SOLUBILITY AND PHYTOAVAILABILITY OF

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CADMIUM IN SOILS TREATED

WITH NITROGEN FERTILIZERS

BY

LESLIE GRANT MITCHELL

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

MASTER OF SCIENCE

Department of Soil Science University of Manitoba Winnipeg, Manitoba

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THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

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CADMIUM IN SOILS TREATED WITH NITROGEN FERTILIZERS

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LESLIE GRANT MITCHELL

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University

of Manitoba in partial fulfillment of the requirements of the degree

of

MASTER OF SCIENCE

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ABSTRACT

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Mitchell, Leslie Grant. M.Sc., The University of Manitoba, February, 1997. <u>Solubility and</u> <u>Phytoavailability of Cadmium in Soils Treated With Nitrogen Fertilizers</u>. Major Professors; Cynthia A. Grant and Geza J. Racz.

Studies were conducted to examine the effects of some commonly-used fertilizers on cadmium extractability, concentration of Cd in the soil solution, and concentration of Cd in plants grown on nitrogen-fertilized soils. Soil extractions were performed on a clay loam soil using different concentrations of fertilizer solutions, and the extracts were analyzed for Cd. Only solutions of ammonium sulfate solubilized a significant amount of Cd, with the increase in extracted Cd being unrelated to pH. The same clay loam soil was incubated at field fertilizers extracted with water and capacity with various and diethylenetriaminepentaacetic acid (DTPA) after 1-28 days to see if time had any effect on Cd solubilization. Time did not significantly affect cadmium extractability. Ammonium sulfate and urea were the only fertilizer salts to increase the amount of extractable Cd, and the increase in cadmium solubility was not related to pH. In a third study, wheat plants were grown in pots containing a fine sandy loam soil with different rates of urea fertilizer. At different stages of plant growth, plant material was analyzed and the soil solution was removed using water displacement. Cadmium concentration in the soil solution and in the plant tissue increased significantly with nitrogen rate. Many of the plant nutrients showed similar increases in the soil solution and in the plant with increasing nitrogen rate. These increases were related to increasing ionic strength of the soil solution and a general reduction

in soil pH. Plant growth and transpiration also increased with increasing nitrogen rate, allowing plants to take up increased amounts of Cd by mass flow. The increase in Cd phytoavailability with increasing nitrogen rate may be caused by the combined effect of increasing ionic strength, decreasing pH, and increasing plant growth.

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WEAL-MARK IN COMPANY

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Mom and Dad are two wonderful people with a world of patience, who give me every opportunity to explore my interests, and are always there to provide love and encouragement. Words cannot express my love and gratitude to them and sister Tracy for being my family and for everything they have ever done for me. None of this would have been possible without them. Finally, I would like to thank my special friend Melanie for coming into my life, for her love and understanding, and for making me smile on a daily basis (it's contagious)!

I have undoubtedly forgotten someone so I would like to thank everyone I have ever known, met, listened to, read about, or watched on a screen. In one way or another, you have all influenced my life!

For J.C. (1971-1995).

FOREWARD

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This thesis was written in manuscript style as outlined in the Department of Soil Science *Guide to Thesis Preparation for Graduate Students*. All three of the following manuscripts are likely to be submitted for publication. The journal(s) to which they will be submitted have yet to be determined.

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1. INTRODUCTION

Cadmium (Cd) is a heavy metal that has garnered considerable interest in recent years because of its association with various human health problems (Alloway 1990; Jackson and Alloway 1992). Cd may be present in the soil-plant environment from both natural and anthropogenic sources. Soils may contain high concentrations of naturally-occurring Cd, while phosphate fertilizers and sewage sludges are anthropogenic sources of Cd. Cd enters plants, either by direct absorption through leaves (especially near smelting plants) or by uptake from soils, thereby allowing Cd into the food chain (John et al. 1972).

Kuboi et al. (1986) showed that many plants are not damaged by the uptake of high levels of Cd and, therefore, healthy crops grown in Cd-polluted soils may contribute substantial amounts of Cd to the food chain. Cd remains in the body for a long period of time, having an estimated half-life between 15 and 1100 years (Alloway 1990). Thus, the long-term consumption of foods high in Cd could lead to chronic toxicity (Jackson and Alloway 1992).

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Cd is a persistent problem in soils because uptake by plants can continue long after the direct addition has ceased (Symeonides and McRae 1977). Therefore, it is vital to be able to predict potential Cd uptake by plants from soils. The availability of soil Cd for plant uptake is determined by various plant and soil factors, as well as environmental conditions and agronomic management practices.

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Soil factors affecting Cd availability include: soil Cd content, pH, metal sorption capacity of the soil, cation exchange capacity, redox potential, organic matter content, presence of other metals, and fertilization. Plant factors affecting the uptake of Cd include: species and cultivar, plant tissue sampled, age of the plant, metal interactions within the plant, and soil rhizosphere effects. Agronomic management practices such as the addition of farmyard manures, sewage sludges, N, P and K fertilizers, and other nutrients play a role in Cd mobility and availability.

Most of the Cd accumulated in grains and seeds is a result of plant uptake from the soil, where Cd levels vary with parent material and anthropogenic input. Cd mobility and bioavailability in the soil is influenced by chemical transformations, which in turn, are affected by soil formation processes and management practices.

High yields in crop production require balanced availability of the plant macronutrients N, P, K, S, Ca, and Mg, and the micronutrients Cu, Mo, Mn, Fe, B, Cl, and Zn. Fertilizers are used to enhance availability of these plant nutrients for continuous or repeated crop production. However, it has been suggested by many researchers that Pfertilizer applications year after year may lead to a buildup of intolerable levels of Cd in the soil (Williams and David 1976; Mulla et al. 1980; Mortvedt 1987).

Application of N and K fertilizers, which may not contain Cd, have also been shown to increase concentration of Cd in crops.

In Western Canada, durum wheat may at times have levels of Cd above acceptable levels (0.1 ppm) proposed by the Codex Alimentarius Commission of the World Health Organization (FAO/WHO 1995). This is of economic concern to producers, as it may impact on the marketability of the grain. Therefore, there is a need to study Cd uptake by durum wheat as part of the overall strategy to reduce Cd uptake by crops. This study evaluates the effect of nitrogen fertilization on Cd bioavailability. Studies were also conducted to elucidate soil-fertilizer reactions and plant interactions which may be responsible for increased bioavailability of Cd in N fertilized soils.

2. LITERATURE REVIEW

2.1 Cadmium In The Environment

Cd occurs naturally in soil, water, and air. Concentrations in agricultural soils are usually less than one ug g^{-1} . The element may occur at higher concentrations, especially with Zn ores or other Cd-bearing deposits (Adriano 1986). Contaminated soils can contain as much as several hundred ug g^{-1} Cd.

Significant amounts of Cd are being released to the environment because of its many industrial uses. Consequently, there is evidence of Cd accumulation in soils near smelters (John et al. 1972), where sewage sludge has been applied to land (Chaney 1973), and where P fertilizer has been utilized (Williams and David 1976). Cd from these sources could conceivably reach into the food chain, and consequently, such sources are of paramount importance when identifying contributors of Cd.

2.2. Cadmium In Soils

2.2.1 Distribution

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In uncultivated, unfertilized soils, the amount of Cd present in the soil is closely correlated with that of the soil parent material. Although the soil parent material determines the source and amount of Cd in uncontaminated soils, atmospheric deposition, mining and smelting industries, farmyard manures, and sewage sludges can all affect Cd concentrations in soils.

Cd is fairly immobile in the soil profile, but it is more highly concentrated in the surface soil, which Alloway (1990) attributed to atmospheric deposition, fertilizer use, and cycling through plants. Andersson (1976) stated that the Cd concentrations parallel that of humus distribution, indicating that the humus content adds to the absorptive qualities of the surface soil.

In sewage sludge-amended soils, most of the Cd generally remains in the top 20 cm. Chang et al. (1984) verified that after six years of continued annual sewage sludge application, 90% of the applied Cd remained in the 0 to 15 cm soil depth. Mulla et al. (1980), in a study of Cd accumulation from heavy long-term (36 years) applications of P fertilizer, found that about 71% of the accumulated Cd, but only 45% of the residual P, remained in the surface soil (0 to 15 cm), which led to the conclusion that Cd was less mobile than P in the soil profile.

Holmgren et al. (1993) studied 3,045 surface soil samples from 307 different soil series, and concluded that metal levels generally increased with higher levels of clay

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concentrations, which is consistent with research showing that most of the heavy metals in soil are associated with the clay fractions, probably adsorbed on the Fe and Mn hydrous oxide surface coatings on clay particles, or the organic matter fraction.

2.2.2 Cadmium Species and Complxes

Alloway (1990) reported that the toxic effect of a metal is determined more by its form than by its concentration, and that the predominant free ion ,Cd²⁺, was more likely than other species to be adsorbed on soil surfaces. Wagner (1993) commented that it is generally expected that the free ion is transported across root membranes and those of other tissues. Therefore, different forms of Cd will have different mobility and reactivity in soil, and will differ in their availability for plant uptake and in their toxicity to organisms.

The forms of Cd in soil are extremely variable. In any soil, there will be different metal cations reacting with numerous inorganic and organic ligands to form various complexes and phases, all of which will affect the concentration and speciation of Cd.

The results of sulfate salinity studies by Bingham et al. (1986) showed that pH and chemical speciation were important when trying to determine Cd availability. In unlimed soils, Cd²⁺, CdCl⁺, and CdSO₄ made up the total Cd concentration of soil solutions, but in limed soils, these chemical species made up only 83-90% of total Cd, with Cd carbonate complexes making up the remaining 10-17%.

The Cl anion could reduce Cd adsorption by the formation of negatively-charged or neutral species like MCl_2^0 , MCl_3^- and MCl_4^- (Petruzzelli et al. 1985). Smolders et al. (1995) demonstrated that the increase in phytoavailability of Cd, with increased concentrations of

NaCl, was due to chloro-complexation of Cd which led to greater total Cd concentrations in the soil solution, and not due to ionic strength or ion exchange effects on Cd²⁺ activities in solution. They suggested that an increase of Cd uptake in the presence of Cl was due, not only to the diffusion of Cd²⁺ through soil to the root, but could also be the result of an increased concentration of CdClⁿ_{2-n} species in solution, which are also absorbed by roots. Chloride ions, occurring in all soils and waters, may be regarded as a selective ligand for Cd because they do not complex strongly with other cations like Al³⁺, Ca²⁺, Mg²⁺, Na⁺, and K⁺, all of which are in concentrations of several orders of magnitude higher than Cd in waters and soils (Hahne and Kroontje 1973). This was in agreement with Garcia-Miragaya and Page (1976) who concluded that both hydrolysis and chloride complexation of heavy metal ions affect the solubility of the metal ion salts, and may promote the mobility of heavy metals.

Some aspects of the chemical behaviour of Cd in soils can be explained by the hardsoft Lewis acid-base (HSAB) principle. Cd is a soft Lewis acid and, therefore, will react and complex more easily with soft Lewis bases, such as chloride and hydroxyl groups (Puls and Bohn 1988).

2.2.3 Sorption of Cadmium in Soils

The variability in the Cd retention capacity of soils may have as much of an effect on Cd transport in soil as the variability in the soil's physical properties (Boekhold and Van der Zee 1992). The degree to which Cd sorbs to soil regulates the amount of Cd that will be available in the soil water for plant uptake (Palm 1994). According to Puls and Bohn (1988), sorption is the predominant process governing metal ion movement in soils. It includes adsorption, precipitation and absorption. Cavallaro and McBride (1978) stated that adsorption, precipitation, and complexation all controlled metal concentrations and activities in soil solution. Their findings not only demonstrated that acid soils have less ability to retain heavy metals than neutral soils, but also indicated an ion exchange mechanism of adsorption in the surface soils, and an occurrence of precipitation in calcareous subsoils. Carbonate minerals present in arid zone soils immobilized Cd by providing an adsorbing or nucleating surface and by buffering pH.

The availability and mobility of Cd in soils amended with fertilizers and sludges may be influenced by the amount of adsorption on soil particles; such adsorption of Cd by hydrous oxides and soils is influenced by pH and the ionic composition of the soil. Christensen (1984a; 1984b) reported that soil pH, Ca concentration, and competition by other elements (especially Zn) affected the K_d value (distribution coefficient) of soils with low Cd concentrations, i.e. these factors affected the ratio between the amount of Cd adsorbed by soil and that remaining in solution. Boekhold and Van der Zee (1992) concluded that pH and organic matter content were the most important soil characteristics regulating Cd sorption in the soil.

Christensen (1984a) found that soil sorption of Cd occurs rapidly, with more than 95% of the sorption completed within 10 minutes, and that equilibrium (a constant distribution of Cd between soil and solute) is reached in one hour. There were no long-term (up to 67 weeks) changes in soil sorption capacity with continued exposure to Cd. Both loamy sand and sandy loam soils had very high affinity for Cd at pH = 6.0. Soil sorption capacities increased approximately three fold for each unit increase in pH (between pH levels

4 to 7), which reaffirmed the critical role that pH plays in determining the distribution of Cd between soil and solute. Increasing the $CaCl_2$ concentration decreased soil sorption capacity for Cd in the sandy loam soil, due to a combination of increased ionic strength and chloride complex formation, as well as competition by Ca for soil sorption sites. Bittell and Miller (1974) found little preferential adsorption of Cd over Ca, but Milberg et al. (1978) reported that Cd was selectively adsorbed over Ca by all three soils tested.

Sorption of Cd in a loamy sand was fully reversible, while there was a small and weak irreversibility in a sandy loam soil (Christensen 1984b). The equilibrium distribution of Cd between soil and solute was independent of whether the Cd was initially present in the soil or the solute. This may be due to sorption sites having higher free energy than average sites, but not high enough to have been caused by specific sorption.

Dudley et al. (1991) concluded that cation exchange, not solid phase formation, was the principal sink for Cd, i.e. controlled Cd retention. They found that Cd transport was most clearly controlled by the exchange reactions, after the pH value had been decreased to the acid range.

McBride et al. (1981), in studies with corn, proposed that although clay and organic matter played significant roles in retarding Cd^{2+} uptake by plants, the best soil indicators of Cd^{2+} availability were the Cd retention capacity (CdRC) and exchangeable base (mainly Ca^{2+}) content. They found that because the CdRC is strongly correlated to the exchangeable base content of the soils, soils with high exchangeable base contents tended to restrict absorption of Cd^{2+} by the plant. Therefore, surface soils were better at limiting Cd^{2+} uptake than subsoils because the Cd^{2+} was bound by the soil organic matter in the surface layers.

The adsorption of Ca may lead to increased positive charges at the soil adsorbing

surfaces, which in turn, would reduce heavy metal adsorption (Petruzzelli et al. 1985). The authors also stated that high salt concentrations may increase Cd availability to plants because the soil has less adsorption capabilities due to these high salt concentrations.

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2.2.4 Soil Factors Affecting The Behaviour and Phytoavailability of Cadmium

The soil solution plays a critical role in controlling ion availability to plants and heavy metal ion solubility and, hence, phytoavailability will vary because of the many factors that affect their concentrations in the soil solution (Lorenz et al. 1994). He and Singh (1993b) showed that the principal factors influencing the extractability of Cd in soils (i.e. total Cd, pH, exchangeable K and Ca, Mn-oxides, available P, and fine sand content) varied with different soils, plant species grown, the length of cultivation, and the extractants used.

Soil factors such as pH, CEC, redox potential, organic matter content, other metals, and fertilization all impact on Cd availability and mobility (Adriano 1986). Variations in any of these factors may influence Cd solubility which directly affects phytoavailability. The total amount of Cd present in the soil is one of the major factors affecting the Cd content of plants. Cd concentration in plants increased linearly with total Cd concentration in the soil in a number of studies (Alloway 1990; He and Singh 1993b). Soil type also influences Cd availability. Eriksson (1990) concluded that, for soils of the same total Cd content, Cd was more soluble and more available to plants in sandy soil than in clay soil, while Mahler et al. (1978) found that Cd uptake by plants was usually higher in acidic than in alkaline or calcareous soils.

Much research has centred on the importance of soil pH as a factor influencing the

solubility of Cd and its rate of uptake by plants (Chang et al. 1987; Andersson and Christensen 1988; El-Kherbawy et al. 1988). Soil pH, within a range, has been shown to be negatively correlated with some plant Cd concentrations; Jackson and Alloway (1992) suggested that the manipulation of soil pH offers the best method of managing Cd phytoavailability. Andersson and Nilsson (1974) found that Cd uptake by fodder rape was inversely related to soil pH. Jackson and Alloway (1992) reported that applying lime reduced Cd availability to cabbage and lettuce, while Alloway (1990) reported that plants grown on acid soils had higher concentrations of Cd than plants grown on neutral or alkaline soils.

According to Alloway (1990), soil pH was the most important soil property controlling the availability of Cd in soil because it affected the adsorption and speciation of metals in the soil. Increasing pH aided in the sorption of Cu, Zn, and Cd by soils (Cavallaro and McBride 1978), and reduced plant uptake of Zn and Cd (John et al. 1972; Andersson and Nilsson 1974). Plant tissue concentrations of Cd generally decreased with increased soil pH when other soil properties remained unchanged. This inverse relationship is well established (Williams and David 1976; Mahler et al. 1980; Eriksson 1990).

Naidu et al (1994) stated that increasing pH led to an increase in the surface negative charge of soils, but the changes in surface charge varied widely among soils. Cd sorption increased with increasing pH, regardless of soil type, but the effect of increased ionic strength of the soil solution on Cd sorption varied with pH, indicating that Cd was retained by both non-specific and specific bonding. He and Singh (1993a) showed that soil pH affected the extractability of Cd in soils, although they noted a lack of consistency with various extractants (NH_4NO_3 , NH_4OAc , HCl, and CaCl₂). The decrease in extractability was

attributed to the increase in Cd adsorption or the decrease in solubility of Cd-minerals such as CdCO₃ and Cd₃(PO₄)₂ with increasing soil pH (McBride et al. 1981; Kuo et al. 1985; King 1988a; Christensen 1989; Kuo 1990).

Page et al. (1981) noted that Cd uptake was inversely related to soil pH, and suggested that liming (which increases soil pH) was one of the best ways of minimizing uptake of Cd by plants grown on acid soils. Jackson and Alloway (1992) reported that liming acid soils to pH 6.5 - 7 usually decreased the phytoavailability of soil Cd. MacLean (1976) detected a decrease in Cd concentration in lettuce when lime was added to acid soils with no addition of Cd. However, with the addition of Cd, the effects of pH on Cd uptake were inconsistent. Other authors, such as Pepper et al. (1983) did not find reduced Cd content in maize after liming sludge-amended soils.

The effects of CEC on the phytoavailability of Cd are variable. Mahler et al. (1978) did not find a consistent relationship between soil CEC and the Cd content of either lettuce or Swiss chard leaves. Haghiri (1974) decreased Cd concentration in oat shoots by increasing the CEC of the soil with the addition of organic matter. Adding organic matter, with no increase in CEC, did not affect Cd concentration in the oat shoots nor the soil exchangeable Cd. Therefore, the author concluded that the retaining power of organic matter for Cd is predominantly through its CEC effects (Haghiri 1974).

Garcia-Miragaya and Page (1978), in studies on Cd sorption of four soils, stated that the structural and chemical nature of the adsorption complex of soils was of more importance . than CEC, per se, in Cd adsorption. John (1976) also reported that Cd bonding increased as organic matter and CEC increased, while Petruzzelli et al (1978) were of the opinion that the amount of organic matter binding could depend upon the type of organic matter. Alloway (1990) reported that the effect of CEC on Cd phytoavailability was still not fully understood because cation exchange was only one of several adsorption mechanisms affecting the solubility of Cd in soils.

Organic matter is effective as an adsorbent of Cd (Andersson and Nilsson 1974). John et al. (1972) reported that the soil's most important property was its ability to adsorb Cd, thus, an increase in organic matter would certainly increase the soil's adsorption capacity. It is considered effective in reducing solubility and plant uptake of Cd because of its high CEC and complexing ability (Eriksson 1990). Adriano (1986) suggested that organic matter was important for Cd sorption because it adsorbed great amounts of inorganic cations. There is a correlation between organic matter content and CEC, and the maximum amount of Cd in soils, suggesting that Cd²⁺ ions are retained by ion exchange and complexation (Levi-Minzi et al. 1976; Singh 1979).

Organic complexing of Cd in soil may be of special interest because certain metals may combine with specific chelating groups in humus and become fixed. For example, Stevenson (1976) found that organic Cd complexes were less stable than Cu and Pb complexes. Haghiri (1974) stated that organic matter was able to retain soil Cd because of its CEC, rather than its chelating ability, therefore making the Cd less available to plants.

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Cd generally occurs with other heavy metals, especially in land application of sewage sludges. Since most of these heavy metals are divalent cations, they compete with Cd for soil sorption sites (Christensen 1989). However, most of the reported studies on competition of Cd with other heavy metals involve very high Cd concentrations, which make it difficult to relate to agricultural soils.

Zinc is known to be an important factor affecting the adsorption of Cd, and Zn

content is usually high in soils with a high Cd content (Eriksson 1990). Zinc had an antagonistic effect on Cd uptake by plants in soils with low Cd concentrations, and either a synergistic or a nil effect on soils with high Cd contents (Haghiri 1974; Page et al. 1981; Choudhary et al. 1994). Christensen (1987) reported that Zn is a major competitor with Cd for exchange sites, especially at Zn concentrations of 100 ug l^{-1} .

According to Adriano (1986), lead in the soil can enhance Cd uptake because it is adsorbed more easily than Cd.

2.2.5 Phytoavailability of Cadmium

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Plant uptake of a metal is very dependent on the concentration of the metal in the soil liquid phase (Boekhold and Van der Zee 1992). This is the phase from which plant roots receive water and nutrients, therefore, the concentration of a metal such as Cd in the soil solution is a better measure of potential hazards than its total content in the soil.

Sposito (1984) stated that the phytoavailability of a chemical element such as Cd in the soil solution may be the result of competition among plant roots, soluble complexing compounds, and the solid phases in soil for the free ionic form of Cd. According to Adriano (1986) and Alloway (1990), Cd mobility and phytoavailability in the soil will be determined by its speciation, adsorption or coprecipitation onto hydrous metal oxides, complexation with organic components and precipitation reactions.

Jackson and Alloway (1992) stated that the potentially phytoavailable amount of soil Cd will be determined by the soil's sorptive properties. According to Eriksson (1990), plant uptake of Cd is very much related to the solubility of Cd, which is regulated by soil sorption processes. Many experiments (Cavallaro and McBride 1978; Singh 1979; King 1988a; Garcia-Miragaya 1980) have indicated that most soils can easily sorb Cd, both in an exchangeable and in a non-exchangeable form.

It is important to recognize and understand the soil chemical processes that will affect these variations because of the potential impact of soil contamination on human health. It does not suffice to rely on the acute Cd toxicity symptoms of leaf chlorosis, wilting and stunted growth, to signal that something is amiss, for Cd can accumulate in plants without visual signs of its presence (Chaney and Giordano 1977).

2.3 Cadmium In Plants

2.3.1 Amounts and Distribution

Under natural conditions, all plants take up small quantities of Cd from the soil. However, when Cd is readily available, the amount taken up by the roots and distributed throughout the plant will vary greatly (Page et al. 1972; Turner 1973; Bingham et al. 1975). Wagner (1993) suggested that a general rule for Cd accumulation in plant tissues is leaves > fibrous roots > seeds = storage organs, with potato tubers accumulating high amounts of Cd. Wagner (1993) also reported on the tendency of tobacco to accumulate more Cd in the leaves than in the roots. Cd concentration appeared to be lower in seed, tuber, and fruit tissues and higher in roots and leafy tissues, according to Bingham et al. (1975). As well, Florjin et al. (1992) showed that young lettuce leaves accumulated smaller amounts of Cd than older leaves. Brown et al. (1988) reported that increases in soil solution concentrations of Cd, either due to sludge amendment or to changes in soil redox potential, led to increased Cd in vegetative parts of oats and rye grass, but not in the grain. They suggested that soil type, plant species and environmental conditions all played a role in plant metal uptake.

Rao and Mathur (1994) developed a mathematical root-soil water flow and Cd movement model to predict the uptake of Cd by plants. However, the effect of soil parameters (pH, organic matter, CEC, etc.) and competition of other heavy metals on Cd distribution between soil and solute were not considered. To accurately simulate crop growth and uptake, parameters other than those considered by Rao and Mathur would have to be part of the model.

2.3.2 Plant Factors Affecting The Uptake of Cadmium From Soil

Plant species and varieties (cultivars) vary greatly in their ability to absorb, accumulate, and tolerate Cd, with lettuce accumulating more Cd than any other crop (Adriano 1986). Li et al. (1993) reported that grain Cd levels were affected by both soil characteristics and plant genotype. The 31 durum wheat lines and 200 sunflower genotypes studied exhibited wide variations in kernel Cd concentration. For non-oilseed sunflowers, both plant genotype and soils appeared to affect Cd concentrations, where heavy-textured soils contained more Cd and caused higher kernel Cd. According to the authors, lower soil pH and high amounts of soil chloride could lead to an increase in kernel Cd concentration.

In addition to physiological differences among plant species, the length of the growth phase, as well as the depth of rooting, can influence plant uptake of Cd. Plant varieties with a small root surface area may take up less metal than plants with a large root surface area. Mullins et al. (1986) applied sewage sludges to four soil types, and found significant uptake of Cd and Zn by corn roots. Using a nutrient uptake model, they concluded that mass flow was the main supply route of Cd, and that root growth constants, average root radius, and water influx rate had the greatest effect of all plant factors on metal uptake. Wagner's (1993) studies indicated that the higher fine root mass of *N. rustica* could have accounted for the high root Cd binding capacity of this species.

The rhizosphere may play a major role in enhancing uptake or decreasing uptake of Cd from the soil. The soil-root interface (the rhizosphere) can change considerably when plants try to adapt to adverse soil chemical conditions. According to Marschner (1992), the changes depend on plant species, the nutritional status of plants, and the soil conditions. Mass flow and diffusion of nutrients from the soil may play a role in nutrient concentration, where an excess of nutrients (more than taken up by plants) could lead to accumulations in the rhizosphere. On the other hand, depletion of nutrients in the soil (e.g. P and K) could lead to a release of K from the non-exchangeable fraction and even induce enhanced 'weathering' of clay minerals (Marschner 1992).

Rhizosphere pH is often quite different from that of the bulk soil. The imbalance in cation-anion uptake results in differences in H^+ excretion and pH changes in the rhizosphere. Because NO₃ is more mobile in the soil, and is delivered very quickly to the roots via mass flow and diffusion, its uptake is often greater than that of NH⁴, leading to an increase in pH in the rhizosphere, even in strongly acid soils. Marschner (1992) suggested that root-induced changes in rhizosphere pH will affect the solubility and acquisition of the mineral nutrient P, and the micronutrients Zn, Fe and Mn. A similar effect may occur with Cd. Eriksson (1989) concluded that because of the wide variance in plant responses to changes in soil pH, physiological differences between plant species might play as large a role as the adsorption characteristics of the soil in trying to determine the influence of pH on Cd uptake. Some plants reduce soil pH near their root systems, and so increase the phytoavailability of different soil components. Furthermore, soluble root exudates can increase metal solubility in the rhizosphere, depending upon plant species and cultivars (Mench and Martin 1991). Root exudates of *Nicotiana* spp. increased Cd solubility, by the formation of complexed cations with organic acids and, to a lesser degree, with amino acids (Mench and Martin 1991). Uren and Reisenauer (1988) stated that root exudates could indirectly affect nutrient solubility and uptake because of their influence on microbial activity, on the physical properties of the rhizosphere, and on root growth patterns. Direct effects would be enhanced because of acidification, chelation, precipitation, and oxidation-reduction processes.

2.4 Effects of Fertilization

Fertilizers can increase the phytoavailability of Cd as a contaminant in the fertilizers and by the effects of fertilizers on pH, ionic strength, complexation, and plant growth. Additions of N, P, and KCl fertilizers can increase Cd accumulation in crops, even when only trace amounts of Cd are present in the fertilizers, although varying opinions have been given regarding the significance of these additions.

Increasing the fertilizer rate can also increase plant growth and transpiration which would result in greater uptake of Cd from the soil solution (deVillarroel et al. 1993; Lorenz et al.

1994; Selles 1995; Grant et al. 1996b).

2.4.1 Fertilizer Salts

Increases in concentrations of Cd in fertilized soils and plants are not due solely to the traces of Cd in fertilizer. Cd content of crops can be increased by as much as 50 %, due to soil chemical reactions resulting from the fertilizer salts (Andersson 1976). Eriksson (1990) stated that fertilizers increased the availability of Cd in soils by increasing the salt content and changing the pH of the soil. Andersson (1976) concurred, stating that salt led to an increase in the solubility of Cd, and therefore, to an increase in plant uptake of Cd. According to Lorenz et al (1994), fertilizers could be an influence on the availability of Cd in soils, due to acidification or increased ionic strength of the soil solution. In experiments on winter wheat, with four different commercial fertilizers (nitrate of lime, NPK 16-5-12, NPK 20-5-9 and PK 8-15) tested at three different rates, Andersson (1976) found that increased rates of fertilization led to higher concentrations of Cd in wheat grain, even with nitrate of lime (which is very low in Cd). The greater amounts of Cd removed by the wheat than was supplied by the fertilizer must have been due to soil reactions, probably ion exchange, where acidity would decrease the pH, releasing some of the easily-soluble Cd of the soil. Therefore, even almost Cd-free fertilizers could bring about increases in the Cd content of plants. The effects of soil chemical reactions resulting from the fertilizer salts could play a prominent role in the short-term. Once the fertilizer salts were dissolved and distributed in the soil plough layer, then the concentration of free salts and pH would determine the Cd concentration of the soil solution.

Studies by Petruzzelli et al. (1985) and Temminghoff et al. (1995) showed that increased ionic strength (by additions of calcium chloride salts) decreased Cd adsorption by soil, as a result of Ca-ions competing for the high energy soil adsorption sites, which adsorbed Cd in trace amounts on a very selective basis. The decrease in Cd adsorption with increased ionic strength was attributed to competition between Cd and cations in the electrolyte (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992). Sparks (1984) stated that although it is universally recognized that ionic activities in soil solution are important influences on nutrient uptake and plant growth, each soil has unique characteristics that define this relationship. Therefore, data and conclusions cannot always be extrapolated from one soil to another, based solely on ion activities.

2.4.2 Nitrogen Fertilizers

Nitrogen fertilizers have been shown to increase Cd accumulation in plants, even though the fertilizer does not usually contain significant levels of Cd (Williams and David 1976; Eriksson 1990; Brown et al. 1994; Grant et al. 1996a). Nitrogen fertilizers containing N in the form of ammonium (ammonium sulfate, ammonium nitrate, urea) are known to have acidifying effects on soil. Eriksson (1990) stated that the difference in N-fertilizer effects on Cd solubility and Cd plant uptake depended on pH. The higher the NH₄⁺ content of the fertilizer, the lower the pH, and the higher the solubility and plant uptake of Cd. Cd contents were lowest after nitrate of lime application and highest after application of ammonium sulfate. Increasing the application rates of the fertilizers led to an increase in Cd availability, an effect which tended to be stronger in sand than in clay soils, due to a lower
CEC and lower soil water content (Eriksson 1990; Grant et al. 1996a).

Nitrogen fertilizers affected the chemical behaviour of mineral elements in the soil, as well as plant uptake, with significant differences among various N fertilizers applied at the same rates (Willaert and Verloo 1982). In their studies, the acidifying fertilizers $(NH_4)_2SO_4$, NH_4NO_3 , and urea all increased exchangeable and water-soluble Mn, Zn and Cd in the soil, illustrating the dominant effects of pH on the solubility of these elements. The non-acidifying fertilizers did not show these increases. Concentrations of Mn, Fe, Cd and Ni in spinach leaves increased significantly when $(NH_4)_2SO_4$ was applied, due to decreased soil pH which increased the water soluble contents of the minerals, and hence, uptake by the plants. Nitrogen fertilizers also increased the contents of Ca, Mg, K, and total N and NO₃, but decreased the plant uptake of P, Cl, and SO₄, which may have been effects of not only the higher concentrations in the soil solution, but also the antagonistic effects between $NO_3^$ and other anions at the moment of root absorption.

The form of nitrogen applied to plants had a major effect on the other nutrients taken up by plants and on the cation/anion uptake (Florijn et al. 1992). The uptake of K, Ca, and Mg was lower in NH_4 -fed plants than in NO_3 -fed plants, due to the balancing of the uptake of cations and anions by the plant. The form of N taken up by the plant may also influence Cd uptake by the effects on rhizosphere pH. In soil, the phytoavailability of Cd is pHdependent. Raising the pH of the soil, e.g. by liming, has been shown by many researchers to decrease the Cd concentration in the soil solution and, therefore, its uptake by plants. If, however, the form of nitrogen affects the rhizosphere pH via the extrusion of OH⁻ or H⁺ ions, it might play a major role in the phytoavailability of Cd and its uptake by plants (Florijn et al. 1992). Both NO_3^- and NH_4^+ are taken up by the plant roots (Riley and Barber 1971).

Rhizosphere pH decreases with plant absorption of NH4⁺ due to H⁺ extrusion and increases with the absorption of NO₃ by OH⁻ extrusion. Florijn et al. (1992) showed that NH₄ led to higher Cd concentration in lettuce shoots and roots compared to NO₃, even at constant pH, but that after uptake, the form of N did not affect Cd distribution within the plant. Approximately 70% of the Cd was found in the shoots. Young leaves had smaller amounts of Cd than old leaves, regardless of source. Thomson et al. (1993) also concluded that the form of nitrogen fertilizer (NH₄-N or NO₁-N) could affect plant growth by influencing the availability of other trace elements. In experiments on beans, they reported significantly higher yields of shoot and root dry matter for plants supplied with KH2PO4 (rock phosphate -Hyperphos) and fertilized with NH_4 -N compared with NO_3 -N. The authors speculated that the increased growth was due to more nutrient availability because of the acidification of the bulk soil. As well, shoot concentrations of P (but not K), and micronutrients such as Fe, Mn, Zn and Cu were also higher with NH₄-N and nitrification inhibitor N-Serve, which the authors stated could only be due to acidification of the rhizosphere. Therefore, Thomson et al. (1993), concluded that ammonium fertilizers reduced the pH of the bulk soil after nitrification, and also reduced the rhizosphere pH during preferential NH₄-uptake. Rhizosphere acidification appeared to be more effective in increasing the uptake of P and micronutrients into bean plants than acidification of the bulk soil by nitrification of NH₄-N.

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Lorenz et al. (1994) suggested that the addition of fertilizer cations, such as K and NH₄, would significantly alter the ionic strength of the soil solution and, therefore, the uptake of heavy metals by plants. In their studies, they added more N and K fertilizer than what the plants required. This excess fertilizer decreased soil pH and increased K, Ca, and Mg, and also Cd and Zn ions in soil solution, probably due to ion exchange and the dissolution

of carbonates. The fertilizer cations K and NH₄ probably were responsible for the desorption of major elements, heavy metals and H⁺ ions that were adsorbed on to exchangeable sites or soil colloids. They suggested that nitrification and uptake by plants of the added NH₄ caused the decrease in soil pH and the desorption of major and heavy metal ions, and that dissolution of carbonates also occurred at the lowered soil pH. A decrease in the amount of excess fertilizer cations, due to plant uptake of ions, led to a decrease in the concentrations of ions in solution, and an increase in soil pH. Lorenz et al. (1994) also reported that concentrations of K, Ca, and Mg in plant parts were quite constant over time and did not appear to be related to their concentrations in the soil solution. In contrast, increased Cd and Zn concentrations in the soil solution led to increased concentrations in plants. It appeared that plant uptake of N, K and Mg were closely correlated with transpiration. Therefore, adding fertilizer according to the rate of transpiration would be sufficient to meet the needs of the plants, and would, perhaps, result in a soil solution unaltered by fertilizer ions (Lorenz et al. 1994).

2.4.3 Phosphorus Fertilizers

The effects of P fertilization on Cd uptake has varied. Mortvedt et al. (1981; 1987) reported that applications of P fertilizers (triple superphosphates) at recommended rates for more than 50 years in nine long-term soil fertility studies did not increase the Cd content of wheat, corn, and soybeans, although there were increases in soil Cd levels by as much as 100 %. He concluded that the plant availability of Cd in P fertilizers was rather low, even at high rates of P fertilization. However, increases in Cd uptake by crops, due to the addition of Cdbearing phosphorous fertilizers have been reported by others (Singh 1991).

Phosphorus fertilizer may also influence Cd availability by its effects on soil pH, ionic strength, and plant growth. An increase in soil pH increases the adsorption of Cd by soils, and thus reduces its extractability (Andersson and Nilsson 1974; Christensen 1984a; Kuo et al. 1985; King 1988a); therefore, liming has been suggested as a way of decreasing plant availability and uptake (Jackson and Alloway 1992).

He and Singh (1994) suggested that increasing pH increased both the deprotonation of hydroxyl and carboxyl groups, and the negative charge density on soil colloids. Thus, an increase in soil pH leads to more adsorption and less extractability of Cd in soils. Levi-Minzi and Petruzzelli (1984) showed that MAP (monoammonium phosphate) and diammonium phosphate (DAP) drastically affected the solubility of Cd in two soils by altering soil pH. According to Xiong (1995), phosphate fertilizers could not decrease soil Cd availability without a simultaneous increase in pH. Phosphate has a very high affinity for soil adsorption sites, and the adsorption of phosphate usually increases soil negative charge (Parfitt 1978). Kuo and McNeal (1984) also observed that phosphate sorbed on oxides increased Cd adsorption, which they attributed to phosphate decreasing the zero point of charge on the surface.

Potassium Fertilizers

Application of KCl may increase plant uptake of Cd by increasing Cd-chloride complex formation, therefore decreasing Cd adsorption (Grant et al. 1996a). Sources of K could also influence Cd availability. In their study of Russet Burbank potatoes grown with banded fertilizer consisting of diammonium phosphate (DAP), and either potassium sulfate (K_2SO_4) or potassium chloride (KCl), Sparrow et al (1994) found lower Cd concentrations, at four of their six sites, when potatoes were grown with K_2SO_4 . They attributed this to sulfate ions increasing soil adsorption of soil and/or fertilizer Cd to a greater degree than chloride ions, thereby decreasing Cd availability. There were no appreciable differences in Cd uptake between K sources at two of their experimental sites, which the authors stated could be due to leaching, or to chloride in irrigation water, or to the addition of more NPK fertilizer than was required by the crop. O'Connor et al (1984) also reported that Cd in poppy seed grown with KCl had more Cd than those grown with K_2SO_4 . Studies by Bingham et al. (1983; 1984) showed that Cl treatments greatly increased Cd in the soil solution and leaf Cd content. Bingham et al. (1986) indicated that the SO_4^{2} ligand was less able to complex Cd than the Cl⁻ ligand, so chloride treatments would form more Cd complexes than sulfate treatments.

2.5 Summary

The literature reviewed and cited shows that the phytoavailability of Cd is influenced by many plant and soil properties and by management. The effect of fertilization, particularly that of nitrogen fertilization, on Cd phytoavailability is not fully understood. Much more information is needed before management practices can be adopted which would mitigate the effects of N fertilization on Cd uptake by crops.

3. EFFECT OF ADDED FERTILIZER ON EXTRACTABILITY OF CADMIUM IN SOIL

3.1 Abstract

The effects of ionic strength of the soil solution, as affected by various fertilizer salts, on Cd extractability in a Newdale clay loam soil were studied. Samples of soil were extracted with various concentrations (ionic strengths) of urea, calcium nitrate, potassium chloride, potassium sulfate, and ammonium sulfate. The extracts were analyzed for Cd. In a second study, soil samples were treated with urea, ammonium nitrate, potassium chloride, potassium sulfate, and ammonium sulfate at 10 000 ug N or K g⁻¹ and incubated for 1, 3, 7, 14 and 28 days at 20° C. Samples were extracted successively with water, 0.01M calcium chloride, 0.1M calcium chloride, and DTPA, and the extracts were analyzed for Cd. Concentrations of Cd in the extracts were quite low, barely above detectable levels. The extracting solutions of ammonium sulfate and urea had the highest Cd concentrations and also the highest pH values. Extracting solutions of calcium nitrate had the lowest Cd concentrations and the lowest pH values. The strengths of the extracting solution did not significantly increase Cd concentration, with the exception of the ammonium sulfate solutions. Only ammonium sulfate increased extractable Cd for soils that were incubated.

3.2 Introduction

Cd, when ingested in large quantities by humans and animals, may cause health problems (Alloway 1990; Jackson and Alloway 1992). Crops grown in soils with high levels of available Cd can accumulate substantial quantities of Cd and transfer this Cd to edible portions of the plant (Kuboi et al. 1986). In the soil, the mobility and phytoavailability of Cd are affected by chemical processes which can, in turn, be influenced by management practices.

Applications of fertilizers, necessary for high yields and sustainability of arable agriculture, have been shown to increase Cd uptake (Brown et al. 1994; Grant et al. 1996a). Fertilizers may influence the availability of Cd by increasing the salt content and changing the pH of the soil (Williams and David 1976; Eriksson 1990). Solubility and plant uptake of Cd increases with increasing fertilizer rate (Andersson 1976; Brown et al. 1994; Grant et al. 1996a). According to Lorenz et al. (1994), fertilizers could increase the availability of Cd to plants, due to acidification or increased ionic strength of the soil solution. Petruzzelli et al. (1985) showed that increased ionic strength of the soil solution decreased Cd adsorption. This was likely caused by competition between Cd and cations in the electrolyte (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992). Potassium fertilizers such as KCl may also increase the solubility of Cd. Grant et al. (1996a) reported that Cd uptake by barley increased when KCl was applied. Sparrow et al. (1994) found higher Cd concentrations in potatoes grown with KCl than those grown with K_2SO_4 . The SO_4^2 ligand is less able to complex Cd than the Cl⁻ ligand (Bingham et al. 1986). Cd solubility is increased by complexation with chloride (Garcia-Miragaya and Page 1976). The increase

in Cd concentration with increasing fertilizer rate may be a combination of pH, ionic strength, and complexation effects.

The relative effects of different fertilizer sources, ionic strength, pH, and complexation on Cd solubility are still not known, therefore the purpose of this study was to investigate the effects of fertilizer source and ionic strength on soil pH and Cd solubility.

3.3 Materials and Methods

3.3.1 Soil

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The soil selected for study was an Orthic Black soil (Newdale clay loam), a fertile Manitoba soil occupying a significant area of the cultivated soils of the upland till plain of Western Manitoba. This soil has a pH of about 7.1, a conductivity of approximately 0.8 dS m^{-1} (Canada-Manitoba Soil Survey 1984), and a DTPA-extractable Cd content of approximately 100 ng g⁻¹ (Bailey et al. 1995).

3.3.2 Effect of Fertilizer Solutions on Cd Extractability

Solutions of five fertilizer salts of reagent grade, varying in ionic strength, were prepared (Table 3.1). Concentrations ranging from very low to saturation were used in order to simulate concentrations of fertilizer salts in soil during and after dissolution of fertilizer granules.

Extracting Solution	Concentration (M)	
Urea	0.05, 0.1, 0.5, 1.0, 2.0, 3.0, 5.0	
Calcium nitrate	0.05, 0.1, 0.5, 1.0, 2.0, 3.0, 5.0	
Potassium chloride	0.05, 0.1, 0.5, 1.0, 2.0, 3.0	
Potassium sulfate	0.05, 0.1, 0.5	
Ammonium sulfate	0.05, 0.1, 0.5, 1.0, 2.0, 3.0	

TABLE 3.1. Concentrations of extracting solutions.

Duplicate five grams samples of air-dried soil were placed in bottles with 50 ml of solution, and the samples shaken for 12 h. The pH of the slurry was measured using a Fisher Scientific 825 MP pH meter with a Ross "Sure Flow" electrode. The extracts were filtered through Whatman #42 filter paper, and purified and concentrated for analysis using a dithizone chelation-extraction procedure similar to that used by Kamata et al. (1989). One ml of ammonium acetate buffer was added to a 2 ml sample and the pH adjusted to 4.5 using 6M hydrochloric acid. One ml of 0.05% dithizone was added and the samples shaken for 15 m. The aqueous layer was discarded and 1 ml of 0.06M nitric acid was added. The samples were shaken for 10 m and the aqueous layer retained for analysis. All pipettes and containers used were glass, and caps were composed of Teflon.

Cd concentration in the extracts was measured using graphite furnace atomic absorption spectrophotometry. The concentration of Cd in the fertilizer solutions was measured before extraction and these background values were subtracted from the values obtained for the soil extracts. Statistical analysis was performed using the SAS General Linear Models procedure (SAS Institute 1990).

3.3.3 Effect of Fertilizer Salts and Time of Incubation on Cd Extractability

Five reagent grade fertilizer salts were used: urea, ammonium nitrate, potassium chloride, potassium sulfate, and ammonium sulfate. Ten grams of air-dried soil were placed in 50 ml centrifuge tubes. The fertilizer salt was mixed with the soil in each tube at a rate of 10 000 ug g⁻¹ N or K. Treatments were duplicated and soils with no fertilizer salt were also prepared. The soils in the tubes were wetted to field capacity and incubated at 20^oC for 1, 3, 7, 14, or 28 d. After incubation, each sample was successively extracted for a 2 h duration with 40 ml deionized water, 40 ml 0.01M calcium chloride, 40 ml 0.1M calcium chloride, and 40 ml diethylenetriaminepentaacetic acid (Lindsay and Norvell 1978; Carter 1993; Bailey et al. 1995). The pH of each extract was measured. The samples were purified, Cd concentrations were determined, and statistical analysis was performed, as previously described.

3.4 Results

3.4.1 Effect of Fertilizer Solutions on Cd Extractability

Cd concentrations in the extractants were very low, and only slightly above detectable levels (Fig. 3.1). In many instances, subtraction of the concentration of Cd in the fertilizer solution (no soil) from the values obtained after extraction resulted in negative values. Despite the above limitation, the data shows that the urea, potassium sulfate, potassium chloride, and calcium nitrate solutions had very little or no effect on Cd



Figure 3.1. Amounts of Cd extracted by various fertilizer solutions (a), and pH values of soil/extractant slurries (b); error = 2.17 (a), 0.27 (b).

extractability in this study. Ammonium sulfate at low concentrations had no effect on Cd solubility. However, at high concentrations of ammonium sulfate, Cd solubility was significantly increased. It should be noted that the calcium nitrate solutions had the lowest pH and yet did not appear to solubilize Cd (Fig. 3.1). In contrast, the ammonium sulfate solutions had intermediate pH values and extracted high concentrations of Cd. The increase in Cd solubility with increasing ammonium sulfate concentration was not related to pH. The potassium salts had little or no effect on pH or Cd extractability. Urea increased soil pH and tended to extract more Cd than the potassium salts, despite the high pH. All figures were plotted using averages of replications. Statistical analysis results are given in Table 3.2. Replications are not true experimental "reps", since the experimental conditions were applied simultaneously and identically to the two samples, therefore the error term reflects measurement error.

Source	df	Cd	рН	_
fertilizer	4	0.0780	0.0001	-
concentration	6	nsª	ns	
error		2.1655	0.2692	

TABLE 3.2.	Probability val	ues from ana	lysis of variance	e of the ef	fect of fertiliz	zer salt an	d
concentra	tion on the pH	and amount o	of Cd extracted l	by various	s fertilizer sol	lutions.	

^a ns indicates not significant at $p \le 0.10$.

3.4.2 Effect of Fertilizer Salts and Time of Incubation on Cd Extractability

Cd concentrations in the water, 0.01M and 0.1M CaCl, extracts of soils treated with fertilizer salts and incubated for various periods of time were also very low (one ng Cd g⁻¹ or less) except for the water extracts from the soil treated with urea. Water consistently extracted 2-3 ng Cd g⁻¹ from the urea-treated soils, despite a pH of approximately 9. Only ammonium sulfate, which had an intermediate pH, significantly increased DTPA-extractable Cd in this study (Fig.3.2). Potassium chloride was the only other salt that solubilized more Cd than the control. Incubation time had no significant effect on extractable Cd. There was no relationship between pH and extractable Cd. There were no effects of fertilizer or time on pH, except that the urea treaments were about 1.5 pH units higher than the other treatments (Fig. 3.2). The DTPA extraction was buffered to a pH of 7.30, so the values given were measured during the water extraction. DTPA-extractable Cd concentration for the urea treatments decreased drastically in the first week, possibly due to the initial pH increase, but increased steadily with time of incubation. Ammonium nitrate and potassium sulfate fertilizers did not influence DTPA-extractable Cd concentration. All figures were plotted using averages of replications. Statistical analysis results are given in Table 3.3. Replications are not true experimental "reps", since the experimental conditions were applied simultaneously and identically to the two samples, therefore the error term reflects measurement error.



Figure 3.2. DTPA-extractable Cd (a) and pH (b), as affected by fertilizer salt and time of incubation; error = 9.76 (a), 0.05 (b).

Source	df	Cd	pH
fertilizer	5	0.0103	0.0001
time	4	ns*	ns
error	-	9.7558	0.0541

TABLE 3.3. Probability values from analysis of variance of the effect of fertilizer and time on soil pH and DTPA-extractable Cd.

^a ns indicates not significant at $p \le 0.10$.

3.5 Discussion

Fertilizer salts are known to solubilize soil constituents and hence, metals such as Cd by affecting pH (Eriksson 1990; Jackson and Alloway 1992; He and Singh 1993a), ionic strength (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992; Temminghoff et al. 1995), and complex formation (Hahne and Kroontje 1973; Petruzzelli et al. 1985). There is generally an inverse relationship between pH and available Cd in the soil (Eriksson 1990; Jackson and Alloway 1992; He and Singh 1993a). This relationship, however, was not evident for either study reported herein. In the extraction experiment, only ammonium sulfate consistently increased solubility of Cd. There was no relationship between pH of the extractant, soil, and fertilizer salt mixtures and Cd in soil solution. Urea, potassium chloride, and ammonium sulfate increased DTPA-extractable Cd in the incubation experiment. Soils treated with urea had very high pH values, and soils treated with the other salts had pH values between 7.0 and 7.5. The inverse relationship between pH and Cd solubility was established in bulk soils, not in fertilizer micro-regions. The ionic environment adjacent to fertilizer granules is very different from that of the bulk soil, and the effects of pH may have been masked by other factors.

Complexation is also an important factor to consider. Chloride ions may be considered as a selective ligand for Cd because they do not complex strongly with most other cations (Hahne and Kroontje 1973). These Cd-chloride complexes are negatively charged or neutral species that are less likely to be adsorbed and are more available (Petruzzelli et al. 1985). According to Bingham et al. (1986), Cd also complexes with sulfate, mainly as CdSO₄. These complexes may also increase solubility of Cd, although not to the extent of complexation with Cl⁻ (Salardini et al. 1993). Theoretically, both chloride and sulfate should have increased Cd in solution. In the first study, Cd solubility was not increased by chloride, but was increased by high concentrations of sulfate as ammonium sulfate. In the second study, amounts of DTPA-extractable Cd were increased by application of potassium chloride and ammonium sulfate. Thus, it appears that complex formation was, at least, partially responsible for increases in Cd solubility.

A third factor important in solubilization is the "salt effect" or ionic strength effect. Salts could increase the solubility of Cd in soil solution due to exchange reactions and an increase in solubility of solid phases which are matrices for Cd. All salts except urea should have had an immediate effect on solubility, and initial ionic strength effects should have been in the order of urea < potassium sulfate < ammonium sulfate < potassium chloride < calcium nitrate = ammonium nitrate. Urea would become more important over time as hydrolysis occurs. The sulfate fertilizers are ranked lower than expected because excess sulfate likely precipitated as calcium sulfate. In the first experiment, calcium nitrate did not solubilize Cd despite a high ionic strength and low pH. Only ammonium sulfate solubilized Cd. In the second experiment, urea, potassium chloride, and ammonium sulfate increased DTPAextractable Cd. Thus, a definitive relationship between ionic strength and Cd solubility was not evident.

3.6 Conclusions

Factors such as ionic strength and complexation appear to have influenced Cd solubility in this study. Since pH did not exhibit its typical inverse relationship with soluble Cd, and most other relevant variables were eliminated in this study, it is likely that ionic strength, pH, and complexation interacted to influence Cd solubility. It is impossible to separate pH, ionic strength, and complexation effects based on these studies alone. However, ionic strength and complexation effects appeared to be as important or more important than the pH effect. Further research is required to separately evaluate the relative importance of ionic strength, pH, and complexation for the specific fertilizers of concern.

4. EFFECT OF NITROGEN APPLICATION ON CONCENTRATION OF CADMIUM AND NUTRIENT IONS IN SOIL SOLUTION

4.1 Abstract

A growth chamber experiment, involving displacement of the soil solution, was performed to study the composition of the soil solution over time, as affected by application of N fertilizer. Sceptre durum wheat was grown, using a fine sandy loarn soil, in separate pots with treatments of 0, 50, 100, 200, 400, and 800 ug N g⁻¹ as urea. The soil solution was removed by water displacement and analyzed for Cd and other nutrient ions at time of seeding, 10, 20, 30, and 40 days after seeding, and at time of crop maturity. Soil was also analyzed at each sampling time. Conductivity measurements were taken as estimators of ionic strength. Both solution Cd concentration and DTPA-extractable soil Cd increased with increasing nitrogen rate. The increases in Cd concentration with N fertilization were greatest immediately after fertilization and appeared to be related to an increase in soil and solution conductivity and a decrease in soil pH. Changes in Cd and K concentrations with N rate were greater than changes in the concentrations of the other elements studied. The soil solution concentration of all nutrients, with the exception of phosphate, increased with N rate. The effects of N fertilization on the amounts of extractable nutrients in the soil were more variable.

4.2 Introduction

All soils contain Cd, therefore uptake by agricultural crops is the main source of Cd entry to the human food chain. The mobility and phytoavailability of Cd in the soil are regulated by chemical processes which are, in turn, influenced by management practices such as fertilization.

Plant nutrients are added to the soil in the form of fertilizers to increase crop yields and quality. However, other soil functions and processes may be affected by fertilizer application. Cd concentrations in soils and plants are influenced by soil chemical reactions resulting from the addition of fertilizer salts (Andersson 1976). Fertilizers can influence the availability of Cd in soils, due to acidification or increased ionic strength of the soil solution (Lorenz et al. 1994). Nitrogen fertilizers affect the chemical behaviour of mineral elements in the soil, with significant differences occurring between various N-fertilizers at the same rate (Willaert and Verloo 1992). Some of these differences were discussed in Chapter 3. The difference in N-fertilizer effects on Cd solubility and plant uptake may depend, at least partially, on pH (Eriksson 1990). Nitrogen fertilizers containing N in the form of ammonium can acidify the soil (Tisdale et al. 1993). Urea has been shown to increase exchangeable and water-soluble Cd in the soil, illustrating the effect of acidification on the solubility of Cd (Willaert and Verloo 1992; Brown et al. 1994). The ammonium ion can also lead to desorption of heavy metals from exchange sites or soil colloids (Lorenz et al. 1994). Once the fertilizer salts are dissolved and distributed in the soil plough layer, the concentration of free salts and pH influence the Cd concentration of the soil solution (Andersson 1976). Increasing the application rates of the fertilizer also increases Cd availability, an effect that

is stronger in sandy soils than in clay soils (Eriksson 1990; Grant et al. 1996a). An increase in the rate of N addition increases the ionic strength of the soil solution, causing more competition between Cd and cations in the electrolyte (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992).

The effect of nitrogen application on solution Cd concentration is important because plant uptake of a metal is very dependent on the concentration of the metal in the soil liquid phase (Boekhold and Van der Zee 1992). The objective of this study was to investigate the effects of added nitrogen on the soil solution concentration of Cd and other nutrient ions.

4.3 Materials and Methods

The soil selected for study was a Rego Black soil (Souris fine sandy loam), a medium textured soil occupying a significant area of the cultivated soils of Western Manitoba. Unamended soil samples were analyzed for pH, conductivity, Cd, and nutrient content (Table 4.1). Field capacity was determined as outlined by Veihmeyer and Hendrickson (1949) and Cassel and Nielsen (1986). Dried soil was placed into each of 111 1.5 kg pots. Granules of fertilizer grade urea were mixed into each pot at rates of 0, 50, 100, 200, 400, and 800 ug N g⁻¹. There were 18 pots of each rate. To ensure good plant growth, 20 ug P g⁻¹, 50 ug K g⁻¹, and 20 ug S g⁻¹ were also added to each pot as reagent grade MAP and K₂SO₄. Soils were watered to field capacity using deionized water, and deionized water was added every second day for a period of two weeks to maintain the soil at field capacity.

Parameter	Value	Parameter	Value
pH	7.7	Mg	295 ug g ⁻¹
conductivity	180 uS cm ⁻¹	Zn	0.5 ug g ⁻¹
Ν	9 ug g ⁻¹	Cu	0.5 ug g ⁻¹
Р	16 ug g ⁻¹	Fe	12 ug g ⁻¹
K	190 ug g ⁻¹	Mn	22 ug g ⁻¹
Ca	2400 ug g ⁻¹	Cd	100 ng g ⁻¹

TABLE 4.1. Soil characteristics of Souris fine sandy loam (0-15 cm).

After incubation of the pots for 14 d, ten seeds of Sceptre durum wheat were seeded in a cross pattern in all but three replicates of each treatment. Soils were maintained at field capacity moisture content by the addition of deionized water, every second day, then daily when the plants began to grow. Samples of the soil solution for each treatment were taken as outlined by Lorenz et al. (1994). Plants were harvested by cutting at the soil surface and deionized water was added to bring soils to field capacity. The soils were then covered and allowed to equilibrate for 24 h. The pots were uncovered and deionized water was added to the soil surface of each, at a rate of 5 ml every 5 m, to gradually push the soil solution out through the drainage holes in the bottom of the pot, through funnels, and into collection tubes (Fig. 4.1). The first 5 ml of leachate were discarded and the next 50 ml were collected. This displacement procedure was performed on 3 pots for each treatment at seeding, 10, 20, 30, and 40 d after seeding, and at crop maturity. The pH of the collected leachates was measured using an Orion SA 520 pH meter with a Ross "Sure Flow" electrode, and electrical



Figure 4.1. Three-tiered soil solution displacement apparatus.

conductivity was measured using a YSI Model 31 conductivity bridge with a Beckman conductivity cell (K=1.00). The samples were analyzed for Cd, nitrate, phosphate, potassium, calcium, magnesium, zinc, copper, iron, and manganese. Analyses were conducted using a Technicon II Autoanalyzer (NO₃, soil P), an ARL 3410 ICP with Minitorch (solution P, K, Ca, Mg, Zn, Cu, Fe, and Mn), and a Varian Spectr AA-400 GFAAS with deuterium background (Cd). For the Cd analysis, a standard curve was made up using standards of 0.3 ng Cd g⁻¹ to 2.2 ng Cd g⁻¹.

Soil samples were taken from each pot, dried, ground, and analyzed for Cd, zinc, copper, iron, and manganese with DTPA extraction (Lindsay and Norvell 1978; Bailey et al.

1995), nitrate and phosphate with sodium bicarbonate extraction (Carter 1993), and potassium, calcium, and magnesium with ammonium acetate extraction (Carter 1993). Soil pH and conductivity were measured on a soil/deionized water ratio of 1:2. Statistical analysis was performed using the SAS GLM procedure (SAS Institute 1990).

4.4 Results

Solution pH did not change appreciably with N rate or time, except for the samples incubated for 10 days, where a decrease in pH occurred at nitrogen rates of 50-200 ug g⁻¹ (Fig. 4.2a). Electrical conductance of solutions increased considerably with N rate for all sampling times (Fig. 4.2b). Cd concentration of the solutions increased with nitrogen rate for samples obtained at seeding and 10 d after seeding (Fig. 4.3a). However concentration of Cd in soil solution was increased only moderately for samples taken 20 and 30 d after seeding and was increased only slightly or not at all for samples taken 40 d after seeding and at plant maturity (Fig. 4.4). The increase in solution Cd concentrations with increasing N rates was related to the higher electrical conductivities for initial harvests, but conductivities remained high as Cd concentrations decreased in the later stages of the experiment. There was no evident relationship between pH and Cd concentration in the solution samples.

Phosphate concentrations in the solutions decreased slightly with increasing nitrogen rate and also decreased with time (Fig. 4.3b). Potassium in the solutions increased considerably with nitrogen rate (Fig. 4.3c), but this increase became less pronounced over time. Manganese in the soil solution increased with N rate and decreased over time (Fig. 4.3d). Calcium and magnesium in solution were nearly identical in their behaviour and both



Figure 4.2. Soil solution pH (a) and conductivity (b) values measured at intervals after seeding; standard error = 0.07 (a), 278.88 (b).







Figure 4.4. The relationship between solution conductivity and solution Cd concentration over time.

increased with N rate (Figs. 4.5a and 4.5c). Iron and zinc in solution increased slightly with nitrogen rate (Figs. 4.5b and 4.5d). Concentration of copper in solution was too low to accurately measure. Data obtained for nitrate were extremely variable and, therefore, not shown. There was no apparent relationship between concentrations of Cd and Zn in soil solution.

Soil pH decreased and soil conductivity increased with increasing nitrogen rate (Figs. 4.6a and 4.6b). Decreases in soil pH and increases in electrical conductance were usually more pronounced for samples taken at 10 and 20 d after seeding than for samples taken earlier or later. DTPA-extractable soil Cd behaved like solution Cd, increasing with increasing nitrogen rate (Fig. 4.7a). These increases became less pronounced over time. Extractable soil Cd was linearly related to soil conductivity and, inversely, to soil pH (Figs. 4.8b and 4.8a). DTPA-extractable Cd was usually highest at the 10 and 20 d sampling times which corresponded to the periods of time at which the largest decreases in soil pH and the largest increases in soil conductivity occurred.

As expected, soil nitrate increased with nitrogen rate and decreased slightly over time (Fig. 4.7b). Soil potassium did not change appreciably with N rate but decreased over time (Fig. 4.7d). Extractable manganese behaved similarly to DTPA-extractable Cd and increased with N rate, with the greatest increase occuring after 10-20 d (Fig. 4.7c). Soil calcium and magnesium changed very little with nitrogen rate but increased over time (Figs. 4.9a and 4.9c). Soil zinc was not related to nitrogen rate but did increase slightly after the first displacement (Fig. 4.9b). Copper was not related to N rate but increased after the first displacement, and gradually decreased for the duration of the experiment (Fig. 4.9e). Extractable iron increased slightly with N rate and time (Fig. 4.9c). There was no



Figure 4.5. The effect of added urea on soil solution concentrations of Ca (a), Fe (b), Mg (c), and Zn (d); standard error = 94.55 (a), 2.21 (b), 17.42 (c), 2.44 (d).



Figure 4.6. Soil pH (a) and conductivity (b) values measured at intervals after seeding; standard error = 0.04 (a), 20.12 (b).



Figure 4.7. The effect of added urea on extractable soil Cd (a), NO₃ (b), Mn (c), and K (d); standard error = 1.91 (a), 4.18 (b), 1.12 (c), 4.03 (d).



Figure 4.8. The relationships between DTPA-extractable Cd and soil pH (a) and conductivity (b).



Figure 4.9. The effect of added urea on extractable soil Ca (a), Zn (b), Mg (c), Fe (d), and Cu (e); standard error = 13.73 (a), 0.09 (b), 2.34 (c), 0.61 (d), 0.03 (e).

relationship between extractable soil Cd and extractable soil Zn. All relationships were determined using second order regression unless other wise indicated. All non-regression figures were plotted using the average for the three replicates. Statistical analysis results are given in Tables 4.2 and 4.3.

Source	df	pH	cond	Cd	P	K
гер	2	ns*	ns	ns	ns	ns
N rate	1	0.0001	0.0001	0.0001	0.0001	0.0001
time	1	0.0001	0.0001	ns	0.0001	ns
rate * t	1	0.0005	ns	0.0001	0.0028	0.0001
st. err.		0.0709	278.88	0.0325	0.2687	9.0608
Source	df	Mg	Mn	Fe	Ca	Zn
Source	df 2	Mg ns	Mn ns	Fe	Ca ns	Zn ns
Source rep N rate	df 2 1	Mg ns 0.0001	Mn ns 0.0001	Fe ns ns	Ca ns 0.0001	Zn ns ns
Source rep N rate time	df 2 1 1	Mg ns 0.0001 <u>0</u> .0001	Mn ns 0.0001 0.0491	Fe ns ns ns	Ca ns 0.0001 0.0001	Zn ns ns 0.0935
Source rep N rate time rate * t	df 2 1 1 1	Mg ns 0.0001 <u>0.0001</u> 0.0193	Mn ns 0.0001 0.0491 0.0141	Fe ns ns ns ns ns	Ca ns 0.0001 0.0001 0.0158	Zn ns ns 0.0935 0.0001

TABLE 4.2. Probability values from analysis of variance and standard errors of effect of nitrogen rate and time on pH, conductivity, and concentration of Cd and nutrient ions in the soil solution.

^a ns indicates not significant at $p \le 0.10$.

Source	df	pН	cond	Cd	NO ₃	P	Zn
гер	2	⊓S ^a	ns	0.0874	ns	0.0424	ns
N rate	1	0.0001	0.0001	0.0001	0.0001	0.0656	ns
time	1	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
rate * t	1	0.0255	0.0062	ns	0.0701	ns	ns
st. err.		0.0419	20.117	1.9142	4.1841	0.9102	0.0870
Source	df	Сп	Fe	Mn	Са	Mg	ĸ
		Çu	10			8	
гер	2	ns	ns	ns	DS	ns	
rep N rate	2	ns 0.0480	ns	ns 0.0001	ns	ns	ns 0.0011
rep N rate time	2 1 1	ns 0.0480 0.0001	ns ns ns	ns 0.0001 0.0122	ns ns 0.0001	ns ns 0.0008	ns 0.0011 0.0001
rep N rate time rate * t	2 1 1 1	ns 0.0480 0.0001 ns	ns ns ns 0.0588	ns 0.0001 0.0122 0.0001	ns ns 0.0001 ns	ns ns 0.0008 ns	ns 0.0011 0.0001 0.0418

TABLE 4.3. Probability values from analysis of variance and standard errors of effect of fertilizer rate and time on soil pH, conductivity, and extractable amounts of Cd and nutrient ions.

^a ns indicates not significant at $p \le 0.10$.

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4.5 Discussion

Increasing ionic strength can cause competition between Cd and other cations for exchange sites, resulting in desorption of Cd (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992; Temminghoff et al. 1995). In this case, the ammonium ions from urea, when in higher concentrations, may be competing with the Cd ions for soil adsorption sites, resulting in more Cd in the soil solution (Lorenz et al. 1994). This competition between cations may also explain the increase of some of the other nutrient ions in solution with increasing nitrogen rate. These other ions, all monovalent or divalent cations, could be replaced in the same manner as Cd, increasing their concentration in the soil solution. Phosphate is the only nutrient that did not increase with N rate, and it is an anion. The decrease of the nutrient ions in solution over time can be attributed to a combination of plant uptake, readsorption, and precipitation. Removal of ions from solution would increase over time and with N rate because of increased plant growth; thus, it would be expected that the slope of the line solution ion concentration / N level would decrease over time. Hydroponic studies by W.T. Buckley (personal communication) have indicated a very rapid absorption of Cd from solution. It is possible that, once the roots spread to all areas of the pot, the plants could take up Cd from the soil solution much faster than the solution could replenish itself, and a measurement of the soil solution could provide misleading low Cd values.

In addition to increasing Cd in the soil solution, high nitrogen rates led to an increase in DTPA-extractable soil Cd. There was an effect of N rate on extractable nitrate and manganese. Acidifying fertilizers increase exchangeable and water-soluble Mn, Zn, and Cd (Willaert and Verloo 1992). There was no strong effect on extractable zinc in this study, perhaps due to low indigenous soil zinc. Similarly, there were no observable nitrogen effects on extractable potassium, copper, iron, calcium, or magnesium in the soil, but extractable soil Cd, nitrate, potassium, manganese, and copper decreased over time. This was probably due to an equilibrium shift, with ions moving from exchange sites to the soil solution to replace those removed by plant uptake (Tisdale et al. 1993). Marschner (1992) also reported that depletion of nutrients in the rhizosphere can lead to a release of minerals from the nonexchangeable fraction and weathering of clay minerals. Plant uptake of calcium and magnesium is low in relation to the available Ca and Mg in the soil (Tisdale et al. 1993).

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The concentrations of these nutrients in solution remained high, and this may have resulted in readsorption and a subsequent increase in exchangeable soil Ca and Mg over time.

An inverse relationship between pH and available Cd has been frequently reported (Eriksson 1990; Jackson and Alloway 1992; He and Singh 1993a). In this study, soil pH and extractable soil Cd and Mn were related. However, the amount of Cd in soil solution was not related to solution pH. Complexation was likely not a significant factor in increasing Cd concentrations. If any Cd-complexing anions were present, each pot should have contained the same amount of these anions. Since complexation was not a factor, the lack of observable relationships between Cd in the soil solution and solution pH may be due to the strong influence of ionic strength, which masked the effects of pH.

4.6 Conclusions

Ionic strength of the soil solution varied greatly with N level applied, and appeared to be most closely correlated to changes in soil and solution ion concentrations observed. The ammonium ions, from the hydrolysis of urea fertilizer, competed with Cd and other cations for exchange sites. An increase in the rate of fertilizer merely increased this competition and more cations became phytoavailable. Manganese and potassium ions were affected in the same manner. Many of the ions measured, both in solution and in the soil itself, decreased with time. A combination of pH and ionic strength effects resulted in an increase in availability of Cd and some nutrient ions, with increased nitrogen application.
5. EFFECT OF NITROGEN APPLICATION ON TRANSPIRATION AND ACCUMULATION OF CADMIUM AND NUTRIENT IONS IN DURUM WHEAT

5.1 Abstract

A growth chamber study was performed to study Cd uptake as a function of rate of nitrogen fertilizer and transpiration rate. Sceptre durum wheat was grown in pots with treatments of 0, 50, 100, 200, 400, and 800 ug g^{-1} N in the form of urea. Water use by plants was recorded for each pot. Above-ground plant material was harvested from each pot 10, 20, 30, and 40 days after seeding, and at crop maturity and analyzed for Cd and other nutrient ions. Plant Cd concentrations increased with increasing N rate to 800 ug g^{-1} , but dry matter yield and transpiration only increased with N rate to 200 ug g^{-1} . Cd was the element most affected by increasing the nitrogen rate. There were minor changes in other elements with N-rate and time.

5.2 Introduction

All soils contain various amounts of Cd and, under natural conditions, all plants take up small quantities of Cd from the soil. Uptake by agricultural crops, however, is of greater concern because it allows Cd into the human food chain. Long-term consumption of plants high in Cd can lead to chronic toxicity (Jackson and Alloway 1992). Plant uptake of Cd is closely related to the solubility of Cd or concentration of Cd in the soil solution, which is regulated by soil sorption processes (Eriksson 1990). These chemical processes can be influenced by management practices such as fertilization.

Many plant nutrients are added to the soil in the form of fertilizers to produce higher crop yields and quality; however, other soil functions and processes may be affected by fertilizer application. Cd concentrations in soils and plants are influenced by soil chemical reactions resulting from fertilizer salts (Andersson 1976). The availability of ions to plants will vary because of the many factors that affect their concentration in the soil solution (Lorenz et al. 1994). Plant uptake of a contaminant is very dependent on the concentration of the contaminant in the soil liquid phase (Boekhold and Van der Zee 1992). Nitrogen fertilizers affect the chemical behaviour of mineral elements in the soil (Willaert and Verloo 1992), and increase the Cd content of plants (Williams and David 1976; Brown et al. 1994; Grant et al. 1996a). The effects of fertilizer on Cd solubility and plant uptake may partially depend on pH (Eriksson 1990). There is a well established inverse relationship between pH and plant uptake of Cd (Williams and David 1976; Mahler et al. 1980; Eriksson 1990). Increased ionic strength of the soil solution, as a result of fertilization, can also influence the availability of Cd to plants (Lorenz et al. 1994). The increasing salt content leads to an increase in the solubility of Cd, and therefore, to an increase in plant uptake of Cd (Andersson 1976). Fertilizers providing the ammonium ion, such as urea, can desorb heavy metals and other nutrient ions from the exchange sites (Lorenz et al. 1994). Many of these ions are then available to plants from the soil solution. An increase in fertilizer rate will also increase Cd availability, by increasing the competition between the fertilizer cations and Cd in the electrolyte (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992). Once the fertilizer salts are dissolved and distributed in the soil plough layer, the resultant changes in concentration of free salts and pH will influence the concentration of Cd and other ions in the soil solution available for plant uptake (Andersson 1976).

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The concentration of trace elements in plant tissue is a function of solute transport processes during plant growth (de Villarroel et al. 1993). Mass flow is a major mechanism by which plants take up trace elements from the soil solution (Mullins et al. 1986; de Villarroel et al. 1993). Increasing the nitrogen rate would enhance plant growth, increasing transpiration and biomass accumulation. Plants grown with higher N rates would have a more extensive root system and a greater mass flow rate, which would result in greater uptake of Cd and other elements from the soil solution (de Villarroel et al. 1993; Lorenz et al. 1994; Grant et al. 1996b).

While studies have individually evaluated the effects of fertilizer salts on the concentrations of Cd in the soil and in plants, little information is available to elucidate the effects of fertilizer N on Cd availability from the soil solution through to plant uptake. Chapter 4 dealt with the soil and soil solution concentrations of Cd as affected by nitrogen application. The objective of this study was to investigate the effects of added nitrogen on plant growth, transpiration, and plant concentrations of Cd and other nutrient ions.

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5.3 Materials and Methods

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The soil used was a Rego Black soil (Souris fine sandy loam), a fine textured soil occupying a significant area of the cultivated soils of Western Manitoba. Unamended soil samples were analyzed for pH, conductivity, Cd and nutrient content (Table 5.1). Instruments used for analysis were a Technicon II Autoanalyzer (NO₃), an ARL 3410 ICP with Minitorch (PO₄, K, Ca, Mg, Zn, Cu, Fe, and Mn), and a Varian Spectr AA-400 GFAAS with deuterium background (Cd), an Orion SA 520 pH meter with a Ross "Sure Flow" electrode, and a YSI Model 31 conductivity bridge with a Beckman conductivity cell (K=1.00).

Parameter	Value	Parameter	Value
pH	7.7	Mg	295 ug g ⁻¹
conductivity	180 uS cm ⁻¹	Zn	0.5 ug g ⁻¹
N	9 ug g ⁻¹	Cu	0.5 ug g ⁻¹
Р	16 ug g ⁻¹	Fe	12 ug g ⁻¹
K	190 ug g ⁻¹	Mn	22 ug g ⁻¹
Ca	2400 ug g ⁻¹	Cd	100 ng g ⁻¹

TABLE 5.1. Soil characteristics of Souris fine sandy loam (0-15 cm).

Field capacity was determined as outlined by Veihmeyer and Hendrickson (1949) and Cassel and Nielsen (1986). Dried soil was placed into each of 111-1.5 kg pots and fertilizer grade urea (containing no detectable Cd) was mixed into each pot at rates of 0, 50, 100, 200, 400, and 800 ug g^{-1} . A total of 18 pots were prepared for each rate. To ensure good plant

growth, 20 ug g⁻¹ P, 50 ug g⁻¹ K, and 20 ug g⁻¹ S as reagent grade MAP and K_2SO_4 were also added to each pot. The pots were placed in a growth chamber, where they were allowed to equilibrate for a two week period. During this two week period, the pots were brought to field capacity with deionized water every second day. With the exception of the first 18, all pots were sown with ten seeds of Sceptre durum wheat in a cross pattern. All seeded pots were brought to field capacity, by the addition of deionized water, every second day, then daily when the plant began to grow. The pots were thinned to four plants each after the 20 d displacement. Water use was recorded for each pot. Transpiration was estimated by subtracting average evaporation measured in three unplanted pots from the water use for each pot.

The soil solution displacement procedure, as outlined by Lorenz et al. (1994), was performed on 18 pots at seeding, 10, 20, 30, and 40 d after seeding, and at maturity. Each time, all above-ground plant material was harvested, dried, weighed, ground, and analyzed for Cd, nitrogen, phosphorus, and potassium with a sulfuric acid / hydrogen peroxide digestion (Westerman 1990), and calcium, magnesium, zinc, copper, iron, and manganese with a nitric acid / perchloric acid digestion (Westerman 1990). For the samples taken at maturity, the grain and the straw were analyzed separately. Statistical analysis was performed using the SAS GLM procedure (SAS Institute 1990). Results of soil and soil solution analyses were discussed in Chapter 4.

.5.4 Results

Plant weight and transpiration were not affected by N rate between seeding and 30 days after seeding (Fig. 5.1). The addition of urea increased dry plant weight and transpiration up to about 200 ug N g⁻¹ at 40 d after seeding and at maturity. At higher rates of urea, dry plant weight and grain yield increased only slightly up to 800 ug N g⁻¹ for the samples taken at maturity. Transpiration decreased slightly at rates above 200 ug N g⁻¹ at all sampling times.

Cd accumulation increased with increasing N rate, especially after the 40 d sampling (Figs. 5.2c and 5.2d), with Cd accumulation only partially related to plant growth and transpiration (Fig. 5.3). Concentration of Cd in the above-ground plant tissue and in the grain increased significantly with increasing N rate to 800 ug g^{-1} for the samples taken at 40 days and maturity, and to 400 ug g^{-1} for the samples taken at the other sampling times. Plant Cd concentration in the mature plant straw increased by 150% between 200 and 800 ug N g^{-1} , while Cd concentration in the grain increased by 50% (Figs. 5.2a and 5.2b).

Nitrogen accumulation increased with increasing N rate, with the greatest increase occurring in the samples taken at maturity (Fig. 5.4b). Nitrogen concentration increased slightly with N rate, but the lowest concentrations were measured at maturity (Fig. 5.4a). The highest N concentrations were measured at the 30 d sampling time. Nitrogen concentration in the grain increased with N rate (Fig. 5.4a). Phosphate was unaffected by nitrogen rate but accumulation increased and concentration decreased with time (Figs. 5.4d and 5.4c).

Potassium accumulation increased with increasing nitrogen rate for the samples taken



Figure 5.1. The effect of added urea on dry plant weight (a) and cumulative transpiration per pot (b) at intervals after seeding; standard error = 0.34 (a), 0.81 (b).



Figure 5.2. The effect of added urea on Cd concentration (a and b) and accumulation (c and d) of plant shoots (maturity and grain concentrations are independent; maturity accumulation includes grain accumulation); standard error = 0.02 (a), 0.02 (b).



Figure 5.3. The relationships between shoot Cd accumulation and both plant growth (a) and transpiration (b) at crop maturity.



Figure 5.4. The effect of added urea on shoot concentration and accumulation of N (a and b) and P (c and d); maturity and grain concentrations are independent; maturity accumulation includes grain accumulation; standard error = 0.16 (a), 0.23 (a grain), 0.17 (c), 0.23 (c grain).



Figure 5.5. The effect of added urea on shoot concentration and accumulation of K (a and b) and Mn (c and d); maturity and grain concentrations are independent; maturity accumulation includes grain accumulation); standard error = 1.23 (a), 0.35 (a grain), 6.00 (c), 3.66 (c grain).

at maturity, but not at the other times (Fig. 5.5b). Concentration of K in the grain and plant tissue was unaffected by N rate but decreased over time (Fig 5.5a). Manganese accumulation and concentration increased significantly with increasing nitrogen rate, especially for the samples taken at maturity (Figs. 5.5d and 5.5c). Concentration of Mn in the grain was not affected by N rate.

Calcium accumulation increased significantly with increasing N rate for the samples taken at maturity and increased slightly for the samples taken at other times (Fig. 5.6b). Calcium concentration generally increased with N rate, but Ca concentration in the grain was not affected (Fig. 5.6a). The accumulation and concentration of magnesium increased with increasing nitrogen rate at maturity only (Figs. 5.6d and 5.6c). Concentration of Mg in the grain was not affected.

Plant accumulation of Zn and Cu increased with increasing N rate and with time (Figs. 5.7b and 5.7d). Shoot concentrations of Zn and Cu increased slightly with N and decreased over time (Figs. 5.7a and 5.7c).

Concentrations of Cd and Zn in the plant shoots were related, although this relationship changed over time (Fig. 5.8).

All relationships were determined using second order regression. All non-regression figures are plotted using averages of replicates. Statistical analysis results are given in Tables 5.2 and 5.3. Accumulation values were calculated from concentrations and plant weight, therefore, no statistical data is given.



Figure 5.6. The effect of added urea on shoot concentration and accumulation of Ca (a and b) and Mg (c and d); maturity and grain concentrations are independent; maturity accumulation includes grain accumulation; standard error = 0.54 (a), 0.03 (a grain), 0.09 (c), 0.05 (c grain).



Figure 5.7. The effect of added urea on shoot concentration and accumulation of Zn (a and b) and Cu (c and d); maturity and grain concentrations are independent; maturity accumulation includes grain accumulation; standard error = 1.04 (a), 2.62 (a grain), 0.29 (c), 0.25 (c grain).



Figure 5.8. The relationship between shoot Cd concentration and shoot Zn concentration over time.

Source	df	dsw	water	Cd	N	P	Zn
rep	2	nsª	ns	ns	ns	ns	ns
N rate	1	0.0001	0.0005	ns	0.0001	0.0407	0.0001
time	1	0.0001	0.0001	0.0068	0.0001	0.0001	0.0001
rate * t	1	0.0001	0.0001	0.0001	0.0027	0.0004	0.0391
st. err.		0.3424	0.8150	0.0237	0.1614	0.1664	1.0350
Source	df	Mn	Fe	Cu	Ca	Mg	K
rep	2	ns	ns	ńs	ns	ns	ns
N rate	1	0.0090	0.0657	0.0001	ns	ns	0.0136
time	1	ns	ns	0.0005	0.0001	0.0735	0.0001
rate * t	1	0.0001	ns	0.0553	0.0001	0.0001	0.0465

TABLE 5.2. Probability values from analysis of variance and standard errors of effect of nitrogen rate and time on transpiration, plant growth, and above-ground plant concentration of Cd and nutrients.

* ns indicates not significant at $p \le 0.10$.

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Source	df	grain wt.	Cd	N	P	Zn	Mn
rep	2	ns ^a	ns	ns	ns	ns	ns
N rate	1	0.0001	0.0001	0.0008	0.0079	0.0056	0.0001
st. err.		0.6308	0.1848	0.2271	0.2267	2.6166	3.6626
Source	df	Fe	Cu	Ca	Mg	K	
rep	2	ns	ns	ns	ns	ns	
N rate	1	0.0414	ns	0.0001	0.0069	0.0106	
st. err.	~	3.1074	0.2522	0.0282	0.0534	0.3534	

TABLE 5.3. Probability values from analysis of variance and standard errors of effect of nitrogen rate and time on grain yield and concentration of Cd and nutrient ions in the grain.

^a ns indicates not significant at $p \le 0.10$.

1

Nitrogen, phosphorus, zinc, and copper concentrations in the grain were higher than in the straw. Addition of nitrogen did not significantly affect the distribution of Cd between the straw and the grain (Table 5.4). The ratio between grain phosphorus concentration and straw phosphorus concentration did increase with increasing nitrogen rate. The other nutrients were generally unaffected, although there were slight decreases in the grain/straw ratios for Zn, Ca, Mg, Mn, and Cd between 100 and 800 ug N g⁻¹.

N_rate .	Ratio of concentration of Cd or nutrient in grain/straw								raw			
(ug g ⁻¹)	Cđ	N	P	K	Mn	Ca	Mg	Zn	Cu			
0	0.36		2.49		0.50	0.08	1.01	3.67				
50	0.40	1. 86	2.90	0.39	0.60	0.10	1.01	3.15	10. 69			
100	0.53	1. 95	3.85	0.37	0.62	0.10	0.96	3.89	9.69			
200	0.39	3.02	8.24	0.41	0.38	0.07	0.77	3.72	1.43			
400	0.27	3.66	9.40	0.37	0.21	0.04	0.51	3.48	1.94			
800	0.22	2.52	9.60	0.40	0.13	0.04	0.39	2.23	0.91			

TABLE 5.4. The effect of urea fertilization on plant distribution of Cd and other nutrients.

5.5 Discussion

Added nitrogen in the form of urea fertilizer increased Cd accumulation and concentration in both above-ground plant tissue and grain. The accumulation of all of the plant nutrients measured also increased with increasing N rate, but their concentrations in the plant did not necessarily increase. For the plant concentration of a nutrient or metal to increase, the addition of fertilizer must increase the concentration of the ion in the soil solution, so that the uptake of that nutrient or metal is more than is required to increase the growth of the plant. The increase in uptake must be proportionately greater than the increase in yield. Cd, nitrogen, manganese, calcium, magnesium, zinc, and copper concentrations were increased by increasing N rate, with Cd, Mn, Ca, and Mg showing the greatest increases in the mature plants. Only N and Cd concentration increased in the grain with increasing nitrogen.

in the mature plants. Only N and Cd concentration increased in the grain with increasing nitrogen.

For Cd and many of the nutrients measured, most of the uptake (or transport from roots) occurred between the 40 d sampling time and plant maturity. The greatest nitrogen effects at this stage of plant growth were from 200 to 800 ug N g⁻¹, although dry plant growth and transpiration levelled off within that nitrogen range. While mass flow may be the main supply route of Cd (Mullins et al. 1986; de Villarroel et al. 1993), transpiration does not correlate with Cd accumulation well enough in this study to suggest that no other factors are involved. Plants grown with higher nitrogen rates produced more extensive root systems and greater biomass accumulation, resulting in greater uptake of Cd and nutrients from the soil solution (Lorenz et al. 1994; Grant et al. 1996b). However, this study showed that plant concentrations of Cd and other elements still increased at very high N rates that may also have hindered plant growth. This would suggest that soil factors also played an important role in the increase of plant Cd accumulation with increasing N rate, as suggested in Chapter 4. Ionic strength was increased and soil pH was decreased with the addition of urea fertilizer, and the result may have been increased Cd solubilization and higher Cd concentrations in the soil solution.

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The amount of Cd moving to the plant through the transpirational stream during any time interval can be expressed by the following equation:

Cd accumulation = water flow x concentration in solution

Total accumulation of Cd by mass flow is the sum of all time intervals. Not only did the

addition of nitrogen increase plant vigor and cause plants to take up more water and Cd in the transpirational stream, the concentration of Cd in the soil water had already been increased by the effects of nitrogen on soil pH and the ionic strength of the soil solution (i.e. the addition of urea increased both water flow and concentration in solution). The result is a cumulative increase in plant uptake of Cd and plant nutrients with increasing nitrogen rate.

5.6 Conclusions

Nitrogen fertilizer as urea increased concentration of Cd in durum wheat grain and straw. Some of the nutrient ions were affected in the same manner. Some of these increases can be attributed to greater plant growth and vigor associated with N fertilization. However, the concentration of Cd and other ions increased further in plants grown with very high rates of urea, where plant growth did not increase further with increasing rates of nitrogen. It appears quite likely that soil factors such as pH and ionic strength are interacting with plant factors such as biomass growth and transpiration to increase the concentration of Cd in the soil solution and in the plant.

6. GENERAL DISCUSSION

The findings in all three studies confirmed that nitrogen fertilizers can increase the solubility of Cd and increase its availability to plants. This had been shown by previous research (Williams and David 1976; Brown et al. 1994; Grant et al. 1996). Eriksson (1990) stated that the effect of nitrogen fertilizer on Cd solubility and plant uptake depended on pH. An inverse relationship exists between pH and Cd solubility (Jackson and Alloway 1992; He and Singh 1993a). That relationship was only evident in one of the three studies. It was likely masked by other effects. A similar instance of salinity effects dominating over pH effects was reported by McLaughlin et al. (1994). An increase in ionic strength can solubilize Cd due to competition between Cd and other cations for adsorption sites (Garcia-Miragaya and Page 1976; Boekhold and Van der Zee 1992; Lorenz et al. 1994). There appeared to be an increase in Cd solubility with increasing ionic strength in these studies. The increase in Cd solubility with increasing fertilizer rate was probably a result of the interaction of lowered soil pH, increased ionic strength of the soil solution, and complexation (usually with chloride and sulfate fertilizers).

This research has shown that urea fertilizer increases Cd concentration in the soil solution and Cd concentration in the plant. The increase of Cd in the soil solution can be explained by the previously mentioned pH / ionic strength interaction but the increase in plant Cd is more complicated. Plants grown with higher rates of nitrogen have a more

extensive root system and transpire more, allowing a greater uptake of Cd and other elements from the soil solution (de Villarroel et al. 1993; Lorenz et al. 1994; Grant et al. 1995). For this research, plant growth increased with increasing nitrogen up to about 200 ug N g⁻¹, then levelled off. Plant Cd concentration increased with increasing N rate up to 800 ug N g⁻¹ and may have continued to increase had even higher rates been tested. While plant growth and Cd concentration appeared to be related, the previously mentioned soil factors must have been involved in the large increase in plant Cd concentration between 200 and 800 ug N g⁻¹. For plant Cd concentration to increase at high N rates when mass flow had levelled off or decreased, the concentration of Cd in the soil solution had to have increased.

7. SUMMARY

In these studies, nitrogen fertilization increased the extractability of Cd and nutrient cations from the soil, the concentration of Cd and nutrient cations in the soil solution, and the concentration of Cd and nutrient cations in the plant. An increase in nitrogen rate caused increased concentrations of Cd and many positively charged plant nutrients in both the soil solution and in the plant tissue.

These increases resulted from the interaction of several plant and soil factors. The addition of nitrogen fertilizer in the form of urea (1) lowered soil pH, (2) increased the ionic strength of the soil solution, and (3) increased transpiration and plant growth, all of which can increase the phytoavailability of Cd and other cations.

There is a need for much more research in this area to further elucidate the factors which cause the fertilizer effects on the behaviour of Cd. There may be other factors involved. Similar work can be done with different fertilizers, different soils, and different conditions. As long as Cd remains a health and economic issue, Cd research of this nature will be important.

8. CONTRIBUTION TO KNOWLEDGE

This work has confirmed that nitrogen fertilization can have a significant effect on the phytoavailability of Cd and serves as a starting point for future research. Through a series of experiments, this research has suggested processes, both in the soil and in the plant. that may be responsible for the increase in Cd phytoavailability with increasing nitrogen rate. Further research is now underway to assess the relative importance of these processes, which may help to determine practices which can be used to decrease the amount of Cd available to the human food chain.

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10. APPENDICES

Time	Temperature	R. Humidity (%)	Fluorescent (%)	Incandescent (%)
09:45	22.0	60	100	100
10:45	22.0	60	100	100
11:00	22.0	60	75	75
11:15	22.0	60	50	50
11:30	22.0	60	25	25
11:45	15.0	60	0	0
19:45	15.0	60	25	25
20:00	15.0	60	50	50
20:15	15.0	60	75	75
20:30	15.0	60	100	100
21:45	22.0	60	100	100

I. Daily Growth Chamber Parameters for Displacement Study.

Source: R. March, personal communication.

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N-rate	Phosphate extracted (ug g ⁻¹) throughout growing season							
(ug g ⁻¹)	Seeding	10 days	20 days	30 days	40 days	Maturity		
0	36.83	32.83	26.92	21.83	20	18.33		
50	24.08	31.25	24.08	21.67	19.42	16.83		
100	29.50	32.58	32.33	11.17	16.50	12.67		
200	37.25	38.00	26.75	23.17	18.58	15.00		
400	32.00	38.17	29.75		20.17	14.33		
800	27.00	36.75	32.83	31.92	20.58	15.00		

II. Sodium Bicarbonate-Extractable Soil Phosphate as Affected by Nitrogen Application.

III. Straw and Grain Concentrations of Iron as Affected by Nitrogen Rate.

N-rate	Iron concentration (ug g ⁻¹) throughout growing season						
(ug g ⁻¹)	20 days	30 days	40 days	Maturity	Grain		
0	244	31	36	176	19		
50	131	35	48	109	25		
100	200	50	40	56	32		
200	204	78	54	536	38		
400	145	75	187	84	33		
800	601	111	302	337	36		