

**Cd CONTENT OF DURUM WHEAT AND CANOLA
AS AFFECTED BY
NITROGEN FERTILIZATION AND TILLAGE PRACTISES**

BY

KIMBERLEY R. BROWN

**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**

©November, 1997



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

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

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

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

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

0-612-32906-2

THE UNIVERSITY OF MANITOBA
FACULTY OF GRADUATE STUDIES

COPYRIGHT PERMISSION PAGE

**Cd CONTENT OF DURUM WHEAT AND CANOLA
AS AFFECTED BY NITROGEN FERTILIZATION AND TILLAGE PRACTISES**

BY

KIMBERLEY R. BROWN

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

Kimberley R. Brown 1997 (c)

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

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

FOREWORD

This thesis was written in manuscript style as outlined in the Department of Soil Science *Guide to Thesis Preparation for Graduate Students*. Both manuscripts are to be submitted for publication, to journals which have yet to be determined.

TABLE OF CONTENTS

	Page
FOREWORD	ii
ABSTRACT	vi
ACKNOWLEDGEMENTS	viii
LIST OF TABLES	x
LIST OF FIGURES	xii
1. INTRODUCTION	13
2. LITERATURE REVIEW	15
2.1 Introduction	15
2.2 Cadmium and Health	15
2.3 Cadmium in Plants	16
2.3.1 Cd in Various Plant Species	20
2.3.2 Root Exudates	23
2.3.3 Mycorrhiza	24
2.4 Cd in Soil	25
2.4.1 Total Cd	25
2.4.2 pH and Ionic Strength	27
2.4.3 Complexation and Speciation	30
2.4.4 Cation Exchange Capacity	33
2.4.5 Other Influences Affecting Soil Cd Uptake	37
2.5 Management	38
2.5.1 Cultural Treatments	39
2.5.2 Sewage Sludge	40
2.5.3 Phosphatic Fertilizers	42
2.5.4 Nitrogen	47
2.5.5 Other Influences Affecting Soil Cd Uptake	49
2.6 Conclusion	50
3. AVAILABILITY OF Cd TO DURUM WHEAT AS AFFECTED BY FERTILIZER RATE, SOURCE AND PLACEMENT	52
3.1 Abstract	52
3.2 Introduction	53
3.3 Materials and Methods	54
3.4 Results	57

3.5 Discussion	66
3.6 Summary and Conclusion	70
4. EVALUATION OF THE INFLUENCE OF TILLAGE AND FERTILIZER MANAGEMENT ON Cd CONTENT OF DURUM WHEAT AND CANOLA	72
4.1 Abstract	72
4.2 Introduction	73
4.3 Materials and Methods	75
4.4 Results	79
4.4.1 Fertilizer Treatments	79
4.4.1.1 Nitrogen	79
4.4.1.2 Phosphorus	94
4.4.2 Tillage and Soil Type	94
4.5 Discussion	98
4.6 Summary and Conclusions	102
5. GENERAL DISCUSSION	104
6. SUMMARY AND CONCLUSIONS	108
7. CONTRIBUTION TO KNOWLEDGE	110
8. REFERENCES	112
9. APPENDICES	124
Appendix I	
Availability of Cd to durum wheat and western red spring wheat as affected by nitrogen fertilization	124
I.1 Abstract	124
I.2 Introduction	125
I.3 Materials and Methods	126
I.3.1 Main Experiment	126
I.3.2 Sub-Experiment	128
I.4 Results and Discussion	128
I.4.1 Main Experiment	128
I.4.2 Sub-Experiment	129
I.5 Summary	129
Table I.1 Influence of nitrogen source and rate on Cd concentration and yield in durum wheat	131
Figure I.1 Grain Cd concentration as a function of N rate and form ..	132

Figure I.2	Concentration of Cd in DT-627 and Katepwa grain and straw	133
Table I.2	Influence of nitrogen source and rate on Cd concentration and yield in DT-627 durum and Katepwa western red spring wheat	134
Appendix II		
Table II.1	List of Cd concentrations and yield of grain and straw for treatment means of the first growth chamber experiment . . .	135
Appendix III		
Table III.1	List of Cd concentrations and yield of grain and straw for treatment means for the growth chamber experiment in Appendix I	136
Appendix IV		
Table IV.1	List of Cd concentrations and yield of grain and straw for treatment means from the growth chamber experiment with two soil types	137

ABSTRACT

Cadmium is an element of concern as certain food crops can accumulate levels of Cd which are not toxic to the plant but may be harmful to humans. Due to high concentrations of Cd currently found in some Canadian grains and oilseeds there is a need to determine the factors responsible for Cd uptake and accumulation in these crops. Two growth chamber studies were conducted to determine the effects of rates and placements of nitrogen fertilizers, including $\text{Ca}(\text{NO}_3)_2$, urea, and $(\text{NH}_4)_2\text{SO}_4$, on Cd concentration in durum wheat (*Triticum turgidum* cv. Medora). Fertilizer effects were examined on two soils, a Newdale clay loam (Orthic Black Chernozem) and a Cobfield fine loam (Gleyed Carbonated Rego Black Chernozem). A field study was conducted from 1992 to 1994 to determine the effects of fertilizer management and tillage practises on Cd concentration in crops. Durum wheat (*Triticum turgidum* cv. Sceptre) and canola (*Brassica napus* cv. Legend) were grown on two Orthic Black Chernozems, a Newdale clay loam and a Marringhurst fine sandy loam. Various commercial fertilizers were applied at 60 kg N ha^{-1} to both crops either under conventional or zero tillage systems.

Growth chamber studies indicated that plant Cd concentration increased as the supply of nitrogen increased from 0 - 400 $\mu\text{g g}^{-1}$. Variation among fertilizer source was significant, with $\text{Ca}(\text{NO}_3)_2$ causing the greatest concentrations and $(\text{NH}_4)_2\text{SO}_4$ the least. Broadcast urea caused higher Cd concentrations in both grain and straw than banded urea. In the first study variation among samples was high for the $(\text{NH}_4)_2\text{SO}_4$ and banded urea treatments, especially at the high rates of N. Comparison of two soil types, in the second study, demonstrated there were significant differences in Cd concentration in plant tissue

even though soil-Cd levels were similar.

Analyses of field data indicated there were few significant differences in durum Cd levels among fertilizers although similar trends were evident on all six site years. The fertilizers which gave the highest yields (NH_3 , banded urea) also tended to cause higher concentrations of Cd in grain and straw. Application of 40 kg P ha^{-1} as monoammonium phosphate did not increase durum Cd concentrations relative to the control. Yields and Cd concentrations in durum tended to be higher under conventional tillage than zero tillage. Cd concentrations in plant tissue were higher on the fine sandy loam site, and yearly variation in durum ranged from $45 \mu\text{g g}^{-1}$ on the 1992 clay loam to $180 \mu\text{g g}^{-1}$ on the 1994 fine sandy loam. Cd concentrations in canola were not affected by either N fertilizers or tillage systems. Both growth chamber experiments confirmed that increasing fertilizer nitrogen rates can elevate Cd concentrations in grain and straw. In the field, plant Cd levels were influenced by soil type, fertilizer management, and tillage practises as well as environmental factors. Application of any nitrogen fertilizer increased Cd concentration relative to the control, while application of MAP had no effect. Since application of high-efficiency fertilizers increased both yield and Cd concentration, total accumulation of Cd in these plots was great.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation for my co-advisors, Dr. C.A. Grant and Dr. G.J. Racz for their patience, advice, encouragement, guidance, and support over the last few years. I have welcomed the opportunity to work with Dr. Grant while finishing my writing as she has given me excellent instruction and has truly been my mentor.

I would also like to thank Dr. Martin Entz from the Department of Plant Science for his excellent advice and helpful suggestions. Although I did not work as closely with him as with my co-advisors, I am grateful for the opportunity to have him on my advisory committee and learn from him.

I am indebted for the support of the Agriculture and Agri-Food Canada Brandon Research Centre, where I completed a substantial part of my work and training. Dr. Loraine Bailey has been a source of valuable advice and knowledge and has made a significant contribution to the skills and abilities I have been able to acquire through my project. I have been lucky to get 'the best of both worlds' - excellent scholastic instruction from the University of Manitoba and then the use of first-rate research facilities in Brandon.

I would also like to extend my appreciation to Brian Hadley, Mike Svistoski, and Val Huzel for their technical support and assistance. Carol Enns, *librarian extraordinaire*, has been wonderful through her technical support and encouragement. I appreciate the help I have received over the years from other academic staff and graduate students in the Department of Soil Science at the University of Manitoba. Mrs. Helen

Nemeth and Mrs. Pearl Novotny helped make my transition into graduate studies smoother and I thank them for their kindness and assistance.

Financial assistance is gratefully acknowledged from Viridian Inc. and the Brandon Research Centre.

Last, but certainly not least, I would like to thank my families for their love and support during this project. Robyn and Sarah Jean have been patient with my absences and generous when allowing me time to work on my thesis. I did this for all of us, and I couldn't have made it without you. My parents, Brian, Arlene, Jean, and Dunc have been wonderfully supportive and encouraging and I will never forget all they have done for us over the last few years. This thesis is dedicated to the memory of Dunc.

LIST OF TABLES

Table	Page
3.1 Characteristics of the two soils used in growth chamber experiments	57
3.2 Probability values from analysis of variance of effect of fertilizer source and nitrogen rate on durum yield and grain Cd concentration in two growth chamber studies	58
3.3 Influence of nitrogen source and rate, and addition of P and/or S in the absence of N, on Cd concentration and yield in durum wheat	61
3.4 Influence of nitrogen source and rate on root, straw, and wheat grain Cd concentration of selected treatments	62
3.5 Influence of nitrogen source and rate on root:straw and straw:grain Cd concentration ratios of selected treatments.	62
3.6 Contrast analysis of soil type and influence of nitrogen source and rate on Cd concentration and yield in durum wheat on two soils	65
4.1 Soil characteristics of the experimental sites at the beginning of the study	77
4.2 Meteorological data of the experimental sites from Licors located at each site	78
4.3 Probability values from analysis of variance of effect of treatment, tillage, and year on grain Cd and yield of durum and canola on a clay loam and a fine sandy loam soil for three years, 1992-1994 inclusive	80
4.4 Wheat yield and contrast analyses of grain and straw on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	81
4.5 Wheat yield and contrast analyses of grain and straw on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	82
4.6 Wheat yield and contrast analyses of grain and straw on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	83
4.7 Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	84

4.8	Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	85
4.9	Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994	86
4.10	Canola yield and contrast analyses of seed and straw on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	88
4.11	Canola yield and contrast analyses of seed and straw on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	89
4.12	Canola yield and contrast analyses of seed and straw on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	90
4.13	Cd concentration and contrast analyses of canola seed and straw (selected samples) on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	91
4.14	Cd concentration and contrast analyses of canola seed and straw (selected samples) on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	92
4.15	Cd concentration and contrast analyses of canola seed and straw (selected samples) on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive	93
4.16	Cd content of wheat grain on two soil types as influenced by phosphorus presence and placement, from 1992-1994	94

LIST OF FIGURES

Figure	Page
3.1 Grain Cd concentration as a function of N fertilizer rate and form	60
3.2 Root Cd:Straw Cd and Straw Cd:Root Cd as a function of N rate and form . . .	63
3.3 Grain Cd concentration as a function of N fertilizer rate and form on two soil types, a Cobfield fine loam and a Newdale clay loam	64
4.1 Regression of durum grain Cd as a function of yield (means of three years, 1992-1994 inclusive, are plotted).	87
4.2 Seed and straw yield of durum wheat and canola as affected by soil type (CL = clay loam and FSL = fine sandy loam) and year, under conventional (CT) and zero tillage (ZT) for the years 1992-1994 inclusive	96
4.3 Grain Cd concentration as affected by year and soil type (CL = clay loam and FSL = fine sandy loam) in durum wheat (A) and canola (B)	97

1. INTRODUCTION

Durum wheat, sunflower and flax tend to accumulate high concentrations of Cd in their edible portions and grains and cereal products tend to be the largest source of Cd in our diets. While food crops can accumulate Cd in their edible portions without decreasing yield, these levels may be potentially harmful to humans. Cadmium has no known biological function and possesses a long half-life in the body which may cause chronic toxicity (NRCC, 1979). To reduce potential danger from this element the FAO/WHO Expert Committee on Food Additives in 1972 suggested a maximum tolerable Cd intake limit of 70-84 $\mu\text{g person}^{-1} \text{ day}^{-1}$. As well, the Codex Alimentarius Commission of the FAO/WHO has suggested a limit of 0.1 mg Cd kg^{-1} for cereal grains traded on international markets. Since our crops have concentrations which may approach or exceed the proposed export limit, it is desirable to monitor and control Cd concentrations entering the food chain from our products.

Since Cd occurs naturally in soil and may be increased due to anthropogenic factors (DeBoo, 1990), management factors affecting crop uptake are being investigated. The amount of Cd present in the soil and soil pH are the two most important soil factors governing bioavailability. Among crops there are large differences in uptake between species and even among cultivars of the same species. Management decisions concerning tillage and fertilizers may be important in determining the amount of Cd taken up by the crop. Phosphorus fertilizers have been shown to increase (Williams and David, 1973; He and Singh, 1994) or have little or no effect (Mortvedt, 1981, 1987; Jeng and Singh, 1995) on Cd concentrations in crops. Nitrogen fertilizers have been shown to

increase Cd accumulation in plants either through increased yield or their effects on soil chemistry (Eriksson, 1990; Andersson and Siman, 1991). Oliver et al. (1993) have reported that crop rotation and tillage can influence Cd concentration in grain crops.

Due to the economic importance of durum wheat in Western Canada it is prudent to investigate accumulation of Cd in this crop. Growth chamber studies were conducted to investigate the effects of fertilizer sources, rates and placements on durum. These experiments were designed to increase understanding of processes affecting Cd uptake from levels found naturally in soils, when no additional Cd was added. Field experiments were initiated to evaluate the effect of management practises on Cd concentrations in durum and canola under field conditions on two high-pH Chernozems representative of soils in Western Canada.

2. LITERATURE REVIEW

2.1 Introduction

Cadmium is a rare element with concentrations in the earth's crust ranging from 0.1 to 0.2 $\mu\text{g g}^{-1}$, ranking it 67th in order of abundance. Cadmium is isolated from an ore called “cadmia” by the ancients, possibly because it was first found near the Cadmean city of Thebes (Asimov, 1969). It is used mainly in thin coatings for ferrous metal surfaces to reduce and retard corrosion, as well as a stabilizer for PVC and other plastics. It is also found in pigments used in plastics and paints, which are usually based on cadmium sulphide. Aylett (1979) offers minor uses for cadmium in production of nickel-cadmium batteries, as a constituent in solders, as control rods in nuclear reactors, and as a hardening agent for copper. Cadmium and zinc form a variety of covalently bound compounds and react readily in the presence of oxygen to form oxides. Cadmium and zinc are geochemically similar minerals and are often associated in nature.

2.2 Cadmium and Health

Cadmium is of concern due to its toxic effects on the human body. This metal has no known biological function and has an unusually long half life in human kidneys, estimated from 10 to 30 years (Spivey Fox, 1988). Excretion rate of Cd is very low and humans are constantly taking in Cd through food. The FAO/WHO Expert Committee on Food Additives in 1972 suggested a maximum tolerable limit of 70 to 84 $\mu\text{g day}^{-1}$ for adults. The National Research Council has estimated Canadian intake to range between 50 and 98 $\mu\text{g person}^{-1} \text{ day}^{-1}$ (NRC, 1979), however a study by Dabeka and McKenzie

(1992) calculated the dietary intake of a Canadian adult to be $14.5 \mu\text{g day}^{-1}$. Daily intake of Cd varies with diet, and potatoes, grains and cereal products, meat, fish, and poultry products tend to be the largest sources of Cd in the Canadian diet.

Long term consumption of foods containing higher amounts of Cd or inadequate diets can cause accumulation of Cd in the kidneys and liver. Renal tubular dysfunction and pulmonary emphysema are attributed to excess Cd exposure (Wagner, 1993). Itai-itai disease has been known to occur in women with poor quality diets and elevated Cd intake through fish and drinking water. This painful and crippling disease is a form of osteoporosis/osteomalacia where Cd is thought to contribute to bone demineralization (Wagner, 1993). As well, Cd in tobacco smoke is thought to be carcinogenic. Although there are concerns about health risks from chronic exposure to Cd, evidence suggests only certain individuals may be 'at risk'. Persons having severe nutritional deficiencies, persons consuming greater than normal levels of visceral meats, fish, and shellfish, pregnant and lactating women having a negative Ca^{2+} balance, nursing infants, persons with kidney ailments, and multiparous, postmenopausal women are groups which have been identified as being at risk from excess Cd exposure (Wagner, 1993). Since food is the primary source of intake for the average population, it may be desirable to control or lower Cd levels in food crops.

2.3 Cadmium and Plants

Photosynthetic organisms are the principal entry points of metals into the food chain leading to animals and man (Rauser, 1990). Primary producers live in aquatic and terrestrial environments that provide both essential and non-essential, as well as possibly

toxic, elements. Plants possess nonprotein metal-binding polypeptides which, although differing in structure and biosynthesis, may be functionally analogous to cysteine-rich metallothioneins (Steffens, 1990). Due to their ubiquity in plant species and their apparent function in sequestering of metal ions, they have been named phytochelatins. Unlike metallothioneins, which are induced during normal development of mammalian systems, phytochelatins are unique in that heavy metals are the primary inducers of synthesis. Cd is one of the strongest inducers while Zn is one of the weakest (Steffens, 1990). Bartolf et al. (1980) discovered the presence of a metallothionein-like protein in tomato roots which appeared to be induced by treatment with Cd^{2+} . Interestingly, Cd also induces heat shock proteins but heat shock does not induce phytochelatin biosynthesis (Steffens, 1990). In contrast to other plant stress responses which may be induced by a number of factors, the availability of metal ions strictly regulates phytochelatin biosynthesis (Steffens, 1990). It is generally assumed that phytochelatin-metal complexes are less toxic to cellular plant metabolism than the free metal ions (Kneer and Zenk, 1992).

Studies have found Cd occurring in the soluble fraction, cell walls, and organelles including vacuoles (Rauser, 1990). Kneer and Zenk (1992) assume free metal ions cross the plasmalemma and activate the phytochelatin-synthase, causing immediate complexation and inactivation of Cd. The sequestered metal may then be transferred to the vacuole where it can undergo transformations which are reflected in the degradation of the phytochelatin complex. Guo and Marschner (1995) suggest Cd-PC complexes may represent a mobile form in the translocation of Cd from roots to shoots. Salt and Wagner

(1993) demonstrated Cd^{2+} transport across the tonoplast in oat seedling roots is coupled to the tonoplast V-type ATPase via a pH gradient. This was shown to occur similarly to the $\text{Ca}^{2+}/\text{H}^{+}$ antiport function in the membrane. This mechanism is believed to work at both high and low Cd^{2+} exposure to transport Cd from the cytoplasm to vacuoles. Costa and Morel (1994) examined Cd uptake in lettuce seedlings and felt uptake processes depending on ATP seemed important in Cd uptake. Their study showed Cd uptake to be mediated by two distinct transport systems, a high affinity and a low affinity. They described the low affinity site as possibly a disorder in the membrane or irreversible binding to root exchange sites. Competition between Zn and Cd was great, possibly due to common transport sites or processes.

Phytochelatins synthesis has been observed within 5-15 minutes of excess metal exposure, and ceases immediately when EDTA or metal-free phytochelatin are added, suggesting a feedback loop (Steffens, 1990). As free metal ions are depleted, accumulation of phytochelatin stops and then levels rapidly decrease, suggesting either the metal-binding capacity of phytochelatin increases or the metal becomes associated with other ligands as the phytochelatin are degraded (Steffens, 1990). Study of absorption of Cd by maize seedlings indicated biphasic accumulation, characterized by a rapid initial phase followed by a slower phase (Girling and Peterson, 1981). Cataldo et al. (1983) studied cadmium uptake kinetics in intact soybean plants using solutions containing 0.0025 to 0.3 μM CdCl_2 . The authors restricted the range of CdCl_2 since in soils of pH 5-7.5, solubility controls result in a Cd^{2+} concentration of $\sim 0.1 \mu\text{M}$ or $11 \mu\text{g l}^{-1}$ soil solution. Under these realistic conditions Cd uptake showed linear absorption for

two hours, exhibited multiphasic absorption kinetics, and was sensitive to metabolic inhibition. A common transport site or process was indicated through competition with Cd, Fe, Zn, and possibly Mn. These characteristics are indicative of a metabolically mediated membrane transport process (Cataldo et al., 1983).

Phytochelatins synthesis is presumed to be cytoplasmic and may be part of a shuttle system for the transfer of metal into the vacuole (Steffens, 1990). The pH in the vacuole is very important and depending on the amount of labile sulfur, Cd may be displaced from phytochelatin, where other ligands may associate with the metal (Steffens, 1990). Mechanisms other than phytochelatin may be used to detoxify metal ions. Citrate, malate, or phytic acid may complex with metals in the vacuole.

Biosynthesis of metal-binding peptides was connected to glutathione synthesis rather than to direct ribosomal protein synthesis (Rauser, 1990). Glutathione (GSH) is believed to be a precursor involved in the synthesis of phytochelatin, and the ratio of Cys-GSH to metal in phytochelatins complexes is 2:1 for Cd, Zn and Pb (Steffens, 1990). Cysteine thiol is the primary metal ligand. Presence of sulfide helps stabilize the pH at which dissociation occurs, as in Cd complexes lacking sulfide are half dissociated at pH 5 versus sulfide-containing complexes which become half dissociated below pH 4 (Steffens, 1990). The association of labile sulfide and sulfite with phytochelatin suggests the possibility that phytochelatin also serve a role in sulfate reduction, with the labile sulfur used to support cysteine biosynthesis (Steffens, 1990). *Brassica juncea*, a wild mustard, was found to accumulate two types of phytochelatins-Cd complexes, including a high molecular weight (10 000 mw) PC-Cd-sulfide form (Speiser et al.,

1992). High rates of sulfur uptake by *B. juncea* may allow a greater rate of phytochelatin synthesis and production of S^{2-} for incorporation. The authors suggest production of these complexes could contribute to higher metal tolerance. Reese et al. (1992) exposed tomato plants to Cd and discovered they produced metal-peptide complexes containing acid-labile sulfur. In low concentrations of Cd, tomatoes produced a low-sulfide phytochelatin complex; higher metal concentrations seem to elicit sulfide production.

Molecular mass of Cd phytochelatin complexes ranges anywhere from 3000 to 10 000 depending on ionic strength, and incorporation of varying amounts of sulfide or sulfite ion may contribute to the differences in size (Steffens, 1990). Weigel and Jager (1980) examined distribution of Cd in beans and determined that more than 70% was in the cytoplasmic fraction and 8-14% was bound as cell wall fractions or in organelles. The authors assumed the Cd to be bound by low molecular weight peptides. Molecular weights were under 5000 to 10 000 in roots and 700 to 5000 in leaves. Cd complexes of 10 000 mw were observed in cabbage and tobacco plants (Wagner and Trotter, 1982) and were found to be constitutive and inducible and to contain sulfur. Additional Cd was found in the <2000 mw fraction and was suggested to be complexed and not free metal.

2.3.1 Cd in Various Plant Species

Plants can accumulate sub-phytotoxic levels of Cd in their tissues which may be cause for human health concerns. Crops accumulate Cd differently depending on species and cultivar. Species known to be metallophytes or hyperaccumulators are able to accumulate higher metal concentrations in tissues than metal intolerant species (Brown et al., 1995). The use of these plants may prove beneficial in phytoremediation of

contaminated sites. Some crops accumulate most of their Cd in the root, followed by stem, leaves, and fruiting organs. Guo and Marschner (1995) found a gradient in bean and rice Cd concentrations in the order roots>>stem/stalk base>>shoots (stems/sheaths)>leaves. Other crops, in particular vegetables, accumulate Cd in the leafy portions. Genetic manipulation through gene fusion with mammalian metallothionein was studied by Maiti et al. (1989). They found transgenic tobacco expressing mouse metallothionein contained about 20% less Cd than non-transformed seedlings. Conversely Brandle et al. (1993) found that expression of mammalian metallothionein in four transgenic tobacco lines did not lead to significantly lower Cd levels in roots or leaves.

Cd can be an element of concern in certain crops, such as durum and flax, while other crops take up very small amounts and thus Cd levels are not an issue. Several authors have noted great differences in Cd accumulation among plant species, both at levels naturally present in soil and where Cd had been added to the system. Kuboi et al. (1987) examined the effects of added Cd on several species grown in an acid (pH 5.6) sandy soil. The authors concluded Cd accumulation characteristics were present at the family level, with Cruciferae>Solonacea>Graminae>Leguminosae. They also found accumulation capacity was associated with Cd tolerance. Page et al. (1972) compared the response of corn, turnips, beets, tomatoes, beans, cabbage, lettuce, green peppers and barley to Cd levels in solution ranging from 0.1 to 10 $\mu\text{g ml}^{-1}$. Turnips, beets, and beans were the most susceptible to solution Cd concentration and cabbage was able to tolerate the greatest amount of Cd in solution. When all species were tested at 1.0 $\mu\text{g Cd ml}^{-1}$

solution concentration, bean and barley leaves had the lowest Cd levels while turnip and lettuce exhibited the highest concentrations. When vegetables were grown with additions of 0, 2.5, and 10 $\mu\text{g Cd g}^{-1}$, Cd concentrations were greatest in the order radish roots < green pepper < celery leaves < celery stalk < radish top < lettuce, both in the control and with added Cd (Haghiri, 1973). Guo and Marschner (1995) found Cd concentrations in above ground parts in the order maize >> curly kale > rice > bean, and yet root Cd concentrations in kale, rice, and bean were higher than in maize. This suggests translocation of Cd from root to shoot was inhibited in kale, rice, and bean. Higher proportions of Cd in the soluble fraction of maize roots as compared to other species agreed with its greater mobility and higher concentrations in the xylem sap (Guo and Marschner, 1995). Cd-phytochelatins were much higher in the roots of maize and rice, possibly contributing to higher Cd translocation to the shoot in maize.

In addition to differences in Cd concentration among species, varietal differences have been noted within a species. Florijn and van Beusichem (1993) studied 19 maize inbred lines and found considerable difference between lines, ranging from 0.9 to 9.9 $\mu\text{g Cd g}^{-1}$ dry weight. They partitioned the cultivars into two main groups, one of which had low shoot Cd concentrations but high root Cd, and the other which had similar Cd concentrations in root and shoot. They termed these groups 'shoot Cd excluder' and 'non-shoot excluder', respectively. The authors concluded internal distribution rather than uptake caused the genotypic differences, as whole plant-Cd for both groups was similar. Eriksson (1990) obtained various cultivars of wheat from production areas in Norway and found certain varieties had higher Cd concentrations than others grown

within the same region. Greenhouse trials involving at least 20 soybean varieties grown on three different soils indicated quantitative differences among varieties (Boggess et al., 1978). With a few exceptions the differences between varieties were similar across all three soils.

2.3.2 Root Exudates

Intact plant roots are capable of producing inorganic and organic substances which are released at the root surface. Root exudation and the contents of the exudates are influenced by both the above-ground and below-ground plant environment and by rhizosphere microorganisms (Bokhari et al., 1979). The amount and composition of root exudates may be influenced by mineral nutrition of the plant. In turn, the release of root exudates may influence the mineralization and immobilization of nutrients by soil microorganisms, thus influencing nutrient acquisition and growth of the plant. Mench and Martin (1991) state root exudates may influence nutrient solubility and uptake indirectly through their effects on microbial activity, rhizosphere physical properties, and root growth patterns. Direct effects include acidification, chelation, precipitation, and oxidation-reduction reactions. Bokhari et al. (1979) studied root exudates of blue gramma (a short grass prairie plant) and found that rhizosphere soil of these plants contained more soluble sugars and polyphenols than non-rhizosphere soil. Non-rhizosphere soil contained more soluble and non-soluble amino N than rhizosphere soil.

Mench and Martin (1991) examined mobilization of Cd by root exudates in two soils, finding the extent of Cd extraction by root exudates was similar to the order of bioavailability to the plants when grown on soil. The authors felt the increases in metal

concentration observed in root exudate extracts was likely due to the formation of complexed cations. Organic acids and amino acids, including phytosiderophores, are the major components responsible for the increased extraction of Cd by root exudates (Mench and Martin, 1991).

2.3.3 Mycorrhiza

Vesicular arbuscular mycorrhiza (VAM) growth is affected by nutrient levels provided to the plants, and in turn mycorrhizal associations with plant roots can influence growth due to increased availability of nutrients. The volume of soil explored by the root system is increased due to the mass of the fungal mycelium, possibly increasing absorption of nutrients as well as other elements in soil like cadmium. Fungi can accumulate metals either through excretion of extracellular substances or through cell walls. Little data is available concerning levels of metals found in fungi, so levels found in higher plants are taken as guidelines and accumulation in fungi is assumed at levels 5 times higher (Lepp, 1992).

Evidence for the presence of metallothionein or other metal-binding proteins was found by Morselt et al. (1986) as the existence of protein-bound disulphides and metal-thiolate clusters was discovered in a metal-tolerant mycorrhizal fungus. Weissenhorn and Leyval (1995) found arbuscular mycorrhizal colonization by a Cd-tolerant strain did not alleviate the negative effect of added Cd on plant growth. They concluded the interaction between fungi, Cd and plants depends on the factors influencing plant and fungal development and Cd availability. El-Kherbawy et al. (1989) studied the interaction between soil pH and inoculation with rhizobia and VAM in an industrially polluted soil.

As pH was increased (6.0-6.7) uptake of Cd decreased with rhizobia and VAM inoculation, however at the highest pH (7.2) the opposite occurred. The authors felt this indicated the influence of VAM on heavy metal uptake was partly dependent on the original soil availability of the metal. Shoot dry weight of VAM-infected plants at pH 7.2 was greatest of all treatments, indicating optimum growth conditions which may have contributed to the higher concentrations.

Accumulation of Cd is evident in edible mushrooms belonging to the genus *Agaricus*. Kojo and Lodenius (1989) found Cd concentrations highest in *Agaricus* specimens with low -SH contents, and found only a weak correlation with mycorrhizal fungi and none in decomposer fungi.

2.4 Cd in Soil

Cadmium that is taken up by the plant is a function of the amount of Cd in soil solution. Solution Cd is affected by a number of factors, including total Cd in soil, pH, ionic strength, CEC, complexation and/or speciation, and other factors. Any chemical, physical, or biological activities which affect the above factors can influence the amount of Cd available to the plant.

2.4.1 Total Cd

Heavy metals in soils are derived either from the weathering of parent material or from numerous external contaminating sources (Singh and Steinnes, 1994). For some metals the amount added through contamination is great and outweighs the amount contributed through soil-forming processes. The amount of Cd present in soil, however,

is usually dictated by the amount present in the parent material. Alloway (1990) states that soils derived from igneous rocks would have Cd contents of 0.1 - 0.3 mg kg⁻¹, those from metamorphic rocks would range from 0.1 - 1.0 mg kg⁻¹ and those derived from sedimentary rocks would contain 0.3 - 11 mg kg⁻¹. According to Singh and Steinnes (1994), Cd concentrations of igneous rocks range from 0.09 to 0.13 mg kg⁻¹ and 0.03 to 0.05 mg kg⁻¹ in sedimentary rocks. Most soils contain less than 1 mg kg⁻¹ Cd, but concentrations in shale can be much higher. A study in Monterey County, CA indicated residual soils developed from shale parent material had the greatest Cd concentrations with a mean of 7.5 µg g⁻¹ (Lund et al., 1981). The authors also found alluvial soils from mixed parent materials had an intermediate mean Cd content of 1.5 µg g⁻¹ while soils developed from sandstone and basalt had the lowest mean Cd concentrations at 0.84 µg g⁻¹. In Manitoba, Mills and Zwarich (1975) determined that background Cd levels ranged from 0.4 mg kg⁻¹ in the A horizon of a Souris loamy sand to 1.7 mg kg⁻¹ in the A horizon of a Keld clay loam. A study in Alberta compared soil Cd concentrations in the Black, Brown and Gray Soil Zones at well drained, poorly drained and Solonetzic sites. Dudas and Pawluk (1975) found little variability among sites, with Cd concentrations ranging from 0.07 to 0.40 mg kg⁻¹. Greatest variability was found in the Gray Soil Zone, and the largest site-to site variation occurred in poorly drained areas. Data collected across 850 000 km² in both the Canadian Prairies and the northern United States showed that Cd concentrations in the Ap horizon varied from <0.2 - 3.8 µg g⁻¹, with a median of 0.3 µg g⁻¹ (Garrett, 1994). Greatest variability is at scales ≤20x20 km, probably due to local changes in soil chemistry, reflecting the composition of the underlying parent material

and differences in local pedological processes (Garrett, 1994).

2.4.2 pH and Ionic Strength

After considering the amount of Cd present in the soil, pH is the second most important factor governing Cd availability. In general, heavy metals are more soluble in acid soils, leading to greater uptake by plants. Cd is present as the divalent ion at pH 6 and is completely soluble in the absence of precipitating anions such as phosphate and sulphide (Hahne and Kroontje, 1973). Since Cd forms relatively insoluble precipitates with carbonates, phosphates, hydroxides and Cl complexes, at higher pH values Cd is less available. Two models have been proposed to describe pH-dependent adsorption mechanisms: (i) metal hydrolysis model and (ii) ion exchange model (Basta and Tabatabai, 1992b). In the first model metal ions undergo hydrolysis and produce protons and the metal ions are subsequently adsorbed by the soil surface. These reactions are favoured at a high pH and are very pH-dependent. In the second model metal adsorption is explained by competition of protons with metal ions for cation-exchange sites. At high pH levels decreased competition of H^+ with metal ions may be responsible for greater amounts of metal adsorption (Basta and Tabatabai, 1992b). In a study of two soils the authors found the shapes of metal adsorption vs. solution pH did not conform to those expected from model (i). Data indicated adsorption of Cd by soils is associated with simple electrostatic and ion-exchange reactions. At high solution pH and/or high metal concentrations, adsorption-desorption or precipitation-dissolution reactions occur. Since metal adsorption curves did not conform to solubility lines of Cd minerals, precipitation-dissolution reactions were rejected (Basta and Tabatabai, 1992b). The authors concluded

that pH-dependent adsorption of Cd can be attributed to exchange reactions and related pH-dependent composition of the CEC of the soils.

When determining sorption isotherms for different pH values (4.0 to 7.7), sorption capacities of two soils were found to increase approximately three times for each increase of one pH unit (Christensen, 1984). These results emphasized pH as the most critical factor governing the distribution of Cd between soil and solute. Korte et al. (1976) used a natural leachate to leach eleven soils and monitor trace element movement. With one exception, a high pH soil with low CEC, Cd was highly mobile in the soils with lower pH's and exhibited moderate to low mobility as the soils became less acid. When examining lime effects on pine forest floor leachate chemistry, Marschner et al. (1992) found that liming increased retention of Cd and Zn, reduced N mineralization and stimulated nitrification. A study done by Basta and Tabatabai (1992b) indicated that differences in metal adsorption were dependent on the initial heavy-metal concentration. At low concentrations (0.02 mM Cd), all of the added metal was adsorbed regardless of the solution pH. At higher concentrations of added metal (1.0 - 2.0 mM Cd), metal adsorption was strongly related to solution pH; metal adsorption increasing with increasing solution pH. This may be due to affinity of metals for highly selective sites (specific adsorption) at low concentrations followed by adsorption of metal for less selective sites at large amounts of metal added (non-specific adsorption) (Basta and Tabatabai, 1992b).

An investigation of monoammonium phosphate (MAP) and diammonium phosphate (DAP), applied to two soils, induced variations in pH values in these soils

influencing the solubility of Cd (Levi-Minzi and Petruzzelli, 1984). In both soils MAP decreased pH and decreased Cd sorption while DAP increased pH and Cd sorption. The effect was greater in the soil with low organic matter and buffering capacity, and the authors felt the acidity induced by the different forms of phosphate was the most important factor controlling Cd adsorption.

Ionic strength and pH affect the surface charge of soils, and can strongly influence adsorption of trace elements, especially in the case of soils with variable charge (Gerritse and van Driel, 1984). In measuring the distribution constants of Cd in 33 temperate soils, the authors found that adsorption of Cd related to organic matter increased with increasing pH. Naidu et al. (1994) found for six soils that adsorption of Cd increased with an increase in pH and most of the variation in adsorption with pH was explained by the variation in negative surface charge. Their study suggests the effect of ionic strength on Cd adsorption varied among the soils and with pH. In soils dominated by variable charge components, there was a characteristic pH below which increasing ionic strength increased Cd adsorption and above which the reverse occurred. In all soils in the normal range ($\text{pH} > \text{PZC}$) the adsorption of Cd decreased with an increase in ionic strength, irrespective of pH. The effect of ionic strength on metal sorption has been attributed to i) change in the activity of free Cd^{2+} and CdOH^+ due to ion-pair formation and effect of ionic strength on pH, ii) competition for the sorption sites on clay surfaces, and iii) changes in electrical potential in the plane of sorption (Naidu et al., 1994). When examining the effect of variable concentrations of CaCl_2 on adsorption of Cd in three soils, Petruzzelli et al. (1985) found that the metal ion was more strongly adsorbed at

lower ionic strengths while any increase in electrolyte concentration decreased Cd adsorption. The authors felt this was attributed mainly to the increasing competition of Ca^{2+} for adsorption sites in the soil. Garcia-Miragaya and Page (1976) investigated the influence of ionic strength of three solutions and found increasing strength decreased the amount of Cd sorbed on the surface of montmorillonite. When modelling reaction kinetics of Cd adsorption and desorption by goethite, Barrow et al. (1989) determined that increasing the concentration of the background electrolyte decreased adsorption. The authors attributed this to decreased activity of metal- OH^- ions in solution counteracted by decreases in negative potentials of the surface. Adsorption of Cd and Cu by single metal-Mn oxide suspension systems increased with increasing pH because H^+ influences surface charge and solution speciation (Fu et al., 1991). Temminghoff et al. (1995) studied Cd sorption by sandy soil (total Cd $1.78 \text{ } \mu\text{mol kg}^{-1}$) and found both increasing ionic strength and decreased pH reduced Cd sorption.

2.4.3 Complexation and Speciation

When determining the bioavailability of various Cd species in soils one must examine the chemical forms in soil solution. Free Cd (Cd^{2+}) is probably the form most available to plants (Sposito et al., 1982). Girling and Peterson (1981) found in eight crop species, >90% of water-soluble Cd was in the ionic form, Cd^{2+} . In the soil solution, metals exist as different chemical species, and it is the metal speciation at equilibrium, and in particular the free metal activity, that determines plant uptake of metals (Kabata-Pendias and Pendias, 1992). Lighthart et al. (1983) state the soluble metal species present in the soil solution would be expected to correlate with toxicity, with the

solid phase serving as a control on solubility or concentration. Metals added to soil in a solid phase, such as sewage sludge, come into equilibrium with soil solids through the soil solution (Candelaria et al., 1995).

Using computer simulated speciation of Cd in two soils, Lighthart et al. (1983) found inorganic ligands such as Cl^- , SO_4^{2-} , NO_3^- accounted for 30%, metal organic complexes accounted for 2-3%, and CdCO_3 , the predominant Cd solid phase, accounted for up to 40% of Cd at 0.5 mmol kg^{-1} . Hirsch and Banin (1990) measured total Cd concentration in three unpolluted arid-zone forest soils to which Cd was added. The ratio of free to total Cd was then measured and Cd^{2+} and CdHCO_3^+ were estimated to make up 35% and 45%, respectively, of total soluble Cd in these calcareous soil solutions. The authors also found organo-Cd complexes present in minor amounts, with CdCO_3^0 appearing in increasing proportions as pH increased above 8. Other species were present, but less common, in order of importance $\text{CdSO}_4^0 > \text{CdCl}^+ > \text{CdOH}^+$. El-Falaky et al. (1991) measured Cd activities in slightly acidic to alkaline soils and found Cd^{2+} activities undersaturated with respect to CaCO_3 at pH 7.0. He suggested that CdFe_2O_4 was the only known mineral which could control Cd^{2+} activity in these soils. Using NaClO_4 , NaCl , and Na_2SO_4 as solutions, Garcia-Miragaya and Page (1976) found sorption of Cd in the chloride system was 25 to 50% less than the ClO_4 system at the same ionic strength. This was due to the presence of CdCl_2^0 , CdCl_3^- and CdCl_4^{2-} rather than Cd^{2+} . The authors noted the SO_4 systems showed a moderate decrease in Cd sorption compared to the ClO_4 system at the same salt concentration, attributed to the presence of CdSO_4^0 .

McBride (1980) studied adsorption and precipitation of Cd in the presence of

calcium carbonate and found initial chemisorption of Cd^{2+} on calcium carbonate was very rapid while CdCO_3 precipitation at higher Cd concentrations was slow. He concluded that even at low solution Cd^{2+} activities Cd could be effectively retained by calcium carbonate surfaces. Papadopoulos and Rowell (1988) found the CaCO_3 surface had a high affinity for Cd whereas precipitation of CdCO_3 on calcite predominated at higher additions. When precipitation occurred, pH decreased and solutions were undersaturated with respect to CaCO_3 , indicating CdCO_3 prevented the CaCO_3 surface from reacting with the acidity generated from CdCO_3 precipitation (Papadopoulos and Rowell, 1988). An experiment conducted by Holm et al. (1996), however, suggested that under environmentally relevant conditions solid phase carbonates are not likely to govern aqueous Cd concentrations in calcareous agricultural soils. Their experiments using Cd-amended soil suspensions and soils showed up to ten times supersaturation for periods of more than fifteen months, indicating Cd is not in equilibrium with CdCO_3 precipitates. The authors felt dissolved organic carbon may act as a precipitation inhibitor, and that Cd concentrations in solution are governed primarily by sorption processes.

In an experiment examining extraction of various Cd fractions in three Norwegian soils, Jeng and Singh (1993) found most of the Cd available in the weakly adsorbed, less in the adsorbed fractions (including carbonate-bound), and a high proportion as strongly adsorbed (organic matter, Mn oxides and amorphous Fe oxides). These soils had slightly acid pH. He and Singh (1993a) found most soil Cd in the exchangeable fraction of three soils, and the smallest proportion was carbonate-bound. Application of P to three soils at 0, 60, and 120 mg kg^{-1} soil altered the distribution of Cd among various chemical pools in

soil (Kaushik et al., 1993). Cd levels generally were reduced in the crystalline Fe oxide, organic matter, and carbonate fractions, and increased in the water soluble + exchangeable and anhydrous Fe oxide pools.

Studies on the chemical form of Cd contaminants in phosphate fertilizer (Mortvedt and Osborn, 1982) suggest that Cd contained in triple superphosphate (TSP) and DAP is $\text{Cd}(\text{H}_2\text{PO}_4)_2$, CdHPO_4 , or a mixture of these salts.

2.4.4 Cation Exchange Capacity

Although total soil Cd can be an indicator of Cd availability to the plant, other factors influence the amount of Cd that becomes available in the soil solution. The buffered cation exchange capacities (CEC) of soil are commonly used to estimate capacity to adsorb heavy metals and retain these metals against plant uptake (McBride et al., 1981). High pH and high base saturation favour strong adsorption of heavy metals. While soil texture and structure has a great effect on uptake of Cd by plants, organic matter may reduce Cd mobility through ion exchange and conversely increase mobility through formation of soluble complexes. McBride et al. (1981), showed that Cd uptake in maize grown on a sandy soil was greater from the B horizon, indicating the effect of organic matter in the A horizon. For soils of the same total Cd content, Eriksson (1989) found Cd was more soluble and plant available in a sandy soil than in a clay soil. Addition of increasing amounts of organic matter increased exchangeable soil Cd but decreased Cd concentrations in ryegrass grown in three soils, with the results most pronounced in the sand (He and Singh, 1993).

In a pot experiment, when 1 mg Cd kg^{-1} was added to the soil, Eriksson (1988)

found organic colloids were more effective than clay colloids in reducing soluble and plant-available Cd in soil. Ryegrass and rapeseed both showed decreases in plant-Cd concentrations from additions of peat to the soil. Haghiri (1974) found cadmium concentration in oat shoots decreased when the CEC of the soil was increased, and felt the retaining power of organic matter for Cd was predominantly through its CEC rather than through chelation. McBride et al. (1981) studied the availability of soil Cd^{2+} in soils from northeastern USA and found a strong correlation with exchangeable bases (mainly Ca^{2+}), buffered CEC and pH, and lesser correlation with clay content and organic matter. In three Norwegian soils the exchangeable fraction of Cd increased significantly with increasing amounts of added organic matter (He and Singh, 1993a). McLean (1976) found Cd levels in lettuce grown on two similar sandy loam soils were significantly lower in the soil with a much higher organic C content. Extractable Cd increased with higher amounts of soil organic matter. Addition of organic matter increased Cd adsorption in acid soil in a batch equilibrium experiment (Xiong, 1994), the results being attributed to the effect of OM on raising the pH of the soil.

Sorption of trace metals in soils takes place in the presence of solution cations which are orders of magnitude higher than those of the trace metals, and Backes et al. (1995) state sorption of trace metals by soil is predominantly due to chemisorption rather than normal cation-exchange reactions. Christensen (1984a) examined the effects of Ca competition, and found an increase in Ca concentration from 10^{-3} to 10^{-2} M reduced the Cd sorption capacity of a sandy loam by one third. Measurement of Cd mobility in 22 soils by thin-layer chromatography found that while mobility was quite variable among

soils, highly significant negative correlations existed with pH, Ca^{2+} , Mg^{2+} , and the sum of exchangeable bases (Sanchez-Camazano and Sanchez-Martin, 1993). The relative mobility of Cd, Cu, Ni, and Zn added to four soils were examined by Tyler and McBride (1982) in soil columns. They found the lowest mobility in soils with high pH, CEC, and exchangeable bases, and found liming acid soils reduced mobility but not to the extent seen in a naturally non-acid soil. Elliot et al. (1986) investigated competitive adsorption of Cd, Cu, Pb, and Zn on four soils using batch adsorption. They found adsorption for two mineral soils was $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$, which corresponds to the increasing pK (hydrolysis product) of these metals. In two soils containing 20-40 g kg^{-1} organic C selectivity was $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$, suggesting organic matter preferentially adsorbs Cd over Zn. These adsorption sequences suggest a greater availability of Cd and Zn compared to Pb and Cu. When comparing competitive adsorption of Cd, Cu, Ni, Pb, and Zn on two soils, Basta and Tabatabai (1992c) found competition between metals for exchange sites was enhanced as the initial metal concentration was increased. This resulted in large differences in adsorption of each metal. The strong relationship between metal adsorption and percentage base saturation could be attributed to replacement of Ca and Mg from exchange sites by transition and heavy metals (Basta and Tabatabai, 1992c). Cd uptake in maize seedlings showed that uptake was greater in the absence of calcium due to the presence of many cell wall exchange sites (Girling and Peterson, 1981). When examining the relative mobility of metals added to soil, Tyler and McBride (1982) found the order of mobility was $\text{Cu} < \text{Zn} \approx \text{Ni} \approx \text{Cd}$. Adsorption of the heavy metals was accompanied by an almost stoichiometric desorption of Ca^{2+} , Mg^{2+} , Al^{3+} , Na^+ , and K^+ . Bittell and Miller

(1974) examined exchange adsorption of Pb, Ca, and Cd on three types of clay minerals and found that while Cd^{2+} may compete fairly evenly with Ca^{2+} , adsorption of Pb^{2+} is favoured by a factor of 2 or 3. This may suggest more Cd^{2+} in solution and thus its greater availability to plants. When investigating Cd sorption on sandy soil Temminghoff et al. (1995) found sorption of Cd by soil could be described by a three-species Freundlich equation in which pH, complexation, Ca competition, and ionic strength effects were taken into account. They showed that increasing ionic strength of reagents from 0.003 to 0.3 decreased Cd sorption by 60% for $\text{Ca}(\text{NO}_3)_2$ and 25% for NaNO_3 . This was due to a decrease of the activity coefficient, increase of organic complexation, and increased competition by Ca.

Short-term kinetic experiments suggest more than 95% of Cd sorption onto soil takes place within 10 minutes and a constant distribution of Cd between soil and solute is obtained in 1 hour (Christensen, 1984a). Nakhone and Young (1992) found added amounts of Cd to a calcareous soil rendered non-labile by rapid precipitation. Desorption experiments with two soils exposed to low Cd concentrations showed full reversibility for a loamy sand and partial irreversibility for a sandy loam (Christensen, 1984b). As well, aging of the soils after exposure did not indicate stronger binding. The study also showed increased solution concentrations of Zn, H^+ , Ca, or EDTA significantly desorbed Cd from the soils (Christensen, 1984b). However, Backes et al. (1995) studied the kinetics of Cd and Co desorption from Fe and Mn oxides and found the longer the contact period between the metal and the oxide the slower the subsequent rate of desorption. They interpreted this as movement of Cd ions to sites with lower desorption reactions. Mn

oxides sorbed larger amounts of Cd than Fe oxides. Buchter et al. (1996) modelled Cd transport in an unsaturated stony subsoil monolith and found their approach which included ion exchange and irreversible sorption described the data well. The authors observed hysteresis which was modelled as irreversible sorption in the solid phase, and found a one-day isotherm was a better predictor for transport than a two-day isotherm.

2.4.5 Other Factors

The amount of Cd present in soil can be increased above naturally occurring levels through various anthropogenic factors. Singh and Steinnes (1994) state that for metals such as Cd, the rate of mobilization associated with industrial activities exceeds by a factor of ten or more the rate of mobilization from natural cycling. Cd levels in soils nearest to mining and smelting sites have been well documented and can be extremely high compared to background levels (Weissenhorn et al., 1995a; Dudley et al., 1991). Atmospheric deposition of pollutants from industrial activities can raise Cd concentration in the soil. Deposition of contaminants occurs near to the source of the contaminant and due to long range transport can occur in areas quite far away. Cadmium may enter the plant through aerial deposition, although it normally enters plants through the root. Lagerwerff (1971) studied uptake of Cd by radish from soil and air, finding increased levels in radish tops nearest to a busy highway. Cd levels decreased as the distance from the highway increased. It was believed that Cd was added through attrition of automobile tires and burning of motor oils.

Hahne and Kroontje (1973) examined the effect of pH and chloride concentration on Cd as hydrolysis and chloride complexation affect the solubility of sparingly soluble

metal salts. They state chlorides like hydroxyl and hydrogen ions occur in all natural soil and water and may be regarded as one of the most mobile and persistent complexing agents with regard to heavy metals. Chlorides do not complex strongly with Al(III) , Ca^{2+} , or Mg^{2+} and thus are more selective for metal cations. The authors found Cd was mainly complexed by chlorides at pH 8.5 and a chloride concentration range from 350-60 000 $\mu\text{g g}^{-1}$. Plant tissue grown on soil treated with reagent DAP + CdCl_2 had greater Cd concentrations than that grown with reagent DAP + $\text{Cd}_3(\text{PO}_4)_2$ (Mortvedt and Osborn, 1982). McLaughlin et al. (1995) examined the relative effects of KCl and K_2SO_4 , finding no effect of the Cl^- ion despite the assumption of Cl^- increasing phytoavailability of Cd. However, tuber Cd concentrations were closely related to levels of water-extractable Cl in soil (which was related to irrigation water quality) and the authors suggested the effects of KCl versus K_2SO_4 were concealed by irrigation water quality factors (McLaughlin et al., 1995). Smolders et al. (1995) studied the influence of chloride on Cd uptake by Swiss chard and found Cd concentrations in plant material and soil solution were significantly increased by increasing NaCl concentrations but unaffected by equivalent concentrations of NaNO_3 . The authors concluded the effect of NaCl on Cd phytoavailability was due to chloro-complexation rather than ionic strength or osmotic effects at the root surface (Smolders et al., 1995).

2.5 Management

Sustainable agriculture requires management of available resources to optimize production without sacrificing economic or environmental sustainability. Methods to reduce Cd concentrations in field crops must be economically viable in order for them to

become adopted by producers. Since Cd levels in crops appear to be influenced by a number of factors, not one method or practise will work in all cases. An integrated management approach is necessary to develop strategies which will influence the amount of Cd taken up by the plant. A combination of plant selection, rotation, tillage, fertilizer management, and other factors will determine Cd uptake in a particular area.

2.5.1 Cultural Treatments

Cultural practises which affect soil quality and productivity will influence Cd availability in the soil as well as the plants' ability to access it. Campbell et al. (1991a) gave results of a 30-yr study on a thin Black Chernozem, showing that cultural treatments (rotations, fertilizers, legumes, cropping frequency) influenced soil organic C and N to about the same extent. Tillage practises and fertilizer management influence soil characteristics as well as crop quality and productivity. Soil moisture, temperature, and structure are influenced by choice of tillage operation. Karlen et al. (1994) found both gravimetric soil water content and volumetric estimates of water-filled pore space in the top layer of soil significantly higher in no-till versus tilled plots. They also found more stable macroaggregates with higher organic C contents under no-till management. Microbial biomass, respiration, ergosterol concentration, and earthworm populations were higher after 12 years of no-till compared to tilled plots (Karlen et al., 1994). Soil organic matter in the first 10 cm has been found to be twice as great in no-till plots versus conventionally-tilled plots after seventeen years of a field trial (Drees et al., 1994).

Oliver et al. (1993) examined the effect of crop rotations and tillage practises on Cd concentration in wheat. In one out of three years direct drilling significantly increased

Cd content in grain over reduced tillage and conventional cultivation. At all rates of nitrogen the highest Cd levels were found in wheat grown after lupins. Wheat grown after legumes, including beans, peas, and pasture, had higher Cd concentrations than wheat following wheat or barley. While comparing the removal or retention of crop residues and their effect on Cd in grain, Andersson and Siman (1991) found Cd levels tended to be higher where crop residues were returned to the soil.

2.5.2 Sewage Sludge

Use of sewage sludge as a soil amendment can increase Cd concentration in the soil, varying with the amount and form of Cd present in the sludge (Jing and Logan, 1992; Korcak and Fanning, 1985). Cd is frequently a contaminant in sewage sludge and many studies have been undertaken to evaluate its effect on soil and plants grown in soil to which sewage sludge has been applied. Some studies have compared the availability of metal salts versus sludge, as the heavy metals applied as soluble salts may be more plant available than the equivalent levels in sludge. The addition of metal salts may be considered the worst-case scenario, as the metals are initially soluble and reactive materials which may bind metals are not added with the metals (Korcak and Fanning, 1985). When examining the addition of sludge to a soil, the chemistry of the sludge may affect the behaviour of metals more so than the properties of that soil, and this may make comparisons across soil types more difficult to assess. A study investigating the effect of sewage sludge Cd concentration on chemical extractability and plant uptake was undertaken by Jing and Logan (1992). They used seventeen anaerobically digested sludges of widely varying Cd content to test whether plant uptake of Cd is proportional to

its concentration in the sludge. Cd uptake by *Sorghum bicolor* varied significantly among the sludges at the same Cd application rate, suggesting that sludge chemistry controls metal uptake. The authors theorize that factors other than Cd content affect Cd uptake, such as Cd-binding metals and ligands such as Fe, Al and PO₄. Sludge P may be important as it may reduce the solubility of sludge Cd by coprecipitating Cd as various phosphates.

Mahler et al. (1978) studied eight soils with pH ranging from 4.8 to 7.8 treated with sewage sludge amended with varying amounts of Cd. The highest plant Cd concentrations were found in plants grown on acid soils. Mitchell et al. (1978) studied metal composition of lettuce and wheat on two soils amended with sewage sludge and found marked soil effects on metal uptake and accumulation. Effects on Cd concentration and uptake were dependent on Cd concentration, as at low levels of added Cd concentrations of Cd in tissue were similar to or higher in the calcareous soil than in the acid soil. However, at all higher soil Cd levels tissue Cd concentrations were higher in the acid soil. Extractability and bioavailability of Cd in three soils sampled five years after application of sewage sludge showed that Cd persisted in the topsoil in forms available to plants (Sanders et al., 1986). The authors found Cd possessed a relatively small bioavailable fraction considered to be exchangeable, and this fraction was susceptible to pH changes.

Korcak and Fanning (1985) applied equal amounts of heavy metals as sulfate salts and sewage sludge to surface and subsurface horizons to six soils. The DTPA metal extractability suggested that phytoavailability of soil Cd levels was greater in both surface

and subsurface material for Cd as metal salts. Metal extractability expressed as a fraction of the applied metal was in the order of $Cd > Zn > Cu > Ni$, and independent of metal source or soil material. Hooda and Alloway (1993) investigated growth of ryegrass in pots with increasing levels of sewage sludge or metal salts. They found addition of both metal sources increased plant uptake, but accumulation was greatest from the metal-salt treated soil.

2.5.3 Phosphatic Fertilizers

Fertilizer management affects nutrient availability to the crop and its subsequent uptake as well as nutrient distribution and stratification in the soil. Application of fertilizers may also increase Cd concentrations in the soil as Cd is present as a contaminant in certain fertilizers. Cadmium is naturally present in phosphate rock and different sources of phosphate rock have varying levels of this contaminant. Cd addition to soil from application of phosphatic fertilizers is of concern due to both short- and long-term effects. In the short-term, the amount of Cd added with the fertilizer, the effect of the fertilizer on soil chemistry, and the fertilizer's effect on plant growth can influence plant uptake of cadmium. Over a longer period of time the accumulation of Cd in the soil from years of fertilizer application and the chemical forms of this Cd will impact on plant growth and Cd uptake. When examining the overall effect of phosphorus fertilization both of these concerns must be addressed.

Cd is present as a contaminant in phosphate rock in amounts ranging from 1 to $>500 \text{ mg kg}^{-1}$ Cd (Alloway, 1990). Most of this contaminant remains present in the resulting fertilizers, ranging from 0.1 to $>200 \text{ mg kg}^{-1}$, as the manufacturing process does

not remove Cd. Rothbaum et al. (1986) studied soils with and without annual additions of superphosphate over a period ranging from 30 to 95 years. The authors determined there was little accumulation due to the fertilizer used on neutral arable soils but appreciable accumulation on acid grassland soil. The fertilizers used in these studies contained low levels of Cd, and very little accumulated in the surface horizon of the arable soil. About one-half of the Cd applied with the triple superphosphate was retained in the surface horizon of the grassland soils.

The Cd contained in phosphate fertilizer is somewhat available to the plant. In Australia, analyses of wheat grain and peas from fields sown with commercial applications of fertilizer, as well as off-the-shelf cereal breakfast food, found low Cd contents. This suggested that in spite of a long history of superphosphate application the cadmium residues had negligible effects on cadmium content of the grain (Williams and David, 1973). Williams and David (1976), found that 80% of the cadmium added through fertilizers was retained in the cultivated layer of the soil. They compared fertilized soil with adjacent unfertilized soil and found increased Cd contents in plants grown on soils with previous history of phosphorus treatment. The increase was attributed to the cadmium residues in the cultivated layer of the soil. This contrasted with results of a study by He and Singh (1993b), who determined Cd levels in newly and long-term cultivated soils in Norway using various extractants. They found significantly higher Cd levels in the long-term cultivated soils, however both oats and ryegrass took up more Cd from the newly cultivated soils. These results mirrored those of Baerug and Singh (1990) who examined long-term use of commercial fertilizers on Cd levels in soil and crops,

comparing newly cleared to old cultivated fields. While Cd levels were higher in old soils, Cd uptake in various plant species grown on these soils was significantly lower.

A pot study by Williams and David (1973), found that application of superphosphate fertilizer brought about increases of up to five-fold in the total Cd content of the soil which in turn increased the cadmium content of oats from seven- to ten-fold and eight- to fourteen-fold in subterranean clover. The soil used came from paired samples, one soil which had received phosphate fertilizer and one which had not, with higher Cd concentrations in the soil which had been fertilized. However, the effect of the fertilizer may have been overestimated because this was a pot study. In this type of trial, where the plant has access to a restricted volume of soil, "mining" of the soil by plant roots may occur. Higher Cd concentrations of plants grown in pot experiments may reflect a greater amount of Cd available than when plants are grown under field conditions. Under field conditions the roots are not restricted to just the upper zone of soil, where Cd levels tend to be the highest, and thus the plants tend to have lower concentrations of Cd in their tissues.

Mortvedt (1987) examined the effects of long term application of TSP on various crops and locations. He found that although soil levels of Cd tended to increase with TSP application there was no corresponding increase in plant Cd concentration. Cadmium concentration tended to be higher in the controls, possibly because of dilution from higher crop yield associated with fertilized soils. Jeng and Singh (1995) examined the Cd status of soil and plants from a 70 year experiment using P fertilizer and/or farmyard manure. They found neither total or plant-available soil Cd was influenced by long-term P

fertilization, and plant-Cd concentrations were unaffected as well. In fact, concentration was highest in the control plots which was attributed to less dilution as yield in the control plots was one-third that of the P-treated plots.

Mortvedt et al. (1981) examined the effect of three DAP fertilizers containing 2, 74, and 153 $\mu\text{g Cd g}^{-1}$ on uptake of Cd by winter wheat grown in the field. They used a P-deficient soil with pH 4.7, with low- and high-lime levels. Cadmium was increased significantly with high Cd-DAP on the low-lime soil, indicating that Cd concentrations in the crop were not significantly affected by phosphate fertilization. Even with low soil pH, high Cd-DAP, and a marked response to P fertilization, Cd concentrations increased only slightly. In contrast, results from a pot experiment comparing five treatments (He and Singh, 1994) indicated the amount of Cd in the plants was affected by the Cd level in the type of P fertilizer added. High-Cd fertilizer tended to give the highest Cd concentrations in the plants, with the results being more pronounced in the sandy soil. Application of phosphate rock with high-Cd levels did not increase plant Cd concentrations, indicating the Cd found in phosphate rock was not very plant available. Results of the second and third phases of the above pot study (He and Singh, 1995), using repeated applications of fertilizers, showed Cd concentrations in plant species increased with increasing Cd content in phosphatic fertilizers. Again, Cd in phosphate rock was not easily available to the plants, and there was no consistent increase in plant Cd concentration over the years of repeated fertilizer application. Fertilizer results were more pronounced in the sandy soil compared to the loam. In a pot experiment, with a limited volume of soil available to the roots, native soil Cd levels in the upper zone of soil may be very important in

determining the amount of Cd which is taken up by the plant. The sandy soil had much lower Cd levels and contained less clay and organic carbon, and may have been more responsive to Cd added through the various fertilizer treatments.

If the amount of Cd present in phosphate fertilizers is important in determining uptake by plants, presumably increasing the rate of P supplied will also increase the amount of Cd available to the plant. Sparrow et al. (1992) examined the effect of increasing rates of high-Cd TSP on potatoes and obtained both increased yield and Cd concentration in the tubers as rate of P increased. Fertilizer placement in proximity to the seed can influence the amount of Cd taken up by the crop. Placement of high-Cd phosphate fertilizer in a band has been noted to increase Cd concentration in potatoes relative to broadcast application (Sparrow et al., 1992). The soils studied were intensively cropped, high P-fixing kraznozems which showed economic yield response to banded P fertilization.

The form of phosphate fertilizer used may be important as some of the influence of P fertilization on Cd phytoavailability may be due to changes in pH, as observed by Levi-Minzi and Petruzzelli (1984) in pot studies. However in field studies, changing the chemical form of phosphatic fertilizers (MAP, DAP, SSP, or reactive phosphate rock), had little influence on potato tuber Cd concentrations, with the largest differences due to inter-site variations (McLaughlin et al., 1995).

Andersson and Siman (1991) analysed plant and soil samples from seven long-term experiments which had been subjected to varying fertilizer rates. Soil Cd levels were slightly elevated with increased fertilizer addition and plant Cd concentrations were

significantly higher at the highest rate. While the authors felt this was due to Cd contamination from phosphorus fertilizers, the results were confounded by increases in N in conjunction with the increased P rates. Eriksson (1990) found in a pot study an increase in NPK fertilizer generally resulted in an increase in levels of soil-Cd and in Cd concentrations in the plants, and plant Cd concentrations were higher in a sand than a clay soil. In contrast, in a field trial examining Cd concentration in Chinese cabbage and carrots, Guttormsen et al. (1995) applied NPK fertilizers with varying rates of Cd at 70 kg P ha⁻¹ and found that increased Cd levels in the fertilizer did not affect Cd concentration of either plant species.

2.5.4 Nitrogen

Although nitrogen fertilizers contain negligible amounts of Cd, application of N fertilizers can increase Cd concentration in plants. Despite the increase in yield associated with N fertilization there appears to be no dilution of Cd, but rather increased concentration, compounding the amount of Cd which accumulates in the crop. When various nitrogen treatments were applied with different amounts of sewage sludge to a permanent grassland, the Cd content of the grass increased considerably with increasing amounts of sludge and nitrogen (Hemkes et al., 1983). In separate cuts of grass at high N levels the Cd content was twice as high as at low N levels. Oliver et al. (1993) studied the effect of crop rotation and tillage on Cd content of wheat, finding that irrespective of crop rotation, concentration of Cd increased in the grain with increasing rates of nitrogen.

Application of ammonium nitrate in a field experiment increased uptake of both native soil cadmium and that from fertilizer residues by up to 50%, but no adequate

explanation could be given (Williams and David, 1976). Mulla et al. (1980) examined the impact of long term phosphorus fertilization on barley grown where orange trees had been established. From 1927 to 1963 the control plot received no P but 400 kg N ha⁻¹ from Ca(NO₃)₂ while the treated plots received P as well as 200 kg N ha⁻¹ from urea and 200 kg N ha⁻¹ from manure. The Cd concentration in the soil was much higher in the treated plots. After 1963 the plots were seeded to barley. Despite the fact the control had received no phosphorus fertilization it contained similar Cd concentrations in the barley grain and higher concentrations in the leaves than the treated plots. This may have been the influence of the nitrogen fertilizer which all plots received. However, pot experiments with Swiss chard, using soil from the field study, showed much higher Cd concentrations when grown on soil from the treated plots. Since the soil Cd levels were greater in the treated soil and in a pot experiment the volume of soil is limited and roots are confined to this small volume of soil, plants grown on treated soil may have had greater access to Cd.

Nitrogen fertilization may increase Cd accumulation through its effects on soil pH as various chemical reactions occur in the soil after N application. Eriksson (1990), used NH₄NO₃, (NH₄)₂SO₄, Ca(NO₃)₂ as fertilizers in a slightly acid soil (pH 6.2 - 6.7) and found both extractable soil-Cd and plant Cd concentrations highest in the (NH₄)₂SO₄ treatment, lowest in the Ca(NO₃)₂ treatment and intermediate when NH₄NO₃ was applied. Tests with NH₄NO₃, (NH₄)₂SO₄, Ca(NO₃)₂ and urea at 87.5 mg N kg⁻¹, along with 3 mg Cd (sulphate) kg⁻¹ in a light sandy loam showed that only (NH₄)₂SO₄ increased Cd concentrations in spinach leaves (Willaert and Verloo, 1992). The (NH₄)₂SO₄ decreased pH and increased NH₄OAc and water-soluble Cd, possibly increasing availability to the

plant. In a time-course experiment conducted by Lorenz et al. (1994), an excess of fertilizer cations in the soil caused drastic changes in concentrations in solution of major ions and heavy metals during certain stages of the experiment. An increase of NH_4^+ and K^+ in solution increased Cd and Zn in the soil solution and increased concentrations of Cd in radish leaves. Grant et al. (1996) examined the effect of N, P, and KCl on yield and Cd concentration of barley and found when soil nitrate levels were low, addition of nitrogen fertilizer increased Cd levels in grain, and these increases in Cd concentrations were generally associated with increases in crop yield.

2.5.5 Other Influences Affecting Soil Cd Uptake

Zinc applied in a pot study at a rate close to field recommendations for reducing Zn deficiency increased seed Zn and decreased seed Cd in flax (Moraghan, 1993). The Cd concentration in flax seed was reduced approximately 50% by increasing availability of soil Zn. The inhibitory effect of high zinc additions on Cd uptake was determined by Girling and Peterson (1981). They found that at equimolar concentrations of Cd and Zn, zinc appeared to stimulate Cd uptake. Gerritse et al. (1983) studied uptake of Cd by several crops in relation to its concentration in soil solution, and found Cd uptake was increased by Zn at high soil solution concentrations of Cd but decreased uptake at low solution concentrations. Increasing rates of zinc application decreased potato tuber Cd concentration at 4 out of 5 sites in southern Australia (McLaughlin et al., 1995). In field studies Grant and Bailey (1997), found that Cd concentration in flaxseed decreased as Zn concentration in flaxseed increased, and Cd concentration in the seed was negatively correlated with Zn concentration in the soil. However, although application of Zn

fertilizer generally decreased Cd concentration it had little effect on Cd accumulation in flaxseed.

In a study of temperature and Zn effects, Haghiri (1974) found addition of Zn from 5 to 50 $\mu\text{g g}^{-1}$ increased Cd concentration in shoots. This may be due to increased displacement of Cd into the soil solution, or perhaps increased metabolic uptake. Total Zn content in soil ranges from 10 to 300 $\mu\text{g g}^{-1}$ and averages approximately 50 $\mu\text{g g}^{-1}$ (Tisdale et al., 1985), so additions of Zn at these levels could be realistic. At added Zn levels of 100 to 400 $\mu\text{g g}^{-1}$, Cd in shoots was reduced, possible due to dilution of Cd in soil solution because excess amounts of Zn. Increased temperatures resulted in higher concentrations of Cd in shoots at given Zn applications (Tisdale et al., 1985).

Investigation of temperature effects on uptake of Cd and Zn from sewage sludge showed that soil heating generally improved yield and Cd uptake (Giordano et al., 1979). Higher Cd uptake due to soil heating was more pronounced for the checks than the sludge-treated soils. The authors found Cd levels higher in vegetative than reproductive parts, and lettuce and other leafy vegetables contained the highest Cd concentrations. In pot experiments, ryegrass grown in a warm environment (25°C) took up more Cd than under cool conditions (15°C) (Hooda and Alloway, 1993).

2.6 Conclusion

Phytoavailability of Cd to plants is complex and dependent upon many interrelated factors. Cultural practises such as fertilization, tillage, and crop sequence will have a combined effect on Cd uptake by crops. Each of these in turn can be influenced by the physical, chemical, and biological characteristics of the soil environment. For

example, fertilizer effects on soil pH may be mediated by soil texture. Crop sequence and tillage influence both quality and quantity of residue to be managed for the following crop. The combination of fertilizer applications, crop sequence, and tillage will have varying effects depending on the site and its history. When relating several factors to plant availability of Cd in cultivated soils, He and Singh (1993c) could not relate an individual factor to extractable Cd and/or plant Cd concentrations. Various extractants as well as soil pH, exchangeable Ca and Mg, total soil Cd, and Fe- and Mn-oxides affected the amounts of Cd extracted as well as Cd availability to plants. This indicates how difficult it may be to predict Cd uptake in a particular crop due to site-specific reactions, making it harder to generalize about patterns of accumulation over large areas. Since many parameters of the plants' growth environment are inherent and cannot easily be manipulated, the producer must look to areas he can influence to control Cd uptake and accumulation. Choice of tillage, rotation, and fertilizer are areas in which the producer has some degree of control over Cd uptake. These factors have not been extensively studied and much needs to be learned about their effect on Cd behaviour in soil and its movement into plants.

3. AVAILABILITY of Cd to WHEAT as AFFECTED by FERTILIZER RATE, SOURCE, and PLACEMENT

3.1 Abstract

Cadmium is a heavy metal taken up by plants which may lead to chronic human health problems. Due to high concentrations of Cd currently found in some Canadian grains and oilseeds there is a need to determine the factors responsible for the uptake and accumulation in these crops. Two growth chamber studies were conducted to determine the effects of rate and placement of nitrogen fertilizers, including $\text{Ca}(\text{NO}_3)_2$, $\text{CO}(\text{NH}_2)_2$, and $(\text{NH}_4)_2\text{SO}_4$, on Cd concentration in durum wheat (*Triticum turgidum* cv. Medora). Fertilizer effects were examined on two Chernozems, a Newdale clay loam (Orthic Black) and a Cobfield fine loam (Gleyed Cumulic Regosol). The study using the Newdale soil indicated that increasing the supply of nitrogen to the plants increased Cd concentration in the plant. Variation among fertilizer source was significant, with $\text{Ca}(\text{NO}_3)_2$ causing the highest and $(\text{NH}_4)_2\text{SO}_4$ the lowest concentrations of Cd in the plants, respectively. Broadcast urea caused higher Cd concentrations in both grain and straw than banded urea. Variation among samples was high for the $(\text{NH}_4)_2\text{SO}_4$ and banded urea treatments, especially at the high rates of N. A second study showed that plants grown on the carbonated soil (Cobfield fine loam) had higher Cd concentrations than plants grown on the Newdale clay loam. As in the initial experiment, application of $\text{Ca}(\text{NO}_3)_2$ caused the highest Cd levels in wheat. In both studies Cd concentrations in grain and straw increased with increasing fertilizer N rates.

3.2 Introduction

Cadmium is a heavy metal which possesses a long half-life within the human body and may cause chronic toxicity (NRCC, 1979). Food crops can accumulate levels of Cd which are potentially harmful to humans, without affecting crop yield. The FAO/WHO Expert Committee on Food Additives in 1972 suggested a maximum tolerable Cd intake limit of 70-84 $\mu\text{g person}^{-1} \text{ day}^{-1}$. The Canadian intake of Cd has been estimated in the range of 14.5 $\mu\text{g day}^{-1}$ (Dabeka and McKenzie, 1992) to 50-98 $\mu\text{g day}^{-1}$ (NRCC, 1979). Since our diets, as well as those of people in other countries, may have Cd levels near the FAO standard it is desirable to keep Cd levels in food crops as low as possible in order to limit exposure. Grains and cereal products tend to be the largest dietary source of Cd. As Cd occurs naturally in soil and may be increased due to anthropogenic factors (DeBoo, 1990), factors affecting crop uptake of this element need to be investigated.

Availability of Cd in soil and its accumulation into crops is dependent upon several factors, including soil and crop processes as well as management practices. Fertilizer source, rate and placement, tillage, micronutrient application, and crop and cultivar choice will affect Cd accumulation in the crop. Phosphatic fertilizers have been shown to either increase (Williams and David, 1973) or have no significant effect (Jeng and Singh, 1995; Mortvedt, 1987) on Cd concentration in grain. Placement of high-Cd phosphate fertilizer in a band has been noted to increase Cd concentration in potatoes relative to a broadcast application (Sparrow et al., 1992). Although they contain no appreciable Cd, nitrogen fertilizers are also reported to increase Cd concentration in wheat (Oliver et al., 1993), with the strength of the effect varying with N source

(Eriksson, 1990).

Although studies have indicated that N source may have an effect on Cd uptake, there is little information on the interactive effects of fertilizer source, rate, and placement on Cd accumulation. Therefore, two growth chamber experiments were conducted to examine the effects of rate and placement of various nitrogen fertilizers on grain Cd levels.

3.3 Materials and Methods

Two growth chamber experiments were conducted to determine the effects of various rates of fertilizer and their placement on Cd concentration in durum wheat (*Triticum turgidum*). The cultivar Medora was chosen as is it a moderate to high accumulator of Cd (Dr. Dave Leisle, pers. comm.). In the first study, soil was collected from the 0-15 cm layer of an Orthic Black Chernozem (Newdale clay loam), air dried and sieved to pass through a 20 x 40 mm screen. This soil came from near Minnedosa, MB and had been under an oilseed-cereal rotation with minimum tillage. Five thousand grams of air dry soil was placed into 6.4 L pots (20.3 cm diameter by 19.7 cm high). The top 4.5 cm of soil was removed and any broadcast fertilizer treatments were incorporated with the remaining soil. Soil beneath the banding depth was then wetted to field capacity by weight using distilled deionized water. For one treatment of urea, bands of fertilizer were placed 2.5 cm to the side of the future seedrow, and 2.5 cm of soil was added to cover the bands. Eleven seeds were placed on each seedrow, the remaining soil was replaced to cover the seeds and the top 4.5 cm of soil was watered to field capacity. Plants were thinned to six plants per pot when seedlings reached the two-leaf stage. Treatments

consisted of 0, 100, 200 and 400 $\mu\text{g g}^{-1}$ of urea, $\text{Ca}(\text{NO}_3)_2$, or $(\text{NH}_4)_2\text{SO}_4$. As 400 $\mu\text{g g}^{-1}$ of $(\text{NH}_4)_2\text{SO}_4$ contains relatively high amounts of sulphur, a treatment of 400 $\mu\text{g g}^{-1}$ urea + the equivalent amount of S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was added. Controls receiving no nitrogen were tested with and without additions of 20 $\mu\text{g g}^{-1}$ S and/or P. 20 $\mu\text{g g}^{-1}$ S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was applied to all pots with the exception of the $(\text{NH}_4)_2\text{SO}_4$ treatments and some of the controls. Twenty $\mu\text{g g}^{-1}$ monoammonium phosphate was applied to all pots except some control treatments. Sulphur was mixed throughout the soil in the pot while phosphorus was banded 2.5 cm below the seed but to the opposite side of the nitrogen fertilizer band. The experiment was a factorial design with four reps of four fertilizers (urea was both broadcast and banded) and four rates of N. In total there were seventeen treatments and four reps in a randomized complete block design. The plants received 16 hours of daylight with temperatures of 22°C during the day and 15°C at night. Relative humidity was maintained at 60%.

The second growth chamber study was conducted to determine the influence of soil type, especially the presence of carbonates, on fertilizer effects. A Gleyed Cumulic Regosol (Cobfield fine loam) which had been under alfalfa production for several years and the Newdale clay loam from the prior experiment were used. The Cobfield soil was part of the crop land of the Brandon Research Centre located on the flood plain of the Assiniboine River. Soil was analysed for NaHCO_3 extractable N and P, NH_4OAc extractable K, pH and conductivity (McKeague, 1981) and DTPA-TEA extractable Cd (Bailey et al., 1995). Characteristics for the two soils prior to use in these studies are given in Table 3.1. Soil was air dried and sieved to pass through a 20 x 40 mm screen. In

this experiment a different type of pot was used to maximize growth chamber space. Square wooden pots with a capacity of 4.7 L (interior 15.2 cm diameter by 20.3 cm high) were lined with plastic bags and filled with 5000 g of air dry soil. The top 2.0 cm of soil was removed and fertilizers were mixed thoroughly with the soil in the pot. Soil beneath the seeding depth was then wetted to field capacity using distilled deionized water. Nine seeds were planted in a row in the centre of the pots, covered with the soil and after seeding the top 2.0 cm was watered to field capacity. Seedlings were thinned when they reached the two-leaf stage and five plants were grown to maturity. All nitrogen fertilizers were broadcast along with $20 \mu\text{g g}^{-1}$ S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $20 \mu\text{g g}^{-1}$ monoammonium phosphate applied to all pots. Since the previous experiment had indicated no significant effect on Cd uptake due to the levels of S or P added, the controls received these nutrients. Treatments consisted of 0, 100, 200 and $400 \mu\text{g g}^{-1}$ of urea, $\text{Ca}(\text{NO}_3)_2$, or $(\text{NH}_4)_2\text{SO}_4$. The experiment was a factorial design with four reps of three fertilizers and four N rates on two soils, with soil type being the main effect. Due to space limitation in the growth chamber $\text{Ca}(\text{NO}_3)_2$ was able to be tested only on the non-carbonated Newdale clay loam soil. Growing conditions were identical to those in the first experiment.

In both experiments pots were watered to field capacity with distilled deionized water every other day and then daily as needed until the plants were harvested at maturity. Total above ground material was dried in a Unitherm oven at 30°C and grain and tissue were separated. Grain was ground with a stainless steel Braun coffee grinder while straw was processed with a Wiley mill, both to pass through a 1 mm sieve. In the first experiment certain treatments were selected and two reps of roots were washed from the

soil using distilled deionized water. Due to the small amount of material obtained, roots were not ground before they were analysed for Cd. After wet-digestion with HNO_3 - HClO_4 , the Cd analyses were performed on the samples by a Varian 300/400 atomic absorption spectrophotometer using a graphite furnace with deuterium correction (detection limit $0.01 \text{ ng Cd mL}^{-1}$). Analysis of standard samples of wheat flour with a mean concentration of $23 \mu\text{g kg}^{-1}$ had a standard error of 2.15. Other analyses were performed by an ICP or Auto Analyser after wet-digestion with $\text{H}_2\text{SO}_4 + \text{SeO}_2$. Soil nutrients were analysed according to procedures specified by M^cKeague (1981).

Table 3.1: Soil characteristics of the two soils used in the growth chamber studies.

	Clay Loam	Carb. Fine Loam
$\text{Na}(\text{HCO}_3)_2$ - $\text{NO}_3\text{-N}$ to 15 cm (kg ha^{-1})	22	25
$\text{Na}(\text{HCO}_3)_2$ - P to 15 cm ($\mu\text{g g}^{-1}$)	16	10
NH_4OAc - K to 15 cm ($\mu\text{g g}^{-1}$)	204	173
DTPA-TEA - Cd to 15 cm ($\mu\text{g kg}^{-1}$)	134	75
pH ¹ to 15 cm	7.1	8.3
Conductance ¹ to 15 cm ($\mu\text{S cm}^{-1}$)	261	217

¹ using a 1:2 soil:H₂O solution.

Statistical analyses were conducted using GLM and CONTRAST procedures of the SAS Institute, Inc. (1989). Means separation was performed using the Student-Newman-Keuls test.

3.4 Results

In the first study grain Cd concentration was significantly affected by both fertilizer source and fertilizer rate (Table 3.2). Cd concentrations in both grain and straw increased as nitrogen rate increased (Table 3.3). Grain Cd levels were significantly lower

with banded urea and $(\text{NH}_4)_2\text{SO}_4$ treatments than with $\text{Ca}(\text{NO}_3)_2$ and broadcast urea treatments, although yield was not influenced by fertilizer source (Table 3.3). Fertilizer sources behaved similarly except at the $400 \mu\text{g g}^{-1}$ N rate, where a significant fertilizer source*N rate interaction was evident (Figure 3.1). The Cd concentration in wheat grain was significantly greater with $\text{Ca}(\text{NO}_3)_2$ and broadcast urea than with $(\text{NH}_4)_2\text{SO}_4$ and banded urea at a rate of $400 \mu\text{g N g}^{-1}$.

In the absence of applied nitrogen, application of P or P+S did not increase Cd concentration in grain or straw. Application of $400 \mu\text{g g}^{-1}$ of urea plus sulphate as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, equivalent to the S applied in the ammonium sulphate treatment, produced significantly higher grain and straw Cd concentrations than any other treatment (Table 3.3).

Table 3.2 Probability values from analysis of variance of effect of fertilizer source and nitrogen rate on wheat yield and grain Cd concentration in two growth chamber studies.

	Study 1		Study 2			
	Clay Loam		Clay Loam		Carb. Fine Loam	
	Cd	Yield	Cd	Yield	Cd	Yield
Fertilizer Source	0.0001	ns ¹	0.0001	ns	0.0001	ns
Nitrogen Rate	0.0001	0.0078	0.0001	0.0016	0.0005	0.0003
Source * Rate	0.0001	0.0016	ns	ns	ns	ns
MSE	218.2	4.2	224.6	3.6	242.4	4.3
CV (%)	9.9	8.6	11.9	11.6	12.6	15.5

¹ ns - not significant at a *p* value ≤ 0.10 .

Comparison of selected root, straw, and grain Cd concentrations indicated that concentrations of Cd in straw and root increased along with increases in grain Cd concentration (Table 3.4). Cadmium was translocated to the straw from the root as

nitrogen rate increased (Table 3.5). Movement of Cd from the straw into the grain appeared to decrease as more nitrogen was supplied (Table 3.5). Fertilizer sources appeared to have similar effects on Cd partitioning (Fig. 3.2).

When fertilizers and N rate effects on Cd concentration were investigated on two soils, Cd concentration differed with fertilizer source and increased with increasing N rate (Table 3.2). In contrast to the previous experiment there was no fertilizer source*N rate interaction, thus Cd concentration in the grain increased to a similar extent with increasing N rates of the various N sources (Figure 3.3). On the clay loam soil, application of $\text{Ca}(\text{NO}_3)_2$ produced the highest grain Cd concentrations, followed by $(\text{NH}_4)_2\text{SO}_4$ and then urea (Table 3.6). On the carbonated fine loam soil, application of $(\text{NH}_4)_2\text{SO}_4$ produced higher tissue Cd concentrations than urea. The $\text{Ca}(\text{NO}_3)_2$ was not applied on the carbonated soil due to space limitations in the growth chamber. Contrast analysis indicated that the Cd concentration in grain from the Newdale soil was significantly lower than that of the Cobfield soil (Table 3.6).

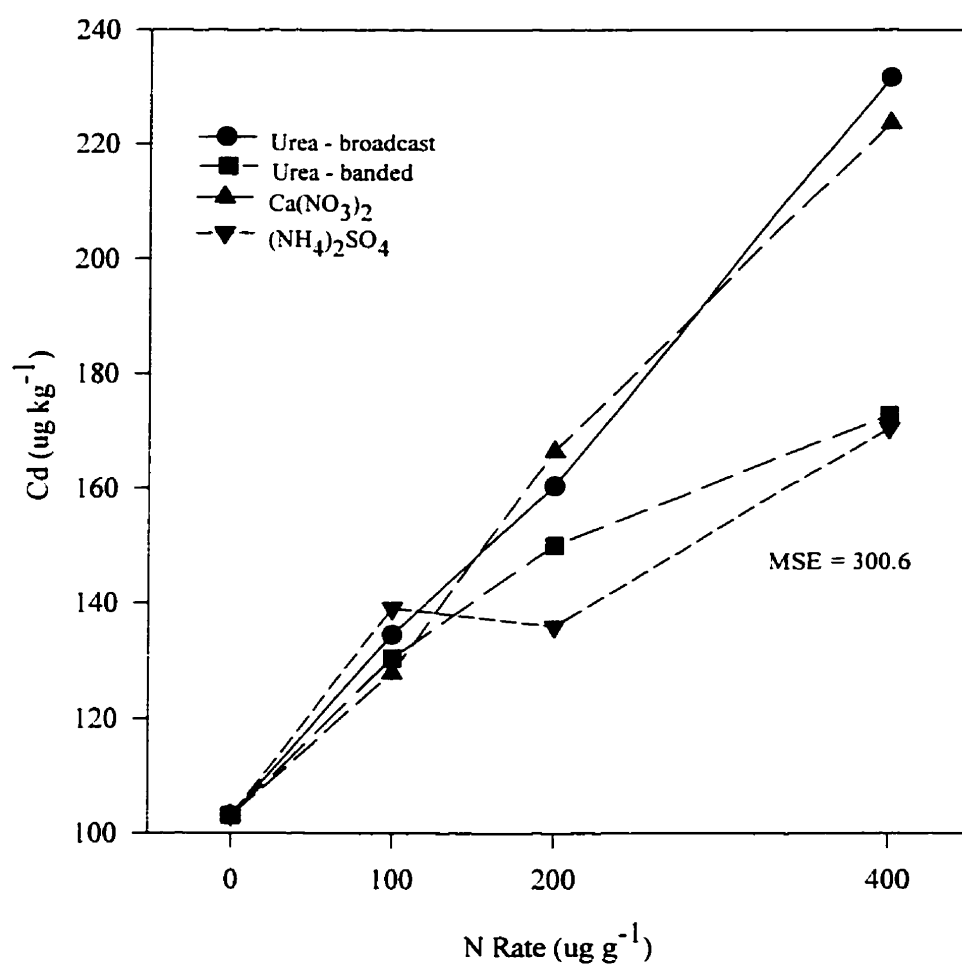


Figure 3.1 Grain Cd concentration as a function of N fertilizer rate and form.

Table 3.3 Influence of nitrogen source and rate, and addition of P and/or S in the absence of N₂ on Cd concentration and yield in wheat.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
Nitrogen Source				
Ca(NO ₃) ₂	173a ¹	26.3a	578a	32.7a
Broadcast Urea	176a	26.5a	599a	33.9a
Banded Urea	151b	25.0a	525b	32.9a
(NH ₄) ₂ SO ₄	147b	24.7a	464c	33.8a
MSE	218	5.5	2276	4.3
Nitrogen Rate				
100 $\mu\text{g g}^{-1}$	133c	27.0a	418c	29.2c
200 $\mu\text{g g}^{-1}$	153b	24.7b	519b	34.1b
400 $\mu\text{g g}^{-1}$	202a	25.3b	685a	36.5a
MSE	224	4.2	2332	3.0
Other Treatments				
Control	103b	14.9c	228d	14.8d
Control + P	100b	16.7c	236d	17.4d
Control + P + S	102b	15.2c	228d	15.7d
Urea + CaSO ₄	258a	29.0a	970a	38.1a
MSE	300	4.5	3221	3.5

¹. Within each group values followed by the same letter are not significantly different at the 5% confidence level.

Table 3.4 Influence of nitrogen source and rate on root, straw, and wheat grain Cd concentration of selected treatments.

Treatment	Root Cd ($\mu\text{g kg}^{-1}$)	Straw Cd ($\mu\text{g kg}^{-1}$)	Grain Cd ($\mu\text{g kg}^{-1}$)
100 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	722ab ¹	442ef	128de
200 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	972a	555d	166cd
400 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	853ab	736c	224b
100 $\mu\text{g g}^{-1}$ Broadcast Urea	745ab	397f	135cde
200 $\mu\text{g g}^{-1}$ Broadcast Urea	780ab	562d	160cd
400 $\mu\text{g g}^{-1}$ Broadcast Urea	900ab	838b	232ab
400 $\mu\text{g g}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$	693b	556d	170c
400 $\mu\text{g g}^{-1}$ Urea + CaSO_4	901ab	970a	258a
Control	732ab	228g	103e
MSE	4316	3222	301

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

Table 3.5 Influence of nitrogen source and rate on root:straw and straw:grain Cd concentration ratios of selected treatments.

Treatment	Root Cd:Straw Cd	Straw Cd:Grain Cd
100 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	1.64b ¹	3.46ab
200 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	1.74b	3.34ab
400 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	1.10b	3.32ab
100 $\mu\text{g g}^{-1}$ Broadcast Urea	2.03b	2.99ab
200 $\mu\text{g g}^{-1}$ Broadcast Urea	1.48b	3.52ab
400 $\mu\text{g g}^{-1}$ Broadcast Urea	1.05b	3.66ab
400 $\mu\text{g g}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$	1.31b	3.20ab
400 $\mu\text{g g}^{-1}$ Urea + CaSO_4	0.92b	3.78a
Control	3.25a	2.23c
MSE	0.18	0.13

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

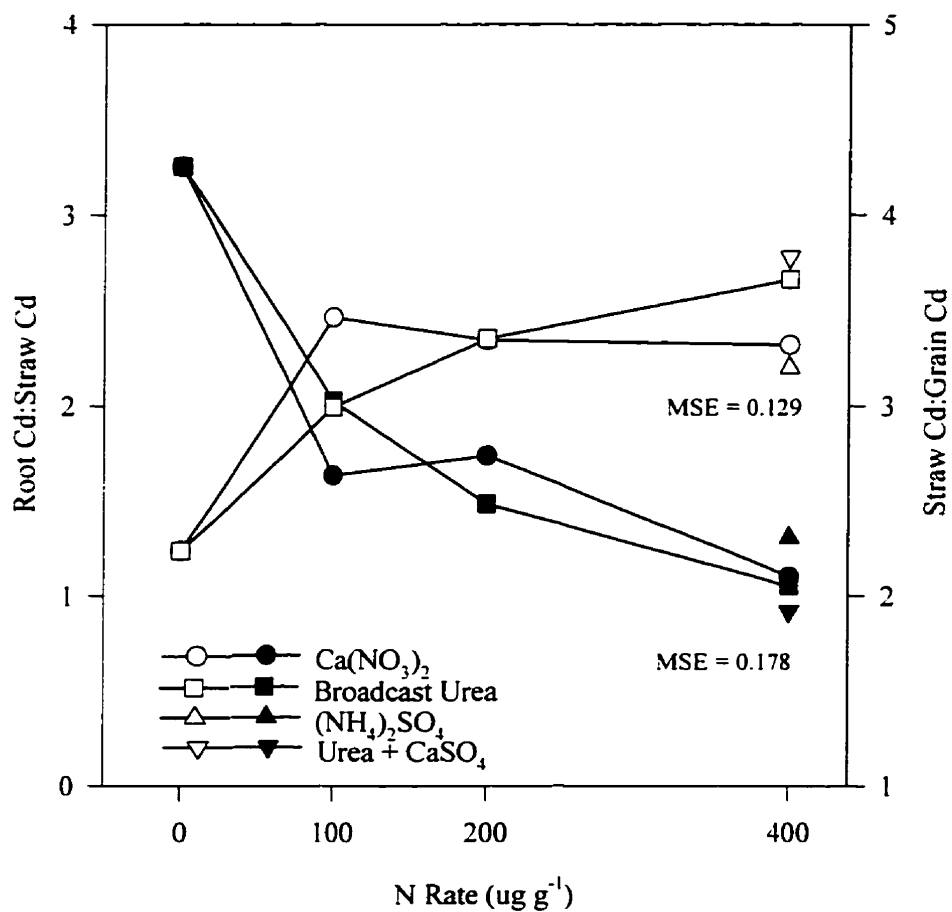


Figure 3.2 Root Cd:Straw Cd (closed symbols) and Straw Cd: Grain Cd (open symbols) as a function of N rate and form.

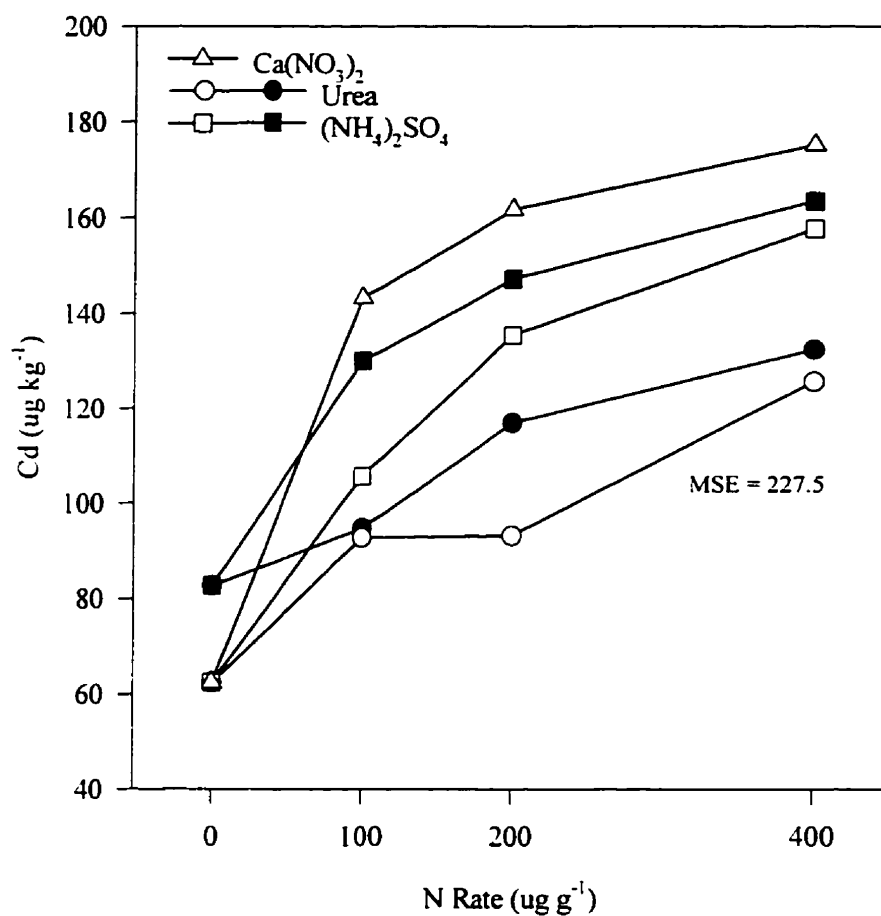


Figure 3.3 Grain Cd concentration as a function of N fertilizer rate and form on two soil types, a Cobfield fine loam (closed symbols) and a Newdale clay loam (open symbols).

Table 3.6 Contrast analysis of soil type and influence of nitrogen source and rate on Cd concentration and yield in wheat on two soils.

Contrast Analysis	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
Newdale CL vs. Cobfield	0.0157	0.0001	ns ¹	ns
<i>Newdale Clay Loam</i>				
<u>Nitrogen Source</u>				
Ca(NO ₃) ₂	160a ²	16.9a	426a	33.3a
Urea	105c	17.1a	298c	23.8b
(NH ₄) ₂ SO ₄	133b	17.9a	371b	27.0b
MSE	225	3.6	1807	12.7
<u>Nitrogen Rate</u>				
Control	62	9.0c	182f	10.7g
100 $\mu\text{g g}^{-1}$	114c	15.8b	288c	24.6b
200 $\mu\text{g g}^{-1}$	133b	17.1ab	374b	31.5a
400 $\mu\text{g g}^{-1}$	153a	18.9a	440a	28.7a
MSE	225	3.6	1807	12.7
<i>Cobfield Carbonated Fine Loam</i>				
<u>Nitrogen Source</u>				
Urea	118b	14.6a	308b	26.4a
(NH ₄) ₂ SO ₄	147a	13.3a	355a	23.7a
MSE	242	4.4	1323	18.5
<u>Nitrogen Rate</u>				
Control	83c	9.4c	105g	11.2g
100 $\mu\text{g g}^{-1}$	112b	15.4a	261c	27.7a
200 $\mu\text{g g}^{-1}$	130ab	16.1a	311b	25.8a
400 $\mu\text{g g}^{-1}$	143a	11.9b	387a	23.1a
MSE	242	4.4	1323	18.5

¹ ns - not significant at a p value ≤ 0.10 .

² Within each group values followed by the same letter are not significantly different at the 5% confidence level.

3.5 Discussion

Increasing nitrogen supply to wheat plants, regardless of source, resulted in higher Cd concentrations in the grain under growth chamber experiments. With all sources of N, concentration of Cd in both grain and straw increased with each increment of fertilizer. One explanation of these results is that increasing the rate of nitrogen may have decreased the pH of the soil solution, leading to increased Cd phytoavailability. Lutz et al. (1977) found that applications of acid-forming fertilizers may affect the plant root environment, as in some soils high nitrate and electrolyte concentrations in the soil solution were accompanied by lower pH. This resulted in increased Al and Mn concentrations in the soil solution. In our experiments the application of nitrate fertilizers, as well as ammonium-based fertilizers which are subsequently nitrified, would be expected to effect changes in ionic strength and pH of the soil solution. In a pot experiment where changes of Cd and Zn in soil solution were studied over time, Lorenz et al. (1994) found excess fertilizers caused substantial increases of these metals as well as other cations in solution. Changes in ionic strength of the soil solution and/or desorption reactions may have produced these results. As concentrations of Cd and Zn increased in soil solution, concentrations in the plants increased as well.

Application of calcium nitrate in the first experiment gave the highest Cd concentrations while the lowest plant Cd concentrations occurred with ammonium sulphate. This contrasted with the findings of Eriksson (1990), who reported the highest plant Cd concentrations for ammonium sulphate fertilizer compared to NH_4NO_3 and $\text{Ca}(\text{NO}_3)_2$. Eriksson found a strong association between the fertilizers' effect on soil pH

and plant Cd levels; however the soils he used were had lower pH and buffering capacity than the soils used in this experiment. The differences in soil characteristics may explain this inconsistency in the behaviour of ammonium sulphate. With ammonium sulphate the increase in Cd concentration as nitrogen rate increased was less pronounced than with the other fertilizers. Yield of plants grown on ammonium sulphate was lower than with other fertilizers, which may have influenced the Cd concentration. Due to its acidifying effect on soil, it was expected that application of ammonium sulphate would cause the highest plant Cd concentrations, however our findings did not support this. Therefore factors other than soil pH may have been important in determining Cd uptake from the soils used in our experiments. This contrasts with other observations in the literature, which suggest a relationship between Cd uptake on the effects of fertilizer application on soil pH.

Thomson et al. (1993) compared the effect of nitrate and ammonium fertilizers on soil pH and plant growth, finding a lower soil pH when ammonium was supplied to the pots.

Shoot concentrations of P as well as micronutrients (Fe, Mn, Zn, and Cu) were higher for plants supplied with NH_4^+ . In a study where lettuce was grown in nutrient solution with added Cd, concentrations as well as whole-plant uptake of Cd was higher when grown on NH_4^+ versus NO_3^- (Florijn et al., 1992). The authors stated rhizosphere acidification after NH_4^+ uptake may have resulted in increased bioavailability of Cd in the soil solution, and subsequently enhanced uptake. However, in our studies the acidifying effect of fertilizers on soil pH did not seem to have a great effect. The effect of fertilizers on ionic strength of the soil solution, the buffering capacity of our soils, or Ca^{2+} substitution in the soil solution may have influenced Cd uptake more than the effect of pH. The second study

revealed calcium nitrate caused the highest Cd concentrations in both grain and plant tissue, followed by ammonium sulphate and then urea. Application of $\text{Ca}(\text{NO}_3)_2$ may have increased Cd phytoavailability through ion exchange of Ca^{2+} for Cd^{2+} , as Ca could have substituted for bound Cd and increased the amount of Cd in soil solution (Christensen, 1984). As well, $\text{Ca}(\text{NO}_3)_2$ may have increased the ionic strength of the soil solution (Temminghoff et al., 1995).

In the first experiment concentrations of Cd in the grain were significantly higher using broadcast urea than banded urea, especially at the highest rate. Yield of banded urea tended to be lower than that of broadcast urea in this study, which may have influenced Cd concentration, especially at the higher rates of N. When the supply of nutrients within the rooting zone is non-uniform, plant roots often proliferate in regions where favourably high concentrations exist (Goss et al., 1993). Banding of fertilizer can create this effect. Drew and Saker (1975, 1978) studied the effect of applied nitrate on barley. When the supply was localized the rate of uptake was five times higher, but when the nutrient supply was uniform the total uptake of nitrate was greater. This explains why Cd concentration in grain was higher when urea was broadcast rather than banded.

In the second experiment plants grown in the carbonated fine loam had higher Cd concentrations than those grown in a non-carbonated clay loam. This is in contrast to other studies in the literature. Chemisorption may control Cd^{2+} activity in some calcareous soils, producing solubilities much lower than predicted by the solubility product of CdCO_3 (McBride, 1980). The ionic radii of Cd^{2+} and Ca^{2+} are very similar and this may account for the strong affinity of Cd^{2+} for calcite surfaces (Papadopoulos and

Rowell, 1988). Thus plants grown in a carbonated soil may be expected to take up less Cd than plants grown in a non-carbonated soil, as there may be less free Cd^{2+} in the soil solution due to chemisorption. Hirsch and Banin (1990) state the high bicarbonate and high pH in the vicinity of an active root grown in a calcareous soil may rapidly change Cd speciation. This could lead to decreased availability of Cd to plants at given total soil Cd levels by increasing CdHCO_3^- and decreasing Cd^{2+} . The contradictory results in the second experiment, where Cd concentrations were higher in wheat grown on a carbonated soil, may have been due to the cropping history of that soil. Although NO_3^- nitrogen levels were similar for the two soils (Table 3.4), the carbonated soil had been in alfalfa production for several years. Residual fertility benefits from a nitrogen-fixing crop such as alfalfa will not be apparent from the nitrate-N soil test, and this may have influenced the amount of nitrogen available to the plants grown in this soil. In addition, the carbonated fine loam soil was much coarser in texture than the clay loam, and yields were significantly decreased at $400 \mu\text{g g}^{-1}$ added nitrogen. Coarse-textured soils with low CEC have been shown to produce higher plant Cd concentrations in response to fertilizer additions (Eriksson, 1990; Grant et al., 1996).

When applying nitrogenous fertilizers containing other nutrients, such as S, substantial amounts of the counter ion will be added along with the nitrogen. In the first experiment, addition of $400 \mu\text{g g}^{-1}$ nitrogen as ammonium sulfate added $462 \mu\text{g g}^{-1}$ of sulphur to the growth medium. Application of $400 \mu\text{g g}^{-1}$ nitrogen as urea plus $462 \mu\text{g g}^{-1}$ of sulphur as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced significantly higher Cd concentrations than the equivalent amount of fertilizer as ammonium sulphate. Since the sulphur concentrations

remained the same as in the treatment of $400 \mu\text{g g}^{-1}$ ammonium sulfate, the added calcium apparently increased Cd concentrations in the plants. This is in agreement with Christensen (1984), who found increasing the Ca concentration in soil reduced the Cd sorption capacity of a sandy loam. The reduction in sorption capacity was explained as a combination of reduced activities (due partly to the increased ionic strength) and competition by Ca for soil sorption sites. Similar results were found by Temminghoff et al. (1995) who found that increasing ionic strength decreased Cd sorption by 60% for $\text{Ca}(\text{NO}_3)_2$ due in part to increased competition by Ca.

3.6 Summary and Conclusions

Increasing the rate of nitrogen supplied to wheat plants consistently increased the Cd concentration of grain and straw. When N was added, yield tended to increase over the control, and total uptake of Cd tended to be greatest where the rate of applied fertilizer nitrogen was the highest. Application of P and S in the absence of applied nitrogen did not affect Cd concentration relative to the control.

The effect of fertilizer additions on soil pH did not appear to be directly related to Cd levels in the plants. Calcium nitrate consistently produced the highest Cd concentrations. The Ca^{2+} competition presumably increased Cd uptake by the plants, possibly due to Cd^{2+} desorption from soil surfaces. In the first study Cd concentrations were similar with broadcast urea and ammonium sulphate, whereas in the second experiment Cd levels in plants were higher when ammonium sulphate had been applied as compared to urea.

Fertilizer placement influenced Cd concentration with broadcast urea producing

higher Cd concentrations than banded urea, in both grain and straw. Yield with banded urea was lower, especially at the higher rates of nitrogen, which may have affected uptake of Cd from the soil.

Cd uptake differed between the two soils studied despite similar soil Cd levels. However, Cd uptake patterns among fertilizer sources remained constant across both soils.

4. INFLUENCE of TILLAGE and FERTILIZER MANAGEMENT on Cd CONTENT of DURUM WHEAT and CANOLA

4.1 Abstract

Cadmium has become an element of concern as certain food crops can accumulate levels of Cd which are not toxic to the plant but may be harmful to humans. Due to high concentrations of Cd currently found in some Canadian grains and oilseeds there is a need to determine the factors responsible for the uptake and accumulation in these crops. A field study was conducted to determine the effects of fertilizer management and tillage practises on Cd concentration in crops. From 1992 to 1994 durum wheat (*Triticum turgidum* cv. Sceptre) and canola (*Brassica napus* cv. Legend) were grown on two Orthic Black Chernozems. Research sites were located near Minnedosa (Newdale clay loam) and Brandon (Marringhurst fine sandy loam). Various commercial fertilizers were applied at 60 kg N ha⁻¹ to both crops under conventional or zero tillage management. While there was little significant difference in wheat Cd levels among fertilizers, similar trends were evident on all six site years. The fertilizers which gave the highest yields (NH₃, banded urea) also tended to cause higher concentrations of Cd in grain and straw. Application of 40 kg P ha⁻¹ as monoammonium phosphate did not increase wheat Cd concentrations relative to the control. Yields and Cd concentrations in wheat tended to be higher under conventional tillage than zero tillage. While both sites had similar DTPA-TEA extractable soil-Cd levels, Cd concentrations in wheat were higher on the fine sandy loam site, and overall yearly variation ranged from 45 µg g⁻¹ on the 1992 clay loam to 180 µg g⁻¹ on the 1994 fine sandy loam. Since application of fertilizers increased both yield

and Cd concentration, total Cd accumulation from high-yielding plots was greater than from plots with lower yields. Application of any nitrogen fertilizer increased Cd concentration relative to the control, while MAP did not. Contrary to wheat, there was no pattern of Cd uptake among fertilizer sources and placements for canola. The effect of nitrogen fertilization on Cd concentration in canola is not clear, as in some cases Cd concentrations at high N levels are lower than that of the control.

4.2 Introduction

Cadmium is a heavy metal which possesses a long half-life within the human body and may cause chronic toxicity (NRCC, 1979). Food crops can accumulate levels of Cd which are potentially harmful to humans, without affecting crop yield. It is desirable to keep Cd levels in food crops as low as possible in order to limit exposure to this metal. As grains and cereal products tend to be the largest dietary source of Cd, we should examine Cd accumulation in these foods to control Cd inputs to our diet. Since Cd occurs naturally in soil and may be increased due to anthropogenic inputs (DeBoo, 1990), factors affecting crop uptake of this element need to be investigated.

Availability of Cd in soil and its accumulation into crops is dependent upon several factors, including soil and crop processes as well as management practices. Fertilizer source, rate and placement, tillage, micronutrient application, and crop and cultivar choice will affect Cd accumulation in the crop. Phosphatic fertilizers have been shown to either increase (Williams and David, 1973) or have no significant effect (Jeng and Singh, 1995; Mortvedt, 1987) on Cd concentration in grain. Nitrogen fertilizers are reported to increase Cd concentration in wheat (Oliver, 1993), and different N fertilizers

have effected varying Cd concentrations in plants (Eriksson, 1990). Growth chamber studies by Brown et al. (Chapter 1) have indicated that Cd concentration in wheat grain increased with increasing rates of nitrogen fertilization, and that at given N rates different nitrogen formulations produced grain with different Cd concentrations.

Effects of soil management on soil quality will influence both crop yield and quality, including nutrient and elemental composition. Soil degradation is a threat to sustainable agriculture as crop quality and productivity are greatly influenced by soil characteristics. Conservation tillage management maximizes surface residue retention and increases organic matter content near the soil surface (Drees et al., 1994). This results in reduced evaporative losses, increased rainfall infiltration, less water runoff, and less wind and rain erosion. In addition to the effects of tillage, effective fertilizer management also affects nutrient availability and uptake by the crop as well as pH and nutrient stratification in the soil. Karlen et al. (1994) found total soil N almost twice as high under long term no-till versus tilled treatments. While tillage had no effect on total-P levels in soil, Weil et al. (1988) found the distribution of inorganic forms of P was significantly affected by tillage. The authors stated that less mixing of applied P fertilizer with the soil may have reduced P-fixation, leaving more unreacted Ca-P present under no-till systems.

Although some information is available on the effect of nitrogen fertilizers on Cd uptake, there have been no studies evaluating the interactive effects on fertilizer source and placement with tillage. Therefore, this study was designed to examine how various commercial fertilizers, using a number of application methods, effect Cd concentration in

wheat and canola under conventional and zero tillage.

4.3 Materials and Methods

Studies were established in Western Manitoba near Minnedosa and Brandon on two Orthic Black Chernozem soils, one a clay loam and the other a fine sandy loam. Using a wheat-canola rotation, Sceptre durum wheat (*Triticum turgidum*) and Legend canola (*Brassica napus*) were grown adjacent to each other, alternating sides each year to provide appropriate stubble for the next crop. Plots were maintained on precisely the same locations for the duration of the trial, allowing individual fertilizer treatments to be put down on the same location each year. Both crops were established on 2 by 5 metre plots with nine rows at 20 cm spacing. Tillage consisted of either conventional tillage, with two fall cultivations and one spring cultivation prior to seeding, or zero tillage where no tillage was done prior to seeding. All plots were seeded with a Seed Hawk air drill using 2.5 cm openers and cultivation was done with a 2.1 m Case IH chisel plow. Fertilizer rates were low to ensure that differences in nitrogen efficiency would be apparent. Plots received 60 kg ha⁻¹ N and either 30 kg P₂O₅ ha⁻¹ for canola or 40 kg P₂O₅ ha⁻¹ for wheat. Fertilizer applications consisted of either spring or fall treatments. Fertilizers included anhydrous ammonia (82-0-0), urea-ammonium nitrate (28-0-0), urea (46-0-0), and ammonium nitrate (34-0-0). Application methods consisted of side banding (2.5 cm below and to the side of the seed row), spoke wheel, dribble banding, and broadcasting. The P was either seed placed or dual banded with the nitrogen. Controls received no nitrogen and had either no P, seed placed P, banded P, or a knifing operation without addition of P to simulate soil disturbance. Herbicide application occurred as

necessary according to recommendations found in the provincial Guide to Crop Protection (Anonymous, 1992-1994), as well as roguing when necessary.

This experiment was conducted over a period of four growing seasons, however only three years of data will be presented here. The test was established in the spring of 1992 so fall treatments for that year were not applied. In the spring of 1992 all plots were seeded and the fall treatments of that year, which should have been applied in the previous autumn, received spring banded applications of N. This was done in order to provide stubble for the 1993 season, to maintain residual N levels similar to the other plots, and to avoid increasing the incidence of weeds in these plots. Wheat was seeded 5 cm deep at a rate of 125 kg ha⁻¹ and canola was seeded 2.5 cm deep at 8 kg ha⁻¹. Canola seed was treated with Counter 5G while wheat seed was untreated. Soil characteristics and nutrient levels for these soils prior to the beginning of this trial are shown in Table 4.1. Soil analyses were in accordance to procedures specified by McKeague (1981). Meteorological data for both sites was collected over the duration of growing seasons (Table 4.2).

At crop maturity the middle five rows of each plot were harvested using a plot combine, leaving approximately 10 cm of standing stubble. Canola was desiccated with Reglone and then straight combined. Grain was dried at 30°C in a Unitherm drying oven to uniform moisture and weights were recorded. Straw yields above the cutting height were taken in the field at harvest using a straw catcher with a scale attached to the combine. Straw was returned to the plot and evenly spread after weighing. Samples of the straw were kept as selected treatments were to be analysed. Grain was ground with a

stainless steel Braun coffee grinder and other plant materials were processed with a stainless steel Wiley mill, both to pass through a 1 mm screen. After wet-digestion with $\text{HNO}_3\text{-HClO}_4$, the Cd analyses were performed on the samples by a Varian 300/400 atomic absorption spectrophotometer using a graphite furnace with deuterium correction (detection limit $0.01 \text{ ng Cd mL}^{-1}$). Analysis of standard samples of wheat flour with a mean concentration of $23 \mu\text{g kg}^{-1}$ had a standard error of 2.15. Other analyses were performed by an ICP or Auto Analyzer after wet-digestion with $\text{H}_2\text{SO}_4 + \text{SeO}_2$.

Table 4.1 Soil characteristics of the experimental sites at the beginning of the study.

	<u>Newdale CL</u>	<u>Marringhurst FSL</u>
$\text{Na}(\text{HCO}_3)_2$ - $\text{NO}_3\text{-N}$ to 60 cm (kg ha^{-1})	47	45
$\text{Na}(\text{HCO}_3)_2$ - P to 15 cm ($\mu\text{g g}^{-1}$)	16	14
NH_4OAc - K to 15 cm ($\mu\text{g g}^{-1}$)	279	127
DTPA-TEA - Cd to 15 cm ($\mu\text{g kg}^{-1}$)	105	83
pH ¹ to 15 cm	7.5	7.3
Conductance ¹ to 15 cm (uS cm^{-1})	234	148

¹using a 1:2 soil:H₂O solution.

The experiment consisted of 18 fertilizer treatments * 4 reps * 2 tillage systems * 2 crops * 2 sites * 3 years for a total of 1728 experimental units. The tests were arranged as a split-plot design with completely randomized blocks. Tillage was the main plot and was randomized from rep to rep while the sub plot consisted of the fertilizer treatments. Statistical analyses were conducted using GLM and CONTRAST procedures of the SAS Institute, Inc. (1989). Means separation was performed using the Student-Newman-Keuls test. Data from all three years at each site has been analysed and presented separately. The effect of each fertilizer and tillage system was similar from year to year although treatment means varied with each growing season. As there was no treatment by tillage

interaction for the clay loam soil, data from the two tillage systems was combined to show the overall effect of each fertilizer. A fertilizer treatment by tillage interaction occurred on the fine sandy loam soil therefore ZT and CT treatments are shown separately. Since crops were not randomized canola and wheat were treated as separate experiments.

Table 4.2 Meteorological data of the experimental sites from Licors located at each

	<u>Newdale CL</u>			<u>Marringhurst FSL</u>		
	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>
<u>May</u>						
Precipitation (mm) ¹	1	nd ²	45	16	nd	43
<u>June</u>						
Solar (Joules)	19	19	nd	21	19	21
Air Temp (°C)	14	14	15	15	14	16
Precipitation (mm)	22	84	84	32	95	69
<u>July</u>						
Solar (Joules)	19	18	nd	20	18	22
Air Temp (°C)	14	15	16	16	16	17
Precipitation (mm)	86	117	68	104	102	22
<u>August</u>						
Solar (Joules)	16	16	nd	17	16	17
Air Temp (°C)	14	15	15	16	16	16
Precipitation (mm)	22	93	82	37	133	88
<u>September</u>						
Solar (Joules)	11	12	nd	11	12	14
Air Temp (°C)	9	8	13	10	9	14
Precipitation (mm)	19	52	53	45	27	53
<i>Total Precipitation</i>	150	346	332	234	357	275

¹Rainfall collection started on:

²nd - data not available.

4.4 Results

4.4.1 Fertilizer Treatments

4.4.1.1 Nitrogen. Grain yield and Cd concentration were significantly affected by fertilizer treatment on both soil types (Table 4.3). Application of N fertilizer increased both wheat grain yield (Tables 4.4-4.6) and Cd concentration (Tables 4.7-4.9). Fertilizer treatments which gave the greatest nitrogen efficiency, as measured by yield, tended to cause Cd concentrations which were as high or higher than the other treatments. Fall and spring banded treatments tended to produce higher Cd concentrations than other treatments. Application of NH_3 , either as a spring or fall band, tended to produce the highest grain Cd concentrations of all the treatments. Within each site-year, Cd concentrations for wheat tended to be highest in those fertilizer treatments which produced the greatest yield. Correlation of wheat grain Cd with grain yield indicates a good relationship between these two parameters (Figure 4.1). Values for canola showed there was no effect of nitrogen fertilizer on Cd concentration in grain, and in some site-years the control was as high or higher in Cd than all other treatments (Tables 4.10-4.15).

Due to the large number of plots only particular treatments were chosen for determination of Cd concentration in straw (Tables 4.7-4.9, 4.13-4.15). As with the grain, Cd concentrations in straw were increased by N fertilization, with effects of fertilizer sources, timing, and placements being similar to their effects on grain. Cd concentration in wheat, for the ratio of grain Cd:straw Cd, increased from 1992-1994. Within each year, this ratio was higher on the fine sandy loam site compared to the clay loam. Thus with higher Cd concentrations in wheat, whether from year to year or site to site within a year,

the ratio of grain Cd:straw Cd increased as well.

Table 4.3 Probability values from analysis of variance of effect of treatment, tillage, and year on grain Cd and yield of wheat and canola on a clay loam and a fine sandy loam soil for three years, 1992-1994 inclusive.

	Wheat		Canola	
	Grain Cd	Yield	Grain Cd	Yield
<i><u>Clay Loam</u></i>				
Treatment	0.0001	0.0001	ns	0.0001
Tillage ¹	ns ²	0.0051	ns	ns
Treatment*Tillage	ns	ns	ns	0.0188
Year	0.0001	0.0001	0.0001	0.0001
Year*Treatment	ns	0.0001	ns	0.0002
Year*Tillage	0.0001	0.0001	0.0319	ns
Year*Treatment*Tillage	ns	0.0034	ns	ns
MSE ³	424.3	3.4 x 10 ⁴	154.4	1.8 x 10 ⁴
MSE ⁴	4974.3	1.1 x 10 ⁵	209.3	1.3 x 10 ⁵
CV (%)	26.3	14.3	21.5	16.7
<i><u>Fine Sandy Loam</u></i>				
Treatment	0.0001	0.0001	ns	0.0001
Tillage	0.0986	ns	ns	0.0215
Treatment*Tillage	0.0004	0.0854	ns	ns
Year	0.0001	0.0001	0.0002	ns
Year*Treatment	ns	ns	ns	0.0001
Year*Tillage	0.0001	0.0040	ns	0.0583
Year*Treatment*Tillage	ns	ns	ns	ns
MSE ³	556.4	5.3 x 10 ⁴	518.3	2.7 x 10 ⁴
MSE ⁴	2914.2	9.1 x 10 ⁴	485.8	9.4 x 10 ³
CV (%)	19.9	17.6	28.9	19.5

¹ using rep(till) as an error term.

² ns - not significant at a p value of ≤ 0.10 .

³ MSE- means square error using rep as the error term.

⁴ MSE- means square error using rep(till) as the error term.

Table 4.4 Wheat yield and contrast analyses of grain and straw on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatment	Grain Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	2668	3734	3201	--	3918	5760	4839
Fall Band, 28-0-0	--	2140	2976	2558	--	4330	4113	4222
Fall Band, 46-0-0	--	2645	2740	2692	--	4055	4200	4126
Spring Band, 82-0-0	2311 ¹	2426	3599	2778	7378	4768	5895	6014
Spring Band, 28-0-0	2291	2550	3770	2870	7055	3755	5505	5438
Spring Band, 46-0-0	2451	2547	3652	2884	7273	3998	5230	5500
Dual Band, 28-0-0	2280	2506	3318	2702	6750	3958	5185	5298
Dual Band, 46-0-0	2505	2377	3608	2830	7415	4200	5835	5816
Spoke Wheel, 28-0-0	2405	2533	3405	2780	7838	3870	5553	5754
Dribble Band, 28-0-0	2319	2497	3276	2698	7265	4330	4893	5496
Dribble Band, 46-0-0	2436	2082	3268	2596	7555	4140	4528	5408
Dribble Band, 34-0-0	2575	2168	3080	2608	7650	2920	4648	5072
Broadcast, 34-0-0	2184	2282	3072	2512	7610	4480	5060	5716
Broadcast, 46-0-0	2324	2475	3083	2628	6860	4333	4623	5272
Control-no N, no P	1829	1589	2308	1908	4628	2083	2905	3206
Control-no N, P seed-placed	2089	1592	2597	2092	5378	2880	3508	3922
Control-no N, P banded	2037	1668	2720	2140	5718	2415	4015	4050
Control-no N, no P, banding operation	1648	1334	2532	1838	4035	2558	3760	3450
<u>Contrasts</u>								
No n vs N	***	***	***	***	***	***	***	***
Phosphate Response	***	ns	*	**	***	ns	ns	***
Spring Band vs Fall Band ²	--	ns	***	ns	--	ns	***	***
Dual band vs Band	ns	ns	*	ns	ns	ns	ns	ns
NH3 Band vs Urea Band	ns	ns	***	**	ns	ns	***	**
NH3 band vs UAN Band	ns	ns	**	**	ns	ns	***	**
34-0-0 Band vs 34-0-0 Broadcast	***	ns	ns	ns	ns	***	ns	*
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	*	**	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	**	ns	ns	*
MSE	45824	146595	126498	134695	475547	615010	711114	767257

¹ Contrast made with 1993 & 1994 data only.

Table 4.5 Wheat yield and contrast analyses of grain and straw on the fine sandy loam site under conventional tillage as affected by by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatment	Grain Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	2535	2938	2736	--	5527	2613	4070
Fall Band, 28-0-0	--	2497	3151	2824	--	4853	2827	3840
Fall Band, 46-0-0	--	2451	3037	2744	--	5060	2833	3947
Spring Band, 82-0-0	2988 ¹	2585	2721	2765	3260	5300	2520	3693
Spring Band, 28-0-0	3071	2488	2483	2680	3587	4760	2300	3549
Spring Band, 46-0-0	2901	2501	2459	2620	3100	5060	2327	3496
Dual Band, 28-0-0	3777	2586	3180	3181	4980	4807	3187	4324
Dual Band, 46-0-0	3721	2490	3084	3098	4880	4893	3007	4260
Spoke Wheel, 28-0-0	3116	2659	3129	2968	4500	4773	3033	4102
Dribble Band, 28-0-0	3061	2439	2724	2741	4173	4960	2780	3971
Dribble Band, 46-0-0	2659	2731	2575	2655	3427	5827	2293	3849
Dribble Band, 34-0-0	2617	2498	2524	2546	3273	5160	2380	3604
Broadcast, 34-0-0	3057	2671	3095	2941	4420	4340	3027	3929
Broadcast, 46-0-0	3170	2423	2785	2793	3447	4573	2587	3536
Control-no N, no P	1694	1819	1970	1828	1967	3120	1740	2276
Control-no N, P seed-placed	2293	1977	2246	2172	2587	3087	2173	2616
Control-no N, P banded	2403	1980	2334	2239	2540	2767	2300	2536
Control-no N, no P, banding operation	1820	1781	2214	1938	1947	2733	1993	2224
Contrasts								
No n vs N	***	***	***	***	**	***	**	***
Phosphate Response	**	ns	ns	**	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	**	ns	--	ns	*	*
Dual band vs Band	**	ns	**	**	**	ns	**	*
NH3 Band vs Urea Band	ns	ns	ns	ns	ns	ns	ns	ns
NH3 band vs UAN Band	ns	ns	ns	ns	ns	**	ns	ns
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	*	*	ns	**	*	ns
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
MSE	228710	39083	166378	195689	1166773	241403	206877	979981

¹ Contrast made with 1993 & 1994 data only.

Table 4.6 Wheat yield and contrast analyses of grain and straw on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatment	Grain Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	3025	3125	3075	--	6533	2653	4593
Fall Band, 28-0-0	--	2584	2360	2472	--	4860	1933	3397
Fall Band, 46-0-0	--	2656	2617	2637	--	4840	2340	3590
Spring Band, 82-0-0	3646 ¹	2853	3332	3277	6280	5027	3327	4878
Spring Band, 28-0-0	3585	2717	2631	2978	5167	5080	2267	4171
Spring Band, 46-0-0	3536	2506	2720	2921	5073	4607	2013	4084
Dual Band, 28-0-0	3536	2629	2583	2916	4333	5060	2353	3916
Dual Band, 46-0-0	3341	2463	2439	2748	3533	5193	2013	3580
Spoke Wheel, 28-0-0	3173	2769	2484	2809	4673	5587	2133	4131
Dribble Band, 28-0-0	3459	2668	2585	2904	4833	4967	2373	4058
Dribble Band, 46-0-0	3295	2705	2801	2934	4400	5540	2567	4169
Dribble Band, 34-0-0	2873	2568	2433	2625	3600	5293	1993	3629
Broadcast, 34-0-0	3322	2677	2581	2860	4100	5587	2187	3958
Broadcast, 46-0-0	3011	2492	2577	2693	4080	4240	2260	3527
Control-no N, no P	1491	1709	1595	1598	1500	2847	1287	1878
Control-no N, P seed-placed	2309	1899	1864	2024	2547	2873	1480	2300
Control-no N, P banded	1925	1878	1577	1793	1807	2673	1407	1962
Control-no N, no P, banding operation	2122	1684	1783	1863	2493	2820	1507	2273
Contrasts								
No n vs N	***	***	***	***	**	***	***	***
Phosphate Response	ns	**	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	ns	--	ns	ns	ns
Dual band vs Band	ns	ns	ns	ns	ns	ns	ns	ns
NH3 Band vs Urea Band	ns	***	*	**	ns	**	ns	*
NH3 band vs UAN Band	ns	***	**	**	ns	**	**	*
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	*	ns	ns	ns	**	ns	ns
MSE	294241	15017	250166	228603	2854718	419728	342917	1815852

¹ Contrast made with 1993 & 1994 data only.

Table 4.7 Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Grain Cd (ug kg ⁻¹)				Straw Cd (ug kg ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	90	123	107	--	--	--	--
Fall Band, 28-0-0	--	91	109	95	--	--	--	--
Fall Band, 46-0-0	--	88	109	98	--	--	--	--
Spring Band, 82-0-0	47 ¹	97	129	91	142	150	183	158
Spring Band, 28-0-0	50	81	118	83	--	--	--	--
Spring Band, 46-0-0	51	82	111	81	128	148	191	155
Dual Band, 28-0-0	45	83	87	72	--	--	--	--
Dual Band, 46-0-0	44	79	90	71	--	--	--	--
Spoke Wheel, 28-0-0	51	82	105	79	--	--	--	--
Dribble Band, 28-0-0	51	76	111	79	--	--	--	--
Dribble Band, 46-0-0	53	76	107	79	--	--	--	--
Dribble Band, 34-0-0	50	77	94	73	--	--	--	--
Broadcast, 34-0-0	51	87	118	85	130	151	136	139
Broadcast, 46-0-0	50	82	100	77	117	129	152	133
Control-no N, no P	40	67	89	65	94	113	149	118
Control-no N, P seed-placed	45	69	94	69	96	102	121	106
Control-no N, P banded	42	71	92	68	104	107	120	111
Control-no N, no P, banding operation	33	64	75	57	--	--	--	--
<u>Contrasts</u>								
No n vs N	**	***	**	***	***	***	**	***
Phosphate Response	**	ns	ns	*	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	**	--	--	--	--
Dual band vs Band	*	ns	***	**	--	--	--	--
NH3 Band vs Urea Band	ns	**	**	**	ns	ns	ns	ns
NH3 band vs UAN Band	ns	***	*	**	--	--	--	--
34-0-0 Band vs 34-0-0 Broadcast	ns	**	**	**	--	--	--	--
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	*	ns	**
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	*	ns	ns	**	ns	ns
MSE	84	103	412	424	661	467	3088	1437

¹ Contrast made with 1993 & 1994 data only.

Table 4.8 Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Grain Cd (ug kg ⁻¹)				Straw Cd (ug kg ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	137	195	166	--	--	--	--
Fall Band, 28-0-0	--	118	169	143	--	--	--	--
Fall Band, 46-0-0	--	137	182	155	--	--	--	--
Spring Band, 82-0-0	99 ¹	141	207	149	180	189	297	213
Spring Band, 28-0-0	103	134	230	156	--	--	--	--
Spring Band, 46-0-0	95	125	242	154	171	202	310	235
Dual Band, 28-0-0	65	127	173	122	--	--	--	--
Dual Band, 46-0-0	71	133	162	122	--	--	--	--
Spoke Wheel, 28-0-0	81	126	178	128	--	--	--	--
Dribble Band, 28-0-0	71	134	174	127	--	--	--	--
Dribble Band, 46-0-0	96	131	232	153	--	--	--	--
Dribble Band, 34-0-0	84	145	204	144	--	--	--	--
Broadcast, 34-0-0	68	110	172	116	117	141	192	150
Broadcast, 46-0-0	80	123	190	131	130	169	253	184
Control-no N, no P	47	115	120	94	73	103	144	107
Control-no N, P seed-placed	56	107	141	101	78	146	139	121
Control-no N, P banded	46	105	140	97	62	133	144	113
Control-no N, no P, banding operation	44	83	132	86	--	--	--	--
<u>Contrasts</u>								
No n vs N	***	**	***	***	***	**	***	***
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	**	ns	---	---	---	---
Dual band vs Band	***	ns	**	***	---	---	---	---
NH3 Band vs Urea Band	ns	ns	ns	ns	ns	ns	ns	ns
NH3 band vs UAN Band	ns	ns	ns	ns	---	---	---	---
34-0-0 Band vs 34-0-0 Broadcast	ns	**	ns	**	---	---	---	---
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	**	ns	**	ns	ns	**
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	*	ns	*
MSE	199	295	1140	614	429	360	1677	1353

¹ Contrast made with 1993 & 1994 data only.

Table 4.9 Cd concentration and contrast analyses of wheat grain and straw (selected samples) on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Grain Cd ($\mu\text{g kg}^{-1}$)				Straw Cd ($\mu\text{g kg}^{-1}$)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	147	199	173	--	--	--	--
Fall Band, 28-0-0	--	112	186	149	--	--	--	--
Fall Band, 46-0-0	--	97	175	136	--	--	--	--
Spring Band, 82-0-0	79 ¹	127	163	123	147	178	167	164
Spring Band, 28-0-0	68	119	146	111	--	--	--	--
Spring Band, 46-0-0	65	117	167	116	128	181	178	162
Dual Band, 28-0-0	82	106	155	114	--	--	--	--
Dual Band, 46-0-0	93	98	176	122	--	--	--	--
Spoke Wheel, 28-0-0	73	101	139	104	--	--	--	--
Dribble Band, 28-0-0	71	96	113	93	--	--	--	--
Dribble Band, 46-0-0	61	113	142	106	--	--	--	--
Dribble Band, 34-0-0	62	113	139	105	--	--	--	--
Broadcast, 34-0-0	77	119	146	114	132	176	165	158
Broadcast, 46-0-0	69	105	120	98	113	143	135	130
Control-no N, no P	37	69	90	65	47	97	119	88
Control-no N, P seed-placed	62	94	107	88	73	111	159	114
Control-no N, P banded	62	88	126	92	64	124	140	109
Control-no N, no P, banding operation	61	77	130	90	--	--	--	--
<u>Contrasts</u>								
No n vs N	***	**	***	***	***	***	ns	***
Phosphate Response	ns	ns	ns	ns	*	*	ns	ns
Spring Band vs Fall Band ²	--	ns	**	**	---	---	---	---
Dual band vs Band	**	ns	ns	ns	---	---	---	---
NH ₃ Band vs Urea Band	ns	**	ns	**	ns	ns	ns	ns
NH ₃ band vs UAN Band	ns	**	ns	**	---	---	---	---
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	ns	ns	---	---	---	---
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	**	*	ns	**	ns	*
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	**	ns	ns
MSE	231	403	773	498	244	185	3060	1311

¹ Contrast made with 1993 & 1994 data only.

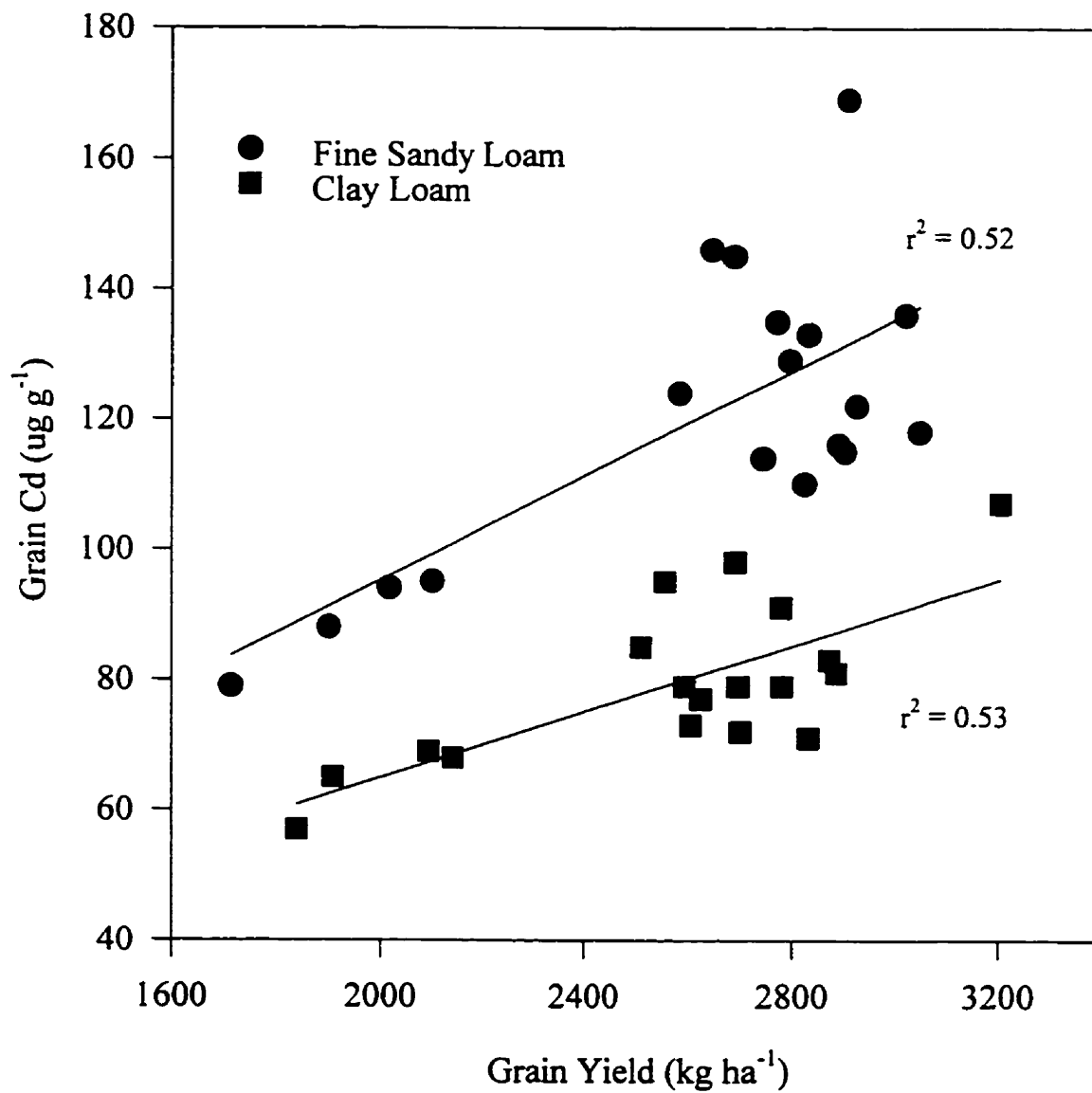


Figure 4.1 Correlation of durum grain Cd as a function of yield and soil type (means of three years, 1992-1994 inclusive, are plotted).

Table 4.10 Canola yield and contrast analyses of seed and straw on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	1921	2050	1990	--	4640	6755	5698
Fall Band, 28-0-0	--	1783	1713	1748	--	4090	5930	5010
Fall Band, 46-0-0	--	1704	1698	1700	--	3960	5950	4956
Spring Band, 82-0-0	1632 ¹	2009	1850	1830	5808	5398	6828	6010
Spring Band, 28-0-0	1441	1893	1944	1760	5223	4660	7365	5750
Spring Band, 46-0-0	1424	1900	1879	1734	5480	4540	6910	5644
Dual Band, 28-0-0	1685	1515	1838	1680	5743	3925	6973	5546
Dual Band, 46-0-0	1326	1846	1783	1652	5293	4850	6388	5510
Spoke Wheel, 28-0-0	1664	1731	1815	1736	6550	4258	5718	5508
Dribble Band, 28-0-0	1433	1818	1749	1666	5890	4888	6680	5820
Dribble Band, 46-0-0	1195	1770	1801	1588	4200	4375	6898	5158
Dribble Band, 34-0-0	1338	1699	1744	1594	5240	4163	6200	5200
Broadcast, 34-0-0	1617	1876	1681	1724	5743	4838	6325	5636
Broadcast, 46-0-0	1585	1665	1777	1676	5440	4353	6273	5356
Control-no N, no P	1253	1290	1179	1240	3495	2693	3121	3104
Control-no N, P seed-placed	1231	1266	1164	1220	3308	2430	3563	3100
Control-no N, P banded	1221	1206	1181	1202	3210	2678	3638	3176
Control-no N, no P, banding operation	1167	993	1168	1110	3090	1998	3828	2972
<u>Contrasts</u>								
No n vs N	***	***	***	***	***	***	***	***
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	ns	--	**	**	**
Dual band vs Band	ns	*	*	ns	ns	ns	ns	ns
NH3 Band vs Urea Band	*	ns	**	**	ns	**	ns	**
NH3 band vs UAN Band	*	ns	**	**	ns	*	ns	**
34-0-0 Band vs 34-0-0 Broadcast	**	ns	ns	*	ns	ns	ns	ns
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
MSE	45281	121506	29000	70255	676475	981319	1311253	1083483

¹ Contrast made with 1993 & 1994 data only.

Table 4.11 Canola yield and contrast analyses of seed and straw on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	2103	2380	2241	--	6247	10473	8360
Fall Band, 28-0-0	--	1634	1985	1809	--	4927	9247	7087
Fall Band, 46-0-0	--	1941	1851	1896	--	6053	7193	6623
Spring Band, 82-0-0	1811 ¹	2037	1959	1936	5940	7140	9287	7456
Spring Band, 28-0-0	1701	1871	2062	1878	6040	6333	9973	7449
Spring Band, 46-0-0	1597	1838	2077	1837	5553	6567	8853	6991
Dual Band, 28-0-0	2220	2154	2035	2136	6713	6860	8527	7367
Dual Band, 46-0-0	2069	1851	1991	1970	7160	6267	8113	7180
Spoke Wheel, 28-0-0	1692	2151	1919	1921	6440	8140	8753	7778
Dribble Band, 28-0-0	1925	1829	2035	1930	6300	6620	9140	7353
Dribble Band, 46-0-0	993	1927	1853	1591	3797	6607	10113	6839
Dribble Band, 34-0-0	1789	1921	2119	1943	5333	6640	9727	7233
Broadcast, 34-0-0	1729	1821	1587	1712	5840	6640	7027	6502
Broadcast, 46-0-0	1873	1494	1835	1734	6273	5447	8133	6618
Control-no N, no P	1579	941	1266	1262	4213	2060	5107	3793
Control-no N, P seed-placed	1401	1048	1409	1286	3733	2680	5040	3818
Control-no N, P banded	1413	1152	1278	1281	4280	3053	4613	3982
Control-no N, no P, banding operation	1729	987	1412	1376	4807	2807	5460	4358
Contrasts								
No n vs N	ns	***	***	***	***	***	***	****
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	ns	--	**	ns	ns
Dual band vs Band	*	ns	ns	*	*	ns	ns	ns
NH3 Band vs Urea Band	ns	ns	ns	*	ns	ns	*	**
NH3 band vs UAN Band	ns	*	ns	**	ns	*	ns	ns
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	**	ns	ns	ns	*	ns
46-0-0 Band vs 46-0-0 Broadcast	ns	*	ns	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	*	ns	ns	ns	ns	ns	ns
MSE	148334	43041	87497	106182	1266699	861987	2917101	1874639

¹ Contrast made with 1993 & 1994 data only.

Table 4.12 Canola yield and contrast analyses of seed and straw on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Yield (kg ha ⁻¹)				Straw Yield (kg ha ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	2330	1976	2153	--	7827	8980	8403
Fall Band, 28-0-0	--	1382	1797	1590	--	3647	6607	5127
Fall Band, 46-0-0	--	1995	1607	1801	--	6113	5973	6043
Spring Band, 82-0-0	1506 ¹	2151	1673	1777	5773	7227	6293	6431
Spring Band, 28-0-0	952	1823b	1884	1553	3453	6033	7573	5687
Spring Band, 46-0-0	1409	1953	1729	1697	4440	6307	5867	5538
Dual Band, 28-0-0	1782	1680b	1693	1718	5707	4987	6227	5640
Dual Band, 46-0-0	1826	1593	1620	1680	7773	5387	6673	6611
Spoke Wheel, 28-0-0	1433	1819	1633	1628	5820	5533	6020	5791
Dribble Band, 28-0-0	1993	1585	1621	1733	6713	5400	6353	6156
Dribble Band, 46-0-0	951	1729	1905	1528	2333	5793	8347	5491
Dribble Band, 34-0-0	1870	1745	1593	1736	6620	5300	6067	5996
Broadcast, 34-0-0	1896	1958	1731	1862	6113	6080	6580	6258
Broadcast, 46-0-0	1866	1767	1573	1735	6133	5613	5147	5631
Control-no N, no P	1658	767	1011	1145	3427	1460	3620	2836
Control-no N, P seed-placed	1642	1011	1316	1323	4660	2373	3727	3587
Control-no N, P banded	1808	845	949	1201	5213	2100	3708	3673
Control-no N, no P, banding operation	1468	1055	805	1110	4013	2213	3027	3084
<u>Contrasts</u>								
No n vs N	ns	***	***	***	**	***	***	***
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	*	--	ns	ns	*
Dual band vs Band	**	**	ns	ns	**	*	ns	ns
NH3 Band vs Urea Band	ns	**	ns	*	ns	ns	**	***
NH3 band vs UAN Band	ns	***	ns	**	**	**	ns	***
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
MSE	184327	39882	73776	106300	1815658	775898	1119572	1595508

¹ Contrast made with 1993 & 1994 data only.

Table 4.13 Cd concentration and contrast analyses of canola seed and straw (selected samples) on the clay loam site as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Cd (ug kg ⁻¹)				Straw Cd (ug kg ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	49	83	66	--	--	--	--
Fall Band, 28-0-0	--	57	65	61	--	--	--	--
Fall Band, 46-0-0	--	59	74	66	--	--	--	--
Spring Band, 82-0-0	31 ¹	58	80	56	307	316	456	360
Spring Band, 28-0-0	35	55	79	57	--	--	--	--
Spring Band, 46-0-0	31	57	73	54	338	293	399	344
Dual Band, 28-0-0	36	56	78	57	--	--	--	--
Dual Band, 46-0-0	34	54	87	58	--	--	--	--
Spoke Wheel, 28-0-0	36	58	81	58	--	--	--	--
Dribble Band, 28-0-0	33	58	74	55	--	--	--	--
Dribble Band, 46-0-0	39	58	68	55	--	--	--	--
Dribble Band, 34-0-0	32	55	81	56	--	--	--	--
Broadcast, 34-0-0	33	61	70	55	304	283	375	318
Broadcast, 46-0-0	34	55	82	57	331	261	471	354
Control-no N, no P	43	58	74	58	357	330	397	362
Control-no N, P seed-placed	44	61	74	60	342	341	434	372
Control-no N, P banded	44	60	77	60	347	323	435	368
Control-no N, no P, banding operation	43	57	79	60	--	--	--	--
Contrasts								
No n vs N	***	ns	ns	ns	**	**	ns	**
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	*	--	--	--	--
Dual band vs Band	ns	ns	ns	ns	--	--	--	--
NH3 Band vs Urea Band	ns	ns	ns	ns	ns	ns	ns	ns
NH3 band vs UAN Band	ns	ns	ns	ns	--	--	--	--
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	ns	ns	--	--	--	--
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	*	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	**	ns
MSE	55	56	263	154	1756	2024	6961	3804

¹. Contrast made with 1993 & 1994 data only.

Table 4.14 Cd concentration and contrast analyses of canola seed and straw (selected samples) on the fine sandy loam site under conventional tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Cd ($\mu\text{g kg}^{-1}$)				Straw Cd ($\mu\text{g kg}^{-1}$)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	70	87	79	--	--	--	--
Fall Band, 28-0-0	--	77	104	90	--	--	--	--
Fall Band, 46-0-0	--	75	104	89	--	--	--	--
Spring Band, 82-0-0	68 ¹	76	88	77	395	382	684	487
Spring Band, 28-0-0	71	79	100	83	--	--	--	--
Spring Band, 46-0-0	65	76	85	86	379	369	658	469
Dual Band, 28-0-0	69	74	93	79	--	--	--	--
Dual Band, 46-0-0	61	87	92	80	--	--	--	--
Spoke Wheel, 28-0-0	69	71	87	76	--	--	--	--
Dribble Band, 28-0-0	86	69	106	87	--	--	--	--
Dribble Band, 46-0-0	72	70	76	73	--	--	--	--
Dribble Band, 34-0-0	66	69	90	75	--	--	--	--
Broadcast, 34-0-0	127	76	72	91	508	364	588	474
Broadcast, 46-0-0	67	78	114	87	424	327	639	463
Control-no N, no P	67	79	60	68	425	366	521	437
Control-no N, P seed-placed	72	81	84	79	569	331	538	479
Control-no N, P banded	74	124	80	93	431	338	512	427
Control-no N, no P, banding operation	67	77	72	73	--	--	--	--
<u>Contrasts</u>								
No n vs N	ns	ns	**	ns	ns	ns	**	ns
Phosphate Response	ns	**	ns	*	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	ns	--	--	--	--
Dual band vs Band	ns	ns	ns	ns	--	--	--	--
NH ₃ Band vs Urea Band	ns	ns	ns	ns	ns	ns	ns	ns
NH ₃ band vs UAN Band	ns	ns	ns	ns	--	--	--	--
34-0-0 Band vs 34-0-0 Broadcast	**	ns	ns	ns	--	--	--	--
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	*	ns	ns	ns	ns	ns
34-0-0 Broadcast vs 46-0-0 Broadcast	**	ns	**	ns	ns	ns	ns	ns
MSE	842	304	409	739	14961	3690	8583	8916

¹ Contrast made with 1993 & 1994 data only.

Table 4.15 Cd concentration and contrast analyses of canola seed and straw (selected samples) on the fine sandy loam site under zero tillage as affected by treatment in 1992-1994 and the mean of 1992-1994 inclusive.

Treatments	Seed Cd (ug kg ⁻¹)				Straw Cd (ug kg ⁻¹)			
	1992	1993	1994	Mean	1992	1993	1994	Mean
Fall Band, 82-0-0	--	68	90	79	--	--	--	--
Fall Band, 28-0-0	--	77	82	79	--	--	--	--
Fall Band, 46-0-0	--	69	87	78	--	--	--	--
Spring Band, 82-0-0	74 ¹	74	99	82	485	347	656	496
Spring Band, 28-0-0	69	66	79	71	--	--	--	--
Spring Band, 46-0-0	72	78	95	82	558	343	717	517
Dual Band, 28-0-0	84	107	87	93	--	--	--	--
Dual Band, 46-0-0	62	67	92	75	--	--	--	--
Spoke Wheel, 28-0-0	73	57	74	68	--	--	--	--
Dribble Band, 28-0-0	87	70	99	86	--	--	--	--
Dribble Band, 46-0-0	74	98	74	82	--	--	--	--
Dribble Band, 34-0-0	71	64	85	73	--	--	--	--
Broadcast, 34-0-0	57	55	60	57	516	326	568	470
Broadcast, 46-0-0	60	63	77	67	391	329	574	431
Control-no N, no P	70	76	89	78	561	420	575	519
Control-no N, P seed-placed	74	83	80	79	588	413	581	527
Control-no N, P banded	80	81	100	88	537	432	566	512
Control-no N, no P, banding operation	78	73	74	75	--	--	--	--
<u>Contrasts</u>								
No n vs N	ns	ns	ns	ns	ns	**	ns	ns
Phosphate Response	ns	ns	ns	ns	ns	ns	ns	ns
Spring Band vs Fall Band ²	--	ns	ns	ns	--	--	--	--
Dual band vs Band	ns	ns	ns	ns	--	--	--	--
NH3 Band vs Urea Band	ns	ns	ns	ns	ns	ns	ns	ns
NH3 band vs UAN Band	ns	ns	ns	ns	--	--	--	--
34-0-0 Band vs 34-0-0 Broadcast	ns	ns	*	**	--	--	--	--
46-0-0 Band vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	*
34-0-0 Broadcast vs 46-0-0 Broadcast	ns	ns	ns	ns	ns	ns	ns	ns
MSE	121	210	285	290	28038	2274	7010	12156

¹ Contrast made with 1993 & 1994 data only.

4.4.1.2 Phosphorus. Cd content of wheat grain was not influenced by the presence and/or placement of phosphorus fertilizer (Table 4.16). The Cd concentration varied little with phosphorus application, and placement of P had no effect on Cd concentration. The physical effect of a banding operation to the plot showed little effect on wheat grain Cd levels, although in some cases this treatment gave the lowest concentrations.

Table 4.16 Cd content of wheat grain on two soil types as influenced by phosphorus presence and placement, from 1992-1994.

<u>Treatment</u>	<u>Newdale CL</u>			<u>Marringhurst FSL</u>		
	1992	1993	1994	1992	1993	1994
No N, No P	40ab ¹	67a	89a	42a	92a	105b
No N, P seed-placed	45a	69a	94a	59a	100a	124ab
No N, P banded	42ab	71a	92a	54a	97a	133a
No N, No P, with banding operation	33b	64a	75a	53a	80a	132a
MSE	67	97	130	332	332	265

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

4.4.2 Tillage and Soil Type

On the clay loam soil, yield of wheat and canola was higher under conventional than zero tillage (Figure 4.2). On the fine sandy loam soil the differences in yield between tillage systems were not as large. On both tillage systems, yield of wheat increased from 2 to nearly 4 tonnes from 1992 to 1994 on the clay loam soil. Lower yields in 1992, with the exception of wheat on the fine sandy loam soil, may have been due to an early fall frost. In contrast, seed yield of canola on both soils increased only slightly from about 1.8 to nearly 2 tonnes from 1992 to 1994.

No treatment by tillage interaction occurred for Cd content in wheat grain or canola seed on the clay loam soil (Table 4.3), therefore data was combined across treatments. There was a significant interaction of treatment*tillage on the fine sandy loam soil, however overall the effect of tillage on grain Cd concentration was only significant at $p = 0.0986$. On both soils Cd concentrations in wheat were consistently higher in conventional tillage than in zero tillage (Figure 4.3a). Concentration of Cd in canola was not significantly affected by tillage, although concentrations tended to be slightly higher under conventional tillage (Figure 4.3b). Contrast analyses indicated a few significant differences between fertilizer treatments (Tables 4.5,4.6,4.8,4.9). However, no pattern of treatment by tillage interactions for either tillage system was observed.

Year to year variation was apparent; there was almost a three-fold increase in Cd concentration from 1992 to 1994 in wheat (Figure 4.3) which appears to be related to a corresponding increase in crop yield. However, increases in Cd concentration in canola seed from 1992 to 1994 were not as large as those seen in wheat. At the fine sandy loam site there were only slight increases in canola seed Cd concentration from year to year. The Cd concentrations tended to be higher on the fine sandy loam even though both sites had approximately the same Cd levels in the soil. Concentrations of Cd in wheat ranged from about 45 to 180 $\mu\text{g kg}^{-1}$ depending on the site and year, while Cd levels in canola were lower, and varied from around 35 to 90 $\mu\text{g kg}^{-1}$.

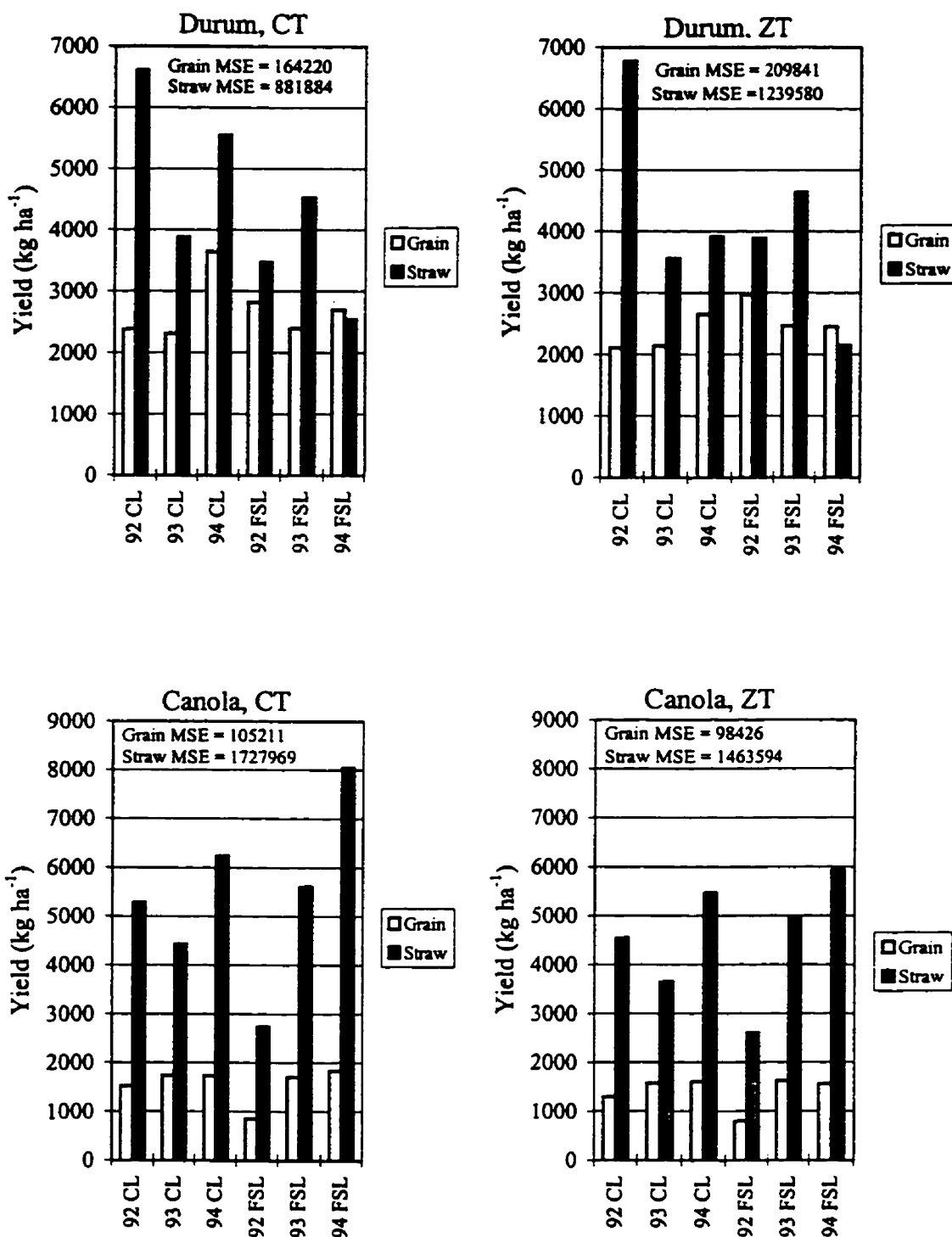


Figure 4.2 Seed and straw yield of durum wheat and canola as affected by soil type (CL = clay loam and FSL = fine sandy loam) and year, under conventional (CT) and zero tillage (ZT) for the years 1992-1994 inclusive.

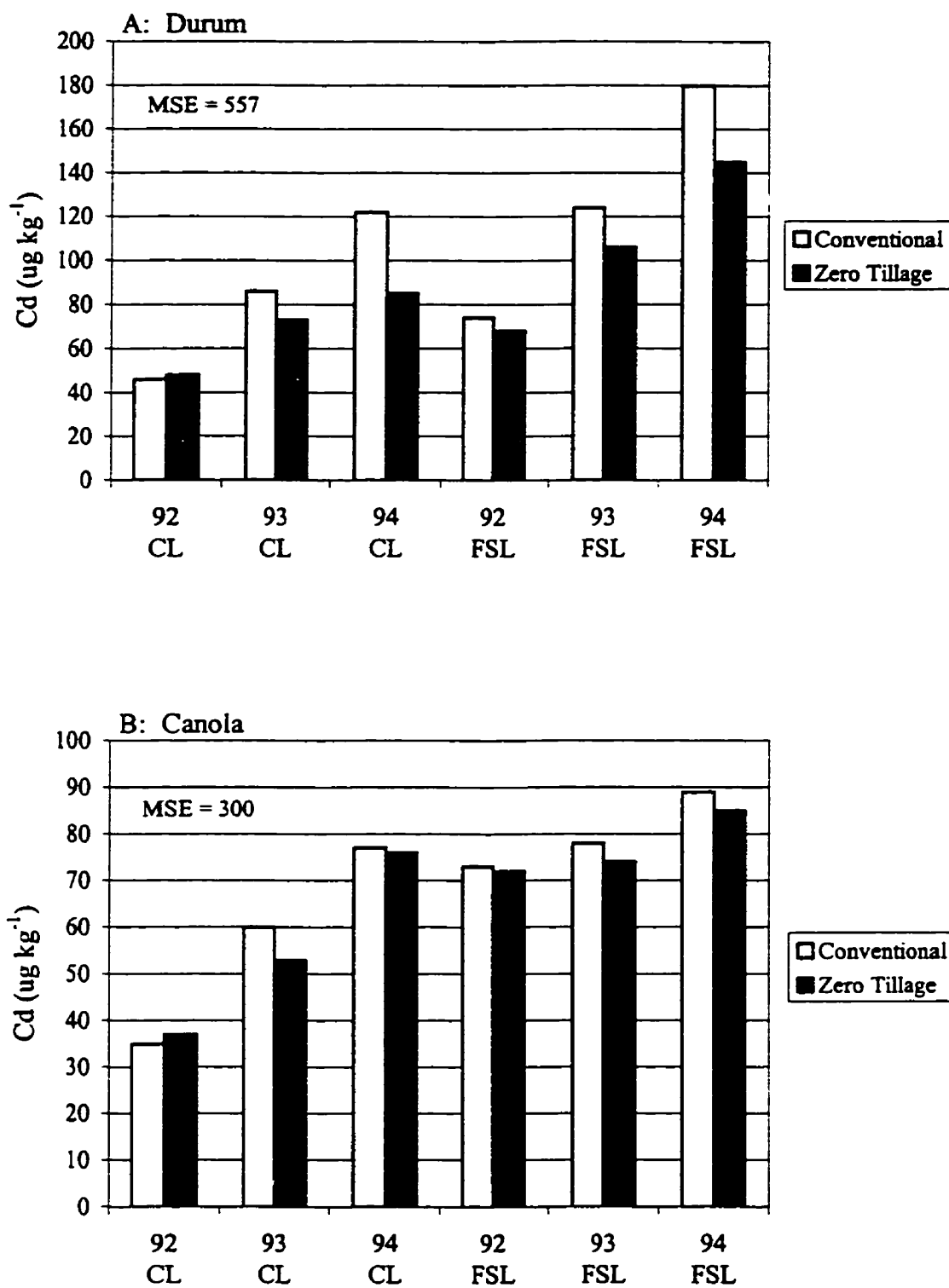


Figure 4.3 Grain Cd concentration as affected by year and soil type (CL = clay loam and FSL = fine sandy loam) in durum wheat (A) and canola (B).

4.5 Discussion

In five out of six site-years, application of nitrogen fertilizers to wheat significantly increased Cd concentration in both straw and grain over that of the control. Similar results were found by Eriksson (1990) and Grant et al. (1996). Application of nitrogen fertilizers can decrease the pH of the soil solution, possibly causing increased Cd phytoavailability. Lutz et al. (1977) found that applications of acid-forming fertilizers may affect the plant root environment, as in some soils high nitrate and electrolyte concentrations in the soil solution were accompanied by lower pH. This resulted in increased Al and Mn concentrations in the soil solution. The application of nitrate fertilizers, as well as ammonium-based fertilizers which are subsequently nitrified, will effect changes in soil solution. The impact of fertilizers on ionic strength of the soil solution will as well as the higher buffering capacity of soils in the present study may have influenced Cd uptake more than the effect of pH. In a pot experiment where changes of Cd and Zn in soil solution were studied over time, Lorenz et al. (1994) found excess fertilizers caused substantial increases of these metals as well as other cations in solution. As concentrations of Cd and Zn increased in soil solution, concentrations in the plants increased as well. In pot experiments Brown et al. (Chapter 1) found increasing nitrogen rate, for several types of N fertilizers, increased Cd concentration in the grain. Plants that have been fertilized may be growing more vigorously than unfertilized plants and may be able to access more Cd in the soil. As yield increased Cd concentration wasn't diluted but instead increased, and thus total uptake of Cd was greater from high yielding plots.

Contrast analyses indicated there were significant differences among fertilizers and application methods affecting Cd concentrations in both wheat grain or straw. In addition, patterns existed among treatments that were fairly consistent from year to year and site to site. Fall and spring banded fertilizers tended to produce the highest Cd concentrations. In particular NH_3 produced the highest grain Cd concentrations in wheat. The ionic strengths of the different fertilizers in soil solution may have influenced the amount of Cd in solution that was taken up by the plant. As yields increased due to fertilization, Cd concentrations in both straw and grain tended to increase as well. While this relationship is one of covariance, it is essential to note that with increased yield dilution of Cd in the grain did not occur, as would be expected.

Pot studies have shown differences among N sources. In a pot experiment testing the fertilizers NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}(\text{NO}_3)_2$ and urea at $87.5 \text{ mg N kg}^{-1}$, along with $3 \text{ mg Cd (sulphate) kg}^{-1}$, in a light sandy loam, Willaert and Verloo (1992) found that $(\text{NH}_4)_2\text{SO}_4$ increased Cd concentrations in spinach leaves. In another pot experiment using NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}(\text{NO}_3)_2$ as fertilizers, Eriksson et al. (1990) showed that both extractable soil-Cd and plant Cd concentrations were highest in the $(\text{NH}_4)_2\text{SO}_4$ treatment, lowest in the $\text{Ca}(\text{NO}_3)_2$ treatment and intermediate when NH_4NO_3 was applied. Brown et al. (Chapter 1) found application of $\text{Ca}(\text{NO}_3)_2$ produced the highest Cd concentrations, followed by $(\text{NH}_4)_2\text{SO}_4$ and then urea. This indicates the effect of fertilizers on Cd concentration is not consistent and warrants further investigation.

Application of 40 kg ha^{-1} as MAP did not significantly increase Cd concentrations. This conflicts with findings from Williams and David (1973) and He and Singh (1994)

where phosphorus fertilization was shown to increase plant Cd concentration in pot experiments. The limited volume of soil available to the plant in a pot as well as the amount of Cd present as a contaminant may have influenced these results. A pot experiment by Brown et al. (Chapter 1) indicated that the addition of low rates of MAP did not increase Cd concentration in the grain. In field experiments Jeng and Singh (1995) found plant-Cd concentrations unaffected by long-term P fertilization, and Mortvedt (1987) determined that application of P fertilizers at recommended rates for >50 years did not result in increased Cd levels in corn, wheat and soybeans. The 40 kg ha⁻¹ of the MAP used, containing approximately 50 mg Cd kg⁻¹, would add about 2 grams Cd per hectare. This is substantially more Cd added to the soil system than what was removed by the crops. While the effects of phosphorus fertilizer may be negligible in the short-term, the long-term effects are cause for concern, as more Cd is being added to the soil system than is being removed by crops. The increasing Cd concentrations in wheat grain from 1992-1994 could possibly be attributed to the increasing amounts of Cd added with the fertilizers, however Cd concentration also increased in the control treatments, which received no P fertilizer. Environmental influence on Cd uptake by plants appears to have a greater effect than application of P fertilizer.

In five out of six site-years Cd concentration in wheat was lower under ZT than CT. Higher Cd concentrations under CT may be due to biocycling of Cd from the canola residue from the preceding crop. Canola has high Cd concentrations in the straw, and incorporation under CT may enhance Cd release from the residue increasing the amount of phytoavailable Cd for the next crop. This is in contrast to findings from Oliver et al.

(1993) where wheat Cd concentrations were highest when the seed was direct drilled. Oliver et al. (1993) also found the crop grown prior to wheat had highly significant effects on cadmium concentration in wheat grain. The highest wheat grain Cd concentrations occurred when the previous crop had been lupins, and they believed this was partly due to rhizosphere acidification. Under ZT the root channels of the previous crop were not disturbed, and the authors felt this may have led to greater Cd concentrations in wheat following lupins. Compaction under ZT could cause root proliferation in the surface layer, where soil was enriched with Cd from years of fertilization with high-Cd phosphorus fertilizer. Eastern Prairie soils tend not to show ZT effects of compaction due to the yearly freeze-thaw cycles. Also, slightly lower yields obtained under zero tillage may have reduced bioaccumulation, as a good relationship between yield and Cd concentration has been demonstrated.

This study consisted of a wheat-canola rotation, with wheat following a crop containing high Cd concentrations in the straw. The amount of Cd in canola straw was much higher than in wheat straw, and canola produces about 1.4 kg straw per litre of grain compared to 1.3 kg straw per litre of wheat (Manitoba Agriculture, 1993). High Cd concentrations coupled with large amounts of biomass may influence Cd levels in the next crop, whether or not the straw was incorporated in the soil or left on the surface. Andersson and Siman (1991) found Cd levels tended to be higher where crop residues were returned to the soil.

Higher concentrations of Cd in wheat grain and straw Cd were generally associated with increased yield, while responses of canola did not seem to follow any

particular pattern. Studies have shown large differences in Cd concentration and uptake patterns between species (Guo and Marschner, 1995; McLean, 1976; and Page et al., 1972).

While trends in Cd concentrations due to the various treatments were similar at each site, the mean Cd concentrations in each crop were much higher on the fine sandy loam soil than on the clay loam. This occurred in spite of the fact that both soils had similar levels of soil Cd. Similar results were found under growth chamber conditions (Brown et al., Chapter 1). He and Singh (1994) found Cd differences more pronounced in a sandy soil than a loam, and Eriksson (1990) found increases in plant Cd concentrations due to fertilizer additions higher in a sand than in a clay soil. The lower organic matter content and CEC capacity of the fine sandy loam soil may affect the amount of Cd retained by soil colloids and increase the amount in soil solution available to the plant. Thus the effect of soil type, which is an inherent property, may influence Cd levels in crops more than other factors and dominate over attempts to control Cd uptake through management decisions such as tillage and fertilizer rate and placement.

4.6 Summary and Conclusions

Cadmium concentration in wheat was increased by nitrogen application, regardless of source, timing, or placement of fertilizer. In contrast, N fertilization had no significant effect on Cd concentration in canola. As fertilizer efficiency increased, as indicated by increased yield, Cd concentration tended to increase as well, although effects were not consistently significant. This led to a much greater total uptake from some plots relative to the control.

Phosphorus applied as MAP did not influence the Cd concentration of either wheat or canola for any site-year. Nitrogen fertilization had a greater effect on Cd concentration and accumulation in crops than phosphorus, despite the fact that P contained Cd as a contaminant while N had virtually no Cd. The effect of nitrogen therefore appears to be due to effects on soil chemical factors such as pH or ionic strength, since the effects cannot be attributed to additions of Cd with fertilizer N. As well, the impact of nitrogen fertilization on plant growth and physiology may affect plant Cd concentration. Concentrations of Cd in wheat were lower under ZT than CT. Yields were slightly lower under ZT than CT, which may have influenced Cd concentrations. Cadmium concentrations in wheat increased from 1992 to 1994, perhaps due to the additive effect of high-Cd residue left from the preceding canola crop or the cumulative effect of application of Cd-containing phosphorus fertilizers to the same location for three years in a row.

5. GENERAL DISCUSSION

It was observed in both growth chamber studies and a field trial that application of nitrogen fertilizers increases Cd concentration in wheat grain. As yield also increased with fertilization, one would expect to see dilution of Cd yet we have seen the opposite. The effects of fertilizer applications on movement of Cd from the soil into the root are complex. Soil solution data may provide the most reliable means of identifying chemical factors limiting plant growth in acid soil (Curtin and Smillie, 1983), and this idea might be extrapolated to include non-acid soils as well as other chemicals that are not limiting. Since the application of nitrogen fertilizers tends to acidify the soil over time, the effects of N fertilization on Cd concentration may be due to its effect on soil solution. Bouman et al. (1995) studied soil acidification after nine years of anhydrous ammonia and urea applications to a moderately acid loam soil. They found significant acidification, especially from NH_3 , and concluded the major effect of acidification was a depletion of exchangeable Ca and Mg. Fertilizer-derived protons that are not neutralized by the H^+ balancing system of the plant react with the soil to reduce the CEC (displacing basic cations) and increase exchangeable acidity (Bouman et al., 1995). In acidic soils, free Cd^{2+} remains in solution even at high pCO_2 in the rhizosphere, and thus Cd availability to plants may be assumed to be higher (Hirsch and Banin, 1990).

Under growth chamber conditions, Cd concentration differed with source of N fertilizer. Some source and placement effects were noticed under field conditions, although results were not as consistent. The type of fertilizer used, whether ammonium- or nitrate-based, can influence the soil solution and subsequent physicochemical

reactions. Lorenz et al. (1994) found an excess of NH_4^+ ions in solution was most closely correlated with concentrations of other ions in soil solution, including Cd and Zn. In contrast to K, Ca, and Mg, increasing concentrations in soil solution of Cd and Zn were mirrored by concentrations in the plants. The authors suggested plants were able to regulate their uptake of K, Ca, and Mg better than Cd and Zn.

Soil management, such as choice of tillage system and fertilizer placement, affects soil quality, which in turn influences crop productivity and quality. Our field studies have shown Cd concentration was consistently higher under CT as compared to ZT. The effects of tillage on yield may also influence Cd concentration, as we saw treatments which produced higher yields also produced higher Cd concentrations. The effects of tillage on soil structure and related chemical and biological components of soil quality are complicated. Nutrient availability under no-till systems can be influenced as aggregate size and structure are influenced by mechanical mixing of the soil. The macropores surrounding aggregates provide very conductive channels that act as sources for water uptake and solute transfer for the aggregates when full of water, but become practically non-conductive and barriers to the transport of water and solutes when dry (Youngs et al., 1994). Thus mass flow of nutrients to the root surface may be affected by tillage system, and uptake of elements such as Cd in soil solution can be influenced. Increased root exudation under mechanical impedance may also reduce the activity in the rhizosphere of certain toxic elements such as aluminum (Goss et al., 1993). This process could affect other elements like Cd as well. Increased penetration resistance, which can occur under no-till systems, may increase the release of exudates which could complex with cadmium

and reduce its availability to the plant. This may have influenced Cd uptake and account for the differences in Cd concentration between CT and ZT in our study.

When chemical and physical properties of the soil are influenced through fertilizer application or tillage practises, root growth may be affected. Elongation of roots is associated with proton release into the cell wall and its subsequent movement to the root surface (Goss et al., 1993). In this way the availability to the roots of mineral nutrients, and other elements such as Cd, could be affected by pH changes. Root growth relative to shoot growth may be reduced by applying nitrogen, yet the total root weight will be increased (Goss et al., 1993). As well, the total length of the root system tends to increase. Increased uptake of nutrients due to root hairs is associated with the small radius of the root hairs, the increased surface for absorption, and the increased volume of the soil accessed (Goss et al., 1993). The presence of mycorrhizal fungus on the root could account for increased nutrient uptake in similar ways, especially as infection by the fungus increases the surface area of the root. Clarkson (1985), states the roots of some species are capable of modifying soil structure directly and increasing nutrient availability by improving soil/root contact and by chemical extraction. Increased nutrient acquisition can also be accompanied by influx of other elements such as Cd. The differences in root growth between canola and wheat may account for the differences in Cd uptake by these species in our study.

Specific reactions involving cadmium are currently under investigation as more needs to be understood about movement of Cd from the soil solution into the root system. Due to its similarity to calcium (i.e. charge, ionic radius), we may look to physiological

processes involving Ca to suggest possible uptake mechanisms for Cd. In spite of ample supplies of calcium in the soil solution, plant uptake is limited because it can only be absorbed by young root tips where the cell walls of the endodermis are unsuberized (Tisdale et al., 1985). Contrary to most ions where a zone of depletion will develop around the root, some such as Ca^{2+} may accumulate because transport by mass flow can exceed uptake (Goss et al., 1993). The relationship between Cd and Ca is complex as Ca may increase Cd availability (Christensen, 1984), or decrease Cd solubility through precipitation of CdCO_3 from calcite surfaces (McBride, 1980; Hirsch and Banin, 1990). Application of $\text{Ca}(\text{NO}_3)_2$ fertilizer in growth chamber studies increased Cd concentration compared to other fertilizers, possibly due to exchange of Ca^{2+} with Cd^{2+} .

6. SUMMARY AND CONCLUSIONS

Studies were conducted to determine the effects of management practises, including fertilizer source, rate, and placement, as well as tillage systems on the uptake of Cd and subsequent concentration in plant tissue. Application of nitrogenous fertilizers significantly increased Cd concentration in wheat and canola seed compared to the control. Growth chamber experiments indicated that as the supply of nitrogen to the plant increased, Cd concentration in tissues increased as well. The source of the nitrogen significantly affected wheat Cd concentrations in growth chamber studies and to a much lesser extent in field trials. Fertilizer nitrogen did not influence Cd concentration in canola; in fact, the control plants sometimes had the highest Cd concentrations, indicating possible dilution by yield. Choice of tillage systems may also significantly affect Cd concentrations in crops. In our field study, zero tillage caused lower Cd concentrations in wheat than conventional tillage in 5 out of 6 site-years. These results may have been influenced by residue management of the preceding crop. Canola has very high Cd levels in its leaves and stems. Residue incorporation and phytoavailability of the cadmium in the residue could affect levels of plant-available Cd in the soil. Yields were slightly lower under zero-tillage which could influence the size of the plants' root systems and their capability to access Cd in the soil.

Significant year-to-year and site-to-site variation were observed in the field study. Since we cannot control this type of variability we must try to understand it as much as possible. The identical crop grown two years in a row on the same soil can have vastly difference Cd concentrations in the grain. This could have significant economic impact

due to WHO/FAO proposed trade limits set for Cd levels in cereal grains.

7. CONTRIBUTION TO KNOWLEDGE

Durum wheat is an important crop for Western Canadian producers. In the last ten years an average of 2.6 million tonnes of wheat is exported yearly from Canada, and in the 1994/95 crop year close to 4 million tonnes were exported to other countries (Canada Grains Council, 1996). At a cost of approximately \$275 tonne⁻¹ (#1 high protein CWAD), this represents an extremely valuable economic crop. Due to the proposed export limits of 0.1 mg kg⁻¹ suggested by Codex Alimentarius, we must be concerned that the quality and integrity of this crop is threatened in international markets. Research has been conducted to investigate wheat Cd levels and how they can be maintained or lowered to comply with the proposed export limits.

We have examined the effect of certain management practises on Cd concentration in wheat grain. From our growth chamber studies it is clearly evident that increasing nitrogen supply to the crop will increase Cd concentration in the grain. Growth chamber experiments indicated a significant difference in Cd concentrations among fertilizer sources, and in the field we saw this to a lesser extent. The fertilizers which tended to have better efficiency and produce higher yields also caused higher Cd concentrations in grain. Our field trials indicated that Cd concentrations in wheat were consistently lower under zero tillage than under conventional tillage. This may be related to the slightly lower yields we obtained with no-till, but crop rotation and residue management may be critical in determining the amount of Cd available to the crop during the next growing season. We observed the effect of different soil types, both with similar DTPA-TEA extractable Cd levels and fairly close geographically, on Cd concentrations in

wheat grain. The fine sandy loam site produced significantly higher Cd concentrations in the grain than the clay loam site. While yields were slightly better on the fine sandy loam and may have influenced Cd uptake, the physical and chemical properties each soil have contributed to the differences as well. Finally, we have noted a large yearly variation in Cd concentrations for the same crop on the same land. That the Cd concentrations steadily increased from 1992 to 1994 could be a coincidence, but could also indicate a build-up of plant-available Cd due to our choice of crop rotation. This demonstrates the difficulty of meeting the proposed export limit of 0.1 mg kg^{-1} in grain, as sites less than fifty km apart can exhibit a large variability in Cd concentration over just a few seasons. Should the Canadian farmer be forced to conform to an export limit of 0.1 mg kg^{-1} for wheat, intensive management of crop type, rotation, soil fertility, and tillage practises will be necessary to maintain grain Cd at acceptable levels.

8. REFERENCES

- Alloway, B.J. 1990. *Heavy metals in soils*. Halstead Press. New York, NY. 124 pp.
- Andersson, A. and G. Siman. 1991. Levels of Cd and some other trace elements in soils and crops as influenced by lime and fertilizer level. *Acta Agric. Scand.* 41: 3-11.
- Anonymous. 1992. *Guide to Chemical Control of Weeds and Plant Diseases*. Manitoba Agriculture. Winnipeg, MB. 147pp.
- Anonymous. 1993. *Guide to Crop Protection*. Manitoba Agriculture. Winnipeg, MB. 193 pp.
- Anonymous. 1994. *Guide to Crop Protection*. Manitoba Agriculture. Winnipeg, MB. 193 pp.
- Asimov, I. 1969. *Words from the Myths*. NAL Penguin Inc., New York, N.Y. 143pp.
- Association of Official Agricultural Chemists. 1965. *Official Methods of Analysis of the Association of Official Agricultural Chemists*. 10th edition. AOAC, Washington, D.C. 957 pp.
- Aylett, B.J. 1979. The chemistry, biochemistry and biology cadmium. *Topics in environmental health*. Elsevier/North-Holland Biomedical Press. New York, NY. 43 pp.
- Backes, C.A., McLaren, R.G., Rate, A.W., and R.S. Swift. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Sci. Soc. Am. J.* 59: 778-785.
- Baerug, R. and B.R. Singh. 1990. Cadmium levels in soils and crops after long-term use of commercial fertilizers. *Nor. J. Agric. Sci.* 4: 251-260.
- Barrow, N.J., Gerth, J. and G.W. Brummer. 1989. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modelling the extent and rate of reaction. *J. Soil Sci.* 40: 437-450.
- Bartolf, M., Brennan, E., and C.A. Price. 1980. Partial characterization of a cadmium-binding protein from the roots of cadmium-treated tomato. *Plant Physiol.* 66: 438-441.
- Basta, N.T. and M.A. Tabatabai. 1992c. Effect of cropping systems on adsorption of metals by soils: III. Competitive adsorption. *Soil Sci.* 153(4): 331-337.

- Basta, N.T. and M.A. Tabatabai. 1992b. Effect of cropping systems on adsorption of metals by soils: II. Effect of pH. *Soil Sci.* 153(3): 195-204.
- Bingham, F.T., Sposito, G., and J.E. Strong. 1986. The effect of sulphate on the availability of cadmium. *Soil Sci.* 141(2): 172-177.
- Bittell, J.E. and R.J. Miller. 1974. Lead, cadmium, and calcium selectivity coefficients on a montmorillonite, illite, and kaolinite. *J. Environ. Qual.* 3(3): 250-253.
- Boggess, S.F., Willavize, S., and D.E. Koeppe. 1978. Differential responses of soybean varieties to soil cadmium. *Agr. Journal.* 70: 756-760.
- Bokhari, U. G., Coleman, D. C., and A. Rubink. 1979. Chemistry of root exudates and rhizosphere soils of prairie plants. *Can. J. Bot.* 57: 1473-1477.
- Bollag, J.-M. and J. Czaban. 1989. Effect of microorganisms on extractability of Cd from soil with NaOH and DTPA. *J. Soil Sci.* 40: 451-459.
- Bollag, J.-M. and W. Barabasz. 1979. Effect of heavy metals on the denitrification process in soil. *J. Environ. Qual.* 8(2): 196-201.
- Bouman, O.T., Curtin, D., Campbell, C.A., Biederbeck, V.O., and H. Ukrainetz. 1995. Soil acidification from long-term use of anhydrous ammonia and urea. *Soil Sci. Soc. Am. J.* 59: 1488-1494.
- Brandle, J. E., Labbe, H., Hattori, J., and B. L. Miki. 1993. Field performance and heavy metal concentration of transgenic flue-cured tobacco expressing a mammalian metallothionein-B-glucuronidase gene fusion. *Genome.* 36: 255-260.
- Brown, S. L., Chaney, R. L., Angle, J. S., and A. J. M. Baker. 1995. Zinc and cadmium uptake by hyperaccumulator *Thlaspi caerulescens* grown in nutrient solution. *Soil Sci. Soc. Am. J.* 59: 125-133.
- Brown, S. M. and T. J. Overcamp. 1991. A simple model for cadmium uptake for crops. 46th Purdue Industrial Waste Conference Proceedings. 46: 379-384.
- Buchter, B., Hinz, C., Gfeller, M., and H. Fluhler. 1996. Cadmium transport in an unsaturated stony subsoil monolith. *Soil Sci. Soc. Am. J.* 60: 716-721.
- Campbell, C.A., Biederbeck, V.O., Zentner, R.P., and G.P. Lafond. 1991a. Effect of crop rotations and cultural practices on soil organic matter, microbial biomass and respiration in a thin Black Chernozem. *Can. J. Soil Sci.* 71: 363-376.

Canada Grains Council. 1996. Canadian Grains Industry Statistical Handbook. Winnipeg, MB. 257 pp.

Candelaria, L. M., Chang, A. C., and C. Amrhein. 1995. Measuring cadmium ion activities in sludge-amended soils. *Soil Sci.* 159(3): 162-175.

Cataldo, D. A., Garland, T. R., and R. E. Wildung. 1983. Cadmium uptake kinetics in intact soybean plants. *Plant Physiol.* 73: 844-848.

Chanmugathas, P. and J.-M. Bollag. 1987. Microbial mobilization of cadmium in soil under aerobic and anaerobic conditions. *J. Environ. Qual.* 16(2): 161-167.

Chanmugathas, P. and J.-M. Bollag. 1987. Microbial role in immobilization and subsequent mobilization of cadmium in soil suspensions. *Soil Sci. Soc. Am. J.* 51: 1184-1191.

Choudhary, M., Bailey, L.D., and C. A. Grant. 1994. Effect of zinc on cadmium concentration in the tissue of durum wheat. *Can. J. Plant Sci.* 74: 549-552.

Christensen, T. H. 1984a. Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. *Water, Air, Soil Pollut.* 21: 105-114.

Christensen, T. H. 1984b. Cadmium soil sorption at low concentrations: II. Reversibility, effect of changes in solute composition, and effect of soil aging. *Water, Air, Soil Pollut.* 21: 115-125.

Clarkson, D.T. 1985. Factors affecting mineral nutrient acquisition by plants. In: *Ann. Rev. Plant Physiol.* 36: 77-115.

Costa, G. and J.L. Morel. 1994. Efficiency of H⁺-ATPase activity on cadmium uptake by four cultivars of lettuce. *J. Plant Nut.* 17(4): 627-637.

Cutler, J. M. and D. W. Rains. 1974. Characterization of cadmium uptake by plant tissue. *Plant Physiol.* 54: 67-71.

Dabeka, R.W. and A.D. M^cKenzie. 1992. Total diet study of lead and cadmium in food composites: preliminary investigations. *J. AOAC Int.* 75(3): 386-395.

De Boo, W. 1990. Cadmium in agriculture. *Tox. and Environ. Chem.* 27: 55-63.

Drees, L.R., Karathanasis, A.D., Wilding, L.P., and R.L. Blevins. 1994. Micromorphological characteristics of long-term no-till and conventionally tilled soils. *Soil Sci. Soc. Am. J.* 58: 508-517.

- Dudas, M.J. and S. Pawluk. 1977. Heavy metals in cultivated soils and in cereal crops in Alberta. *Can. J. Soil Sci.* 57: 329-339.
- El-Falaky, A. A., Aboulroos, S. A., and W. L. Lindsay. 1991. Measurement of cadmium activities in slightly acidic to alkaline soils. *Soil Sci. Soc. Am. J.* 55: 974-979.
- El-Kherbawy, M., Angle, J.S., Heggo, A., and R.L. Chaney. 1989. Soil pH, rhizobia, and vesicular-arbuscular inoculation effects on growth and heavy metal uptake of alfalfa (*Medicago sativa* L.). *Biol. Fertil. Soils.* 8: 61-65.
- Elliot, H. A., Liberati, M. R., and C. P. Huang. 1986. Competitive adsorption of heavy metals by soils. *J. Environ. Qual.* 15(3): 214-219.
- Eriksson, J. E. 1988. The effects of clay, organic matter and time on adsorption and plant uptake of cadmium added to the soil. *Water Air Soil Pollut.* 40: 359-373.
- Eriksson, J. E. 1989. The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil. *Water Air Soil Pollut.* 48: 317-335.
- Eriksson, J. E. 1990. A field study on factors influencing Cd levels in soils and in grain of oats and winter wheat. *Water Air Soil Pollut.* 53: 69-81.
- Eriksson, J. E. 1990. Effects of nitrogen-containing fertilizers on solubility and plant uptake of cadmium. *Water Air Soil Pollut.* 49: 355-368.
- Florijn, P.J. and M.L. van Beusichem. 1993. Uptake and distribution of cadmium in maize inbred lines. *Plant and Soil.* 150: 25-32.
- Florijn, P. J., Nelemans, J. A., and M. L. van Beusichem. 1992. The influence of the form of nitrogen nutrition on uptake and distribution of cadmium lettuce varieties. *J. Plant Nutrit.* 15(11): 2405-2416.
- Fu, G. F., Allen, H. E., and C. E. Cowan. 1991. Adsorption of cadmium and copper by manganese oxide. *Soil Sci.* 152(2): 72-81.
- Garcia-Miragaya, J. and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. *Soil Sci. Soc. Am. J.* 40: 658-663.
- Garrett, R. G. 1994. The distribution of cadmium in A horizon soils in the prairies of Canada and adjoining United States. *Current Research 1994-B*; Geological Survey of Canada: 73-82.

- Gerritse, R. G. and W. Van Driel. 1984. The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. *J. Environ. Qual.* 13(2): 197-204.
- Gerritse, R.G., Van Driel, W., Smilde, K.W., and B. Van Luit. 1983. Uptake of heavy metals by crops in relation to their concentration in soil solution. *Plant and Soil.* 75: 393-404.
- Giordano, P. M., Mays, D. A., and A. D. Behel, Jr. 1979. Soil temperature effects on uptake of cadmium and zinc by vegetables grown on sludge-amended soil. *J. Environ. Qual.* 8(2): 233-236.
- Girling, C.A. and P.J. Peterson. 1981. The significance of the cadmium species in uptake and metabolism in crop plants. *J. Plant Nutr.* 3(1-4): 707-720.
- Goss, M.J., Miller, M.H., Bailey, L.D., and C.A. Grant. 1993. Root growth and distribution in relation to nutrient availability and uptake. *Eur. J. Agron.* 2(2): 57-57.
- Grant, C.A., and L.D. Bailey. 1997. Effects of Phosphorus and Zinc Fertiliser Management on Cadmium Accumulation in Flaxseed. *J. Sci. Food Agric.* 73: 307-314.
- Grant, C.A., Bailey, L.D. and M.C. Therrien. 1996. The effect of N, P and KCl fertilizers on grain yield and Cd concentration of malting barley. *Fert. Res.* 45: 153-161.
- Guo, Y. and H. Marschner. 1995. Uptake, distribution, and binding of cadmium and nickel in different plant species. *J. Plant Nutr.* 18(12): 2691-2706.
- Guttormsen, G., Singh, B.R., and A.S. Jeng. 1995. Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH. *Fert. Res.* 41: 27-32.
- Haghiri, F. 1973. Cadmium uptake by plants. *J. Environ. Qual.* 2(1): 93-96.
- Haghiri, F. 1974. Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. *J. Environ. Qual.* 3(2): 180-183.
- Hahne, H.C.H. and W. Kroontje. 1973. Significance of pH and chloride concentration on behaviour of heavy metal pollutants: mercury(II), cadmium(II), zinc(II), and lead(II). *J. Environ. Quality.* 2(4): 444-450.
- He, Q.B. and B.R. Singh. 1993a. Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. *J. Soil Sci.* 44: 641-650.
- He, Q.B. and B.R. Singh. 1993b. Plant availability of cadmium in soils. I. Extractable cadmium in newly and long-term cultivated soils. *Acta Agric. Scand.* 43: 134-141.

- He, Q.B. and B.R. Singh. 1993c. Plant availability of cadmium in soils. II. Factors related to the extractability and plant uptake of cadmium in cultivated soils. *Acta Agric. Scand.* 43: 142-150.
- He, Q.B. and B.R. Singh. 1994a. Crop uptake of cadmium from phosphorus fertilizers: I. Yield and cadmium content. *Water, Air, Soil Pollut.* 74: 251-265.
- He, Q.B. and B.R. Singh. 1994b. Crop uptake of cadmium from phosphorus fertilizers: II. Relationship with extractable cadmium. *Water, Air, Soil Pollut.* 74: 267-280.
- He, Q.B. and B.R. Singh. 1995. Cadmium availability to plants as affected by repeated applications of phosphorus fertilizers. *Acta. Agric. Scand. Sect. B, Soil and Plant Sci.* 45: 22-31.
- Hemkes, O.J., Kemp, A., and L.W. van Broekhoven. 1983. Effects of applications of sewage sludge and fertilizer nitrogen on cadmium and lead contents of grass. *Neth. J. Agric. Sci.* 31: 227-232.
- Hirsch, D. and A. Banin. 1990. Cadmium speciation in soil solutions. *J. Environ. Qual.* 19: 366-372.
- Holm, P.E., Anderson, B.B.H., and T. H. Christensen. 1996. Cadmium solubility in aerobic soils. *Soil Sci. Soc. Am. J.* 60: 775-780.
- Holmgren, G. G. S., Meyer, M. W. , Chaney, R. L., and R. B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. *J. Environ. Qual.* 22: 335-348.
- Hooda, P. S. and B. J. Alloway. 1993. Effect of time and temperature on the bioavailability of Cd and Pb from sludge-amended soils. *J. Soil Sci.* 44: 97-110.
- Jeng, A.S. and B. R. Singh. 1993. Partitioning and distribution of cadmium and zinc in selected cultivated soils in Norway. *Soil Sci.* 156(4): 240-250.
- Jeng, A.S. and B.R. Singh. 1995. Cadmium status of soils and plants from a long-term fertility experiment in southeast Norway. *Plant and Soil.* 175: 67-74.
- Jing, J. and T. L. Logan. 1992. Effects of sewage sludge cadmium concentration on chemical extractability and plant uptake. *J. Environ. Qual.* 21: 73-81.
- Kabata-Pendias, A. and H. Pendias. 1992. *Trace elements in soils.* CRC Press. Boca Raton, FL.

- Karlen, D.L., Wollenhaupt, N.C., Erbach, D.C., Berry, E.C., Swan, J.B., Eash, N.S., and J.L. Jordahl. 1994. Long-term tillage effects on soil quality. *Soil and Till. Res.* 32: 313-327.
- Kaushik, R.D., Gupta, V.K. and J.P. Singh. 1993. Distribution of zinc, cadmium, and copper forms in soils as influenced by phosphorus application. *Arid Soil Res. and Rehab.* 7: 163-171.
- Kneer, R. and M. H. Zenk. 1992. Phytochelatins protect plant enzymes from heavy metal poisoning. *Phytochemistry.* 31(8): 2663-2667.
- Kojo, M.R. and M. Lodenius. 1989. Cadmium and mercury in macrofungi - mechanisms of transport and accumulation. *Angew. Bot.* 63: 279-292.
- Korcak, R. F., and D. S. Fanning. 1985. Availability of applied heavy metals as a function of type of soil material and metal source. *Soil Sci.* 140(1): 23-34.
- Korte, N.E., Skopp, J., Fuller, W.H., Niebla, E.E. and B.A. Alesii. 1976. Trace element movement in soils: influence of soil physical and chemical properties. *Soil Sci.* 122:350-359.
- Kuboi, T., Noguchi, A., and J. Yazaki. 1987. Relationship between tolerance and accumulation characteristics of cadmium in higher plants. *Plant and Soil.* 104: 275-280.
- Lagerwerff, J. V. 1971. Uptake of cadmium, lead, and zinc by radish from soil and air. *Soil Sci.* 111(2): 129-133.
- Lepp, N.W. 1992. Uptake and accumulation of metals in bacteria and fungi. *Biogeochemistry of Trace Metals.* 277-298.
- Levi-Minzi, R. and G. Petruzzelli. 1984. The influence of phosphate fertilizers on Cd solubility in soil. *Water, Air, and Soil Pollution.* 23: 423-429.
- Lighthart, B., Baham, J., and V. V. Volk. 1983. Microbial respiration and chemical speciation in metal-amended soils. *J. Environ. Qual.* 12(4): 543-548.
- Lorenz, S. E., Hamon, R. E., McGrath, S. P., Holm, P. E., and T. H. Christensen. 1994. Applications of fertilizer cations affect cadmium and zinc concentrations in soil solutions and uptake by plants. *Eur. J. Soil Sci.* 45: 159-165.
- Lund, N.J., Betty, E.E., Page, A.L. and R.A. Elliott. 1981. Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation. *J. Environ. Qual.* 10(4): 551-556.

- Lutz, J.A. Jr., Kroontje, W., and H.C.H. Hahne. 1977. Nitrogen Fertilization: II. Effect on the soil solution composition, acidity, and nitrate adsorption. *Soil Sci. Soc. Am. J.* 41: 568-572.
- Mahler, R. J., Bingham, F. T., and A. L. Page. 1978. Cadmium-enriched sewage sludge application to acid and calcareous soils: effect on yield and cadmium uptake by lettuce and chard. *J. Environ. Qual.* 7(2): 274-281.
- Maiti, I.B., Wagner, G.B., Yeagen, R., and A.G. Hunt. 1989. Inheritance and expression of mouse metallothionein gene in tobacco. *Plant Physiol.* 91: 1020-1024.
- Manitoba Agriculture. 1993. *Crop Residue Facts*. Handling crop residue produced at harvest. Winnipeg, MB. 3pp.
- Marschner, B., Stahr, K., and M. Renger. 1992. Lime effects on pine forest floor leachate chemistry and element fluxes. *J. Environ. Qual.* 21: 410-419.
- M^cBride, M.B. 1980. Chemisorption of Cd²⁺ on calcite surfaces. *Soil Sci. Soc. Am. J.* 44: 26-28.
- M^cBride, M. B., Tyler, L. D., and D. A. Hovide. 1981. Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. *Soil Sci. Soc. Am. J.* 45: 739-744.
- M^cKeague, J.A. 1981. *Manual on Soil Sampling and Methods of Analysis*. 2nd edition. Canadian Society of Soil Science, Ottawa, ON.
- M^cLean, A.J. 1976. Cadmium in different plant species and its availability in soils as influenced by organic matter and additions of lime, P, Cd, and Zn. *Can J. Soil Sci.* 56: 129-138.
- M^cLaughlin, M.J., Maier, N.A., Freeman, K., Tiller, K.G., Williams, C.M.J., and M.K. Smart. 1995. Effect of potassic and phosphatic fertilizer type, fertilizer Cd concentration and zinc rate on cadmium uptake by potatoes. *Fert. Res.* 40: 63-70.
- Mench, M. and E. Martin. 1991. Mobilization of cadmium and other metals from two soils by root exudates of *Zea mays* L., *Nicotiana tabacum* L. and *Nicotiana rustica* L. *Plant and soil.* 132: 187-196.
- Mills, J.G. and M.A. Zwarich. 1975. Heavy metal content of agricultural soils in Manitoba. *Can. J. Soi Sci.* 55:295-300.

Mitchell, G. A., Bingham, F. T., and A. L. Page. 1978. Yield and metal composition of lettuce and wheat grown on soils amended with sewage sludge enriched with cadmium, copper, nickel, and zinc. *J. Environ. Qual.* 7(2): 165-171.

Moraghan, J. T. 1993. Accumulation of cadmium and selected elements in flax seed grown on a calcareous soil. *Plant and Soil.* 150: 61-68.

Morselt, A.F.W., Smits, W.T.M., and T. Limonard. 1986. Histochemical demonstration of heavy metal tolerance in ectomycorrhizal fungi. *Plant and Soil.* 96: 417-420.

Mortvedt, J. J. and G. Osborn. 1982. Studies on the chemical form of cadmium contaminants in phosphate fertilizers. *Soil Sci.* 134(3): 185-192.

Mortvedt, J. J., Mays, D. A., and G. Osborn. 1981. Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers. *J. Environ. Qual.* 10(2): 193-197.

Mortvedt, J. J. 1987. Cadmium levels on soils and plants from some long-term soil fertility experiments in the United States of America. *J. Environ. Qual.* 16(2): 137-142.

Mulla, D. J., Page, A. L., and T. J. Gange. 1980. Cadmium accumulations and bioavailability in soils from long-term phosphorus fertilization. *J. Environ. Qual.* 9(3): 408-412.

Naidu, R., Bolan, N. S., Kookan, R. S., and K. G. Tiller. 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Eur. J. Soil Sci.* 45: 419-429.

Nakhone, L. N. and S. D. Young. 1993. The significance of (radio-) labile cadmium pools in soil. *Environ. Pollut.* 82: 73-77.

National Research Council Canada, Associate Committee on Scientific Criteria for Environmental Quality. 1979. Effects of cadmium in the Canadian environment. 148pp.

Oliver, D. P., Schultz, J. E., Tiller, K. G., and R. H. Merry. 1993. The effect of crop rotations and tillage practices on cadmium concentration in wheat grain. *Aust. J. Agric. Res.* 44: 1221-1234.

Oliver, D. P., Gore, P. J., Moss, H. J., and K. G. Tiller. 1993. Cadmium in wheat-grain and milling products from some Australian flour mills. *Aust. J. Agric. Res.* 44: 1-11.

Page, A. L., Bingham, F. T., and C. Nelson. 1972. Cadmium absorption and growth of various plant species as influenced by solution cadmium concentration. *J. Environ. Qual.* 1(3): 288-291.

Papadopoulos, P. and D. L. Rowell. 1988. The reactions of cadmium with calcium carbonate surfaces. *J. Soil Sci.* 39: 23-36.

Petruzzelli, G., Guidi, G., and L. Lubrano. 1985. Ionic strength effect of heavy metal adsorption by soil. *Commun. in Soil Sci. Plant Anal.* 16(9): 971-986.

Rausser, W. E. 1990. Phytochelatins. *Annu. Rev. Biochem.* 59: 61-86.

Reese, R. N., White, C. A., and D. R. Winge. 1992. Cadmium-sulfide crystallites in Cd-(vCE)_nG peptide complexes from tomato. *Plant Physiol.* 98: 225-229.

Rothbaum, H. P., Goguel, R. L., Johnston, A. E., and G. E. G. Mattingly. 1986. Cadmium accumulation in soils from long-continued applications of superphosphate. *J. Soil Sci.* 37: 99-107.

Salt, D.E. and G.J. Wagner. 1993. Cadmium transport across tonoplast vesicles from oat roots. *J. Bio. Chem.* 268(17): 12297-12302.

Sanchez-Camazano, M. and M. J. Sanchez-Martin. 1993. Mobility of cadmium as influenced by soil properties, studied by soil thin-layer chromatography. *J. Chrom.* 643: 357-362.

Sanders, J. R., Adams, T. M., and B. T. Christensen. 1986. Extractability and bioavailability of zinc, nickel, cadmium and copper in three Danish soils sampled 5 years after application of sewage sludge. *J. Sci. Food Agric.* 37: 1155-1164.

Singh, B. R. 1991. Unwanted components of commercial fertilisers and their agricultural effects. *Proceedings of the Fertiliser Society of London.* 312: 3-28.

Singh, B.R. and E. Steinnes. 1994. Soil and water contamination by heavy metals. *Soil processes and water quality.* Lewis Publishers. Boca Raton, FL. pp. 233-270.

Smolders, E., Lambregts, R.M., McLaughlin, M.J. and K.G. Tiller. 1995. The influence of chloride on cadmium uptake by Swiss chard (*Beta vulgaris* L. cv. Fordhook giant). I. Soil Experiments. *Proc. 3rd. Int. Conf. Biogeochem. Trace Elements, Paris.*

Sparrow, L.A., Chapman, K.S.R., Parsley, D., Hardman, P.R., and B. Cullen. 1992. Response of potatoes (*Solanum tuberosum* cv. Russet Burbank) to band-placed and broadcast high cadmium phosphorus fertilizer on heavily cropped krasnozems in north-western Tasmania. *Aus. J. Exp. Agr.* 32: 113-119.

Speiser, D. M., Abrahamson, S. L., Banuelos, G., and D. W. Ow. 1992. *Brassica juncea* produces a phytochelatin-cadmium-sulfide complex. *Plant Physiol.* 99: 817-821.

Spivey Fox, M. R. 1988. Nutritional factors that may influence bioavailability of cadmium. *J. Environ. Qual.* 17: 175-180.

Sposito, G., Bingham, F.T., Yadav, S.S. and C.A. Inouye. 1982. Trace metal complexation by fluvic acid extraction from sewage sludge: II. Development of chemical models. *Soil Sci. Soc. Am. J.* 46: 51-56.

Steffens, J. C. 1990. The heavy metal-binding peptides of plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 41: 553-575.

Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., and F.A.M. de Haan. 1995. Speciation and calcium competition effects on cadmium sorption by sandy soil at various pHs. *Eur. J. Soil Sci.* 46: 649-655.

Thomson, C.J., Marschner, H., and V. Romheld. 1993. Effect of nitrogen fertilizer form on pH of the bulk soil and rhizosphere, and on the growth, phosphorus, and micronutrient uptake of bean. *J. Plant Nutr.* 16(3): 493-506.

Tisdale, S. L., W. L. Nelson and J. D. Beaton. 1985. *Soil Fertility and Fertilizers*. MacMillan Publishing Co. New York, NY. 754pp.

Tyler, L.D. and M.B. McBride. 1982. Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns. *Soil Sci.* 134(3): 198-205.

Wagner, G. J., and M. M. Trotter. 1982. Inducible cadmium binding complexes of cabbage and tobacco. *Plant Physiol.* 69: 804-809.

Wagner, G. J. 1993. Accumulations of cadmium in crop plants and its consequences to human health. *Adv. Agron.* 51: 173-212.

Weigel, H. J. and H. J. Jager. 1980. Subcellular distribution and chemical form of cadmium in bean plants. *Plant Physiol.* 65: 480-482.

Weil, R.R., Benedetto, P.W., Sikora, L.J., and V.A. Bandel. 1988. Influence of tillage practices on phosphorus distribution and forms in three ultisols. *Agron. J.* 80: 503-509.

Weissenhorn, I. and C. Leyval. 1995. Root colonization of maize by a Cd-sensitive and a Cd-tolerant *Glomus mosseae* and cadmium uptake in sand culture. *Plant and Soil.* 175: 233-238.

Willaert, G. and M. Verloo. 1992. Effects of various nitrogen fertilizers on the chemical and biological activity of major and trace elements in a cadmium contaminated soil. *Pedologie.* 43(1): 83-91.

Williams, C.H. and D.J. David. 1976. The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. *Soil Sci.* 121(2): 86-93.

Williams, C.H. and D.J. David. 1973. The effect of superphosphate on the cadmium content of soils and plants. *Aust. J. Soil Res.* 11: 43-56.

Youngs, E.G., Leeds-Harrison, P.B., and R.S. Garnett. 1994. Water uptake by aggregates. *Eur. J. Soil Sci.* 45: 127-134.

9. APPENDICES

APPENDIX 1

note - this section has been placed here as there is some question as to the accuracy of the Cd analysis. It is believed there was some analytical error, possibly to do with dilution factors, so the Cd concentrations are a bit low, probably half as much as they should be. The experiment was designed well and carried out accurately, and any patterns among fertilizer sources or rates would still be valid but the magnitude of the Cd concentrations would be off. I felt I should include this work but do not intend to publish it.

AVAILABILITY of Cd to DURUM WHEAT and WESTERN RED SPRING WHEAT as AFFECTED by NITROGEN FERTILIZATION

I.1 Abstract

Cadmium is an element of concern as certain food crops can accumulate levels of Cd which are not toxic to the plant but may be harmful to humans. Due to high concentrations of Cd currently found in some Canadian grains and oilseeds there is a need to determine the factors responsible for the uptake and accumulation in these crops. A growth chamber study was conducted to determine the effects of rate and placement of nitrogen fertilizers on the concentration of Cd in durum wheat (*Triticum turgidum* cv. Medora). Fertilizers included urea, $\text{Ca}(\text{NO}_3)_2$, Prolong (a nitrification inhibitor), and a controlled release urea. A sub-experiment studied the effects of different rates of urea on Cd concentration in Canadian Western Red Spring wheat (*Triticum aestivum* cv. Katepwa) and DT-627, an experimental line of wheat which concentrates low levels of Cd in its tissues. Fertilizer effects were examined on an Orthic Black Chernozem (Newdale clay loam). Results indicated that increasing the supply of nitrogen to Medora durum wheat increased Cd concentration, with little variability among source of fertilizer. Use of Prolong, a nitrification inhibitor, as well as the controlled release urea did not reduce

Cd concentration in the grain. DT-627 and Katepwa wheat behaved similarly to Medora durum wheat, although concentrations of Cd in tissue were much lower at all rates of N fertilization.

I.2 Introduction

Cadmium is a heavy metal which possesses a long half-life within the human body and may cause chronic toxicity (NRCC, 1979). Food crops can accumulate levels of Cd which are potentially harmful to humans, without affecting crop yield. The FAO/WHO Expert Committee on Food Additives in 1972 suggested a maximum tolerable intake limit of 70-84 $\mu\text{g person}^{-1} \text{ day}^{-1}$. Grains and cereal products tend to be the largest dietary source of Cd. Since Cd occurs naturally in the soil and may be increased due to anthropogenic inputs (DeBoo, 1990), factors affecting crop uptake of this element need to be investigated.

Availability of Cd to the crop and the amount which accumulates in plant tissue is dependant upon soil and crop processes as well as management practises. Fertilizer source, rate, and placement will affect the timing of and amount of nitrogen available to the crop. A previous growth chamber experiment had indicated placement of nitrogen in a band decreased Cd concentration in wheat grain (Brown et al., Chapter 1). Fertilizers which delay the period over which nitrogen becomes available, whether through biological action or other means, may influence the amount of Cd which gets taken into the plant. Although they contain no appreciable Cd, nitrogen fertilizers are also reported to increase Cd concentration in wheat (Oliver, 1993), with the strength of the effect varying with N source (Eriksson, 1990).

Some studies have indicated there is an effect of nitrogen fertilization on Cd concentration in plant tissue, however little information is available on fertilizers where urea is released slowly. CWRS wheat usually has lower concentrations of grain Cd than wheat, and we were interested in its behaviour at different N rates, as well as concentration of Cd in the straw. As well, the uptake patterns of Katepwa CWRS and a low-Cd durum wheat variety, DT-627, are of interest to note whether translocation of Cd within the plant influences grain Cd levels.

I.3 Materials and Methods

I.3.1 Main Experiment

A growth chamber experiment was designed to evaluate various sources of nitrogen fertilizer as well as the effect of increasing rates of N on Cd accumulation in durum wheat (*Triticum turgidum*). Medora wheat, which accumulates moderate to high levels of Cd, was chosen as the test variety. Soil was collected from the 0-15 cm layer of a Black Chernozemic Clay Loam, air dried and sieved to pass through a 20 x 40 mm screen. 4.7 L square wooden pots (interior 15.2 cm diameter by 20.3 cm high) were lined with plastic bags and filled with 4500 g of air dry soil. Any broadcast treatments were added to the soil and mixed thoroughly. The soil was then added to pots to fill to banding depth and watered to field capacity to here by weight using distilled deionized water. Bands of fertilizer were added 2.5 cm away from the seedrow, and more soil was added to cover the bands 2.0 cm deep. The top 4.0 cm of soil was then taken to field capacity by weight using distilled deionized water. Eleven seeds were placed on each seedrow, and then soil was added to cover them to a 2.0 cm depth. When seedlings

reached the two-leaf stage they were thinned to six plants per pot. Treatments consisted of 100, 200 and 400 $\mu\text{g g}^{-1}$ of each source of nitrogen with 20 ppm S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 20 $\mu\text{g g}^{-1}$ monoammonium phosphate applied to all pots. Fertilizer grade urea (46-0-0) and reagent grade $\text{Ca}(\text{NO}_3)_2$ were used as well as two products which are designed to lengthen the time, after initial application, over which nitrogen becomes available to the crop. Prolong (32-0-0), or dicyandiamide is a commercially available product, with 26% of the N present as urea and 6% present as ammonia. It acts as a microbial inhibitor in the soil and thus slows down microbial degradation of ammonium to its other forms. The controlled release urea was an experimental product consisting of urea covered with a polymer coating. This coating acted as a physical barrier to the release of nitrogen from the fertilizer granule. The particular product used was designed to release 80% of its nitrogen over a 52 day period, and the thickness of the polymer coating gave the end product an analysis of 44.7-0-0.

Pots were watered to field capacity with distilled deionized water every other day and then daily as needed until the plants were harvested at maturity. The plants received 16 hours of light with temperatures of 22°C during the day and 15°C at night. Relative humidity was maintained at 60%. Total above ground material was dried in a Unitherm oven at 30°C and grain and tissue were separated. Grain was ground with a stainless steel Braun coffee grinder while straw was processed with a Wiley mill, both to pass through a 1 mm sieve. After wet-digestion with $\text{HNO}_3\text{-HClO}_4$, the Cd analyses were performed on the samples by a Varian 300/400 atomic absorption spectrophotometer using a graphite furnace with deuterium correction (detection limit 0.01 ng Cd mL⁻¹). Analysis of standard

samples of wheat flour with a mean concentration of $23 \mu\text{g kg}^{-1}$ had a standard error of 2.15. Other analyses were performed by an ICP or Auto Analyzer after wet-digestion with $\text{H}_2\text{SO}_4 + \text{SeO}_2$. Soil nutrients were analysed according to procedures specified by M^cKeague (1981).

I.3.2 Sub-Experiment

Within the main experiment DT-627, an experimental line of durum wheat (*Triticum turgidum*), as well as Katepwa, a western red spring wheat (*Triticum aestivum*) were grown. Urea (46-0-0) was applied to both crops at 100, 200, and $400 \mu\text{g g}^{-1}$. All other procedures were carried out as in the main experiment.

I.4 Results and Discussion

I.4.1 Main Experiment

As indicated in a previous experiment, grain Cd concentration increased regardless of N source. There was no difference in Cd accumulation in either grain or straw from source to source (Table I.1). Sources were similar in their effects on Cd concentration in grain and straw (Figure. I.1) Contrast analyses (data not shown) indicated that Prolong produced higher Cd concentrations than $\text{Ca}(\text{NO}_3)_2$ in the grain but all other contrasts among sources are not significant. The $400 \mu\text{g g}^{-1}$ Urea + CaSO_4 treatment produced higher Cd concentration than $400 \mu\text{g g}^{-1}$ Urea ($p < 0.001$), indicating that addition of CaSO_4 has positively affected the uptake of Cd into the plant. There is no difference between $400 \mu\text{g g}^{-1}$ of Urea and $400 \mu\text{g g}^{-1}$ Urea + $300 \mu\text{g g}^{-1}$ K_2SO_4 .

There was no difference in grain yield among any of the sources (Table I.1), and only slight differences among the straw yields. The two slow-release products showed

little difference between grain yields but slightly greater differences among the straw yields. As might be expected, for all fertilizer sources there was a significant increase in yield as the supply of N was increased.

I.4.2 Sub-Experiment

DT-627 and Katepwa HRSW behaved similarly regarding both grain and straw accumulation of Cd. As seen in the main experiment, increasing rates of nitrogen supplied to the plants resulted in greater concentrations of Cd. Grain Cd levels were similar while DT-627 tended to have greater concentrations of Cd in the straw, although this difference was not significant (Fig I.2). Both DT-627 and Katepwa contrasted significantly from the control when comparing grain Cd levels. Yield as influenced by N rates behaves similarly to wheat (Table I.2).

I.5 Summary

Increasing the rate of nitrogen which is applied, regardless of source, significantly increased Cd concentration in the plant. Varying the source from which N nutrition is supplied did not significantly affect the amount of Cd taken into the plant. Only Prolong and $\text{Ca}(\text{NO}_3)_2$ differed significantly from each other regarding Cd concentration. Differences among application methods, banding versus broadcasting, did not create differences in Cd uptake. Cd increased with rate to a greater degree in straw, possibly indicating that increasing rates affects translocation of Cd within the plant. Addition of high amounts of CaSO_4 increased Cd uptake in the plant, possibly related to production of cysteine-rich peptides which bind Cd, or competition of Cd^{2+} for Ca^{2+} sites. Addition of K_2SO_4 did not affect Cd accumulation.

DT-627 and Katepwa wheat behaved similarly regarding Cd accumulation in the plant. Normally durum wheats uptake greater amounts of Cd than western red spring wheat, but this experimental line contained Cd levels of the same magnitude. Straw levels of Cd between these two species are significantly different, perhaps due to differences in translocation.

Table I.1 Influence of nitrogen source and rate on Cd concentration and yield in wheat.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
Nitrogen Source				
Prolong	86a ¹	11.3b	201a	12.4c
Urea (broadcast)	75a	14.9a	205a	18.9a
CaNO ₃	66a	14.6a	191a	17.7ab
CR Urea	80a	15.1a	209a	16.4b
Urea (banded)	79a	15.6a	192a	16.9b
MSE	408	3.8	2484	3.3
Nitrogen Rate				
100 $\mu\text{g g}^{-1}$	57b	12.1c	144c	13.3c
200 $\mu\text{g g}^{-1}$	69b	14.6b	192b	16.5b
400 $\mu\text{g g}^{-1}$	106a	16.3a	266a	19.5a
MSE	408	3.8	2484	3.3
Other Treatments				
Control	55c	5.9c	97c	6.1c
Urea + K ₂ SO ₄	131b	18.4a	338b	23.3a
Urea + CaSO ₄	215a	17.5ab	563a	21.4a
MSE	454	4.1	2611	5.2

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

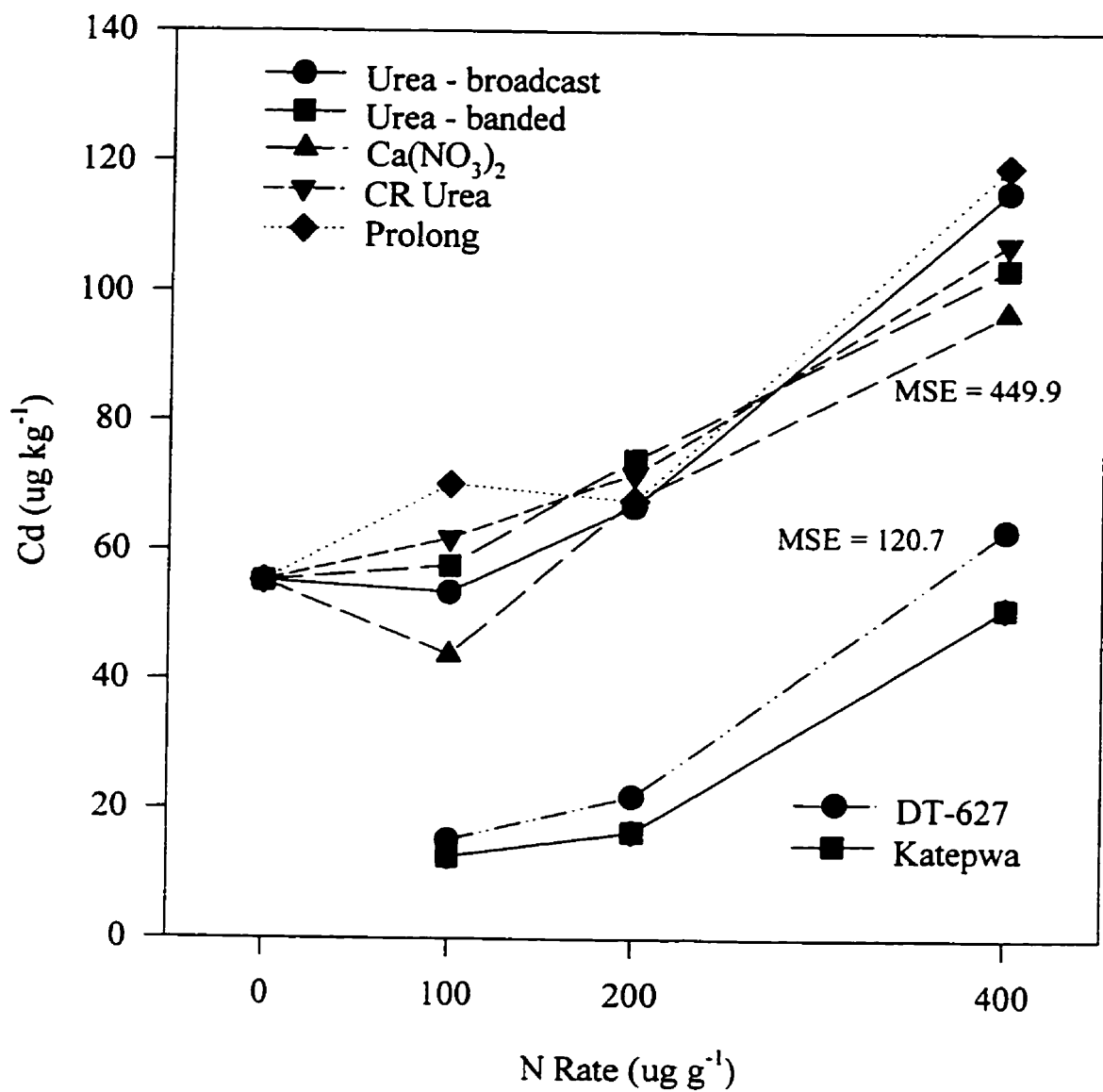


Figure I.1 Grain Cd concentration as a function of N fertilizer source and rate.

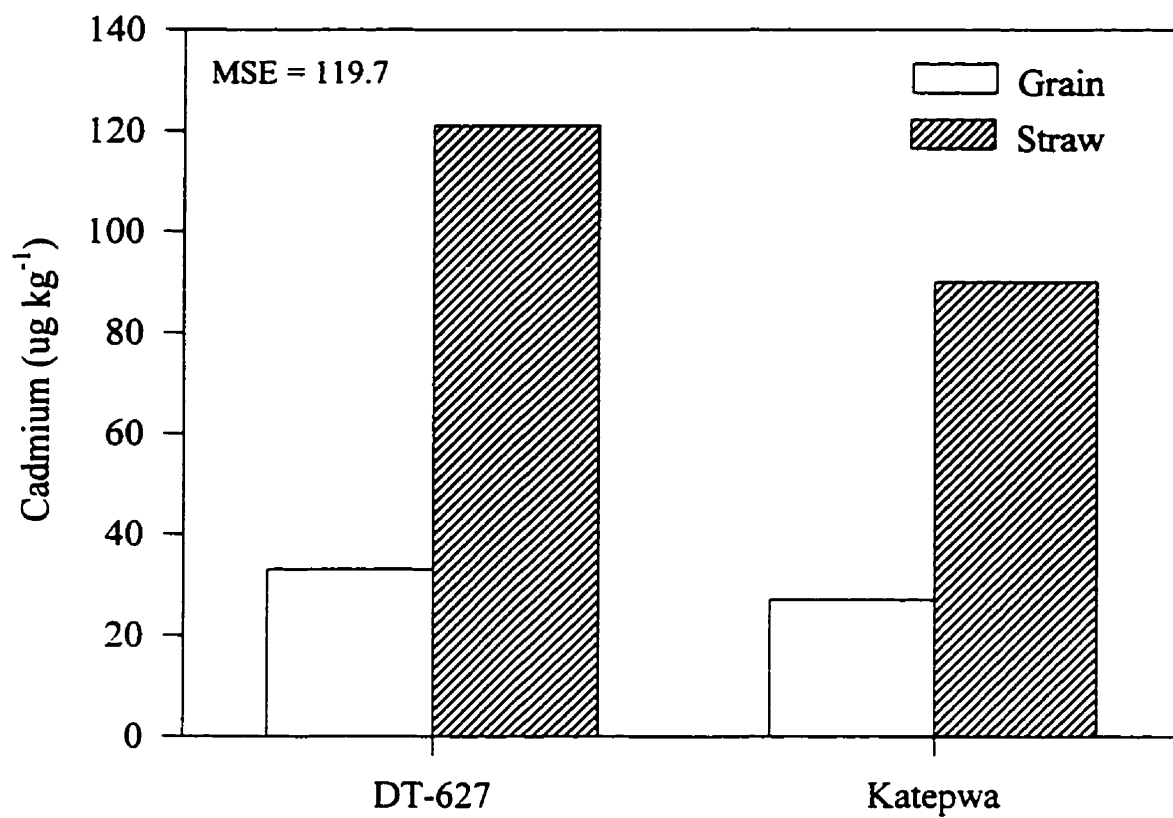


Figure I.2 Concentration of Cd in DT-627 and Katepwa grain and straw.

Table I.2 Influence of nitrogen rate on Cd concentration and yield in DT-627 wheat and Katepwa western red spring wheat.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
Cultivar				
DT-627	33a ¹	14.7a	121a	22.2a
Katepwa	27a	14.5a	90a	19.9b
MSE	107	3.1	1317	1.9
Nitrogen Rate				
100 $\mu\text{g g}^{-1}$	14b	12.7b	52c	17.7c
200 $\mu\text{g g}^{-1}$	19b	15.6a	101b	21.2b
400 $\mu\text{g g}^{-1}$	57a	15.6a	163a	24.2a
Control	55	5.9	97	6.1
MSE	107	3.1	1317	1.9
Contrasts				
Control vs DT-627	**	***	ns	***
Control vs Katepwa	***	***	ns	***
DT-627 vs Katepwa	ns	ns	*	**
MSE	103	3.4	1168	2.3

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

APPENDIX II

Table II.1 List of Cd concentrations and yield of grain and straw for treatment means of the first growth chamber experiment.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
100 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	128e ¹	27.0abc	442ef	30.4cde
200 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	167cd	22.8bc	555d	35.1ab
400 $\mu\text{g g}^{-1}$ $\text{Ca}(\text{NO}_3)_2$	224b	29.1a	736c	32.7bcd
100 $\mu\text{g g}^{-1}$ Broadcast Urea	135cde	27.2abc	397f	29.4de
200 $\mu\text{g g}^{-1}$ Broadcast Urea	160cd	26.4abc	562d	433.8bc
400 $\mu\text{g g}^{-1}$ Broadcast Urea	232ab	26.0abc	838b	38.6a
100 $\mu\text{g g}^{-1}$ Banded Urea	130de	26.2abc	433ef	28.1e
200 $\mu\text{g g}^{-1}$ Banded Urea	150cd	25.9abc	533de	33.9bc
400 $\mu\text{g g}^{-1}$ Banded Urea	173c	22.8bc	610d	36.7ab
100 $\mu\text{g g}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$	139cde	27.8a	393f	28.8e
200 $\mu\text{g g}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$	136cde	23.7bc	426ef	33.5bc
400 $\mu\text{g g}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$	170c	23.4bc	556d	37.9a
Control	103e	14.9d	228g	14.8f
Control + P	100e	16.7d	236g	17.4f
Control + P + S	102e	15.7d	228g	15.7f
400 $\mu\text{g g}^{-1}$ Broadcast Urea, no P or S	248ab	22.5c	870b	35.2ab
400 $\mu\text{g g}^{-1}$ Urea + CaSO_4	258a	28.9a	970a	38.1a
MSE	301	4.5	3222	3.5

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

APPENDIX III

Table III.1 List of Cd concentrations and yield of grain and straw for treatment means for the growth chamber experiment in the Appendix.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
100 $\mu\text{g g}^{-1}$ Prolong	70cdef ⁱ	8.3ef	165efghi	9.6h
200 $\mu\text{g g}^{-1}$ Prolong	68cdef	10.6de	184efgh	12.6gh
400 $\mu\text{g g}^{-1}$ Prolong	119b	14.8abcd	254bcde	15.2defg
100 $\mu\text{g g}^{-1}$ Broadcast Urea	53efghi	13.1abcd	128fghij	15.8cdefg
200 $\mu\text{g g}^{-1}$ Broadcast Urea	67cdef	14.5abcd	202defg	19.1bcde
400 $\mu\text{g g}^{-1}$ Broadcast Urea	115b	17.9a	310bc	22.6ab
100 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂	44fghi	12.2bcde	123fghij	14.1fg
200 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂	68cdef	14.9abcd	209defg	18.7bcdef
400 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂	97bcde	16.6abc	241cdef	20.2bc
100 $\mu\text{g g}^{-1}$ Controlled Release Urea	62defg	13.4abcd	150efghij	12.9gh
200 $\mu\text{g g}^{-1}$ Controlled Release Urea	72cdef	17.3ab	181efgh	16.4cdefg
400 $\mu\text{g g}^{-1}$ Controlled Release Urea	107bc	14.6abcd	296cdef	19.9bcd
100 $\mu\text{g g}^{-1}$ Banded Urea	58efgh	13.4abcd	155ghij	14.3efg
200 $\mu\text{g g}^{-1}$ Banded Urea	74cdef	16.1abc	180defg	15.6cdefg
400 $\mu\text{g g}^{-1}$ Banded Urea	104bcd	17.7a	238bcdef	20.4bc
Control	55efgh	5.9f	97ghij	6.0i
DT-627 + 100 $\mu\text{g g}^{-1}$ Urea	15i	13.5abcd	59ij	18.9bcde
DT-627 + 200 $\mu\text{g g}^{-1}$ Urea	22ghi	15.3abcd	124fghij	22.6ab
DT-627 + 400 $\mu\text{g g}^{-1}$ Urea	63cdef	15.3abcd	179efgh	25.2a
Katepwa + 100 $\mu\text{g g}^{-1}$ Urea	13i	11.8cde	44j	16.6cdef
Katepwa + 200 $\mu\text{g g}^{-1}$ Urea	16hi	15.9abc	79hij	19.9bcd
Katepwa + 400 $\mu\text{g g}^{-1}$ Urea	51efghi	18.9abc	147efghij	23.2ab
400 $\mu\text{g g}^{-1}$ Urea + 300 $\mu\text{g g}^{-1}$ K ₂ SO ₄	131b	18.4a	338b	23.3ab
400 $\mu\text{g g}^{-1}$ Urea + CaSO ₄	215a	17.5ab	563a	21.4ab
MSE	353	4.3	2254	4.4

ⁱ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

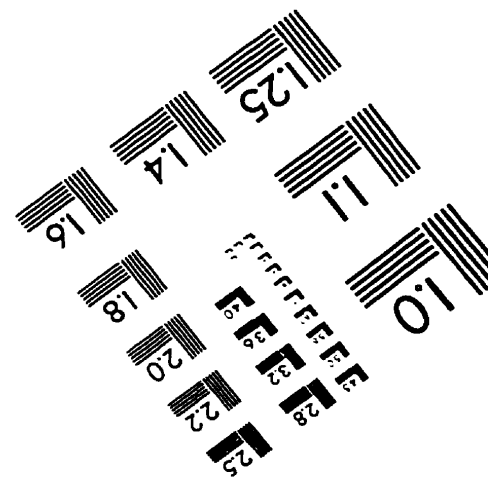
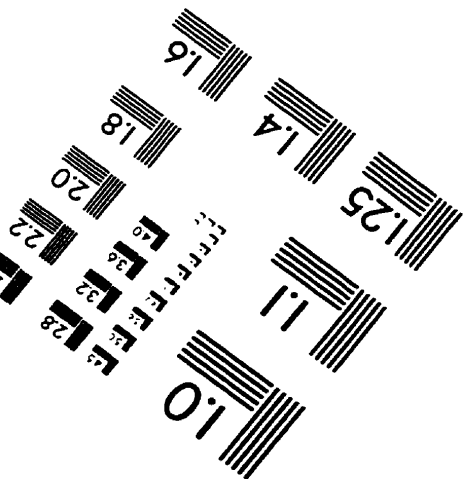
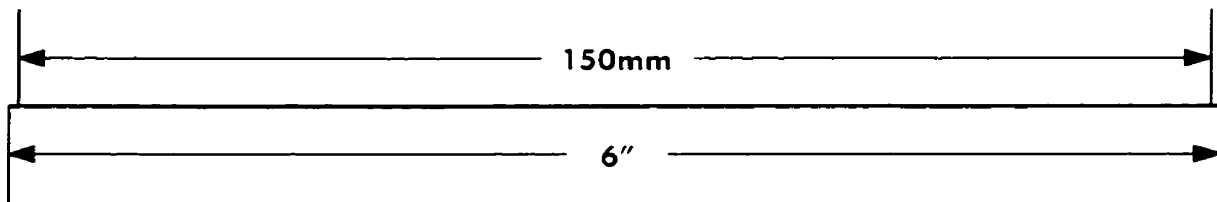
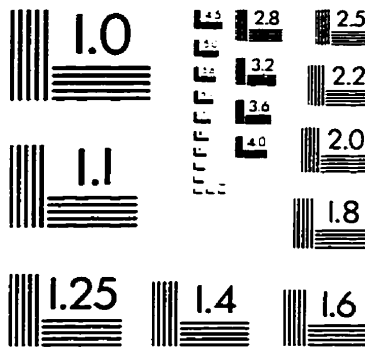
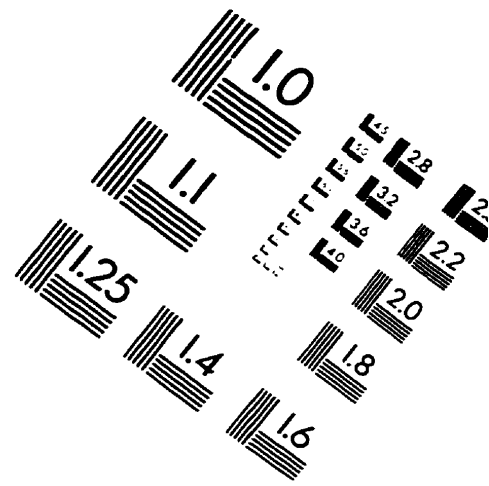
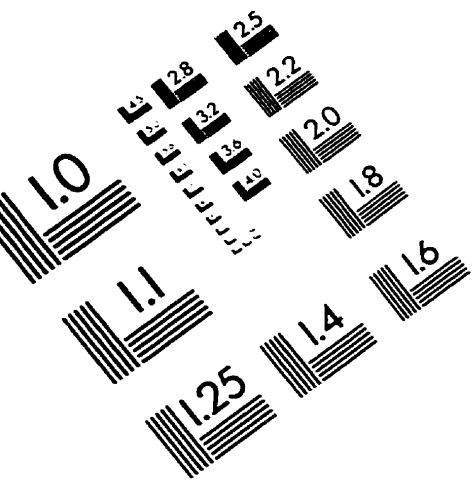
APPENDIX IV

Table IV.1 List of Cd concentrations and yield of grain and straw for treatment means from the growth chamber experiment with two soil types.

	Grain		Straw	
	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)	Cd ($\mu\text{g kg}^{-1}$)	Yield (g)
100 $\mu\text{g g}^{-1}$ Urea on Cobfield FL	95fg ¹	15.3bc	238f	28.1abcd
200 $\mu\text{g g}^{-1}$ Urea on Cobfield FL	117def	16.2abc	290ef	27.0bcd
400 $\mu\text{g g}^{-1}$ Urea on Cobfield FL	130bcde	11.0d	341de	21.9d
100 $\mu\text{g g}^{-1}$ Urea on Newdale CL	93fg	16.3abc	266ef	19.8d
200 $\mu\text{g g}^{-1}$ Urea on Newdale CL	105efg	16.5abc	292ef	24.7cd
400 $\mu\text{g g}^{-1}$ Urea on Newdale CL	126cdef	18.3abc	343de	27.0cd
100 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Cobfield FL	130bcde	15.4bc	284ef	27.3bcd
200 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Cobfield FL	139bcde	16.1abc	334de	25.0cd
400 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Cobfield FL	163ab	9.4d	438bc	19.7d
100 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Newdale CL	106efg	16.7abc	271ef	20.5d
200 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Newdale CL	135bcde	17.8abc	380cd	32.2abc
400 $\mu\text{g g}^{-1}$ (NH ₄) ₂ SO ₄ on Newdale CL	158abc	19.1ab	463ab	28.2abcd
100 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂ on Newdale CL	143bcd	14.4c	326de	33.6ab
200 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂ on Newdale CL	162ab	16.8abc	437bc	35.6a
400 $\mu\text{g g}^{-1}$ Ca(NO ₃) ₂ on Newdale CL	175a	19.4a	514a	30.8abc
Control on Cobfield FL	83gh	9.4d	105h	11.2e
Control on Newdale CL	62h	9.0d	182g	10.7e
MSE	249	2.7	1535	13.0

¹ Within each group values followed by the same letter are not significantly different at the 5% confidence level.

IMAGE EVALUATION TEST TARGET (QA-3)



APPLIED IMAGE, Inc.
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989

© 1993, Applied Image, Inc.. All Rights Reserved