shallow band.

The transport by runoff of certain soluble elements was increased following urea addition to the soil. These elements included C, in inorganic and organic forms, as well as N, P, Al, Fe, Cu. The transport of Ca and Mg was reduced. The null hypothesis can be rejected for these elements as it applies to runoff. Manganese and Zn transport were not significantly altered by urea addition and the null hypothesis can be accepted.

Interpretation of the leachate results with respect to the null hypothesis is not as clear cut. The differences in leachate discharge from the four soil-treatment combinations affected the estimates of export quantities for the different analytes. These differences in leachate quantity may accentuate or mask differences in leachate exports. Effects of treatment on export through leachate were significant for NH_4^+–N, urea-N, K and S. Urea application increased export of the first two analytes and decreased export of the latter two. For NH_4^+–N and urea-N, quantities exported were higher from the urea treatments even though leachate volumes were lower compared to the control. The original hypothesis can be rejected. Potassium export and S export were higher from the controls. Apparently, urea addition reduced K and S export and the null hypothesis can be rejected. Whether these reductions were a result of reduced discharge volume alone or also included changes in soil solution concentrations was not clear. To investigate further, flow weighted mean concentrations (FWMC) were calculated and analyzed statistically. Treatment had a significant effect on FWMC of S but not K, suggesting that treatment effects on S transport were not simply a result of differences in leachate volume. Although treatment effects were not significant with respect to export of Ca and Mg in leachate, they were significant when FWMC's were compared. Urea addition reduced the FWMC of Ca by 9 and 25% in leachate from the Borys and Chamulka soil respectively. The comparable values for Mg were 9 and 33%. The original hypothesis holds in terms of the quantity of Ca and Mg exported, but the lack of difference was a result of treatment effects. Treatment effects on FWMC were not significant for TIC, DOC, P or the trace elements.

Nitrogen, mainly as NH_4^+–N in runoff, was the main FRZ reaction product transported from the application zone. A portion of this NH_4^+–N may have been brought into solution by exchange with K^+ in the rainwater. The reduction in K concentration in runoff versus rainwater supports this hypothesis. The mass balance of K inputs with rainwater and outputs with runoff suggested that K^+ exchange would account for 10% of the NH_4^+–N in runoff. The concentration curves show that even towards the end of the rainfall simulation, the attenuation of K concentration by urea treated soils is an order of magnitude lower than the concentration of NH_4^+–N in runoff. The analytical technique used for NH_4^+–N captures NH_3 as well. The NH_3 to NH_4^+ ratio in solution is strongly pH dependent. At the pH values measured in runoff from urea treatments, NH_3 concentrations would be 8-10% of NH_4^+ in urea treatments and 3-5% in controls. The concentration curves suggest that in the early stages of runoff, NH_4^+–N was flushed from the soil. As rainfall continued the concentration of NH_4^+–N in runoff from the urea treated soils approached equilibrium far above that for the controls. Conversion of NH_3 to NH_4^+ was not the primary process responsible for recharging runoff, neither was ion exchange with K^+. Continual dilution of the soil solution and release of NH_4^+ from exchange sites must have been the main process loading NH_4^+ into runoff.

Losses in runoff approached 20% of applied N in both soils. These losses were one to two orders of magnitude higher than runoff losses of fertilizer N measured under field conditions (Hubbard and Sheridan 1983, Hubbard *et al.* 1991, Lowrance 1992). It is also generally an order of magnitude higher than losses reported when simulated rainfall was applied to *in situ* soils by Gascho *et al.* (1998) or Torbert *et al.* (1999). However, the latter measured losses exceeding 10% in their highest loss treatments -a blend of monoammonium phosphate and ammonium sulphate surface applied to wet soils. The results of the current study suggest that urea application, even subsurface application as used here, can create conditions conducive to overland transport of NH_4^+.

In this study, DOC export in runoff was increased three-fold by urea addition. This is consistent with the increased DOC transport following urea or anhydrous ammonia additions reported in other studies (Ogner 1975, Otchere-Boateng and Ballard 1978, Homann and Grigal 1992, Clay *et al.* 1995). However, these studies examined leaching rather than runoff. In the current study, leaching of DOC was not increased when urea was added. All of the cited studies included either multiple rainfall events, real or simulated, and/or leaching with multiple pore volumes. The leachate volumes in the current experiment would make up approximately 20 and 10% of a pore volume in the Borys and Chamulka soils respectively. These volumes were likely too low to transport DOC through the profile in quantities that would allow separation of treatment effects.

Calcium and Mg concentrations were lower in runoff from the urea treated soils. This was consistent with the differences in soil solution concentrations measured in earlier experiments (Chapters 2 and 3). Kissel *et al.* (1988) attributed lower Ca and Mg to precipitation with CO_2^{2-}. Otchere-Boateng and Ballard (1978) examined leaching of Ca and Mg following urea application to forest soils in southwestern British Columbia. They reported leaching of Ca and Mg initially decreased during the high pH phase associated with urea hydrolysis. In their study, Ca and Mg leaching started to increase 100 days after application, once nitrification reduced the pH.

Urea application enhanced both the concentration and total export of Al, Fe and Cu. The linkage between soluble carbon and metal transport has been examined by a large number of researchers. Simonson (1959) in presenting his generalized theory of pedogenesis reported that there was a wealth of evidence supporting the downward translocation of metal ions complexed with soluble organic ligands. In a more recent review, Stevenson and Fitch (1986) stressed the role of fulvic acid complexes in metal migration. Pohlman and McColl (1988) found that Fe and Al displacement from soil columns was strongly correlated to organic acid concentrations in the eluent, which they prepared by leaching forest litter.

Similarity between the DOC and Cu curves for runoff from urea treatments ($r^2 = 0.96$, $p < 0.001$) suggested transport of metal-organic complexes. To examine this further, the first three runoff samples from the urea treatments from each replicate were filtered using SEP-PAK® C18 cartridge filters, which remove a portion of DOC. Filtering reduced Cu concentrations in runoff. The average reductions were 37 and 35% from the Borys and Chamulka soils respectively. These measurements provide direct evidence that a significant portion of the Cu solubilized in the FRZ was transported in complexed form with DOC. More sophisticated techniques would be required to determine the exact nature of these metal-organo complexes, and the nature of the remaining two-thirds of the mobile Cu.

The Al and Fe concentration curves were not similar in shape to the DOC curve. If viewed in isolation the Al and Fe concentration results could easily be dismissed as noisy data. The close correlation between Al and Fe concentrations suggests that the variability was not random noise. The Al and Fe measured in runoff may be colloidal clay, such as an Fe substituted smectite, rather than metal ions associated with organic ligands. There is other evidence such as greater erosion from urea treatments that suggests structural breakdown and dispersion of clays. Water dispersible colloids have been implicated in the transport of trace metals, those with high surface charge being particularly effective (Karathanasis 1999).

Application of urea increased erosion rates and total sediment discharge. This is consistent with the dissolution of SOM brought about by urea. Furthermore, increased pH tends to disperse permanent charge layer silicate clays (McBride 1994, Chapter 8). Clay-organic matter complexes are essential in the formation of water stable aggregates (Tisdall and Oades 1982), so it is not surprising that urea addition increased erosion rates. A number of other workers have established that NH_3 can disrupt soil structure (Cecconi and Vidrich 1970, Epshteyen and Agafonaov 1977, Gifford and Strikling 1958). Sediment transport is an important mechanism in nutrient transport from soil. Reducing the sediment portion of runoff, through conservation tillage for example, reduces fertilizer nutrient loss, particularly if the fertilizer is applied below the surface (Beyrouty *et al.* 1986, Timmons *et al.* 1973, Whitaker *et al.* 1978). Outside of the results reported here, there appears to be no studies directly linking fertilizer effects on structure to increased sediment loads in runoff.

Total transport of trace metals with sediment would likely be much higher than with solution. For example, DTPA extractable Cu in the 0-2 cm depth of the Borys and Chamulka soil was on average 550 μmol kg^{-1}. Assuming concentrations in sediments were similar to soil, Cu export in sediment at 314 μmol m^{-2} for controls and 515 μmol m^{-2} for urea treatments would be one to two orders of magnitude higher than export in solution. This would be a very conservative estimate because sediment would be clay rich and thus enriched with adsorbed metals.

Urea fertilizer additions enhanced transport of a number of nutrient elements in both soluble and solid form. Would this have any significant impact on nutrient availability to crops or water quality? With the exception of N availability, the effects of liquid runoff losses on crop production would be negligible in the short-term. Copper losses through runoff were 17 μmol Cu m^{-2}. This converts to 0.01 kg Cu ha^{-1}, 20-40% of the annual requirement of a cereal crop. However, the losses were less than 0.1% of the Cu added. Phosphorus losses were 0.3 kg P ha^{-1}, 1 to 2% of annual crop requirements. Nutrient losses with sediment were likely larger. Assuming Cu concentration in sediment were one to three times those in the soil after rainfall, losses due to urea application would still only be 1 to 3% of added Cu. The added soil loss from the urea treatments, equivalent to increasing from 4-6 to 8-10 Mg ha^{-1}, would be considered substantial and serious from a soil quality point of view.

With respect to water quality, dissolved-P concentrations in liquid runoff from urea treatments exceeded 1.6 μmol L^{-1} (50 μg P L^{-1}), the value generally used to separate oligotrophic from eutrophic systems. Trace element concentration in runoff were several orders of magnitude below those considered harmful to aquatic environments. Again the sediment, should it reach surface water, would likely have more of an effect on water quality than the liquid portion of runoff.

Conclusions

The transport of a number of elements in runoff was increased when urea was applied below the surface of two soils. These included NH_4^+–N, urea-N, dissolved-P, TIC, DOC, Al, Fe, and Cu. It decreased the transport of Ca, Mg and K in runoff and had no measurable effect on S, Mn, and Zn. In leachate, NH_4^+–N and urea-N exports were increased, while K and S exports were decreased. There were no significant effects on export of other elements.

An additional finding of this study was that urea additions increased sediment loads by approximately 40%. Losses of nutrient and trace elements in solution were small relative to those lost in sediment. Further study of both solution and solid phase losses caused by urea fertilizer under field conditions are required, before their impact on crop production and water quality can be put in perspective.

Table 6.1. Characteristics of soils, urea and water used in rainfall simulation experiments.

Soil Analysis

Soil	pH	EC	Organic Matter	Sand	Silt	Clay	Exchangeable Cations				CEC
							Ca	Mg	Na	K	
		dS m^{-1}	*g kg^{-1}*		*%*			*mmol kg^{-1}*			*mmol (+) kg^{-1}*
Borys	6.2	0.30	73	22	40	38	129	23	10	11	318
Chamulka	6.3	0.30	67	42	37	21	102	11	10	14	236

Urea Analysis

	TIC[x]	Ca	Mg	K	Na	S	Al	Fe	Cu	Mn	Zn
			mmol kg^{-1}						*µmol kg^{-1}*		
In Urea	1300	0.8	0.3	2.6	1.3	0.56	BDL	BDL	16	BDL	BDL
Soil[y]	6.5	0.004	0.002	0.013	0.007	0.003	nil	nil	0.08	nil	nil

Water Analysis

	pH	I^z	NH_4-N	NO_3-N	TIC	DOC[u]	Ca	Mg	K	S	Al	Fe	Cu
					mmol L^{-1}							*µmol L^{-1}*	
Mean	7.8	4.24	0.10	0.05	1.43	0.15	0.019	0.0065	3.09	0.59	0.35	0.069	0.01
Std Dev	0.1	0.16	0.10	0.05	0.08	0.01	0.009	0.0016	0.28	0.03	0.31	0.096	0.03
CV (%)	1	4	95	89	6	10	50	25	9	4	88	139	361
Maximum	8.00	4.5	0.27	0.16	1.62	0.18	0.038	0.009	3.53	0.65	0.86	0.259	0.12
Minimum	7.60	3.9	BDL	BDL	1.33	0.13	0.009	BDL	2.72	0.56	BDL	BDL	BDL
Detection Limit	NA	NA	0.007	0.007	NA	NA	0.005	0.004	0.01	0.003	0.10	0.100	0.05
Samples BDL	NA	NA	4	4	NA	NA	0	0	0	0	4	7	9

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[x] Total inorganic carbon.

[y] Contribution of urea contaminants to soil used in the 0-2 cm layer for rainfall simulation.

[z] Ionic strength, mol L^{-1} X 10^3.

[u] Dissolved organic carbon.

Table 6.2. Extractable trace metals and mineral-N in two soils before incubation, and after incubation followed by simulated rainfall.

Soil	Treatment	Depth	Sampling Time[x]	DTPA Extractable Trace Metals				Mineral-N	
				Fe	Mn	Cu	Zn	NH_4^+-N	NO_3^--N
		cm		*µmol kg^{-1}*				*mmol kg^{-1}*	
Borys	Control	0-2	Pre-incubation	1680a[y]	320a	580a	54a	0.75a	1.01a
			Post-rain	1640a	310a	410a	53a	0.59a	0.80b
		2-10	Pre-incubation	1740a	410a	22a	78a	0.47a	1.68a
			Post-rain	1700a	350a	25a	71a	0.72a	2.12b
	Urea	0-2	Pre-incubation	1650a	320a	590a	56a	1.56a	1.20a
			Post-rain	1510b	210b	410b	76a	95.5b	1.57a
		2-10	Pre-incubation	1740a	410a	22a	78a	0.47a	1.68a
			Post-rain	1680a	320b	19b	61a	7.61a	4.01b
Chamulka	Control	0-2	Pre-incubation	1870a	400a	500a	120a	1.02a	9.81a
			Post-rain	1950a	420a	360a	88a	0.50a	6.55b
		2-10	Pre-incubation	1930a	640a	22a	140a	0.84a	9.43a
			Post-rain	1870a	450b	24a	94a	0.55a	11.8b
	Urea	0-2	Pre-incubation	1870a	400a	500a	95a	0.59a	9.74a
			Post-rain	1580b	300b	300b	84a	84.0b	8.02b
		2-10	Pre-incubation	1930a	640a	22a	140a	0.84a	9.43a
			Post-rain	1860b	430b	16b	100a	8.99a	16.0b

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[x] Pre-incubation samples were taken immediately prior to addition of urea. Post-rain samples were taken following 5 days incubation and a 90 minutes simulated rainfall.

[y] Pre-incubation and Post-rain mean pairs for each soil/treatment/depth combination are different if followed by different letters. Means were compared using Student's t ($p < 0.05$).

Table 6.3. Total export of NH_4^+–N, NO_3^-–N, urea-N, total inorganic carbon, and dissolved organic carbon in runoff and leachate during simulated rainfall on two soils treated with urea.

Soil	Treatment	Runoff					Leachate				
		NH_4^+–N	NO_3^-–N	Urea-N	TIC	DOC	NH_4^+–N	NO_3^-–N	Urea-N	TIC	DOC
							$mmol\ m^{-2}$				
Borys	Control	6.4a[x]	8.8a	BDL[y]	101a	18a	1.0a	49	BDL	6.3	26
	Urea	590b	15a	7.1a	145b	69b	4.2bc	43	7.5a	5.9	24
Chamulka	Control	5.8a	50b	BDL	108a	23a	1.5ab	64	BDL	5.4	29
	Urea	600b	46b	3.1b	157c	53c	5.0c	33	8.7a	4.9	24
Source							ANOVA				
							P				
Block		ns	ns	ns	0.0015	ns	ns	0.0115	ns	ns	ns
Soil (A)		ns	0.0001	0.0027	0.0130	0.0416	ns	ns	0.0051	ns	ns
Treatment (B)		0.0001	ns	0.0001	0.0001	0.0001	0.005	ns	0.0396	ns	ns
Soil X Treatment (AB)		ns	ns	0.0027	ns	0.0032	ns	ns	ns	ns	ns

[x] Means in columns are significantly different if followed by different letters ($p < 0.05$).

[y] Below detection limit. BDL values are significantly different from other mean values in the same column.

Table 6.4. Total export of Ca, Mg, K, P and S in runoff and leachate during simulated rainfall on two soils treated with urea.

Soil	Treatment	Runoff					Leachate				
		Ca	Mg	K	P[x]	S	Ca	Mg	K	P	S
		mmol m^{-2}									
Borys	Control	21a[y]	6.3a	197a	0.48a	48a	14a	5.2a	16.6ab	0.15	14a
	Urea	6.6b	1.5b	176b	0.81ab	50ab	10ab	3.6ab	13.8ab	0.14	10ab
Chamulka	Control	18c	3.9c	236c	0.58a	52b	7.9bc	2.1bc	17.3a	0.16	8.0bc
	Urea	4.3b	1.3d	210d	1.09b	51b	4.8c	1.3c	13.6b	0.12	5.9c
Source		ANOVA									
		P									
Block		ns	ns	0.0001	ns	0.0096	ns	ns	ns	0.0433	ns
Soil (A)		0.0174	0.0001	0.0001	ns	0.0391	0.0081	0.0026	ns	ns	0.0041
Treatment (B)		0.0001	0.0001	0.0001	0.0124	ns	ns	ns	0.0218	ns	0.0469
Soil X Treatment (AB)		ns	0.0109	ns	ns	ns	ns	ns	ns	ns	ns

[x] Phosphorus means and ANOVA based on two replicates.

[y] Means in columns are significantly different if followed by different letters ($p < 0.05$).

Table 6.5. Total export of Al, Fe, Cu, Mn, and Zn in runoff and leachate during simulated rainfall on two soils treated with urea.

Soil	Treatment	Runoff					Leachate				
		Al	Fe	Cu	Mn	Zn	Al	Fe	Cu	Mn	Zn
						µmol m^{-2}					
Borys	Control	170a^{x}	39a	2.6a	BDL^{y}	BDL	14	3.4a	2.0	17	1.3
	Urea	470b	100b	17b	BDL	1.5	19	3.7a	1.5	7.6	1.3
Chamulka	Control	240ab	38a	2.2a	BDL	2.5	18	4.4ab	1.4	19	2.0
	Urea	440ab	80ab	17b	0.45	0.9	28	7.1b	1.1	3.9	1.5
Source						ANOVA *P*					
Block		ns	0.0188	ns	ns	ns	ns	0.0043	ns	ns	ns
Soil (A)		ns	ns	ns	ns	ns	ns	0.0469	ns	ns	ns
Treatment (B)		0.0046	0.0238	0.0003	ns	ns	ns	ns	ns	ns	ns
Soil X Treatment (AB)		ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

[x] Means in columns are significantly different if followed by different letters ($p < 0.05$).

[y] Below detection limit.

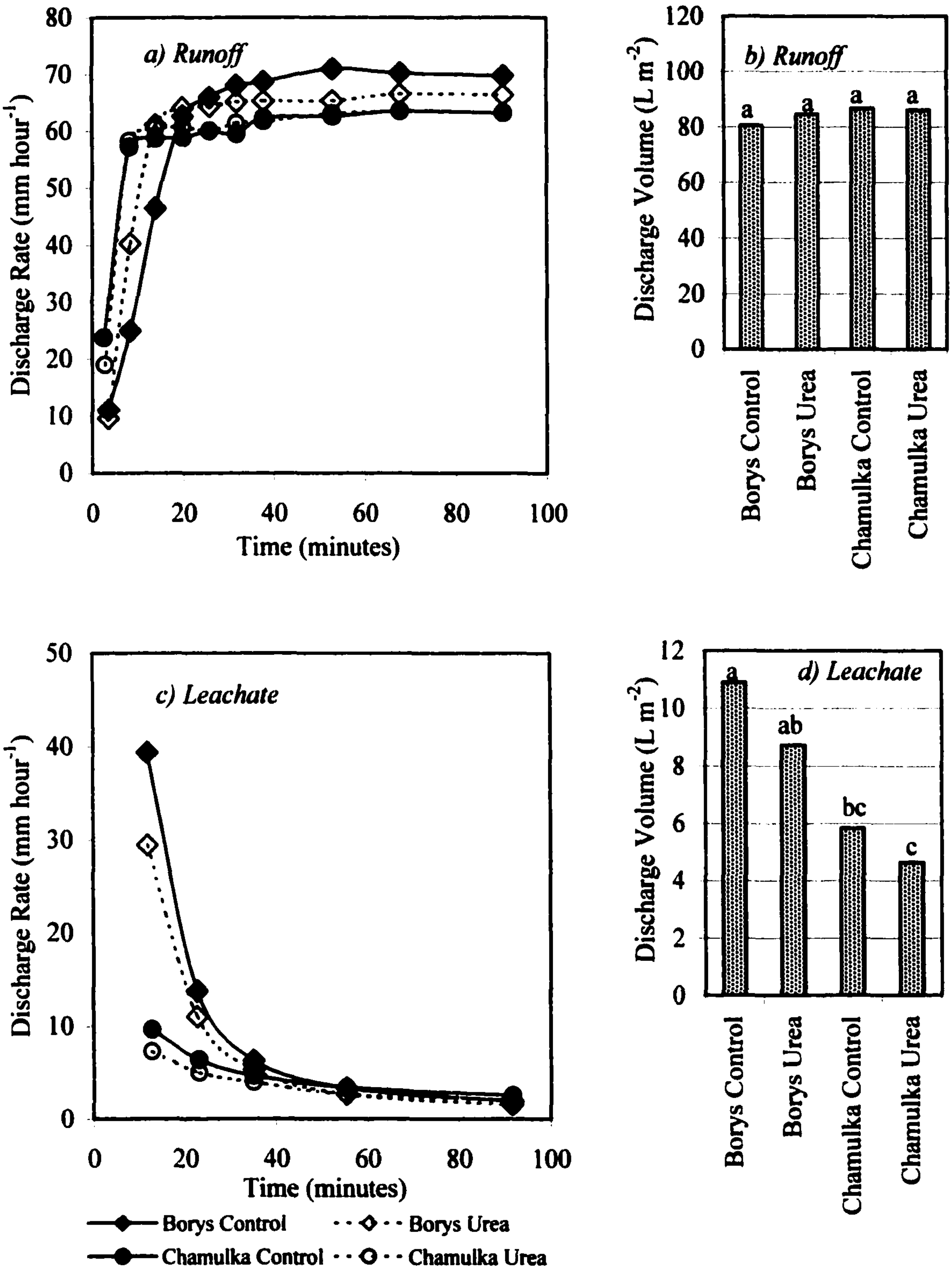

Figure 6.1. Discharge rate and volume from two soils during simulated rainfall.

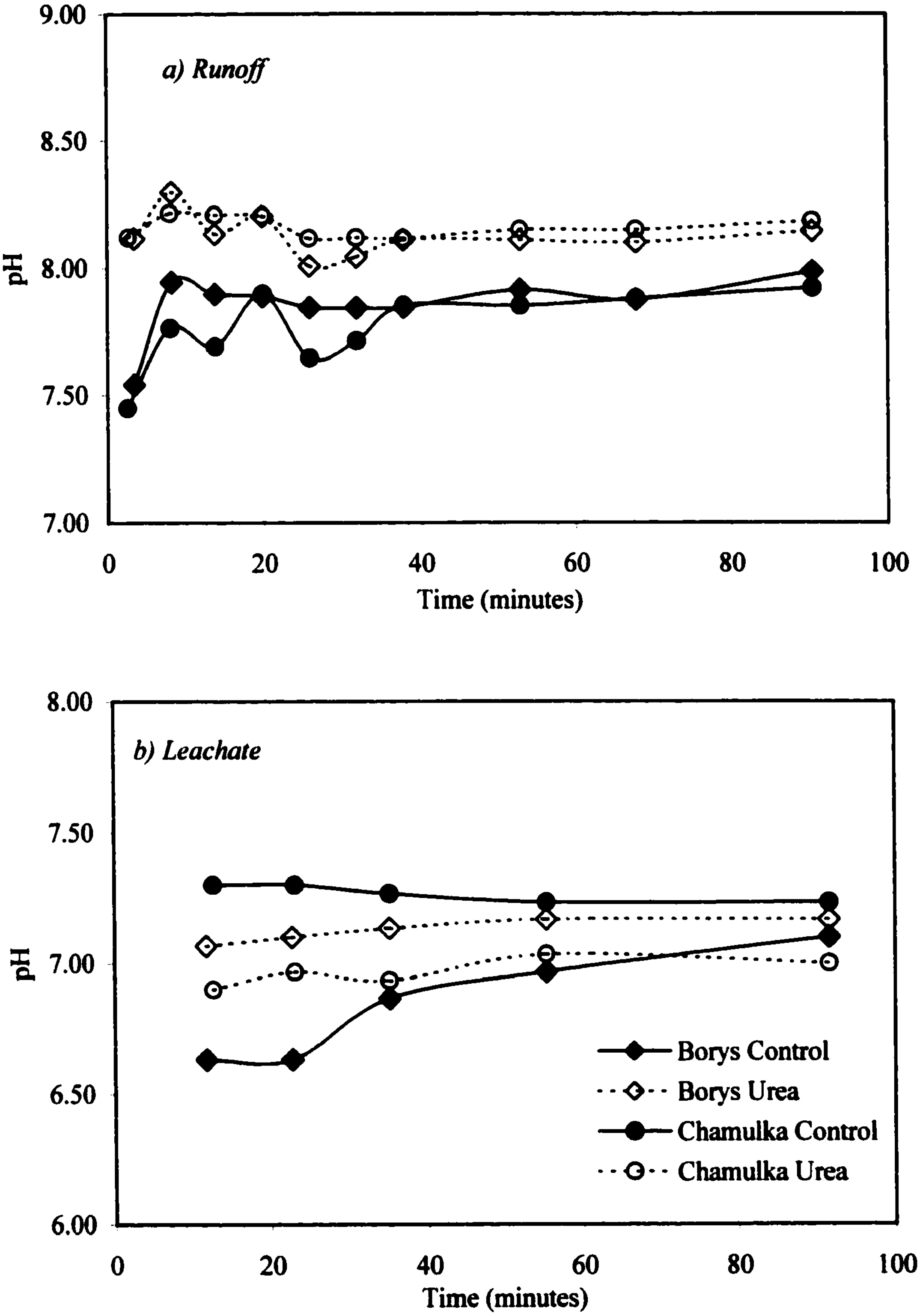

Figure 6.2. Runoff and leachate pH during simulated rainfall on two soils.

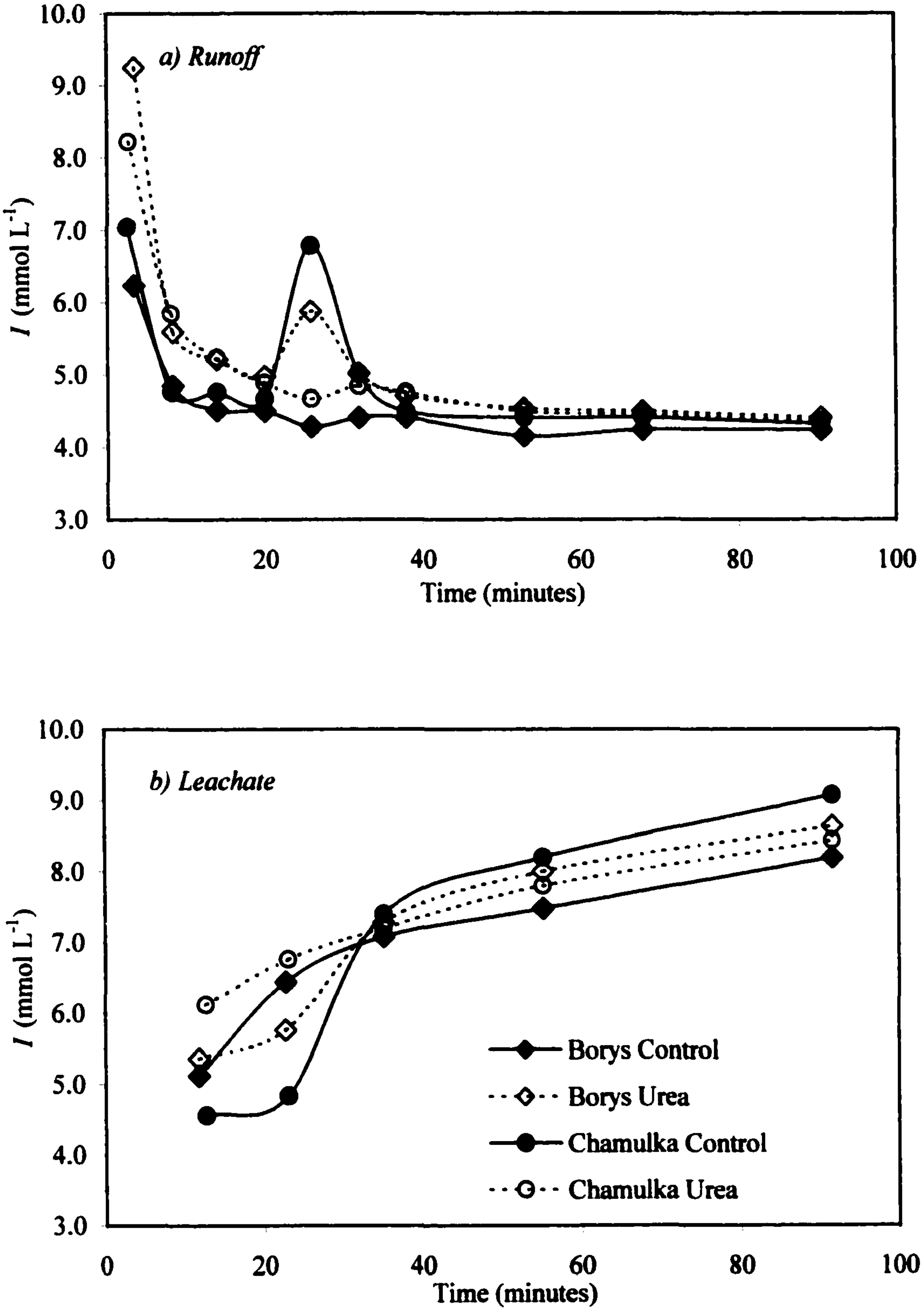

Figure 6.3. Ionic strength of runoff and leachate during simulate rainfall on two soils.

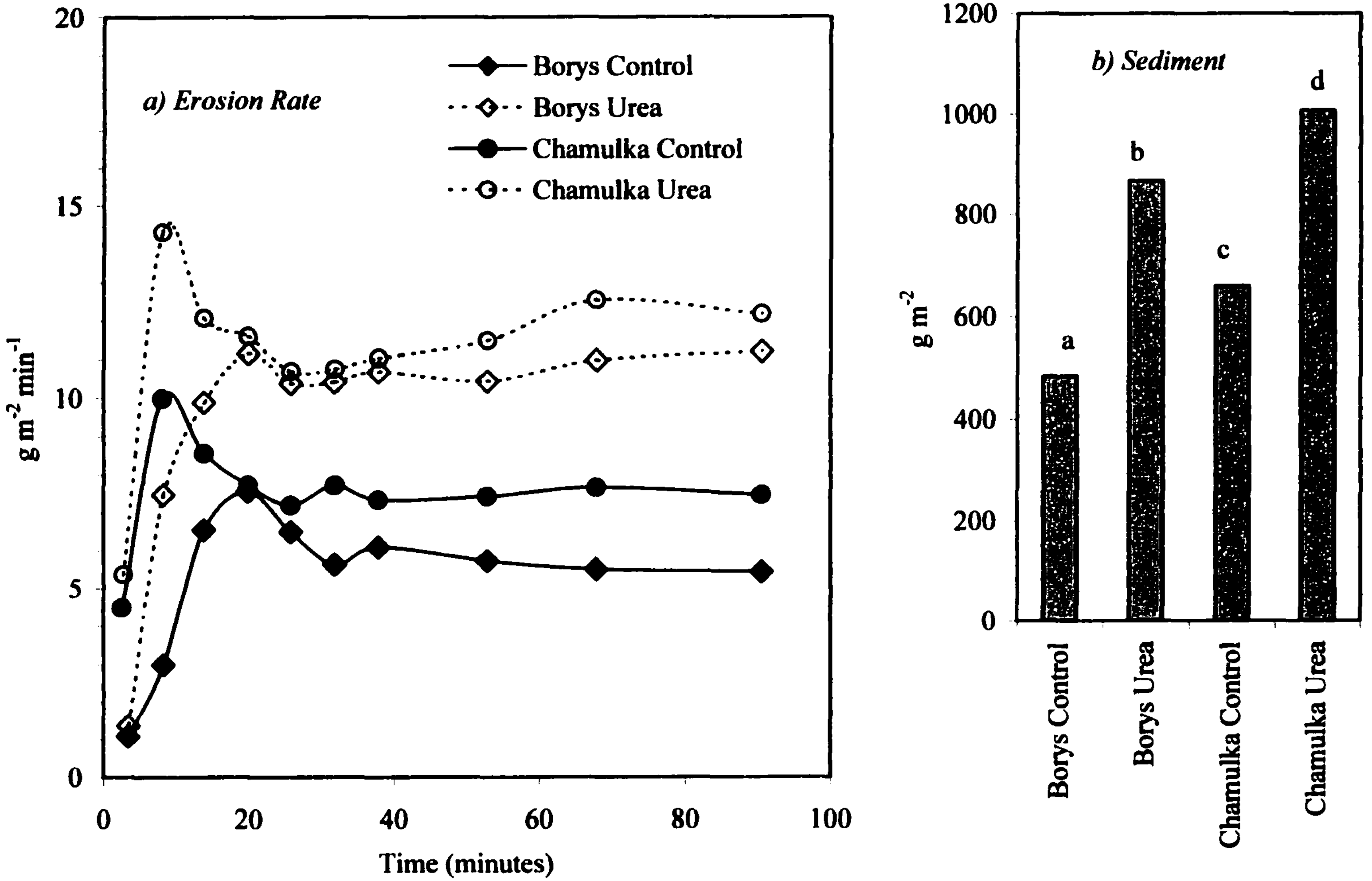

Figure 6.4. Erosion rate and total sediment export from two soils treated with urea and rained on for 90 minutes.

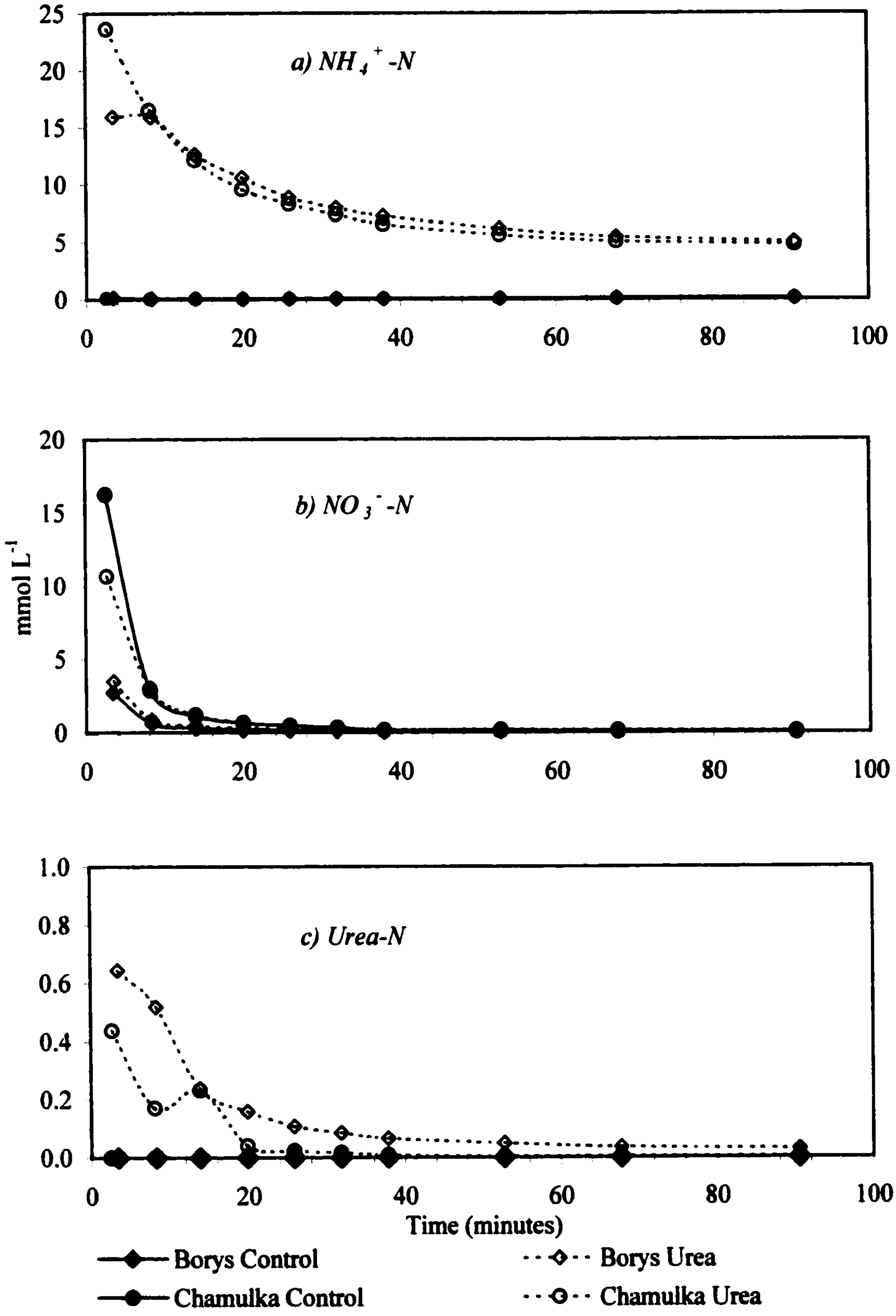

Figure 6.5. Nitrogen in runoff from two soils treated with urea.

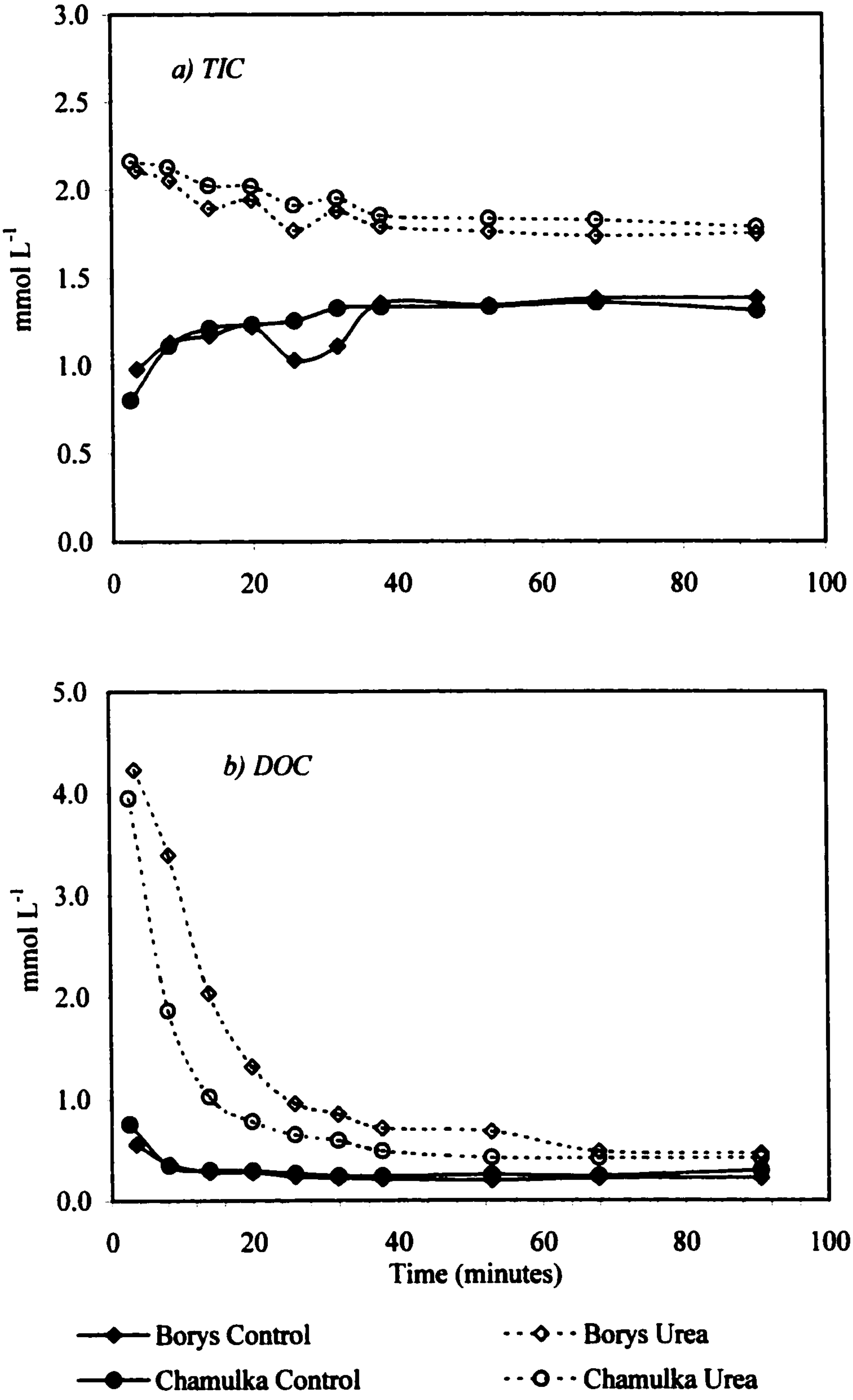

Figure 6.6. Total inorganic carbon and dissolved organic carbon in runoff.

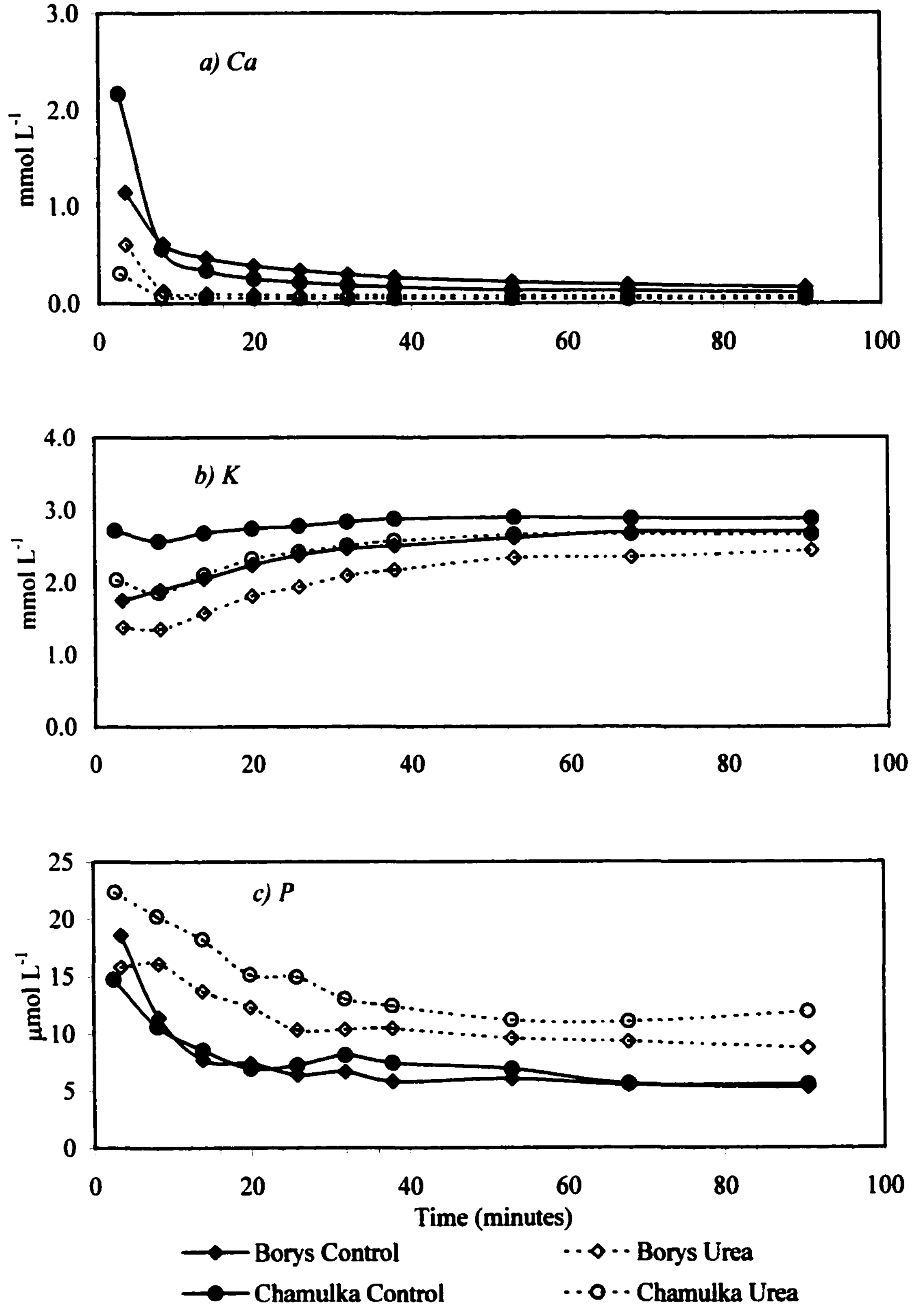

Figure 6.7. Total soluble Ca, K, and P in runoff from two soils.

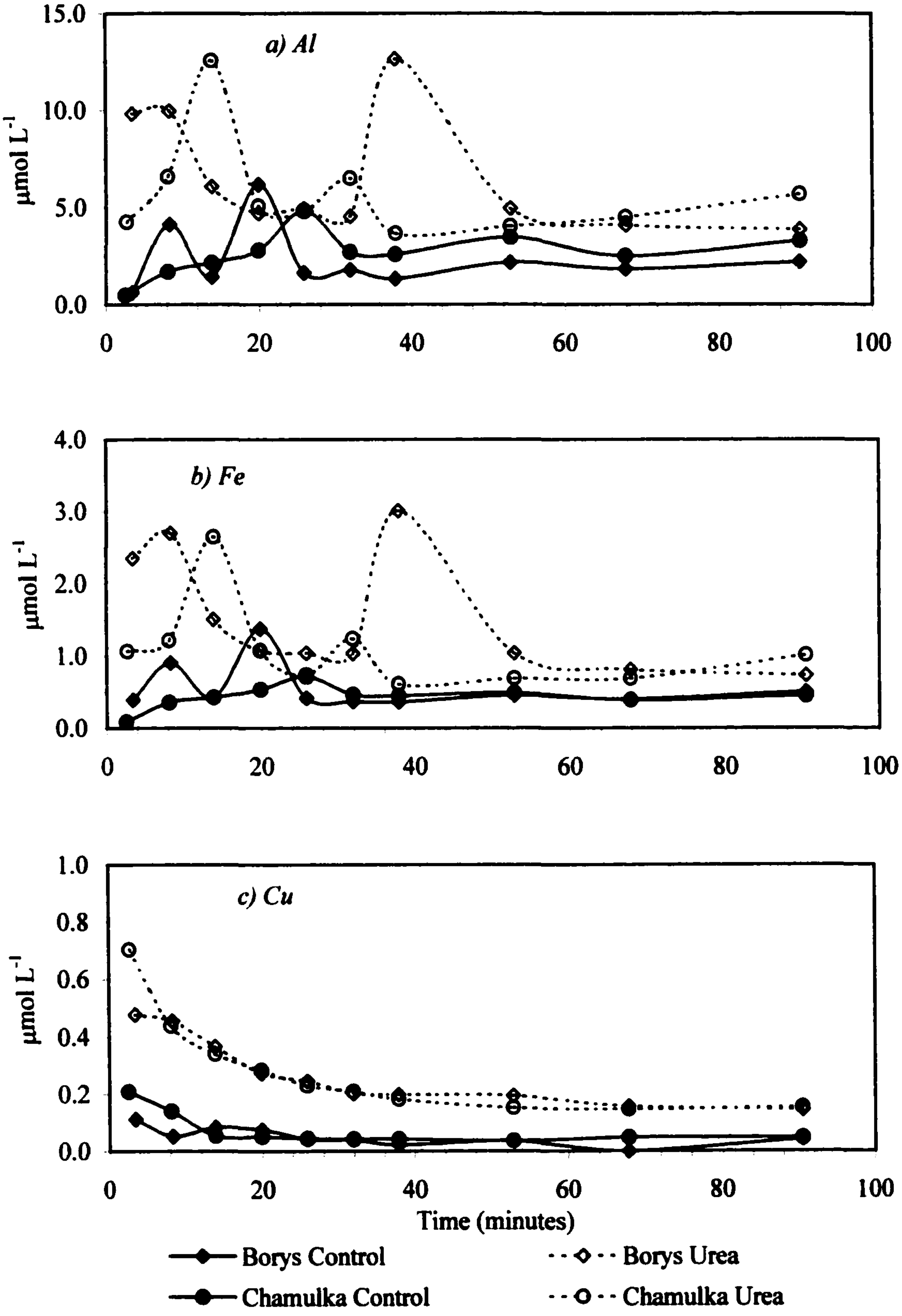

Figure 6.8. Total soluble Al, Fe, and Cu in runoff from two soils.

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CHAPTER 7

PRODUCTS OF UREA HYDROLYSIS IN SOIL ALTER THE SOLUBILITY, PLANT UPTAKE, AND TRANSPORT OF ELEMENTS: SYNTHESIS, HYPOTHESIS, AND FUTURE RESEARCH

Results from the five experiments reported in previous chapters support the following:

- Urea hydrolysis products altered the solubility of a variety of metal and non-metal elements within the soil solution of the fertilizer reaction zone (FRZ).
- Urea reacted in soil in ways that altered plant availability of soil derived and fertilizer elements other the N.
- Changes in solubility led to enhanced transport of soil derived and fertilizer elements in surface runoff.

Although the experiments quantified the changes brought about by urea additions, they did not directly identify the processes involved. Earlier Kissel *et al.* (1988) had described the effects of urea hydrolysis products on Ca and Mg and verified the precipitation processes responsible. There was, however, at the onset of the research described in this thesis, little information in the literature on changes in soluble organic carbon (SOC) or other elements in soil solution following urea fertilizer additions. Consequently, the first objective was to measure changes in soil solution under conditions that approximated the FRZ around a urea granule. The second and third objectives were to determine if changes found in soil solution brought about measurable changes in plant availability and element mobility respectively. As so little was known about the direction and magnitude of these changes, it was difficult to formulate specific hypothesis concerning process. Now, having quantified what occurred, the appropriate questions of how it occurs can be formulated and tested in future work. The purpose of the following discussion is to link the experiments in terms of what was observed and develop hypothesis on process consistent with the results.

Urea Hydrolysis Products and Soil Solution

Towards the purpose stated, limited soil solution modeling was done using the thermodynamic solution model GEOCHEM. Thermodynamic solution models are based on adsorption, exchange, precipitation, and complexation reactions under equilibrium conditions. They ignore a number of important factors such as reaction kinetics and biologically mediated reactions. None-the-less, application to systems not in equilibrium, such as those described in Chapter 2 and 3, may provide insight into process. Such insights may support or contradict existing data interpretations and thereby, suggest alternative hypothesis and new area of research.

GEOCHEM was used to speciate soluble metals and ligands using data obtained from an Orthic Dark Brown Chernozem (Soil 16) and a Dark Gray Solodized Solonetz (Soil 29) in Chapter 3. Solutions from all three treatments – control, urea, and ammonium sulphate (AS) – were modeled. Model boundary conditions, input, and output are summarized in tabular form in Appendix A. In brief, solution pH was fixed at the measured solution values. The model treated all SOC as fulvic acid (FA) at 50% carbon and with a molecular weight of 1000 g mol^{-1}. The controls and AS treatments were modeled as open systems and pCO_2 was allowed to equilibrate with the atmosphere. The urea treatments were modeled as closed systems to account for CO_2 production during urea hydrolysis.

The metal-ligand distribution illustrates several interesting trends (Table A4,A5). The soil solution of the urea treatments is supersaturated with respect to $CaCO_3$. This agrees qualitatively with the soil solution results from a number of soils that suggested $CaCO_3$ was precipitating. Interestingly the model output suggests that $Fe(OH)_3$, $Al(OH)_3$, $ZnCO_3$, and $MnCO_3$ are also precipitating. Significant amounts of Mn and Zn, but not Cu, are complexed with FA in the model solution. Soluble Cu is almost exclusively (97%) speciated with NH_3 to form complex cations. There is also significant pairing of Zn with NH_3, 63% in Soil 16 and 25% in Soil 29. This supports the discussion presented in Chapter 2 suggesting that the formation of ammoniated complexes may be drawing Cu and Zn into solution.

The model results need to be kept in perspective. The SOC was treated as FA rather than the mixture of FA, humic acid (HA), low molecular weight organic acids, and phenols which are normally found in soil solution. Humic acid contains a lower concentration of functional groups than FA, but tends to complex Cu and Zn more strongly (Schnitzer 1986). Homann and Grigal (1992) found in a forest soil that more HA than FA was solubilized following urea additions. A more exact characterization of the soluble organics in the FRZ would be required before the relative importance of ammonia and organic ligands in complexing metals could be quantified with certainty. More directly, information on Cu-NH_3 complexes in the FRZ could be obtained spectrographically as several of the more stable species absorb strongly in the visible range. Metal-ammonia complexes are positively charged, for example $[Cu(NH_3)]^{2+}$, and an unanswered question is whether they are occurring as free ions or are complexed or adsorbed themselves by SOC. GEOCHEM cannot answer that question as K values for the reactions involved are not available. It could be answered relatively easily using techniques that selectively remove organic complexes from solution.

Synthesizing the results of the various experiments, the point made by the model output is that metal-ammonia complexes are likely to form in the FRZ of urea. This may have been a significant process in relation to the high soluble Cu and Zn concentrations measured in the soil solution experiments as well as the increased Cu export measured under simulated rainfall. Metal-ammonia complexes need to be considered along with organic ligands in any further examination of metal solubility or mobility in soils fertilized with urea. The same would hold for soils fertilized with anhydrous ammonia, and based on the GEOCHEM results for AS (Appendix A, Table 6), ammonium salts as well.

From Soil Solution to Plant Uptake

In the plant uptake experiments, the data showed that urea reaction products alter availability of nutrient elements. Not all elements were affected and the results were not consistent enough to allow generalization to all soils. Whether the changes in plant availability, when they occurred, were linked to the initial stage when hydrolysis controls pH or the subsequent acidification stage, or both was not readily discernible. Since plant sampling was not linked explicitly to hydrolysis or nitrification in the soil, the results were generalized over the growing season. Certainly, nitrification of ammonium-based fertilizers like AS can increase availability and uptake of pH sensitive elements like Mn (Petrie and Jackson 1984a,b). Solution values from Chapter 3 showed that in the more acidified AS treatments, Soil 28 and 29, soluble Mn increased substantially. As an aside, the GEOCHEM data for soil 29 (Appendix A, Table A4) suggest that speciation with SO_4^{2-} as well as pH may be important in raising total Mn concentration in AS treated soil. Nitrification of urea derived N will also acidify the soil but not to the degree that AS does. The data reported in Chapter 2 and 3 showed that total Mn increased in solution relative to the control when urea was added in a number of soils. This increase was accompanied by a two order of magnitude increase in SOC. Similar trends are visible in the Cu, Zn, Fe, and Al results. Plant availability of Mn was commonly increased in urea treatments relative to CN treatments or controls in the experiments reported in Chapters 4 and 5. Plant availability of Zn and Fe was also enhanced in some soils following urea addition. Copper availability was only enhanced when Cu was added to the FRZ as Cu-EDTA. Interestingly, Cu-EDTA also enhanced availability of Mn when urea was the N source. Post harvest soil sampling in the greenhouse experiment of Chapter 5 showed that urea addition resulted in increased DTPA extractable Mn, but overall had no effect on soil pH.

The soil solution and plant results together suggest that while urea hydrolysis products generally increase solubility of micronutrient metals, this increased solubility may or may not increase plant availability. Furthermore, the increased plant availability, when it occurs, may or may not be a result of reduced pH as nitrification proceeds. This apparent confusion may be understandable if spatial variation in pH is considered. For example, the initial high pH in the FRZ solubilizes SOM. Elements bound to these now mobile organic ligands would be transported out of the fertilizer microsite by mass flow or diffusion (Figure 7.1). Acidification along the margins of the FRZ, where nitrification is likely to occur, or in the rhizosphere would tend to release complexed metals increasing the free metal concentration. Plants would then take up free metals. Ester bonded elements like P or S could be transported and then detached from carbon in the rhizosphere via exo-cellular enzymes. Soluble organic carbon transported from the urea microsite may be mineralized in soil or rhizosphere also releasing nutrients. In terms of metal transport, the ligands involved need not be organic, other ligands such as NH_3, CO_3^{2-}, and OH^- involved in the formation of pH-controlled complex ions could also be involved. Under this hypothesis, two types of metal behavior would likely be observed. The more weakly complexed metals, such as Mn and Zn, would be mobilized as complexes. They would tend to dissociate to release free metals as they were transported out of the FRZ as their solubility is also strongly pH-dependent (M1, Figure 7.2). Metals that tend to be strongly complexed and less pH-dependent may be mobilized with SOC or other ligands, but this would not enhance activity of the plant available free metal to any great extent (M2, Figure 7.2). Copper would likely prove to be this latter type of metal.

The above hypothesis is conceptually similar to theories of trace element transport to plants put forward by Mitchell (1972) and Zunino and Martin (1977). Both stressed the role played by organic complexes in transport of nutrient metals from soil solution to the rhizosphere. The difference is that in a urea treated soil, high SOC concentrations may create a stronger diffusion gradient between the FRZ and the root surface than would normally be found in untreated soil.

From Soil Solution to Runoff

The time for development of the FRZ in the soil solution experiments was from 4-20 days. It was 5 days in the rainfall experiment. Data from both sets of experiments suggest that within these times, urea hydrolysis rather than nitrification was the dominant process controlling pH. Since the two sets of experiments were comparable in time, a more direct link can be made between what was observed in the soil solution and what was observed in runoff than was possible with the plant uptake results. The soil solution and runoff results generally agree. Soluble organic carbon increased in the soil solution experiments following urea hydrolysis and elevated SOC concentrations were also observed in runoff. Calcium and Mg were precipitated in the FRZ and less was exported with runoff from urea treated soils compared to the controls. Export of several of the transition metals and non-metals solubilized in the FRZ was also higher in runoff from the urea treated soil. These included Al, Fe, Cu, and P. Although Zn and Mn levels tended to be elevated following urea addition in the soil solution experiments, the concentrations found in runoff tended to be below detection so export could not be estimated. In the soil solution experiments, the SOC concentrations correlated significantly with the more strongly complexed elements such as Al, Fe, and Cu. This was also the case for SOC and Cu in runoff. Filtration to remove a portion of SOC significantly reduced soluble Cu in runoff, suggesting the soluble Cu was organically complexed.

Although sediment-sorbed elements were not measured in runoff, sediment loss was substantially higher from the urea treated soils. This increased erosion rate is likely brought about by disruption of soil structure similar to that reported for anhydrous ammonia by a number of researchers (e.g. Cecconi and Vidrich 1970). When DTPA extractable micronutrient concentrations from post-rain soil analysis were used as a proxy for available micronitrients on sediments, the results suggested that losses of sediment sorbed nutrients were likely one to two orders of magnitude higher than losses in the solution portion of runoff. Other work with these same soils shows that the sediment removed by simulated rainfall is clay enriched (Mohamed Amrani, personal communication). Therefore, the estimate of nutrient loss calculated in Chapter 6 was conservative.

Differences in leachate composition between urea and control treatments were minor in the rainfall simulation experiment. The leachates from the urea treatments did not contain elevated metal concentrations relative to the control, nor was there a clear difference in pH. However, less than a fifth of a pore volume of water had moved through the soil profile. Increasing the duration of the rainfall event would have provided a more definitive comparison between treatments, but this was not possible due to water constraints. Long-term studies have shown that urea enhances downward movement of metals within the soil profile (Goh *et al.* 1987). Whether or not movement of metals to groundwater is increased in urea fertilized systems has not been determined. Many prairie soils, particularly those used for agricultural production, contain calcareous C horizons. Free metal ions moving downward in percolating water would tend to precipitate out of solution as hydroxides and carbonates in the C horizon. This may not be the case, for metals complexed with SOC. If the SOC is HA, then movement into a calcareous horizon would not reduce its solubility or the mobility of attached metals. In an acid subsoil, the

HA would tend to precipitate, but dissociation of the complex would free metal ions that may remain mobile.

Future Research

Most of the relevant research questions have been stated as part of the preceding discussion or in the appropriate chapters. Those chosen for elaboration below reflect the author's priorities in each of the three areas –solubility, availability, mobility– explored in this thesis.

Regarding the soil solution, there are two priority projects. One is to characterize the SOC brought into solution in the urea microsite. There are a number of possible approaches. Separation into humic and fulvic fractions, either through classic acidification or physical separation techniques, would link the results to a rich literature on humic substances. While classic techniques are simpler, chromatographic or centrifugation methods would allow quantification of complexed metals within each fraction (Homman and Grigal 1992, Karathanasis 1999). The results in Chapter 3 show that the quantity of SOC solubilized by urea hydrolysis varies among soils. Characterization of the SOC in the microsite should be performed on a range of soil types to determine if there are qualitative as well as quantitative differences among soils. One use of the results would be more realistic speciation of the soil solution within the FRZ using GEOCHEM.

The second priority is to confirm the presence of metal-ammonia complexes in the FRZ. Spectrophotometric techniques may be useful in measuring the complex ions in soil solution as a number of the more stable ones for both Cu and Zn absorb strongly in the visible spectrum. Determining if they bind to humic substances could be accomplished by extracting FA and HA from soil and then reacting the isolated humic materials with solutions containing metal-ammonia complexes. The complex ions are readily produced by reacting metal sulphate with NaOH until precipitation occurs, and then ammoniating the resulting suspension.

The priority question concerning plant uptake is to quantify availability in time relative to the stage when urea hydrolysis or NH_4^+ nitrification controls soil pH. This could be combined with testing the hypothesis presented graphically in Figure 7.2. Techniques for separating rhizosphere soil from bulk soil using permeable membranes have been used to quantify the effects of plant roots on soil chemical and biochemical properties (Dormaar 1988, McKenzie *et al.* 1995). Use of these techniques to create a FRZ, transmission zone, and rooting zone would set up the physical circumstances required. Extraction of soil solution and measuring pH and total soluble metals could be accomplished using the techniques employed in Chapters 2 and 3. It would, however, be worth exploring use of *in situ* techniques for measuring pH and non-destructive techniques for extracting soil solution. This may alleviate some of the variability problems associated with measurements made over time using destructive techniques. Manganese and Cu would be appropriate metals to examine, as they provide a good contrast in terms of pH sensitivity and affinity for SOM. With respect to measuring available ion species, anodic stripping voltammetry using a Hg electrode has been used to measure free metal activity in systems where soil solution pH and organic ligands have been manipulated (e.g. Sauve *et al.* 1998). The technique is selective and sensitive, can be used on a wide selection of metals, works over a wide concentration range, and can be applied without pre-separation of the target analyte from the soil solution (Street and Peterson 1982).

Attenuation within the soil profile would be the area chosen for further study of mobility. The question of subsoil pH effects stated earlier could be answered with a relatively simple column leaching experiment in which solution extracted from the FRZ are passed through soil materials varying in pH. Measuring attenuation processes would be more difficult. Trace metal fractionation techniques as detailed by Shuman (1991) might be useful in characterizing precipitation and adsorption along the attenuation path. Sensitivity would likely be an issue with these techniques, as soil variability would tend to mask small changes. Increasing replication would not really be an option as the techniques are time consuming and tedious. Combining stable or radioisotope tracer enrichment with fractionation would provide direct quantitation rather than difference-based estimates of metal movement into the various solid phases. Choice of metals for such an approach would be limited to those with a useable and available radio or stable isotope. Adding ^{14}C to the FRZ and then leaching through a subsoil layer could be used to quantify C loss along the attenuation path. Using soil in the FRZ that had been ^{14}C enriched sometime previously and contained the isotope in more stable forms of SOM would provide information on transport of humic substances. Enriching the biomass with ^{14}C, disrupting it with urea hydrolysis products, and then leaching would provide information on the attenuation of biomass derived carbon forms.

Final Thoughts on Agricultural and Environmental Significance

Like all ammonium-based fertilizers, continued urea use will eventually acidify soil. Factors controlling acidification, including soil properties, fertilizer rates, and application timing, have been addresses by other authors through long-term studies (Intrawech *et al.* 1982, Goh *et al.* 1987, Bouman *et al.* 1995, Ukrainetz *et al.* 1995). In the short-term, urea reaction products solubilize nutrient elements. Losses of some of these elements like P to surface waters may be important ecologically, but the quantities involved are not likely to be significant in crop production in the short-term. Fertilizing with urea may enhance plant uptake of soil-derived micronutrients under certain circumstances, but for the soils and crops used in this study this was not expressed as higher yield. One of the findings that does have agronomic significance was the synergism between urea and chelated Cu fertilizer. When banded with urea, Cu-EDTA was more available than either CuO or $CuSO_4$. Fertilizer blends which contain urea and chelated Cu are likely to be more effective in supplying Cu than those based on inorganic Cu products.

The results of the soil solution and rainfall experiments suggest urea may increase losses of SOM. Although this may be interpreted as detrimental to soil quality, Intrawech *et al.* (1982) and Goh *et al.* (1987) showed that long-term urea use increases SOM relative to unfertilized controls. The increased crop yields and subsequently higher residue returns to soil with nitrogen fertilizer apparently compensate for any losses induced by SOM dissolution.

The rainfall simulation study showed directly that urea additions enhance transport of soluble nutrients and sediment. Indirectly the results suggested that nutrient loss through sediment was likely to be greater than loss through solution. Regardless of mechanism, the issue is whether the quantities moved and distances transported would be ecologically important downstream. The results of the rainfall simulation study cannot answer that question. Further rainfall simulation studies comparing fertilizer sources and application methods would be useful in determining relative differences among systems. Information that could then be used to design minimum impact systems. Determining whether these systems actually meet agronomic and environmental goals would require a larger scale agro-ecosystem approach.

This thesis shows that the hydrolysis products of granular urea alter solubility, bioavailability, and mobility of a range of elements in soil. These changes are initially brought about within the fertilizer reaction zone surrounding the granule. What then is the larger significance of this work? Perhaps this, fertilizers can be manipulated to produce desirable agronomic and environmental outcomes, knowledge of the microsite is crucial in achieving this end.

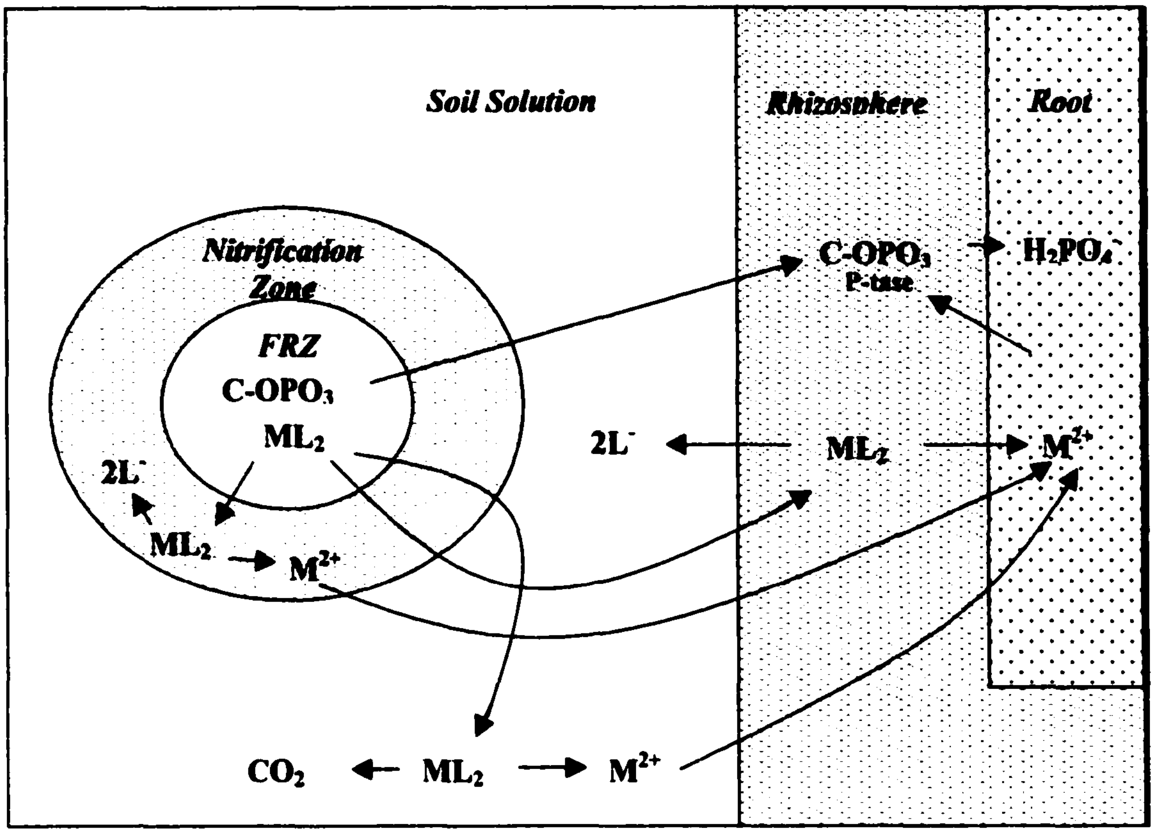

Figure 7.1. Possible movement and uptake of metal and non-metal nutrient elements solubilized in the FRZ of urea (L = ligand, M = metal, C = carbon).

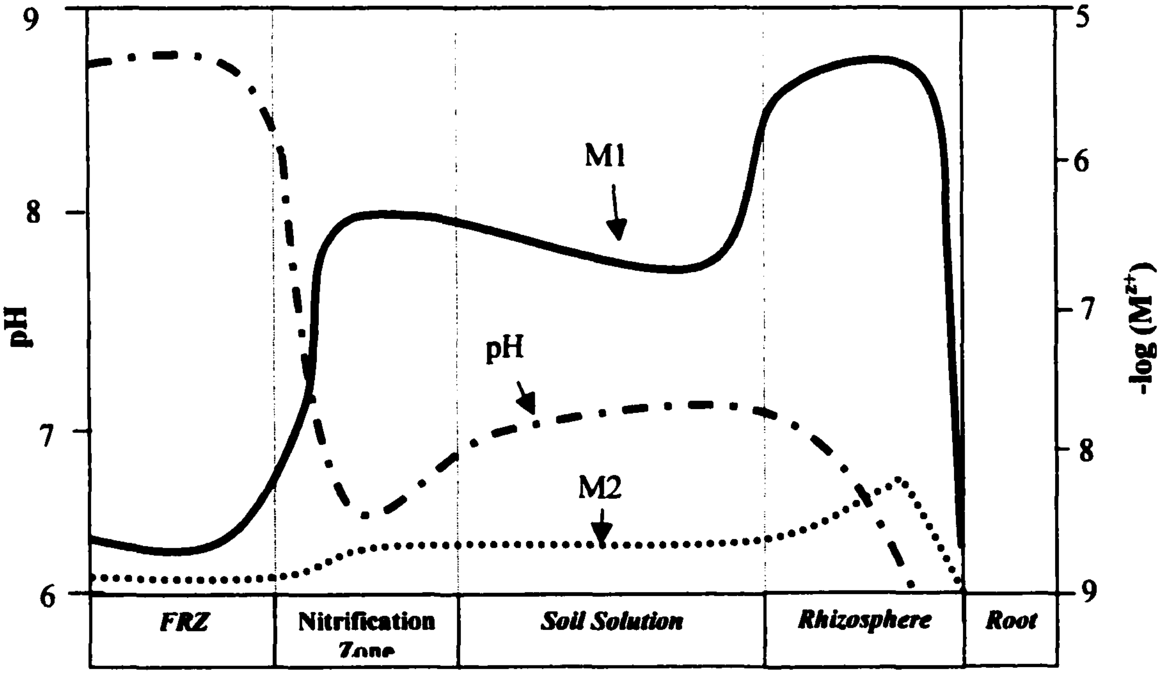

Figure 7.2. Hypothetical free metal activity in urea treated soil for a poorly complexed pH sensitive metal (M1) and a strongly complexed pH insensitive metal (M2).

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APPENDIX A: INPUT AND OUTPUT DATA GEOCHEM

Table A1. Soil solution data used in GEOCHEM.

Soil No.	Ionic Strength	pH	Total Soluble														
			NH_4^+	Ca	K	Mg	Na	Cu	Fe	Mn	Zn	Al	P	S	TIC	SOC	NO_3^-
	mol L^{-1}		*mmol L^{-1}*					*µmol L^{-1}*				*mmol L^{-1}*					
Case 1 Control																	
16	0.012	8.83	1	7.2	4.3	2.4	4.1	0.35	3	3.1	0.1	0.01	0.06	19.02	3.6	8	1
29	0.004	8.42	1	0.7	0.1	0.2	3	0.33	140	13	1	0.47	0.02	0.83	4.6	13	1
Case 2 Urea																	
16	0.059	8.31	100	1.6	2.8	0.9	5.4	29	510	200	6.5	0.92	0.75	2.84	58.7	331	25
29	0.061	8.19	100	6.8	1	1.1	4.1	60	6100	540	18	3.81	1.26	3.58	61.1	627	25
Case 3 Ammonium Sulphate																	
16	0.27	7.28	50	15.8	12	9.8	4.9	0.58	4.1	8.2	0.9	0.01	0.13	79.16	3.8	13	20
29	0.21	6.49	50	10.9	1.9	6.4	4.5	0.68	32	680	5.3	0.18	0.07	86.44	2.3	10	20

Table A2. Concentration of free ligands and complexed metal in soil solution, Soil 16.

	Free Metal	CO_3^{2-}	SO_4^{2-}	NH_3	PO_4^{3-}	NO_3^-	Fulvic	OH^-
				-log(mol L^{-1})				
				Case 1 Control				
Free Ligand		5.06	1.79	3.45	9.20	3.00	4.48	5.09
Ca^{2+}	2.68	5.15	2.83	6.22	6.19	10.81	3.89	6.80
Mg^{2+}	2.82	5.24	3.08	6.16	6.62	9.42	4.53	5.74
K^+	2.39	10.07	3.61	-	-	-	-	8.15
Na^+	2.40	5.96	3.82	-	-	-	-	7.86
Fe^{3+}	22.24	-	20.77	-	18.38	24.74	-	9.04
Mn^{2+}	5.84	7.04	6.00	8.59	-	-	6.25	8.23
Cu^{2+}	9.98	9.01	10.04	9.05	10.37	12.81	10.50	6.46
Zn^{2+}	8.11	9.05	8.27	9.32	10.27	11.04	8.93	7.07
Al^{3+}	17.64	-	16.71	-	17.28	27.54	-	5.68
H^+	8.75	3.81	8.87	3.19	6.08	13.32	-	-
				Case 2 Urea				
Free Ligand		2.96	2.56	1.87	6.65	1.60	2.15	5.58
Ca^{2+}	4.58	4.89	5.71	6.54	5.63	11.40	3.57	9.30
Mg^{2+}	3.74	4.06	4.97	5.50	4.81	7.70	3.22	7.62
K^+	2.56	8.45	4.64	-	-	-	-	8.86
Na^+	2.30	3.46	4.59	-	-	-	-	8.31
Fe^{3+}	20.46	-	20.10	-	13.95	21.71	-	9.31
Mn^{2+}	6.28	5.51	7.41	7.43	-	-	4.47	9.30
Cu^{2+}	9.46	6.20	10.48	4.55	7.60	10.99	7.74	7.08
Zn^{2+}	7.23	6.26	8.36	5.38	7.10	8.86	5.81	6.90
Al^{3+}	15.86	-	16.17	-	12.85	21.86	-	6.18
H^+	8.20	1.25	9.19	1.06	3.12	11.43	-	-
				Case 3 Ammonium Sulphate				
Free Ligand		5.15	1.21	3.17	8.98	1.70	4.42	6.59
Ca^{2+}	2.39	4.17	2.32	5.64	5.15	9.38	3.71	8.18
Mg^{2+}	2.30	4.17	2.33	5.35	4.92	6.57	4.12	6.90
K^+	1.98	9.60	2.80	-	-	-	-	9.35
Na^+	2.35	4.82	3.36	-	-	-	-	9.42
Fe^{3+}	17.21	-	15.62	-	12.31	18.66	-	9.15
Mn^{2+}	5.49	6.57	5.43	7.95	-	-	6.01	9.59
Cu^{2+}	7.82	7.27	7.65	6.34	8.50	9.52	8.44	7.54
Zn^{2+}	6.47	7.84	6.40	7.35	8.50	8.27	7.39	7.62
Al^{3+}	12.61	-	11.43	-	11.21	19.14	-	7.18
H^+	7.15	2.40	6.87	1.31	4.31	10.52	-	-

Table A3. Concentration of free ligands and complexed metal in soil solution, Soil 29.

	Free Metal	CO_3^{2-}	SO_4^{2-}	NH_3	PO_4^{3-}	NO_3^-	Fulvic	OH^-
				$-\log(mol\ L^{-1})$				
				<u>Case 1 Control</u>				
Free Ligand		4.20	3.10	3.71	8.51	3.00	3.69	5.54
Ca^{2+}	3.89	4.99	5.00	7.70	5.98	11.84	4.13	8.29
Mg^{2+}	3.82	4.91	5.03	7.44	5.95	9.85	4.57	7.02
K^+	4.00	12.15	6.35	-	-	-	-	10.12
Na^+	2.53	4.68	5.07	-	-	-	-	8.35
Fe^{3+}	21.42	-	20.76	-	15.69	23.65	-	8.76
Mn^{2+}	5.65	5.59	6.76	8.66	-	-	5.09	8.33
Cu^{2+}	9.46	7.20	10.47	8.78	8.63	12.11	9.00	6.27
Zn^{2+}	6.97	6.68	8.08	8.45	7.87	9.72	6.85	6.23
Al^{3+}	16.82	-	16.83	-	14.59	26.18	-	5.54
H^+	8.38	2.39	9.63	3.09	4.73	12.86	-	-
				<u>Case 2 Urea</u>				
Free Ligand		3.09	2.45	1.98	6.55	1.60	1.87	5.70
Ca^{2+}	4.44	4.81	5.48	6.51	5.33	11.27	3.16	9.28
Mg^{2+}	3.85	4.24	4.98	5.71	4.72	7.82	3.06	7.49
K^+	3.00	9.48	5.00	-	-	-	-	9.43
Na^+	2.42	3.61	4.61	-	-	-	-	8.55
Fe^{3+}	20.09	-	19.65	-	13.38	21.34	-	9.35
Mn^{2+}	6.14	5.48	7.18	7.40	-	-	4.06	9.28
Cu^{2+}	8.81	5.76	9.74	4.24	6.86	10.35	6.82	6.67
Zn^{2+}	6.84	6.01	7.88	5.35	6.64	8.48	5.16	6.64
Al^{3+}	15.49	-	15.71	-	12.28	21.52	-	6.31
H^+	8.08	1.27	8.97	1.05	2.89	11.31	-	-
				<u>Case 3 Ammonium Sulphate</u>				
Free Ligand		6.29	1.13	3.96	9.93	1.70	4.55	7.38
Ca^{2+}	2.45	4.62	2.32	6.49	5.32	9.45	3.92	9.05
Mg^{2+}	2.52	4.78	2.48	6.36	5.35	6.50	4.48	7.91
K^+	2.79	12.69	3.53	-	-	-	-	10.95
Na^+	2.40	5.24	3.33	-	-	-	-	10.95
Fe^{3+}	14.82	-	13.03	-	10.11	16.29	-	8.21
Mn^{2+}	3.58	5.13	3.45	6.82	-	-	4.24	8.48
Cu^{2+}	6.86	7.39	6.62	6.54	8.45	8.56	7.62	7.80
Zn^{2+}	5.68	8.21	5.54	7.40	7.99	7.48	6.74	7.27
Al^{3+}	10.22	-	8.70	-	9.01	16.29	-	7.24
H^+	6.36	2.65	6.00	1.30	4.22	9.74	-	-

Table A4. Distribution of metals and ligands, Soil 16.

Metal

Case 1 Control
Ca
29.30 % as a free metal
.10 % complexed with CO3
47.19 % in solid form with CO3
20.38 % complexed with SO4
1.22 % in solid form with PO4
1.79 % complexed with FULV1
Mg
63.39 % as a free metal
.24 % complexed with CO3
35.03 % complexed with SO4
.03 % complexed with NH3
1.23 % complexed with FULV1
.08 % complexed with OH-
K
94.29 % as a free metal
5.71 % complexed with SO4
Na
96.29 % as a free metal
.03 % complexed with CO3
3.68 % complexed with SO4
Fe +3
.03 % complexed with OH-
99.97 % in solid form with OH-
Mn +2
46.51 % as a free metal
2.91 % complexed with CO3
32.35 % complexed with SO4
.08 % complexed with NH3
17.96 % complexed with FULV1
.19 % complexed with OH-
Cu +2
.03 % as a free metal
.28 % complexed with CO3
.03 % complexed with SO4
.26 % complexed with NH3
.01 % complexed with PO4
99.39 % complexed with OH-

Ligand

CO3
.24 % as a free ligand
.20 % complexed with Ca
95.03 % in solid form with Ca
.16 % complexed with Mg
.03 % complexed with Na
4.33 % complexed with H+
SO4
85.78 % as a free ligand
7.71 % complexed with Ca
4.42 % complexed with Mg
1.29 % complexed with K
.79 % complexed with Na
NH3
35.81 % as a free ligand
.06 % complexed with Ca
.07 % complexed with Mg
64.06 % complexed with H+
PO4
1.07 % complexed with Ca
97.16 % in solid form with Ca
.40 % complexed with Mg
1.36 % complexed with H+
NO3
100.00 % as a free ligand
FULV1
17.13 % as a free ligand
67.24 % complexed with Ca
15.34 % complexed with Mg
.29 % complexed with Mn +2

Table A4. Distribution of metals and ligands, Soil 16 (continued).

Metal

- Zn
  - 7.72 % as a free metal
  - .90 % complexed with CO3
  - 5.37 % complexed with SO4
  - .47 % complexed with NH3
  - .05 % complexed with PO4
  - 1.19 % complexed with FULV1
  - 84.29 % complexed with OH-
- Al
  - 20.79 % complexed with OH-
  - 79.21 % in solid form with OH-

Case 2 Urea

- Ca
  - 1.63 % as a free metal
  - .80 % complexed with CO3
  - 80.35 % in solid form with CO3
  - .12 % complexed with SO4
  - .02 % complexed with NH3
  - .15 % complexed with PO4
  - 16.93 % complexed with FULV1
- Mg
  - 20.28 % as a free metal
  - 9.70 % complexed with CO3
  - 1.20 % complexed with SO4
  - .36 % complexed with NH3
  - 1.72 % complexed with PO4
  - 66.74 % complexed with FULV1
- K
  - 99.19 % as a free metal
  - .81 % complexed with SO4
- Na
  - 93.11 % as a free metal
  - 6.41 % complexed with CO3
  - .48 % complexed with SO4
- Fe +3
  - 100.00 % in solid form with OH-

Ligand

- CO3
  - 1.89 % as a free ligand
  - .02 % complexed with Ca
  - 2.19 % in solid form with Ca
  - .15 % complexed with Mg
  - .59 % complexed with Na
  - .28 % in solid form with Mn +2
  - 94.88 % complexed with H+
- SO4
  - 97.83 % as a free ligand
  - .07 % complexed with Ca
  - .38 % complexed with Mg
  - .80 % complexed with K
  - .92 % complexed with Na
- NH3
  - 13.45 % as a free ligand
  - .09 % complexed with Cu +2
  - .01 % complexed with Zn
  - 86.44 % complexed with H+
- PO4
  - .03 % as a free ligand
  - .31 % complexed with Ca
  - 2.06 % complexed with Mg
  - .01 % complexed with Zn
  - 97.58 % complexed with H+

Table A4. Distribution of metals and ligands, Soil 16 (continued).

Metal

Mn +2
.26 % as a free metal
1.55 % complexed with CO3
81.10 % in solid form with CO3
.02 % complexed with SO4
.02 % complexed with NH3
17.05 % complexed with FULV1
Cu +2
2.19 % complexed with CO3
97.37 % complexed with NH3
.09 % complexed with PO4
.06 % complexed with FULV1
.29 % complexed with OH-
Zn
.91 % as a free metal
8.55 % complexed with CO3
.07 % complexed with SO4
63.59 % complexed with NH3
1.24 % complexed with PO4
.02 % complexed with NO3
23.69 % complexed with FULV1
1.95 % complexed with OH-
Al
.07 % complexed with OH-
99.93 % in solid form with OH-

Ligand

NO3
100.00 % as a free ligand
FULV1
88.58 % as a free ligand
3.41 % complexed with Ca
7.56 % complexed with Mg
.43 % complexed with Mn +2
.02 % complexed with Zn

Case 3 Ammonium Sulphate

Ca
25.94 % as a free metal
.43 % complexed with CO3
30.27 % complexed with SO4
41.38 % in solid form with SO4
.01 % complexed with NH3
.04 % complexed with PO4
.68 % in solid form with PO4
1.24 % complexed with FULV1
Mg
51.04 % as a free metal
.69 % complexed with CO3
47.32 % complexed with SO4
.05 % complexed with NH3
.12 % complexed with PO4
.77 % complexed with FULV1

CO3
.19 % as a free ligand
1.78 % complexed with Ca
1.78 % complexed with Mg
.40 % complexed with Na
95.84 % complexed with H+
SO4
77.29 % as a free ligand
6.04 % complexed with Ca
8.26 % in solid form with Ca
5.85 % complexed with Mg
2.02 % complexed with K
.55 % complexed with Na
NH3
1.34 % as a free ligand
98.64 % complexed with H+

Table A4. Distribution of metals and ligands, Soil 16 (continued).

Metal

K
86.67 % as a free metal
13.33 % complexed with SO4
Na
90.87 % as a free metal
.31 % complexed with CO3
8.82 % complexed with SO4
Fe +3
.02 % complexed with OH-
99.98 % in solid form with OH-
Mn +2
39.10 % as a free metal
3.29 % complexed with CO3
45.63 % complexed with SO4
.14 % complexed with NH3
11.84 % complexed with FULV1
Cu +2
2.62 % as a free metal
9.30 % complexed with CO3
3.85 % complexed with SO4
78.05 % complexed with NH3
.54 % complexed with PO4
.05 % complexed with NO3
.63 % complexed with FULV1
4.96 % complexed with OH-
Zn
37.76 % as a free metal
1.61 % complexed with CO3
44.07 % complexed with SO4
4.94 % complexed with NH3
.35 % complexed with PO4
.60 % complexed with NO3
4.55 % complexed with FULV1
6.11 % complexed with OH-
Al
.66 % complexed with OH-
99.34 % in solid form with OH-

Ligand

PO4
5.39 % complexed with Ca
55.48 % in solid form with Ca
9.25 % complexed with Mg
29.88 % complexed with H+
NO3
100.00 % as a free ligand
FULV1
12.23 % as a free ligand
63.12 % complexed with Ca
24.33 % complexed with Mg
.31 % complexed with Mn +2
.01 % complexed with Zn

Table A5. Distribution of metals and ligands, Soil 29

Metal

Case 1 Control

- Ca
  - 18.32 % as a free metal
  - 1.46 % complexed with CO3
  - 68.15 % in solid form with CO3
  - 1.43 % complexed with SO4
  - .15 % complexed with PO4
  - 10.49 % complexed with FULV1
- Mg
  - 75.01 % as a free metal
  - 6.12 % complexed with CO3
  - 4.67 % complexed with SO4
  - .02 % complexed with NH3
  - .56 % complexed with PO4
  - 13.58 % complexed with FULV1
  - .05 % complexed with OH-
- K
  - 99.55 % as a free metal
  - .45 % complexed with SO4
- Na
  - 99.02 % as a free metal
  - .70 % complexed with CO3
  - .28 % complexed with SO4
- Fe +3
  - 100.00 % in solid form with OH-
- Mn +2
  - 17.13 % as a free metal
  - 19.61 % complexed with CO3
  - 1.34 % complexed with SO4
  - .02 % complexed with NH3
  - 61.87 % complexed with FULV1
  - .04 % complexed with OH-
- Cu +2
  - .11 % as a free metal
  - 17.70 % complexed with CO3
  - .01 % complexed with SO4
  - .34 % complexed with NH3
  - .72 % complexed with PO4
  - .30 % complexed with FULV1
  - 80.82 % complexed with OH-

Ligand

- CO3
  - 1.38 % as a free ligand
  - .22 % complexed with Ca
  - 10.36 % in solid form with Ca
  - .27 % complexed with Mg
  - .46 % complexed with Na
  - .06 % complexed with Mn +2
  - 87.25 % complexed with H+
- SO4
  - 96.57 % as a free ligand
  - 1.21 % complexed with Ca
  - 1.12 % complexed with Mg
  - .05 % complexed with K
  - 1.02 % complexed with Na
  - .02 % complexed with Mn +2
- NH3
  - 19.41 % as a free ligand
  - 80.58 % complexed with H+
- PO4
  - .02 % as a free ligand
  - 5.20 % complexed with Ca
  - 5.58 % complexed with Mg
  - .01 % complexed with Cu +2
  - .07 % complexed with Zn
  - 89.13 % complexed with H+
- NO3
  - 100.00 % as a free ligand
- FULV1
  - 65.13 % as a free ligand
  - 23.53 % complexed with Ca
  - 8.71 % complexed with Mg
  - 2.58 % complexed with Mn +2
  - .05 % complexed with Zn

Table A5. Distribution of metals and ligands, Soil 29 (continued).

Metal

Zn
10.64 % as a free metal
20.84 % complexed with CO3
.83 % complexed with SO4
.34 % complexed with NH3
1.35 % complexed with PO4
.02 % complexed with NO3
15.30 % complexed with FULV1
50.68 % complexed with OH-
Al
.16 % complexed with OH-
99.84 % in solid form with OH-

Case 2 Urea

Ca
.53 % as a free metal
.23 % complexed with CO3
88.91 % in solid form with CO3
.05 % complexed with SO4
.07 % complexed with PO4
10.22 % complexed with FULV1
Mg
12.92 % as a free metal
5.20 % complexed with CO3
.95 % complexed with SO4
.18 % complexed with NH3
1.75 % complexed with PO4
79.00 % complexed with FULV1
K
98.99 % as a free metal
1.01 % complexed with SO4
Na
93.43 % as a free metal
5.97 % complexed with CO3
.60 % complexed with SO4
Fe +3
100.00 % in solid form with OH-
Mn +2
.13 % as a free metal
.61 % complexed with CO3
83.01 % in solid form with CO3
.01 % complexed with SO4
16.23 % complexed with FULV1

Ligand

CO3
1.34 % as a free ligand
.03 % complexed with Ca
9.91 % in solid form with Ca
.09 % complexed with Mg
.40 % complexed with Na
.73 % in solid form with Mn +2
87.48 % complexed with H+
SO4
98.64 % as a free ligand
.09 % complexed with Ca
.29 % complexed with Mg
.28 % complexed with K
.69 % complexed with Na
NH3
10.51 % as a free ligand
.18 % complexed with Cu +2
.01 % complexed with Zn
89.29 % complexed with H+
PO4
.02 % as a free ligand
.37 % complexed with Ca
1.53 % complexed with Mg
.01 % complexed with Cu +2
.02 % complexed with Zn
98.05 % complexed with H+
NO3
100.00 % as a free ligand

Table A5. Distribution of metals and ligands, Soil 29 (continued).

Metal

Cu +2
2.90 % complexed with CO3
96.26 % complexed with NH3
.23 % complexed with PO4
.25 % complexed with FULV1
.36 % complexed with OH-
Zn
.80 % as a free metal
5.43 % complexed with CO3
27.54 % in solid form with CO3
.07 % complexed with SO4
24.84 % complexed with NH3
1.38 % complexed with PO4
.02 % complexed with NO3
38.66 % complexed with FULV1
1.26 % complexed with OH-
Al
.01 % complexed with OH-
99.99 % in solid form with OH-

Ligand

FULV1
88.97 % as a free ligand
4.63 % complexed with Ca
5.78 % complexed with Mg
.58 % complexed with Mn +2
.05 % complexed with Zn

Case 3 Ammonium Sulphate

Ca
32.27 % as a free metal
.22 % complexed with CO3
43.95 % complexed with SO4
22.40 % in solid form with SO4
.04 % complexed with PO4
1.11 % complexed with FULV1
Mg
47.62 % as a free metal
.26 % complexed with CO3
51.52 % complexed with SO4
.07 % complexed with PO4
.52 % complexed with FULV1
K
84.48 % as a free metal
15.52 % complexed with SO4
Na
89.49 % as a free metal
.13 % complexed with CO3
10.38 % complexed with SO4

CO3
.02 % as a free ligand
1.04 % complexed with Ca
.72 % complexed with Mg
.25 % complexed with Na
.32 % complexed with Mn +2
97.64 % complexed with H+
SO4
86.54 % as a free ligand
5.53 % complexed with Ca
2.82 % in solid form with Ca
3.81 % complexed with Mg
.34 % complexed with K
.54 % complexed with Na
.41 % complexed with Mn +2
NH3
.22 % as a free ligand
99.78 % complexed with H+

Table A5. Distribution of metals and ligands, Soil 29 (continued).

Metal

Fe +3
- 99.99 % in solid form with OH-

Mn +2
- 38.33 % as a free metal
- 1.09 % complexed with CO3
- 52.21 % complexed with SO4
- .02 % complexed with NH3
- 8.36 % complexed with FULV1

Cu +2
- 20.46 % as a free metal
- 5.91 % complexed with CO3
- 35.08 % complexed with SO4
- 32.67 % complexed with NH3
- .52 % complexed with PO4
- .40 % complexed with NO3
- 3.54 % complexed with FULV1
- 1.42 % complexed with OH-

Zn
- 39.74 % as a free metal
- .12 % complexed with CO3
- 54.13 % complexed with SO4
- .74 % complexed with NH3
- .19 % complexed with PO4
- .62 % complexed with NO3
- 3.45 % complexed with FULV1
- 1.01 % complexed with OH-

Al
- 99.99 % in solid form with OH-

Ligand

PO4
- 6.83 % complexed with Ca
- 6.84 % complexed with Mg
- .01 % complexed with Zn
- 86.32 % complexed with H+

NO3
- 100.00 % as a free ligand

FULV1
- 11.71 % as a free ligand
- 50.61 % complexed with Ca
- 13.88 % complexed with Mg
- 23.71 % complexed with Mn +2
- .01 % complexed with Cu +2
- .08 % complexed with Zn