

**PEDOGENIC INFLUENCES ON SOIL CADMIUM,
AND PHYTOAVAILABILITY
IN SELECTED AGRICULTURAL SOILS FROM THE PRAIRIE ECOZONE**

BY

ROSS C. MALEGUS

**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
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ABSTRACT

Malegus, Ross Christopher. M.Sc., The University of Manitoba, May, 1997.
Pedogenic Influences on Soil Cadmium, and Phytoavailability from Selected Agricultural Soils in the Prairie Ecozone.
Major Professor; Tee Boon Goh.

Recent grain Cd analyses by the Canadian Grain Commission has identified the Brown soil zone and the Morden, Manitoba region in the prairie ecozone as annually producing higher Durum wheat grain Cd than other parts of the prairies. Codex Alimentarius Commission of the World Health Organization (FAO/WHO 1995) has proposed a grain cadmium (Cd) limit of 0.1 ppm (f.w.) for export.

The agroecosystems from the prairie ecozone producing higher grain Cd must be better understood so that advances in all agronomic fields to control grain Cd content will be relevant to each other. A soil Cd map would be a valuable resource for cereal producers and private or government extension workers. Should it become necessary for specific soil types to be taken out of Durum wheat production, a soil Cd map would identify these regions in the prairie ecozone.

An investigation of some prairie ecozone soils was undertaken to compare the pedogenesis in the regions producing grain with higher Cd to pedons from areas producing grain with lower Cd. Two soil forming factors: parent material and climate were studied from a general survey of the prairie ecozone. Soil samples were collected

from a climosequence of 13 pedons on a genetic basis from the Brown, Dark Brown, Black, and Dark Gray Soil zones including soils from the Dark Gray Luvisol soil zone. A lithosequence representing different parent materials was also used to select sites for this general survey.

The Ap horizon contained the largest amount of total soil Cd for the horizons in the pedons except those horizons that had been geochemically enriched. Historical biopedological cycling occurred in all pedons. Cadmium enrichment factors (A horizon / C horizon) for the Brown, Dark Brown, Black, Dark Gray, and Gray Luvisol Great Groups were 1.38, 1.73, 2.04, 0.787, and 0.833, respectively. Biopedological Cd cycling increased from the Brown to the Black soil zones because of greater annual precipitation and lower annual temperatures. This change in climate corresponds with a change in vegetation moving from short prairie grasses to tall prairie grasses and greater below ground biomass. The decrease in Cd enrichment factor for the Dark Gray and Gray Luvisol soils represents a shift in vegetation to Aspen forests and greater above ground biomass due to greater annual precipitation and lower annual temperatures.

Lacustrine parent material from the Brown soil zone was 0.296 mg Cd kg⁻¹ (o.d.) and mixed till parent material from the Brown soil zone was 0.410 mg Cd kg⁻¹ and 0.256 mg Cd kg⁻¹. In the Black soil zone one mixed till parent material sample was greater (0.346 mg Cd kg⁻¹) than the lacustrine parent material (0.293 mg Cd kg⁻¹). Two other mixed till parent material samples were 0.096 and 0.108 mg Cd kg⁻¹. The Cd content in a shale till parent material from the Dark Gray Luvisol was 0.461 mg Cd kg⁻¹. A mixed till Dark Gray Luvisol soil was 0.351 mg Cd kg⁻¹. Cadmium content in parent

material followed the order: shale till > lacustrine > mixed till parent material. Different rock sources for parent material accounted for the Cd lithosequence.

In order to examine more fully the influence of topography within a lithofunction, a more detailed survey was initiated from a specified area of lacustrine parent material known for producing grain with high Cd. This survey occurred over an 80-kilometre transect of the Red River Valley of southern Manitoba. The transect included eleven agricultural fields. Soil samples were collected on a genetic basis representing the surface and sub-surface horizons from three slope positions at each field. Grain samples were also collected from each slope position.

Results from this detailed survey indicated that the mean surface soil total Cd content was 0.876 mg Cd kg⁻¹. The mean grain Cd content from this portion of the study was 0.094 ppm (f.w.).

Four wheat classes were sampled from the transect. Canada Western Amber Durm, Canada Western Extra Strong, Canada Western Red Spring, and Canada Prairie Spring had a mean Cd value of 0.092, 0.075, 0.063, and 0.042 ppm (f.w.), respectively.

Toposequence results indicated that soil Cd was greater in the surface soil compared to sub-surface soil. The mean value for soil Cd in the crest slope position was 0.938 mg Cd kg⁻¹, and 0.839 and 0.850 mg Cd kg⁻¹ for the mid and toe-slope positions, respectively. Grain Cd had a mean value of 0.103 ppm (f.w.) in the crest position and 0.093 and 0.081 ppm (f.w.) for the mid and toe-slope positions, respectively.

Lithosequence results indicated soil Cd and grain Cd increased with increasing clay content.

A statistically significant positive correlation ($r = 0.54^{**}$) was observed between the surface soil total Cd and grain Cd. A statistically significant negative correlation ($r = -0.50^{**}$) was observed between the sub-surface ratio of total soil Zn / total soil Cd and grain Cd.

A soil Cd map for the prairie ecozone could be developed from parent material. If it becomes necessary to remove certain soils from Durum wheat production, a soil Cd map could be used by producers and industry / government extension workers to make these decisions.

The relationship between Zn:Cd ratios and grain Cd should be further investigated, especially in Zn deficient soils. These are likely to be the more coarse textured soils.

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Val Huzel from the Department of Soil Science, University of Manitoba, assisted

with laboratory analyses. I am indebted to Dr. Russell Tkachuk and Eugene Gawalko from the Canadian Grain Commission, Grain Research Laboratory for heavy metals analyses of grain samples. Jim Griffiths generated the map for Chapter 4. Dr. Walter Michalyna confirmed my identification of soil series. Thanks to Llwellyn Armstrong and Dr. Manas Banerjee for statistical assistance. Thanks to Department of Soil Science graduate students Brian Wiebe, Bill Dubbin, and Dale Tomasiewicz, for their kindly help.

Helen Nemeth and Pearl Novotny helped make everyday life more enjoyable for graduate students.

FOREWORD

This thesis was written in manuscript style as outlined in the Department of Soil Science *Guide to Thesis Preparation for Graduate Students*. Various parts of this thesis have been presented and published as conference proceedings as: Malegus, R.C. and Goh, Tee Boon. 1995. Soil and wheat grain cadmium levels from a 50 mile transect in southern Manitoba. Proceedings from the Manitoba Society of Soil Science. 38:11-20.

The following manuscripts are planned to be submitted for publication. The journal(s) to which they will be submitted have yet to be determined.

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LIST OF ABBREVIATIONS

Word	Abbreviation
fresh weight	f.w.
monoammonium phosphate	MAP
mean annual precipitation	maP
mean annual temperature	maT
cadmium retention capacity	CdRC
zero point charge	ZPC
saturation extract cadmium	Cd _{SE}
diethylenetriaminepentaacetic acid	DTPA
parent material	P.M.
lacustrine	lac
mixed till	till
shale till	sh till
not detectable	n.d.
oven dry	o.d.

1. INTRODUCTION

Cadmium (Cd) is a naturally occurring element that is found in all soils. It serves no known biological purpose. Concern about the accumulation of Cd in the environment has been increasing since Cd was identified as the causative factor in Itai-Itai disease in Japan in the mid-70's. Since that time world-wide efforts have attempted to limit the uses of Cd to prevent its accumulation in the environment. Worldwide production of Cd is expected to decrease in the future (Stoeppler 1991).

In nature, Cd is commonly found as a substitute for zinc in zinc sulphide minerals like sphalerite. Cadmium is collected as a by-product from zinc mining. Cadmium has a number of industrial uses. It is used as a strengthening agent for plastics, a coloring agent, and an energy source in nickel-cadmium batteries. Cadmium can also be found as an impurity in phosphatic fertilizers. The level of impurity in the fertilizer is dependent upon the location of the source of the rock phosphorus. There are concerns about the accumulation of Cd in soil from past and future use of phosphatic fertilizers.

Concern about Cd in the environment is due in part to its uptake by plants. In human consumers of the plants, Cd is stored in the renal cortex of the kidney where it can eventually cause kidney damage. It has a biological half-life of 10 - 30 years depending on age of the individual (Ryan et al. 1982).

Countries with populations that use grains as a staple food source and rely on

importing cereals have been developing stringent grain Cd levels for acceptable grain shipments from foreign countries. This has significant implications for Canadian grain exports if Canada's grains exceed these levels.

Some of the current work in controlling the level of Cd in cereal grains include plant breeding and crop management practices. Basic to these efforts is knowing the background levels of soil Cd, and whether there is a correlation between soil Cd levels and grain Cd contents.

The agricultural region where grain farming occurs in the prairie ecozone includes a number of soil zones; the Brown, Dark Brown, Black, and Dark Gray soil zones from the Chernozemic soil Order. Some grain production also occurs in the Dark Gray Luvisol soil zone. Grain production in the prairie ecozone occurs mostly in the Black soil zone where moisture is less a limitation for crop growth than in the Brown or Dark Brown soil zones. In the Dark Gray and Dark Gray Luvisol soil zones, compared to the Black soil zone, the number of frost free days is a limitation to grain production.

The soils from the prairie ecozone are young soils having developed since the last glaciation approximately 10,000 years ago. The underlying bedrock for much of the prairie ecozone is from the Cretaceous period and usually consists of sedimentary materials such as shale. The Cd content of shale can be enriched compared to other rock sources. Most of the parent material for the soils of the prairie ecozone is mixed till. The till matrix consists of varying proportions of granitic, carbonate, and shale rocks. The proportion of these source rocks is largely a factor of the movement of the glaciers and regional bedrock locations.

The objectives of this study are to: 1) determine the background soil Cd levels for some Chernozemic and Gray Luvisol soils from the prairie ecozone; 2) identify the relationship between parent material and soil Cd levels; 3) ascertain the biopedological influence within the climatic zones on soil Cd levels; 4) correlate physical and chemical soil properties with total soil Cd levels; 5) characterize the relationship between total soil Cd and 0.01 M CaCl₂ - extractable Cd and Cd levels in wheat grain.

2. LITERATURE REVIEW

2.1 Introduction

A literature review on soil cadmium (Cd) and grain Cd for the purposes of this thesis focuses on subjects that can have a direct effect on the level of Cd found in soil and grain. Research is reported that examines the partitioning of Cd in plant parts important to the potential accumulation of Cd in the human diet. Research on biopedological cycling of Cd in the soil system is also reviewed. Literature on how edaphic factors affect soil Cd availability including agronomic factors to manage the uptake of Cd is presented.

2.2 Sources of Cadmium in Soil

2.2.1 Geochemical Sources of Cadmium in Soil

Cadmium is referred to as a "heavy metal" based on an atomic density of $>6 \text{ g cm}^{-3}$ or as a "trace element" because it occurs in concentrations of less than 1% in the soil. Trace elements occur as trace constituents of primary minerals in igneous rocks. They become incorporated into these minerals by isomorphously substituting in the crystal

lattice for ions of one of the major elements at the time of crystallisation. This substitution is governed by the ionic charge, ionic radius, and electronegativity of the major element and of the trace element replacing it. Substitution can occur when the radii of the major constituent ion and that of the trace metal are within 15% of each other and when the charges differ by not more than one unit (Krauskopf 1979).

Sedimentary rocks comprise approximately 75% of the rocks outcropping at the earth's surface (Alloway 1990a). In sedimentary rocks, substitution in silicate lattices of primary minerals is less important than the partitioning of elements which occurred during weathering cycles. As the primary minerals decompose during weathering, the alkaline earths and alkali metals tend to remain in solution and some of the metallic micronutrients pass into the lattices of the secondary or clay minerals (Wild 1988). Shales are formed from organic-rich sediments under anaerobic conditions, and the heavy metals accumulate as sulphides and organic complexes. The trace metal concentrations in sedimentary rocks are dependent upon the mineralogy and adsorptive properties of the sedimentary material, the matrix and the concentrations of metals in the water in which the sediments were deposited (Alloway 1990a). Trace element concentrations in sandstones are generally low since these rocks are frequently dominated by quartz (Wild 1988).

Cadmium is classified as a member of the chalcophile group in Goldschmidt's geochemical classification of the elements. This classification describes elements having a high affinity for sulphur and normally occurring in sulphide deposits. Cadmium is closely associated with Zn in its geochemistry; these elements have similar ionic

structures and electronegativities and both are strongly chalcophile although Cd has a higher affinity for S than Zn (Alloway 1990b). Zinc occurs widely in a number of minerals, but the main source is sphalerite [(ZnFe)S], which commonly occurs with galena (PbS). Cadmium minerals are scarce (Table 2.1), but as a result of its chemical similarity to Zn, Cd occurs by isomorphous replacement in almost all zinc ores (Cotton and Wilkinson 1988). Cadmium is also found in wurtzite, another ZnS, tetrahedrite, and a variety of other sulphides and sulfosalts. Its most common compound is CdS. Cadmium ions form insoluble white compounds, usually hydrated, with carbonates, arsenates, phosphates, oxalates, and ferrocyanides (Adriano 1986). Many carbonate rocks are impure and their trace element contents may be boosted by iron/manganese oxides and clays. Geochemical generalizations are useful when considering young soils where composition is broadly similar to that of the parent material (Wild 1988).

Parent material (p) is one of the state factors in the soil formation equation.

$$\text{Soil} = f(\text{cl}, \varnothing, \text{r}, \text{p}, \text{t}, \dots) \text{ (Jenny 1980)}$$

Where cl is climate, \varnothing is vegetation, r is relief, t is time, and ... are periodic natural occurrences. Thus, the geochemical nature of cadmium and its occurrences allow us to predict natural background levels of Cd in residual or transported soils. The same reasoning can also help to predict where anomalously high levels of Cd could be expected to occur in soil. In non-contaminated, non-cultivated soils, the concentration of Cd is largely governed by the amount of Cd in the parent material (Adriano 1986). In general, most soils possess a Cd content of $< 1 \text{ mg kg}^{-1}$ except soil developed on parent material with anomalously high Cd contents, e.g., black shales (Alloway 1990b).

Table 2.1 Range and mean concentrations of cadmium in various natural materials.

Natural Material	Cadmium, mg kg ⁻¹	
	Range	Average
Ultramafic Igneous ^a	n.d. - 0.2	0.05
Basaltic Igneous ^a	0.006 - 0.6	0.2
Granitic Igneous ^a	0.003 - 0.18	0.15
Shales and Clays ^a	n.d. - 11	1.4
Black Shales ^a	<0.3 - 8.4	1.0
Deep-Sea Clays ^a	0.1 - 1	0.5
Limestones ^b		0.028
Sandstones ^b		0.05
Phosphorites ^a	n.d. - 170	30

^aSource: Connally et al. (1978).

^bSource: Alloway (1990b).

n.d. = not detectable

A survey by Garrett (1994) of soils across the prairie ecozone and immediately adjoining States, covering 850,000 km² and 1,273 Ap horizons, found that geological factors influenced soil composition. The range in data was < 0.2 - 3.8 mg kg⁻¹ Cd, with an arithmetic mean of 0.28 mg kg⁻¹ and a median of 0.3 mg kg⁻¹. The median value of 0.3 mg kg⁻¹ is referred to as the average background level of Cd in the prairie ecozone surface soil. Garrett (1994) suggested that most of the variation in soil Cd is due to local changes in soil chemistry, reflecting the composition of the underlying parent material and differences in local pedological processes, together with sampling and analytical variability, rather than broad prairie-wide factors. The parent materials of the prairie ecozone soils are dominantly glacially transported materials. The distribution of soil Cd reflected a number of regional geological features. These features include the fact that the elevated Cd levels in eastern Saskatchewan, Manitoba, and North Dakota reflect Cretaceous shales, including the Riding Mountain, Vermilion River, Favel, Ashville, and Pierre shales. The lower black shale units, i.e., beneath and older than the Riding Mountain, are generally thought to be the most enriched in heavy metals, and it is over and down-ice from these that the elevated Cd pattern is observed. This pattern does not continue into central Saskatchewan because much of this area is covered by glacial deposits that average 100 m in thickness. The parent material in this area is reworked through the glacial sequence surfaces at diluted concentrations well down-ice from the source area (Garrett 1994). Garrett (1994) suggested that the low Cd areas in the east and north of the survey area, and in the south-central area were related to natural geochemical abundance. For example, the east and northern margin areas contained tills

made up largely of Precambrian Shield and /or Palaeozoic carbonate material which would be expected to be low in Cd. The tills in the southern area contain a significant Cretaceous and Tertiary sandstone component that would also be expected to possess relatively low Cd values. Garrett (1994) found that 95% of the values fell below 0.5 mg Cd kg⁻¹ and 99% below 0.7 mg Cd kg⁻¹. A number of scattered but elevated Cd levels were found in parts of southwestern Alberta and north central Manitoba that may be reflecting the presence of grains of sphalerite or galena in the tills (Garrett 1994).

A study involving 3,045 surface soil samples from 307 different soil series from agricultural soils of the United States found values of the minimum, maximum, 5th, 50th, and 95th percentiles for Cd (mg kg⁻¹ dry soil) to be: <0.005, 2.0, 0.036, 0.20, 0.78, respectively (Holmgren et al. 1993). Areas with moderately high Cd values include the lower Mississippi River Valley and the glacial areas of the north central states. These values could be due to Cd being a lattice contaminant in CaCO₃ or the Cretaceous age Pierre shales from this area (Holmgren et al. 1993).

Pierce et al. (1982) found that the highest total Cd concentrations occurred in calcareous soils developed in the lacustrine sediments and the Des Moines Lobe Till and, in general, in surface soils with free carbonates. Concentrations in the Minnesota soils were low, with total Cd ranging from 0.06 to 0.74 mg kg⁻¹. The authors concluded that the differences among soils could be attributed to differences in the Cd concentrations of their parent materials.

Lund et al. (1981) found surface soils from a region of California derived from shale parent material had a mean value of 7.5 mg kg⁻¹ and ranged in Cd content from 1.4

to 22 mg kg⁻¹. Soils from basalt and sandstone parent material ranged from 0.01 to 3.5 mg kg⁻¹ and averaged 0.79 mg kg⁻¹. Fragments of the shale parent material taken at lithic contacts within the pedons had a mean content of 8.0 mg kg⁻¹. Alluvial soils that were derived from shale generally had a lower Cd content than the residual soils developed on shale. Variations in the Cd content amongst the alluvial soils reflected their source material (Lund et al. 1981).

2.2.2 Anthropogenic Sources of Cadmium in Soil

Besides the natural background levels of cadmium in the soil, Cd levels in the soil can also be influenced by the cultural practices of man, and from industrial pollution adding to the natural load of Cd in the parent material of soils. If the ratio of Cd in surface soil/Cd in subsoil is appreciably greater than 1, it is argued that anthropogenic contamination of the soil has occurred (Holmgren et al. 1993). Although fertilization and atmospheric deposition are sources of Cd, quantities added to rural agricultural soils from these sources are small and amount to a few grams or less per hectare per year (Page et al. 1987).

2.2.2.1 Phosphatic Fertilizers. Phosphatic fertilizers contain various levels of cadmium as a contaminant in the phosphate rock depending on where it is mined (Table 2.2). approximately 175 kg P ha⁻¹ year⁻¹ (as triple superphosphate, TSP) over a 36-year period had Cd levels in the four treated plots that decreased rapidly with soil depth.

Table 2.2 Cadmium concentrations in phosphorites and phosphatic fertilizers.

Origin of Rock	Cd in Phosphorite	Cd in Fertilizer	
	Range, mg kg ⁻¹	Range, mg kg ⁻¹	g Cd / t P ₂ O ₅
Various	< 1 - 75	0.1 - 170	
Pacific Islands	31 - 90	18 - 91	
Various	3.6 - 92	3.3 - 40	
Western USA	< 500	< 200	
Florida USA		< 20	
Morocco		60	
USA		35	
Togo		160	
Senegal		255	
USSR		0.8	
Tunisia/Algeria		60	
Israel/Jordan		35	

Source: Alloway (1990b)

Anderson (1977) found that with increasing fertilization only a slight increase in the Cd in grain was observed. It seems that the level of available soil phosphate may affect the Cd content of plants mainly through effects of phosphorus supply on plant growth and vigour (Williams and David 1977).

Soils from a citrus grove that had been fertilized with the equivalent of P and total

Calculations based on Cd levels in the soil profile indicated that about 71% of the accumulated Cd resided in surface soil (0 to 15 cm). A linear correlation between total Cd in surface soil of all plots was highly significant ($r = 0.89$). Correlation between P and Cd persisted into the 15 to 30 cm increment of soil, where the correlation coefficient, r , was 0.79 (Mulla et al. 1980).

Roberts et al. (1995) reported that based on 1994 phosphorus application rates of 33 kg monoammonium phosphate (MAP) ha^{-1} with 55 mg Cd per kg MAP would amount to an addition of 1.8 g Cd $\text{ha}^{-1} \text{yr}^{-1}$ to prairie ecozone soils resulting in an increase of 6.9×10^{-4} mg Cd kg^{-1} (assuming the plow layer of soil weighs 2.6×10^6 kg ha^{-1}).

2.2.2.2 Farmyard Manure. Values of 0.3 to 1.8 mg kg^{-1} dry weight of cadmium have been reported for farmyard manure (Alloway 1990b).

2.2.2.3 Sewage Sludge. Sewage sludges are commonly used as soil conditioners and as a source of plant nutrients in particular, nitrogen and phosphorus. Sewage contains Cd from human excretion, domestic products containing Zn, and industrial effluents. Almost all the Cd in the sewage accumulates in the sludge produced during the treatment. Cadmium in sewage sludge ranges widely from <1 to 3650 mg kg^{-1} dry weight in western Europe and North America (Alloway 1990b).

2.2.2.4 Atmospheric Deposition. The primary sources of air pollution rank as follows: smelters > incineration of plastics and cadmium pigments > fossil fuel, including coking

> steel mills > metallurgical industries. Other sources of atmospheric Cd originate from the combustion of coal, oil, paper, and urban organic trash. Near roads, motor oils and tread wear from vehicular tires are sources of Cd and other metals. Increased levels of Cd have been found closer to the source of air pollution (Ritter and Rinefield 1983). Cadmium levels as high as 95.40 mg kg⁻¹ on the surface soil were found within 15 m of a battery smelter decreasing to 1.65 mg kg⁻¹ 300 m away (John et al. 1972). Contamination of soil from atmospheric deposition in the agricultural regions of the United States, except near point emission sources, has been described as amounting to a few g or less ha⁻¹ yr⁻¹ (Page et al. 1987).

2.3 Cadmium Uptake by Plants

The general Cd concentration in different plant organs has been characterized in the sequence, roots > leaves > fruiting parts > seeds (Munshower 1986).

Hickey and Kittrick (1984) found that using chemical partitioning in soils and sediments that had formerly received massive additions of heavy metals indicated the greatest percentage (37%) of total Cd was in the 1.0 M MgCl₂ exchangeable fraction. They concluded that Cd should be considered quite mobile and biologically available compared to copper, nickel, and zinc. Others described cadmium's comparatively high mobility on the basis of water solubility of the metal as an important factor of its mobility (Bojakowska and Kochany 1985). Bingham et al. (1984) found that increasing the Cl⁻ content resulted in increasing the CdCl⁺ component of the total Cd at the expense of

Cd^{2+} . Also, leaf Cd was primarily a function of the Cd^{2+} concentration.

Hinesly et al. (1982) demonstrated that, generally, soil CEC inversely affected the uptake of Cd by corn and its growth when Cd was supplied as a soluble salt but not when it was supplied as a constituent of municipal sewage sludge. They concluded that the source of Cd was the most important factor affecting its uptake and impact on plant growth. Experiments by Williams and David (1977) using pot cultures showed that uptake of Cd by subterranean clover was elevated by using increasing amounts of Cd added to the soil up to the 10 mg kg^{-1} level. Also, soil acutely deficient in P had increasing Cd uptake with increasing amounts of phosphate added. They suggested that adding phosphate to soil acutely deficient in soil P resulted in increased root growth in the zone of phosphate enrichment which then increased uptake of Cd. Mahler et al. (1980) found that under acid soil conditions, Cd tended to approach a maximum concentration in shoots as total soil Cd increased, suggesting a carrier-mediated transport process which is possibly energy dependent. Under calcareous soil growth conditions, Cd uptake was primarily a function of the total soil Cd concentration characteristic of a diffusive transport process not requiring energy. In their interpretation of results Mahler et al. (1980) could offer no explanation for how pH or proton activity affects transport processes. Miller et al. (1977) found that there was a tendency for soil Pb to increase the shoot concentration of Cd in soils amended with Pb and Cd. They speculated that Cd concentrations in the soil solution, and thus in the plant, are elevated by Pb as it has been shown that Pb more effectively competes for exchange sites on colloidal surfaces than Cd.

Street et al. (1977) found that more Cd accumulated in plants on soils treated with inorganic Cd than with Cd+sludge, reflecting a possible decreased availability of organically-sorbed Cd. The Cd concentration of plants grown on sandy soils was greater than plants grown on a loam or clay loam soil. They also observed a higher concentration of Cd in the root tissue than in the above ground tissue and that this might reflect a physiological or chemical mechanism for reduced transport of Cd from the roots to the tops of corn plants. They also found that DTPA(diethylenetriaminepentaacetic acid)-extractable Cd showed a highly significant correlation ($r = 0.96$) with Cd concentration in corn seedlings.

White and Chaney (1980) applied Zn and Cd to two different surface soils and found that greater amounts of Cd were absorbed and translocated to the leaves of soybean trifoliolate leaves of plants on the soil with less organic matter, and on both soils, more at pH 5.5 than at pH 6.3. They also found when Zn and Cd were present in the soils, 0.01M CaCl₂-extractable Cd was curvilinear for the soil with the higher organic matter and linear for the soil with the lower level of organic matter at both pH levels. They concluded that the organic matter rich, low Fe and Mn oxide soil bound Cd more strongly.

Miller et al. (1976) found that the threshold of vegetative yield reduction on soybean occurred at 3 to 5 $\mu\text{g Cd g}^{-1}$ dry weight of tissue. They also found that the uptake of Cd by soybeans was related to the amount of Cd in the soil relative to the soil's capacity to sorb Cd.

John et al. (1972) found that although Cd was translocated from root to the top

portions of oat plants, accumulation takes place at root absorption sites. In a separate study, John (1972) found that with radish plants, Cd was translocated to and accumulated in the tops at higher concentrations than in the root part of the plants.

Recently McLaughlin et al. (1994a) found that environmental conditions played a dominant role in determining Cd uptake in potatoes. Higher tuber Cd concentrations tended to occur at sites having sandy soils and where soils were acidic.

2.3.1 Storage Site for Cadmium in Plants

In a review of the mechanisms of Cd uptake and translocation, Jastrow and Koepe (1980) reported a hypothesis that suggests Cd uptake by barley roots involved three mechanisms. The first mechanism is exchange adsorption, in which Cd is reversibly bound to exchange sites on the root and can be readily exchanged by desorption solutions (solutions containing a large excess of another transition type of metal cation, eg. Zn, Cu, Hg) or Ca solutions. The second proposed mechanism is an irreversible, nonmetabolic binding or sequestering to a limited number of sites on the cell wall or other cellular macromolecules. The third mechanism, diffusion, accounts for movement across cell membranes, which is necessary for translocation from roots into above-ground portions of the plant.

Jastrow and Koepe (1980) also reported that the rate of plant uptake and loss (transpiration) affects the movement of essential plant nutrients, and also that of Cd. This suggests that Cd translocation within the radish plant occurs upwards via the transpiration stream.

Wagner (1993) reviewed Cd storage in plants and described a model which speculates on the control of Cd uptake/exclusion/accumulation in plant cells. The first mechanism involves binding of metals in the cell wall. The second mechanism involves limitation of Cd movement across the plasmalemma. Very little is known about Cd transport across plant plasmalemma. Mechanism 3 involves an anion efflux mechanism in plants such as that found in bacteria. A plasmid-encoded, plasmalemma Cd-translocating, Cd-efflux ATPase was characterized in *Staphylococcus*. Mechanism 4 involves sequestration in the cytosol via protein or peptide complexes, organic acids, or inorganic (phosphate, sulfide) complexes. Phytochelatins (PCs) have been suggested as possible chelators of Cd in the cytosol and elsewhere. Under low-level exposure such as in agriculture, PCs may not be abundant and therefore may not be significant in Mechanism 4. Another possible cytoplasmic Cd chelator may be plant metallothionein. The relevance of these potential Cd chelators, if they exist as stable proteins, is not known. Mechanism 5 is an extension of Mechanism 4: chelation of Cd in the cytosol by proteins/peptides and organic or inorganic anions and subsequent transfer of complexes or metal to the vacuole. The possibility that PC or plant metallothionein or their Cd complexes are transported into the vacuole has apparently not yet been tested. There is no evidence in plants for complex-facilitated transport of Cd into the vacuole of plants exposed to low or high levels of Cd. Mechanism 6 involves transfer of free Cd²⁺ to the vacuole via a Cd/H antiporter energized by (change in) pH generated by the well-established tonoplast V-type ATPase. This was observed in tonoplast vesicles isolated from roots of oat seedlings grown in the presence or absence of Cd. It was proposed that

under low- or high-Cd exposure conditions, Cd may enter the cell as free Cd^{2+} via channels in response to the plasma membrane potential and then may be transported into the vacuole via a tonoplast Cd/H antiporter activity. Mechanism 7 is the last mechanism speculated and involves transfer of cytosolic Cd complexes outside the cell.

2.3.2 Biopedological Cycling of Cadmium

Metals in the unharvested portion of vegetation may be returned to the soil as plant residues. This process of metal accumulation by the aerial part of the plant followed by the return of the unharvested residue contributes to metal cycling from the subsurface zone to the soil surface (Sposito and Page 1984). Surface enrichment of elements by plant material is also referred to as the biogeochemical cycle (Brooks 1972).

Microorganisms are important to metal cycling in soils through their role in the decomposition of organic matter and in microbial synthesis. They provide a wide variety of ligands capable of forming both soluble and insoluble metal complexes (Sposito and Page 1984).

Hawkes and Webb (1962) indicate that the composition of residual soil and glacial till does not differ greatly from that of the rocks from which they were derived. Thus, the data on rocks can be used as a first approximation to the background composition of the overburden. However, background metal levels in soils are also subject to appreciable variation, according to soil type and soil horizon, particularly in well-differentiated profiles characterized by marked enrichment of some constituent, such as

iron oxide or organic matter.

Also metals indigenous to the parent material vary in their response during the development of the soil horizons. Soluble metals and those incorporated or adsorbed on clays and colloids are liable to be removed from the A horizon, whereas those contained in resistant primary minerals are liable to be enriched, relative to soluble metals in that horizon. Metals taken up by deep-rooted plants will be returned to the surface in the organic debris, and their subsequent fate will depend on the stability of their organic compounds in the A_1 horizon. Some of the metals which are removed from the A horizon may tend to accumulate along with hydrous Fe and Mn oxides or clays in the B horizon. Deep-rooted plants offset leaching to some extent by taking up elements which are returned to the surface soil when the plant dies or sheds its leaves.

Living vegetation has a profound effect on the dispersion of weathering products. The uptake of a given element by the root system of a plant is a function of the relative solubility of the element in the soil solution, as modified by the extremely corrosive environment created by the plant in the vicinity of its root tips. The biogenic processes whereby elements may be solubilized from relatively stable mineral phases and absorbed into the plant's circulatory system vary with different species of plants.

The net effect of these combined inorganic and organic factors is an uptake of substantial quantities of inorganic matter which is then distributed in greater or less amount through the body of the plant. As the leaves and other plant organs fall to the ground and decay, rain water leaches out the more soluble constituents. A part, however, may again be taken up by living plants or reprecipitated with Fe, Mn, and Al

in the B horizon of many soils. The less soluble constituents released by plant decay tend to remain in the humus layer, wherein ions may also be retained by adsorption on organic matter. This effect is cumulative, and over the years very appreciable enrichment may take place. The entire sequence of processes is referred to as the biogeochemical cycle.

Brooks (1983) refers to the biogenic enrichment of elements as the Goldschmidt Enrichment Principle. The degree of enrichment of trace elements by plants follows the so-called Irving-Williams Rules. These rules state that the stability of metal-organic complexes is independent of the nature of the ligand and that for divalent cations the order of stability (most stable first) is in the sequence: Pt, Pd, Hg, UO₂, Be, Cu, Ni, Co, Pb, Zn, Cd, Fe, Mn, Ca, Sr, Ba. For monovalent cations, the sequence is Ag, Tl, Li, Na, K, Rb, Cs. The corresponding values for trivalent ions are Fe, Ga, Al, Sc, In, Y, Pr, Ce, and La.

Fortescue (1980) describes Perel'man's general characteristics of the four landscape groups ie. 1) wooded landscapes; 2) meadow and steppe landscapes; 3) tundra landscapes; 4) primitive desert lanscapes. Under the Wooded landscape in forests there is a great biological accumulation of organic matter which far exceeds the annual primary production. This landscape requires decades to reach the mature state and involves two kinds of biopedological cycles: (a) annual cycles of leaf fall and related activity and (b) whole tree cycles which are much longer. In these landscapes, the mineral elements (Ca, Mg, P, etc.) may be removed from the soil in the woody parts of the trees for a relatively long time. In such areas most of the organic matter is above the soil surface.

Heinrichs and Mayer (1980) described the role of forest vegetation in the

geochemical cycling of heavy metals by comparing atmospheric input and seepage water output with the rate of accumulation of metals in the noncycling fraction of vegetation (wood, bark) and the amounts retained in the aboveground cycling fraction (leaves, needles, fruits, etc.). The metals incorporated in the noncycling fraction are withdrawn from the geochemical cycle for the lifetime of the forest, and will be partially exported from the ecosystem when the forest is harvested. The metals bound in the cycling fraction reach the soil together with litterfall within a short time, ie., after $< \approx 1$ year in the beech forest, after < 7 years in the spruce forest. Very often there is a strong binding in organic matter and the metals are accumulated in the organic topsoil or humus fraction again being withheld from further cycling.

Metal cycling for forest ecosystems has been studied in Europe and Scandinavian countries. Bergkvist et al. (1989) defined an ecosystem metal budget as the difference between the total deposition to the canopy and the amount that leaves the ecosystem, either with the soil percolate below the rooting zone or with the output from the catchment. A positive ecosystem budget accumulates the metal and acts as a net sink for the metal. Whereas a negative ecosystem budget is associated with metal release from the ecosystem which acts as a net source. The ecosystem budget for Cd is usually negative. This loss is via the soil solution under the rooting zone and remarkably high from a spruce stand (Bergkvist et al. 1989). The low pH of forest soils would likely explain the negative ecosystem budget for Cd. The dominating tree species was important for the metal cycling and acid-base properties of the soils. The acidifying potential of spruce was definitely greater than that of deciduous trees, eg. beech or birch.

Under the meadow and steppe landscapes there are no reserves of living matter and the total amount of living organic matter is usually not more than 30 - 40 tons ha⁻¹. The annual accumulation of organic matter in this type of landscape may equal, or exceed, that of forests although, because the majority of plants are annuals, the elements are kept out of the circulation for short periods only. Organic matter tends to accumulate below the Earth's surface in these landscapes.

Akin (1991) describes the cycling of nutrients in the forest ecosystem versus the grassland ecosystem in terms of the natural vegetation present, i.e., quantity of organic matter produced and the level of nutrient demand. Most grass-produced organic matter dies annually and thus adds to soil humus; even extensive root systems of perennial grasses are replaced every few years. As a result, the upper horizons of grassland soils generally are much darker than those of forest soils. On the other hand, trees and their root systems live longer than grasses and contribute less each year to the accumulation of soil humus. Also trees are less demanding of soil nutrients, particularly bases, so do not recycle these nutrients to the surface to the extent that grasses do.

Eyre (1970) notes that the aerial parts of grasses form a much denser "sod" or "turf" as they die down and accumulate. Furthermore, grasses form a dense rooting network throughout the entire depth of the soil beneath the surface. Roots decay in an almost continuous process so that humus, in a finely-disseminated form, is actually implanted in the soil by the vegetation. This intimate penetration by roots and humus not only ensures deep inherent fertility but also gives the soil a fine crumb structure and perviousness, regardless of differences in original parent-material. Grasses also take up

greater quantities of mineral nutrients, particularly Ca, than do forest trees (Eyre 1970). The humus returned to the soil by grasses is therefore commensurately richer in nutrients. In turn, as the humus decays, the nutrients are released only to be caught up again by the efficient rooting systems. In this way a very rich nutrient cycle is maintained.

2.4 Soil Factors Affecting Cadmium Availability

The two most important factors governing the uptake of cadmium by crops are the soil pH and the concentration of Cd in the soil. Factors of less importance include soil temperature, content of hydrous oxides of iron and manganese in soils, redox potential in soil, and interactions with other metals (Page et al. 1987) and complexation with halides (McBride 1994).

2.4.1 Total Soil Cadmium

Repeated annual applications of fertilizers and/or soil conditioners which contain Cd (eg. municipal sewage sludges), even though they increase the concentration of Cd in the soil each subsequent year, may or may not increase contents of Cd in the crop from year to year (Page et al. 1987). However, Adriano et al. (1982) found that in general, Cd absorption by crops almost always increased with an increasing level of substrate Cd. Lund et al. (1981) used seven soils representing a range in Cd contents from 0.02 to 22 mg kg⁻¹ for a greenhouse study to investigate the uptake of naturally

occurring Cd by three common vegetables: Swiss chard (*Beta vulgaris* var. *cicla*); radish (*Raphanus sativa* L.); and pepper (*Capiscum frutescens* var. *grossum*). They found that the Cd concentrations in the three vegetables tested increased as the Cd concentrations in the soils increased, and were significantly related to both total soil Cd and DTPA-extractable Cd.

2.4.2 Cation Exchange Capacity

A correspondence between soil texture, CEC, and organic matter for total Cd is consistent with the expectation that most of the Cd in soil is associated with the clay fraction (probably adsorbed on the Fe and Mn hydrous oxide surface coatings on clay particles) or the organic matter (Holmgren et al. 1993). The increased ability of soil to adsorb Cd with increasing CEC results in a decrease in Cd availability as judged by the reduction in the Cd concentration of the soil extract. The retaining power of organic matter for Cd predominately is through its CEC property (Mahler et al. 1980). Haghiri (1974) reported that increasing CEC resulted in decreased Cd concentration in oat shoots. Hinesly et al. (1982) found that soil CEC inversely affected the uptake of Cd by corn when Cd was applied as a soluble salt but not when it was applied as a constituent of municipal sewage sludge. Miller et al. (1976) found that CEC was the primary factor controlling the Cd sorption capacities of the soils used in their experiment.

Conflicting views exist on the value of CEC for predictive purposes with natural soils (Korte et al. 1976). Although the adsorption of cations usually is related to the CEC of soils, none of the adsorption equation parameters were significantly correlated

with CEC according to John (1972).

Soil texture can influence Cd uptake. In an attempt to study the mobility of Cd and other trace elements Korte et al. (1976), found that soil texture was an important soil property in providing information for predicting a soil's effectiveness for trace element retention. Increasing the clay content provides an increase in CEC which decrease the availability of Cd for uptake.

2.4.3 Organic Matter Content

Soil organic matter serves a dual role in controlling the mobility and availability of cadmium in soil. A number of authors have found that Cd was considerably higher in Ap horizons than in C horizons. Probably because there was a greater association of Cd with organic matter in the Ap horizon than in the C horizon (Dudas and Pawluk 1980; Whitby et al. 1978; Andersson 1977; Holmgren et al. 1993). However, in poorly drained soils from different soil zones in Alberta, Dudas and Pawluk (1977) found no significant correlation ($r = 0.38$, $n = 18$) between contents of Cd and organic matter. This may have due to their choice of HCl as the extractant for the soils.

Soil organic matter plays an important role in retaining soil Cd through its high CEC which in turns renders Cd less available to plants (Haghiri 1974; Mahler et al. 1980; Street et al. 1977; Krishna Murti 1987; McBride et al. 1981).

A fraction of the heavy metals are adsorbed by functional groups of soil organics in the surface soils. The Cu^{2+} ion is known to complex strongly with fulvic and humic acids, Cd^{2+} would be expected to behave much like Zn^{2+} and associate more weakly with

organics. Cavallaro and McBride (1978) suggested that Cd^{2+} would be more susceptible to Ca^{2+} ion competition, while Cu^{2+} is less replaceable.

The other significant role of organic matter involves complexation of Cd with soluble organic matter. Chelates of Cd appeared to be more soluble than those of other metals (Krishna Murti 1987). Neal and Sposito (1986) found that the sorption of Cd at soil solution concentrations between 0.001 and 0.1 $\mu\text{mol Cd kg}_a^{-1}$ (solution concentration; a = aqueous) was inhibited by the formation of soluble Cd-organic associations in aqueous solution. The S-curve isotherms reflected a preferential complexation of Cd at low concentrations with soluble organic material that is not sorbed by the soil solid phases. It has been shown that soluble organic matter contains two distinguishable groups of exchange sites; one of which can bind with the following ions; Ca(II), Mg(II), Cu(II), Zn(II), Ni(II), Co(II), Mn(II), Cd(II), Pb(II), Fe(III) and protons, the second can bind protons, copper and lead only (Fletcher and Beckett 1987). White and Chaney (1980) found that a soil rich in organic matter reduced the amount of Cd uptake compared to another soil low in organic matter when Cd was added to the potted soils. He and Singh (1993) reported that the Cd concentration in ryegrass decreased with increasing amounts of organic matter added to three soils of varying texture, with the decrease being more pronounced in the sand. Haghiri (1974) concluded that Cd concentration in oat shoots was not significantly affected by the addition of organic matter. From his observations, it appeared that the retaining power of organic matter for Cd was predominantly through its CEC property and not its chelating ability.

2.4.4 Soil pH

If other soil conditions remain unchanged, the Cd concentration of plant tissue would decrease as the pH of the soil increased (Page et al. 1987). Under acid soil conditions, Cd tends to approach a maximum concentration in shoots as total soil Cd is increased (Mahler et al. 1980; Mahler et al. 1978; White and Chaney 1980). Thus, liming is an important means of reducing the mobility of added Cd in soils (Jarvis and Jones 1980).

As the soil solution becomes increasingly acidic, the influence of organic ligands on heavy metal adsorption diminishes due to a decreasing ability of the ligands to bind the metal. Changes in metal speciation with increasing H^+ concentration results from an enhanced advantage of H^+ over Cd^{2+} for ligand binding and complexation by products of soil dissolution (Fe^{3+} and Al^{3+}). Concern is justified when heavy metals and strong organic chelators are codisposed on soils at neutral or alkaline conditions (Elliot and Denny 1982).

Williams and David (1976) demonstrated that the uptake of soil Cd increased in subterranean clover when pH was decreased by the addition of $CaSO_4 \cdot 2H_2O$ and decreased when soil pH was increased.

Cadmium solubility decreases with increasing pH. This suggests that calcareous soils are a more efficient sink for both Cd and Pb when compared to noncalcareous soils (Santillan-Medrano and Jurinak 1975).

Garcia-Miragaya and Page (1978), using four soil separates of different chemical and mineralogical properties, found there was a decrease in the amount of Cd sorbed as

the pH decreased. This was to be expected, due to the effect of increasing concentration of H^+ and Al in solution, both of which compete with Cd for ion sorption sites on the soil sorbent surfaces, as well as the concomitant decrease of negative charge of the same surfaces. The increase in Cd sorption with increment in pH was due to the formation of new sorption sites, together with the diminishing of the competition of H with Cd for soil sorption sites. The mechanisms responsible for the charge increase of iron oxide between pH 6 and 7 seemed to be more effective at increasing the Cd sorption capacity between these pH's than those of organic matter (mainly dissociation of carboxylic, phenolic and enolic groups).

The sorption capacities of soils were found to increase approximately three times for each increase in pH of one unit in the pH-interval 4 to 7 (Christensen 1984a). Adsorption of Cd and Pb related to increasing pH. For Cd, the relative change in distribution constant/soil organic matter with pH increases only slightly with increasing ionic strength of the soil solution. Also, for Cd the distribution constant per unit weight of soil organic matter at a given pH decreases strongly with increasing ionic strength of the soil solution. The solution concentration of Cd increases very strongly with increasing ionic strength at a given pH and soil organic matter content. Thus, the soil solution concentration of Pb and Cu is affected much less by pH than by Zn and Cd. The pH at which reversal of the effect of the ionic strength on soil solution concentration and adsorption constants occurs decreases in the order $Cd > Zn > Pb > Cu$. Lead in soils is thus less accessible than Cd, Zn, and Cu (Gerritse and Van Driel 1984).

2.4.5 Other Cations

It is expected that Ca^{2+} in the soil solutions would compete with Cd^{2+} for exchange sites at the root surface and thereby depress uptake. Similarly, Mn^{2+} and Zn^{2+} may also reduce Cd^{2+} uptake from soils (Mahler et al. 1978). Christensen (1987) found that Zn competes effectively for Cd soil sorption sites. Nevertheless, soil application of Zn as an agent in reducing the uptake of Cd by soybean tops did not appear to be practical since the suppression of Cd occurred only when large amounts of Zn were added at which level the yield was drastically reduced (Haghiri 1974). Zinc on an equivalent basis is not a strong competitor for sorption sites. Increasing the soil solution concentrations of Zn, H^+ , Ca, or EDTA (as a model for organic ligands) significantly desorbed Cd from the soils (Christensen 1984b).

The tendency for soil Pb to increase corn shoot Cd concentrations and uptake was less obvious and only speculative. Speculation is that Cd concentrations in the soil solution, and thus in the plant, are elevated by Pb as it has been shown that Pb more effectively competes for exchange sites on colloidal surfaces than Cd (Miller et al. 1977).

An increase in Ca concentration from 10^{-3} to 10^{-2} was found to reduce the Cd sorption capacity of a sandy loam approximately to one third. Competing ions such as Ca^{2+} shift the adsorption equilibria for Cd^{2+} drastically, suggesting that ion exchange is responsible for Cd^{2+} adsorption (Cavallaro and McBride 1978). This fact may significantly affect the distribution of Cd between soil and solute, and hence availability of Cd to plant uptake and leaching, since it is common that Ca concentrations of soil solutions vary widely as a function of time. Calcium present in the soil solution was

found to compete effectively with Cd for adsorption sites in the soil (Christensen 1984b).

The exchangeable Ca^{2+} and sum of bases gave the highest correlation coefficients to the soils CdRC (cadmium retention capacity) (McBride et al. 1981). Their results strongly suggest that Cd^{2+} was adsorbed in the soils by exchange of basic cations (mainly Ca^{2+}) from clays and organic matter. They concluded then, that the quantity of Cd^{2+} adsorption should be largely determined by the number of surface charge sites on clay and organic colloids occupied by basic cations. In general, the sum of exchangeable bases, exchangeable Ca^{2+} , and the CdRC had stronger correlation with Cd^{2+} uptake than the buffered CEC, a soil parameter commonly used to estimate capacity to adsorb heavy metals. Thus, soils with high exchangeable base contents tend to restrict absorption of Cd^{2+} by the plant.

Kuo and Baker (1980) found that the sorption of Cd was drastically reduced when Cu and Zn were present. Since the sorption of Cu, Zn, and Cd occurs at a pH well below the zero point charge (ZPC) of each soil used, the sorption can proceed even in the presence of electrostatic repulsion between the positively charged surfaces and the metal cations.

2.4.6 Other Soil Factors

Factors such as soil mineralogy, soil temperature, soil water stress, soil microorganisms, and Cl^- can also have an affect on the mobility and availability of cadmium in soil.

Based on the hard-soft-acid-base principle, kaolinite shows a preference for the

softer Cd^{2+} compared to the soft Zn^{2+} and Ni^{2+} . Montmorillonite showed no apparent difference in preference for Cd or Zn (Puls and Bohn 1988). The physical differences between kaolinite and montmorillonite that might explain differences in sorption are (i) kaolinite has a greater percentage of hydroxyl edges and (ii) montmorillonite has a larger percentage of ditrigonal cavities formed by six corner-sharing silica tetrahedra on the siloxane planar surface. The reactivity of these cavities are dependent on the excess negative charge distribution due to isomorphous substitution in the silicate structure. If there is no substitution then the cavity functions as a hard Lewis base.

An increase in the concentration of Cd in soybean shoots was associated with increased soil temperature (Haghiri 1974). Giordano et al. (1979) found that heating the soil did not appear to influence the movement of Cd in the soil profile. Haghiri (1974) reported that Cd concentration increased in soybean with increased soil temperature from 15.5 to 26.6 °C.

The availability of soil water may also affect Cd uptake and accumulation. When corn was grown in Cd-amended nutrient solution (0 to 40 $\mu\text{g Cd ml}^{-1}$) and subjected to various levels of water stress induced by additions of polyethylene glycol (an osmoticant) to the solution, Cd uptake was significantly reduced by increasing water stress (Jastrow and Koeppel 1980).

A study by Chanmugathas and Bollag (1987) of the microbial impact upon the fate of Cd in soil showed that it is different under aerobic and anaerobic conditions. In their aerobic studies, Cd was released after its immobilization, whereas no subsequent Cd mobilization occurred during a longer period of anaerobic incubation. Instead, Cd was increasingly immobilized as a result of microbial activity. They concluded from their

studies that soil microorganisms are an important factor in determining the fate of Cd in soil suspensions. In a short-term exposure, Cd added to soil was immobilized as a result of both microbial activity and soil sorption. However, in the long-term, Cd immobilization was followed by its release into solution (including free Cd^{2+}) under aerobic conditions, whereas no Cd mobilization occurred under reduced conditions. In general, the degree of immobilization was considerably greater under anaerobic than under aerobic conditions. Furthermore, the rate and degree of microbial immobilization and mobilization of Cd varied depending on the soil type (Chanmugathas and Bollag 1987). These authors were unable to describe the mechanism involved in the immobilization and mobilization of Cd through microbial activity.

The influence of chloride on Cd bioavailability has been noted by a number of authors. The relatively low Cd-sorption capacity of two southern California soils may have been caused by their higher concentrations of Na^+ and Cl^- , since they are saline, which may result both in competition between cations and, the formation of Cd-Cl complexes that are sorbed to a lesser extent than Cd^{2+} (Neal and Sposito, 1986). The Cl^- treatment of soil resulted in a significant increase in the solubility of the saturation extract cadmium (Cd_{SE}), probably through exchange of adsorbed Cd by the cation associated with the Cl salt and by enhanced solubility of Cd through the formation of soluble Cl complexes of Cd. The increased concentration of Cd_{SE} promoted a greater accumulation of Cd in the test plant, to the extent that the concentration of plant Cd inhibited growth. Cadmium forms relatively strong complexes with Cl and SO_4 ions. The net effect of salinizing to levels frequently encountered in arid-zone soils is for increased solubility of the metal and possibly increased mobility of Cd because of the change in $\text{Cd}^{2+}/\text{CdCl}^+$ or

$\text{Cd}^{2+}/\text{CdSO}_4^0$ ratios. Uptake and accumulation of Cd_{SE} appear to be related more to the activity of Cd^{2+} than to total Cd (Bingham et al. 1983).

2.5 Crop Management Factors Affecting Cadmium Availability

From the above sections it is apparent that a number of soil chemical and physical properties are important factors in the amount of Cd uptake to plants. Plant genetics will also determine the level of Cd uptake which is likely to occur (McLaughlin et al. 1994b).

Soil factors which influence the uptake of soil Cd such as pH, and CEC can be managed. In the case of soil pH reducing soil pH by liming could reduce the level of Cd uptake (Reddy and Patrick 1977). Increasing CEC to sandy soils by addition of organic matter could increase the level of CEC for the soil and increase the level of Cd adsorption while decreasing Cd availability (Lo et al. 1992; Saviozzi et al. 1983). Nevertheless, these two practices may not be agronomically practical for economical reasons.

Limiting the level of Cd in phosphorus fertilizers by selecting a phosphate rock source low in Cd or through processing phosphorus rock for P fertilizer are possible ways for reducing the amount of Cd added to the soil on an annual basis (Roberts et al. 1995; Williams and David 1973). This may be possible at a likely increased cost to producers through increased P fertilizer prices.

The use of Zn fertilizer on Zn deficient soils may offer a management tool for producers to decrease the level of Cd in their crop(s) (Choudhary et al. 1994; Grant et al. 1995; Oliver et al. 1994; McLaughlin et al. 1995).

3. A SURVEY OF SOIL CADMIUM ACROSS THE PRAIRIE ECOZONE

3.1 Abstract

High grain Cd levels (0.1 - 0.2 ppm f.w.) across western Canada have been identified by the Canadian Grain Commission, Grain Research Lab, Winnipeg. A number of these locations are in the Brown soil zone. In order to determine the influence soil genesis has on soil Cd levels, two soil forming factors were studied; climate and parent material. A climosequence consisting of 11 Chernozemic soils from the Brown, Dark Brown, Black, and Dark Gray soil zones, and two Gray Luvisols were sampled for this study. A lithosequence of pedons representative of different parent materials was also included in the study.

Biopedological redistribution of Cd was evident in all the pedons. The intensity of biopedological Cd cycling observed in this study followed a climatic gradient. Solum Cd depletion was more prominent along the climatic gradient of drier and hotter Brown soil zone to the wetter cooler Dark Gray Luvisol soils. Surface soil Cd enrichment factors (A horizon / C horizon) increased along the climosequence from Brown, Dark Brown, and Black soil zones, but decreased in the Dark Gray and Dark Gray Luvisol soil zones 1.38, 1.73, 2.04, 0.787, and 0.833, respectively.

This study also found that the parent material from which a pedon is developed

has a strong influence on the background Cd levels characteristic of a soil. Lacustrine parent material from the Brown soil soil zone was 0.296 and 0.410 mg Cd kg⁻¹ and 0.256 mg Cd kg⁻¹ in the mixed till parent material. In the Black soil zone one mixed till parent material sample was greater (0.346 mg Cd kg⁻¹) than the lacustrine parent material (0.293 mg Cd kg⁻¹). Two other mixed till parent material samples were 0.096 and 0.108 mg Cd kg⁻¹. The Cd content in a shale till parent material from the Dark Gray Luvisol was 0.461 mg Cd kg⁻¹. A mixed till Dark Gray Luvisol soil was 0.351 mg Cd kg⁻¹. Cadmium content in parent material followed the order: shale till > lacustrine > mixed till parent material. Different rock sources for parent material accounted for the Cd lithosequence. Regional total soil Cd levels were related to the Cd content of the underlying Upper Cretaceous shales from which most of the prairie ecozone mixed glacial till soils are in part derived.

3.2 Introduction

High grain Cd levels (0.1 - 0.2 ppm f.w.) across western Canada have been identified by the Canadian Grain Commission from some grab samples taken from grain elevators across the prairie Provinces. Durum wheat is the wheat class with the high grain Cd levels. Grain Cd levels tended to be elevated in the Brown soil zone of the prairie ecozone. For durum grain harvested in 1991 the average Cd content from Alberta was 0.122 ppm, Saskatchewan was 0.104 ppm and Manitoba was 0.091 ppm (f.w.). The data from the Canadian Grain Commission indicates a relationship may exist for

grain Cd which corresponds to the soil zones of the prairie ecozone.

The Cd "Rechvert" (guide values) of cereals exported to Germany are currently 0.1 ppm (f.w.) for wheat. The European Union (1997) is proposing a grain Cd limit of 0.2 ppm (f.w.) in all cereals. Codex Alimentarius Commission of the World Health Organization (FAO/WHO 1995) has proposed a grain cadmium (Cd) limit of 0.1 ppm (f.w.) for export. Therefore, depending on the country Canada is exporting its wheat to, it may be necessary in the future to be able to manage the grain Cd content. This is, and would continue to be managed to some extent by compositing Canadian grain shipments. Nevertheless, other methods of controlling grain Cd need to be investigated should Canadian grain Cd levels need to be lowered.

Canada is attempting to control grain Cd levels by conducting research in three different areas. First, plant breeding is being used to develop low Cd accumulators. Second, agronomic aspects of crop management such as fertility practices are being developed as a the means for limiting the uptake of soil Cd. Thirdly, background soil Cd levels need to be investigated to identify regions capable of producing higher grain Cd, so that these can be taken out of durum production, if necessary.

Jenny (1980) used a mathematical description to describe soil genesis. He considered the five soil-forming factors: cl , climate; σ , biotic factors; r , topography; p , parent material; t , time; and ..., the dot factors (periodic natural occurrences) as ecosystem determinants. As a group he referred to them as state factors. Thus as an ecosystem property, soil properties (S) are a function of these five state factors. Jenny described this mathematically as $S = f(cl, \sigma, r, p, t, \dots)$

A lithosequence $S = f(p)_{cl, \sigma, r, t, \dots}$ can be studied if the parent material (geochemistry) of the rock source is known for the pedon sites and all the other variables in the soil forming equation are constant. The influence of parent material on the soil Cd levels from different soil zones across the prairie ecozone will be reflected in the geology of the source rock from which the parent material is derived. Typically, shale rocks contain higher levels of Cd than other rock sources (Alloway 1990b). Therefore the relative proportion of shale rock in the till material will also influence the level of Cd in the soil.

A climosequence $S = f(cl)_{\sigma, r, p, t, \dots}$ (vegetation) can be studied using different climatic zones and knowing which soils share the same parent material (geochemistry) so that along with parent material all the other state factors except climate are constant to satisfy the soil forming equation. Climate will influence soil genesis in the different soil zones across the prairie ecozone due to the type of native vegetation associated with a particular climatic region. Going from the Brown soil zone to the Dark Gray soil zone the climate changes from arid with short grasses to sub-humid which has a transition vegetation consisting of grasses and forrest trees. The difference in climate and its influence on the type of native vegetation will in turn influence the intensity of biopedological cycling.

This study was initiated to determine the pedogenic influences two soil forming factors; climate, $S_{Cd} = f(cl)_{\sigma, r, p, t, \dots}$ and parent material, $S_{Cd} = f(p)_{cl, \sigma, r, t, \dots}$ have on soil Cd levels in the prairie ecozone.

3.3 Materials and Methods

3.3.1 Soils

Study Area

Grassland and Forested soils:

A map of the study area is given in Figure 3.1. Sampling sites were selected on the basis of regions which have shown repeatedly higher levels of grain Cd from data obtained by the Canadian Grain Commission. All sites selected are from agricultural fields. A total of thirteen sites were selected. Sites were selected based on similarity in surface texture (clay loam) to eliminate the influence of soil texture on soil Cd levels. All sites were sampled from the mid-slope position to allow for sampling of the modal soil for the sub group classification.

Thirteen pedons were sampled from two soil orders. Eleven pedons from the Chernozemic soil order, and two pedons from the Luvisolic soil order. A climosequence represented by five different soil zones: Brown, Dark Brown, Black, Dark Gray, and Dark Gray Luvisol was used for this study. This climosequence represents a transect through soil zones reflecting a change in climate and vegetation in each. Sites sampled in the lithosequence represented three different parent material types: mixed till, lacustrine, shale till. The locations, soil series sampled, their subgroups and parent material are given in Table 3.1. A complete soil description for each pedon and their profile location is provided in Appendix I.

Pedon Sites Key:

Pedon	Soil Series	P.M.
a	Chin	lac
b	Maleb	till
c	Ardill	till/lac
d	Readymade	till
e	Weyburn	till
f	Beaverhills	till
g	Mayfair	till
h	Newstead	till
i	Niverville	lac
j	Falun	till
k	Whitewood	till
l	Nayler	sh till
m	Pembina (2)	till

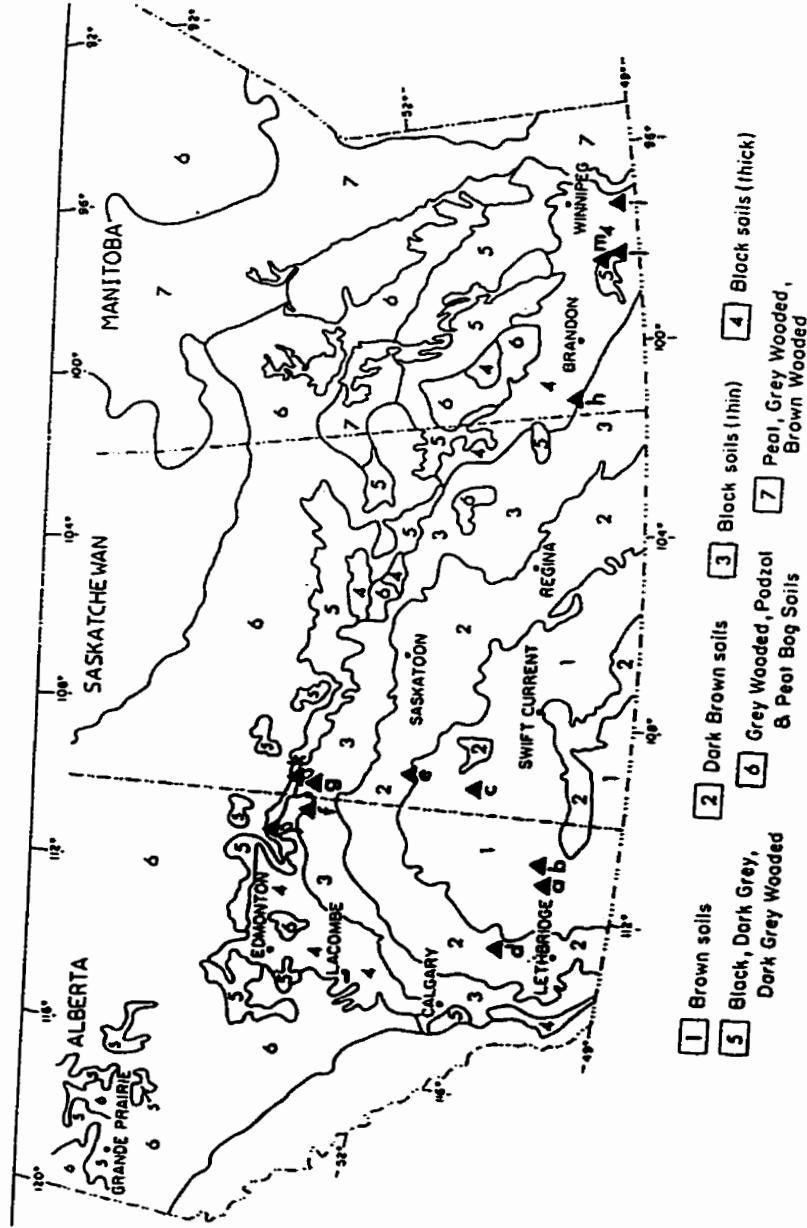


Figure 3.1 Selected pedon sites from soil zones in the prairie ecozone for this study.

Table 3.1 Locations, soil series names, Canadian System of Soil Classification and United States Soil Taxonomy of pedons.

Location	Legal Description	Physiographic District	Soil Series	Soil Subgroup	U.S. Soil Taxonomy	Parent Material
Mantario, SK	SE32-26-27-W3	Neutral Hills Uplands	Ardill	Orthic Brown	Aridic Haploboroll	mixed till
Bow Island, AB	NE10-12-9-W4	Etzikom Plain	Maleb	Orthic Brown	Aridic Haploboroll	mixed till
Bow Island, AB	NE31-11-10-W4	Etzikom Plain	Chin	Orthic Brown	Aridic Haploboroll	lacustrine
Vulcan, AB	SE26-17-21-W4	Majorville Upland	Readymade	Orthic Dark Brown	Aridic Haploboroll	mixed till
Major, SK	NE16-33-26-W3	Neutral Hills Uplands	Weyburn	Orthic Dark Brown	Aridic Haploboroll	mixed till
St.Jean, MB	NE28-2-1-E1	Red River Plain	Niverville	Gleyed Rego Black	Typic Haploboroll	lacustrine
Viriden, MB	NE27-9-28-W1	Oxbow Till Plain	Newstead	Orthic Black	Typic Haploboroll	mixed till
Lloydminster, SK	SW6-49-27-W3	Missouri Couteau Upland	Mayfair	Orthic Black	Typic Haploboroll	mixed till
Kitscoty, AB	NW7-50-3-W4	Viking Upland	Beaverhills	Orthic Black	Typic Haploboroll	mixed till
St. Walburg, SK	SE6-52-23-W3	Missouri Couteau Upland	Whitewood	Orthic Dark Gray	Boralfic Agriboroll	mixed till
Myrnam, AB	NW5-55-9-W4	Myrnam Upland	Falun	Orthic Dark Gray	Boralfic Agriboroll	mixed till
Somersset, MB	W30-5-9-W1	Pembina Hills	Naylor	Dark Gray Luvisol	Typic Eutroboralf	shale till
Altamont, MB	SW32-5-8-W1	Pembina Hills	Pembina (2)	Dark Gray Luvisol	Typic Eutroboralf	mixed till

Field Methods

The profiles were exposed to a depth of 1.0 m at each site. Each pedon was photographed and described in the field. One kg soil samples were collected on a genetic horizon basis, from the middle of each horizon. Subsamples for bulk density determination were also collected in duplicate on a genetic basis using a core sampler. All soil samples were stored in plastic bags.

3.3.2 Analytical Procedures

Sample Preparation

Soil samples were air-dried then passed through a No. 10 plastic sieve with 2.0 mm mesh openings. Any soil aggregates which were too large to pass through were broken using a wooden rolling pin to allow all soil aggregates less than 2.00 mm to be collected. The hygroscopic water content was determined for the soil samples to allow all analytical determinations to be expressed on an oven-dry basis. All analytical determinations were performed in triplicate. The mean values of the particle size fractions, CaCO₃, soil pH, exchangeable cations, cation exchange capacity, and the heavy metals contents were reported.

Physical Analyses

Particle size distribution was determined using the pipette method (McKeague 1981).

Chemical Analyses

Inorganic carbon content was determined using the Bundy and Bremner (1972) titrimetric method. Organic carbon content was determined using a modified Mebius method (Yeomans and Bremner 1988). Soil pH was determined using 0.01 M CaCl₂ at 1:2 soil to solution ratio. Exchangeable cations and cation exchange capacity were determined using a modified version of the Hendershot and Duquette (1986) method of BaCl₂ saturation followed by MgCl₂ replacement, respectively. These analyses were conducted on the fine earth fractions.

Representative subsamples of the fine earth fraction were ground using an agate mortar and pestle then passed through a plastic mesh sieve with 150 μm diameter openings. Soil samples were weighed out to approximately 0.2 g into block digestion tubes, two blanks and two standard reference soil samples were included with each set of 40 tubes. To each tube 5 mL of HNO₃, and 2.5 mL of HClO₄ were added, the samples were mixed and allowed to sit for 1 hour. The samples were then placed in a block digester and brought to 230° C and maintained at this temperature for two hours. The samples were then allowed to cool, filtered through wetted #42 Whatman filter paper and brought to 25 mL using deionized water. Samples were then stored in plastic scintillation vials for further analysis. About 10 mL of the sample was removed for analysis of Cu, Fe, Ni, Pb, and Zn on a Perkin-Elmer, 1100 B atomic absorption spectrophotometer, using flame directly. The remaining 15 mL of extract was treated with 0.05% dithizone at a pH of 4.5 to remove background interferences and concentrate the HNO₃ - HClO₄ digestible Cd. The samples were then analyzed using a Perkin-Elmer, 1100 B atomic absorption spectrophotometer with graphite furnace, with a detection limit of 0.250 ppb.

3.4 Results and Discussion

3.4.1 Climosequence of total soil cadmium and other heavy metals

Morphological descriptions, including physical and chemical properties for the pedons are provided in Appendix I.

Different climatic influxes are occurring along the climosequence. The mean annual precipitation (maP) from the sites in the Brown soil zone was 335 mm, Dark Brown soil zone was 404 mm, Black soil zone was 459 mm, Dark Gray soil zone was 428 mm, and the Gray Luvisol soils was 547 mm (Table 3.2). The mean annual temperature (maT) from the sites in the Brown soil zone was 4.7 °C, Dark Brown soil zone was 3.0 °C, Black soil zone was 1.8 °C, Dark Gray soil zone was 0.7 °C, and the Gray Luvisol soils was 1.8 °C (Table 3.3).

There is evidence of a net downward movement of water into the soil system based on the profile development in the pedons studied. The supplemental data in Appendix I. shows that as the amount of rainfall to a pedon increases along this climatic gradient, the depth to calcium carbonate (CaCO_3), and solum depth increases and the % base saturation decreases.

The pedogenesis of the pedons studied displayed soil chemical properties reflecting the soil zones the pedons were located. All of the soils except the Nayler Series have formed from calcareous parent materials (Appendix I). The Niverville Series had the highest CaCO_3 content in the surface horizon (71 g kg^{-1}). The CaCO_3 content of the soils

Table 3.2 Precipitation (normals) for selected weather stations based on the period 1951 to 1980 (Environment Canada 1982).

Soil Series	Weather Station Location	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
mm														
Ardill	Sibbald, Ab	17.6	10.8	17.6	22.1	31.1	62.1	44.5	42.7	31.5	13.5	13.8	14.0	321.3
Maleb	Bow Island, AB	19.2	12.9	14.4	31.9	50.3	70.6	28.1	38.4	34.3	13.7	14.9	13.7	342.4
Chin	Bow Island, AB	19.2	12.9	14.4	31.9	50.3	70.6	28.1	38.4	34.3	13.7	14.9	13.7	342.4
Readymade	Vulcan, AB	16.2	17.3	16.4	32.9	51.2	80.9	51.4	51.8	37.0	18.3	13.4	17.7	404.5
Weyburn	Denzil, SK	21.7	17.5	21.2	27.1	38.6	73.7	71.7	49.6	29.0	15.3	17.2	21.4	404.0
Niverville	Altona, MB	26.3	17.7	24.2	40.8	58.7	76.7	77.1	63.9	54.6	27.4	19.9	23.3	510.6
Newstead	Virden, MB	21.3	22.5	17.9	29.7	45.1	72.0	67.9	66.4	49.4	30.0	17.1	22.4	461.7
Mayfair	Waseca, SK	25.7	16.1	26.7	24.1	39.4	75.7	76.2	67.9	34.3	19.3	18.4	25.2	449.0
Beaverhills	Kitscoty, AB	20.1	14.3	17.1	17.8	36.9	85.7	73.8	62.4	36.5	14.7	16.2	19.1	414.6
Whitewood	Frenchman Butte, SK	24.9	15.2	21.3	17.9	33.2	70.4	78.0	58.7	29.8	20.4	12.7	20.7	403.2
Falun	Elk Point, AB	22.9	14.9	20.3	20.8	40.7	70.1	83.0	73.5	45.7	19.4	18.9	23.3	453.5
Nayler	Sommerset, MB	20.3	22.5	29.6	41.7	71.0	77.1	78.1	62.8	60.4	33.1	28.0	22.2	546.8
Pembina (2)	Sommerset, MB	20.3	22.5	29.6	41.7	71.0	77.1	78.1	62.8	60.4	33.1	28.0	22.2	546.8

Table 3.3 Temperature (normals) for selected weather stations based on the period 1951 to 1980 (Environment Canada 1982).

Soil	Weather Station	°C												
Series	Location	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
Ardill	Sibbald, Ab	-17.0	-12.3	-6.3	3.6	10.9	15.2	18.1	17.0	10.8	4.5	-5.3	-12.5	2.2
Maleb	Bow Island, AB	-11.3	-6.3	-1.5	6.4	12.7	17.1	20.0	19.0	13.1	8.2	-0.6	-6.5	5.9
Chin	Bow Island, AB	-11.3	-6.3	-1.5	6.4	12.7	17.1	20.0	19.0	13.1	8.2	-0.6	-6.5	5.9
Readymade	Vulcan, AB	-12.1	-7.4	-3.3	4.3	10.3	14.3	17.6	16.5	11.5	6.4	-2.3	-7.6	4.0
Weyburn	Denzil, SK	-17.8	-12.9	-7.6	3.3	10.9	15.3	17.6	16.7	11.0	5.2	-5.7	-13.5	1.9
Niverville	Altona, MB	-18.7	-14.8	-7.4	3.8	11.9	17.6	20.0	18.8	12.9	6.5	-4.0	-13.0	2.8
Newstead	Viriden, MB	-19.1	-15.0	-7.6	3.5	11.3	16.3	19.3	17.7	11.7	5.5	-5.0	-14.1	2.0
Mayfair	Waseca, SK	-19.1	-13.7	-8.5	2.7	10.4	14.2	16.8	15.5	10.1	4.3	-6.2	-14.1	1.0
Beaverhills	Kitiscoty, AB	-18.1	-12.9	-8.0	2.8	10.5	14.4	16.9	15.6	10.2	4.5	-5.8	-13.4	1.4
Whitewood	Frenchman Butte, SK	-20.2	-15.2	-9.5	3.0	10.7	14.6	17.0	15.5	9.7	4.0	-6.6	0.0	0.6
Falun	Elk Point, AB	-19.5	-13.8	-8.3	2.8	10.2	14.0	16.4	14.9	9.4	3.8	-6.8	-14.7	0.7
Nayler	Sommerset, MB	-19.1	-15.1	-8.5	2.5	10.5	16.2	18.7	17.7	11.7	5.8	-5.1	-13.7	1.8
Pembina (2)	Sommerset, MB	-19.1	-15.1	-8.5	2.5	10.5	16.2	18.7	17.7	11.7	5.8	-5.1	-13.7	1.8

ranged from 0 to 6 g kg⁻¹, 0 to 3 g kg⁻¹, and 0 to 71 g kg⁻¹ in the Brown, Dark Brown, and Black soils, respectively. The CaCO₃ content in the Dark Gray soils were both 1 g kg⁻¹. The CaCO₃ content in the Gray Luvisol soils ranged from 0 to 20 g kg⁻¹. The Ardill Series, Maleb Series, Weyburn Series, and the Niverville Series soils have had some lixiviation of CaCO₃ resulting in calcification indicated by the Cca horizon designation within these pedons. Most sola contained little in the amount of CaCO₃ and the depth at which larger amounts of carbonates were present was deeper for the sites from the more subhumid to humid climatic region; Whitewood, Falun, Nayler, and the Pembina (2) Series soils.

Generally the % base saturation increased with depth in the pedons (Appendix I). Some of the pedons with the highest % base saturation were those soils from the Brown soil zone. Soils from this soil zone had % base saturation values for their surface horizon ranging from 74.5 to 134.1%. Values greater than 100% likely indicate the presence of CaCO₃ and a high degree of base saturation. All the horizons for the Chin Series pedon had % base saturation values > 100%. It is not surprising that the more arid Brown soil zone had pedons with the greatest degree of base saturation. The level of base saturation is closely associated with climate and the annual amount of rainfall a region receives (Tan 1993). The % base saturation in the surface horizons from soils in the Dark Brown soil zone ranged from 79.8 to 82.4%. The % base saturation in the surface horizons from soils in the Black soil zone ranged from 73.8 to 79.8%. The % base saturation in the surface horizons from soils in the Dark Gray soil zone ranged from 65.5 to 88.7%. Since the surface horizon for the Falun Series soil had the lowest % base saturation value (65.5%) of all the pedons it would suggest that the level of annual precipitation in this region is probably greater than other regions sampled in this study. It is expected that the % base saturation would be the least for the Nayler and Pembina (2) Series pedons since the mean monthly precipitation (45.6 mm, Table 3.2) for these sites is greater than for any of the other

sites studied.

The solum depths' soils ranged from 0.45 - 0.57 m, 0.26 - 0.30 m, 0.32 - 0.70 m, 0.47 - 1.00 m, and 0.67 - 0.70 m for the Brown, Dark Brown, Black, Dark Gray, and Gray Luvisol soils, respectively (Appendix I). The difference in solum depth between soil zones is likely a reflection of annual precipitation from the study sites.

The total (HNO_3 - HClO_4 digestible) soil Cd, and Zn contents for the thirteen pedons is presented on a horizon basis in Table 3.4. The range in values for total soil Cd in the A horizon was 0.067 to 0.615 mg Cd kg⁻¹ soil for the Falun and Chin Series soils, respectively (Table 3.4). The range in values for total soil Cd in the 9 uniform parent materials was 0.096 to 0.461 mg Cd kg⁻¹ soil for the Mayfair and Nayler Series soils, respectively (Table 3.4). All of the soil horizons in the study contained total Cd within typical background levels for soil, i.e., 1.0 mg kg⁻¹ (Plant and Raiswell 1983). Generally the level of soil Cd in this study was greatest in the surface horizon. The soil Cd levels from this study are similar to other reported values in the literature of other Canadian studies. A recent study of the A horizon in soils from the prairie ecozone found the mean value to be 0.3 mg Cd kg⁻¹ soil (Garrett 1994). A study in Northwestern Alberta (Soon and Abboud 1990) reported the mean total soil Cd (HNO_3 - HF - HClO_4 digestible) for the surface horizon as 0.3 mg Cd kg⁻¹ and 0.2 mg Cd kg⁻¹ in the subsoil. The background level of Cd in Canadian soils from the Interior Plains has been reported as < 1 mg kg⁻¹ (McKeague and Wolynetz 1980). Supplemental data on total (HNO_3 - HClO_4 digestible) soil Cu, Ni, and Pb contents for the thirteen pedons is listed in Appendix II.

There is very little in the literature which describes the vertical distribution of soil Cd on a horizon (ie. genetic) basis. Pierce et al. (1982) described the vertical distribution of Cd on the basis of surface soil, subsoil, and parent material. The surface horizon was based on a 0 to 15 cm depth, the subsoil depth was from 15 cm to the top of the C horizon, and the layer below the

Table 3.4 Profile distribution of Cd and Zn^a in the pedons studied.

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd \pm sd mg kg ⁻¹	Zn \pm sd	
Ardill	Ap	0 - 0.10	0.232 \pm 0.084	44.9 \pm 10	193
	Bm	0.10 - 0.30	0.139 \pm 0.090	43.2 \pm 20	311
	Bmk	0.30 - 0.45	0.103 \pm 0.087	34.6 \pm 16	337
	Cca	0.45 - 0.60	0.240 \pm 0.044	52.4 \pm 18	218
	IIck	0.60 - 0.92	0.610 \pm 0.073	77.5 \pm 12	127
	IIIck	0.92 - 1.15	0.410 \pm 0.121	81.7 \pm 23	199
Maleb	Ap	0 - 0.20	0.521 \pm 0.242	67.1 \pm 22	129
	Ahe	0.20 - 0.30	0.424 \pm 0.286	66.7 \pm 46	157
	Bmk	0.30 - 0.46	0.332 \pm 0.031	49.4 \pm 26	149
	Cca	0.46 - 0.57	0.217 \pm 0.157	65.3 \pm 50	301
	Ck	0.57 - 1.00	0.256 \pm 0.159	67.9 \pm 43	265

sd = standard deviation, ^a all values reported on an oven-dry basis

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd ———— mg kg ⁻¹ ————	Zn ± sd ————	
Chin	Ap	0 - 0.15	0.615 ± 0.297	89.5 ± 37	146
	AB	0.15 - 0.24	0.343 ± 0.029	67.5 ± 8	197
	Btj	0.24 - 0.42	0.296 ± 0.049	78.6 ± 25	265
	BC	0.42 - 0.57	0.214 ± 0.033	83.2 ± 38	388
	Ck1	0.57 - 0.70	0.296 ± 0.067	60.3 ± 7	204
	HCk	0.70 - 1.00	0.275 ± 0.010	42.5 ± 10	155
Readymade	Ap	0 - 0.10	0.383 ± 0.054	68.3 ± 26	178
	Bm	0.10 - 0.30	0.204 ± 0.027	55.6 ± 12	272
	Ck1	0.30 - 0.70	0.273 ± 0.110	31.3 ± 27	115
	Ck2	0.70 - 1.00	0.247 ± 0.067	37.5 ± 7	152

sd = standard deviation

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd	Zn ± sd	
			mg kg ⁻¹		
Weyburn	Ap	0 - 0.13	0.424 ± 0.084	63.6 ± 6	150
	Bm	0.13 - 0.26	0.088 ± 0.076	46.6 ± 7	531
	Cca	0.26 - 0.56	0.180 ± 0.069	50.9 ± 22	283
	Ck1	0.56 - 0.66	0.161 ± 0.031	44.6 ± 11	278
	Ck2	0.66 - 1.10	0.136 ± 0.086	46.0 ± 6	338
Niverville	Apk	0 - 0.15	0.516 ± 0.176	96.4 ± 26	187
	AC	0.15 - 0.32	0.159 ± 0.012	64.2 ± 7	404
	Cca	0.32 - 0.80	0.245 ± 0.024	47.7 ± 17	195
	HCk	0.80 - 1.00	0.293 ± 0.030	91.2 ± 8	311

ND = not determined, sd = standard deviation

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd —— mg kg ⁻¹ ——	Zn ± sd	
Newstead	Ap	0 - 0.20	0.386 ± 0.029	63.8 ± 3	165
	Bm	0.20 - 0.40	0.319 ± 0.135	65.5 ± 3	205
	IIcK1	0.40 - 0.65	0.283 ± 0.014	40.1 ± 0	142
	IIcK2	0.65 - 0.95	0.346 ± 0.027	57.4 ± 27	166
Mayfair	Ap	0 - 0.10	0.100 ± 0.104	49.3 ± 19	493
	Btj	0.10 - 0.28	0.043 ± 0.037	43.8 ± 20	1020
	Bm	0.28 - 0.37	0.056 ± 0.049	40.9 ± 23	730
	Ck1	0.37 - 0.60	0.231 ± 0.117	39.8 ± 6	172
	Ck2	0.60 - 0.88	0.132 ± 0.042	84.2 ± 73	636
	Ck3	0.88 - 1.12	0.096 ± 0.084	47.9 ± 4	499

ND = not determined, sd = standard deviation

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd —— mg kg ⁻¹ ——	Zn ± sd	
Beaverhills	Ap	0 - 0.14	0.317 ± 0.052	61.0 ± 23	193
	AB	0.14 - 0.21	0.204 ± 0.044	66.9 ± 16	328
	Bm	0.21 - 0.40	0.058 ± 0.100	39.1 ± 14	674
	Bt	0.40 - 0.62	0.105 ± 0.045	48.3 ± 17	460
	BC	0.62 - 0.70	0.165 ± 0.026	48.7 ± 23	296
	Ck	0.70 - 1.10	0.108 ± 0.030	45.9 ± 23	425
Whitewood	Ap	0 - 0.10	0.169 ± 0.014	44.5 ± 43	264
	Bt1	0.10 - 0.27	0.054 ± 0.050	55.7 ± 35	1036
	Bt2	0.27 - 0.47	0.044 ± 0.022	38.3 ± 16	862
	Ck1	0.47 - 0.72	0.132 ± 0.066	41.8 ± 30	316
	Ck2	0.72 - 1.00	0.132 ± 0.088	35.5 ± 32	269

sd = standard deviation

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd mg kg ⁻¹	Zn ± sd	
Falun	Ap	0 - 0.20	0.067 ± 0.064	246.7 ± 353	3659
	AB	0.20 - 0.25	0.004 ± 0.050	41.2 ± 25	11353
	Btj1	0.25 - 0.49	0.006 ± 0.010	44.5 ± 26	7854
	Btj2	0.49 - 0.76	0.019 ± 0.028	37.6 ± 18	2003
	BC	0.76 - 1.00	0.069 ± 0.060	36.7 ± 14	530
	Ck	1.00+	0.169 ± 0.061	37.5 ± 14	222
Nayler	Ap	0 - 0.20	0.384 ± 0.132	96.6 ± 4	252
	Ae	0.20 - 0.30	0.092 ± 0.040	78.7 ± 12	856
	Bt	0.30 - 0.50	0.078 ± 0.022	149.0 ± 15	1911
	BC	0.50 - 0.70	0.056 ± 0.006	109.0 ± 67	1946
	C	0.70 - 1.00	0.461 ± 0.639	141.0 ± 13	306

ND = not determined, sd = standard deviation

Table 3.4 (continued).

Soil Series	Horizon	Depth m	Total		Zn / Cd
			Cd ± sd mg kg ⁻¹	Zn ± sd	
Pembina (2)	Ap	0 - 0.25	0.490 ± 0.045	80.8 ± 21	165
	Ae	0.25 - 0.30	0.273 ± 0.033	87.5 ± 23	320
	Bt1	0.30 - 0.37	0.140 ± 0.019	187.5 ± 129	1339
	Bt2	0.37 - 0.67	0.129 ± 0.011	55.6 ± 9	431
	Hk1	0.67 - 0.95	0.314 ± 0.009	58.7 ± 1	187
	Hk2	0.95 - 1.30	0.351 ± 0.013	35.5 ± 4	101

ND = not determined, sd = standard deviation

top of the C horizon represented the parent material. Others have described the vertical distribution of Cd on a limited depth basis.

The discussion on the soil Cd profile distribution as a function of climate will be limited to those pedons which have developed from uniform parent material (ie. pedons developed from a single parent material source or pedons of a single parent material with no textural stratification) with all other state factors constant $S_{Cd} = f(cl)_{s, r, p, t, \dots}$. The soil series from this study which meet this criteria are Maleb, Chin, Readymade, Weyburn, Mayfair, Beaverhills, Whitewood, Falun, and Nayler. Those pedons (Ardill, Niverville, Newstead, and Pembina(2) Soil Series) possessing Roman numeral horizon prefix designations will not be included in the discussion of climosequence because they are pedons developed from more than one parent material or are developed from parent material which is texturally stratified. The one exception to a pedon possessing a Roman numeral horizon prefix designation is the Chin Series. The Chin soil Series is developed from glaciolacustrine material over clay loam till. This characterization is supported by the difference in calcium carbonate content between the Ck1 and the IICk. This pedon will be considered in the discussion on climosequence even though it possesses a IICk horizon. In this case the overlying Ck1 will be considered as the parent material.

A comparison of the pedons clearly displays the influence of climate / vegetation on soil development and the distribution of Cd in their profiles. The climatic data for the Maleb soil Series indicates that the maP is 342.4 mm and the maT is 5.9 °C (Table 3.2 and Table 3.3). The total soil Cd profile distribution for this soil indicates a greater amount of soil Cd for the Ap, Ahe, and Bmk horizons over the Ck horizon and a slight

decrease in total soil Cd in the Cca horizon over the Ck horizon. The Chin soil Series has a maP of 342.4 mm and a maT of 5.9 °C. The total soil Cd distribution for the Chin series indicated that the Ap horizon contained the largest amount of Cd. The Cd content decreased with depth in the solum, and then increased in the Ck1 horizon. The Readymade soil Series has a maP of 404.5 mm and a maT of 4.0 °C. The total soil Cd profile distribution for this soil displays the largest amount of soil Cd in the Ap and a slight increase in total soil Cd in the Ck1 horizon over the Ck2 horizon. There was a slight decrease in total soil Cd in Bm horizon compared to the Cd content in the Ck2 horizon. The climatic data for the Weyburn soil Series indicates that the maP is 404.0 mm and the maT is 1.9 °C. The total Cd profile distribution for this soil also displayed a greater amount of soil Cd in the Ap horizon and only a slight increase in soil Cd in the Cca and Ck1 horizons over the soil Cd content in the Ck2 horizon. There was only a slight decrease of total soil Cd in the Bm horizon compared to the Ck2 horizon. The Mayfair soil Series has a maP of 449.0 mm and a maT of 1.0 °C. The total Cd profile distribution for this soil displayed a similar total soil Cd contents in the Ap and Ck3 horizons. The total soil Cd content decreased in both the Btj and Bm horizons by approximately half the content of the Ck3 horizon. The total soil Cd in the Mayfair soil Series profile was highest in the horizons which contained CaCO₃ in the range from 8.9 to 11.8 g CaCO₃ kg⁻¹. The higher total soil Cd content at the lower depths may be a reflection of CdCO₃ being present in these horizons where Cd²⁺ has substituted for Ca²⁺ (Vlasov 1966). The climatic data for the Beaverhills soil Series indicates that the maP is 414.6 mm and the maT is 1.4 °C. The total Cd profile distribution for this soil

displayed a larger amount of total soil Cd in both the Ap and AB horizons. There was a decrease by half the total soil Cd content in the Bm horizon compared to the Ck horizon. The Whitewood soil Series has a maP of 403.2 mm and a maT of 0.6 °C. The total soil Cd profile distribution for this soil displayed a slight increase in total soil Cd in the Ap horizon over the Ck2 horizon and half the content of total soil Cd from the Bt1 and Bt2 horizons compared to the Ck3 horizon. The climatic data for the Falun soil Series indicates that the maP is 453.5 mm and the maT is 0.7 °C. The total Cd profile distribution for this soil displayed a decrease in all the horizons overlying the Ck horizon. The greatest decrease in total soil Cd occurred from the AB and Btj horizons. The Nayler soil Series has a maP of 546.8 mm and a maT of 1.8 °C. The total soil Cd distribution for the Nayler Series indicated that the Cd content in the Ap horizon was 0.384 mg kg⁻¹. The Cd content then decreased with depth in the solum and was largest in the C horizon, 0.461 mg kg⁻¹. A shale band and shale fragments were observed in the BC and C horizons, respectively (Appendix I). This would likely account for the higher Cd content for the C horizon compared to the Ap horizon for this pedon.

Cadmium does not appear to be a very mobile heavy metal within the soil. Any pedons indicating pervention of clay in a horizon (Appendix I i.e., the Chin Series, Beaverhills Series, Whitewood Series, Falun Series, Nayler Series, and Pembina (2) Series soils) did not display a correspondingly higher total soil Cd concentration. Instead, it appears that once Cd has been removed from the soil by the vegetation and probably forms an organo-metal complex (Fletcher and Beckett 1987; Linehan 1985; Lo et al. 1992), the Cd tends to remain at the surface and not move down the profile.

A biopedological redistribution of Cd from the solum is evident in all of the soil pedons. Generally the accumulation of Cd in the profiles was greatest in the surface horizon, decreasing with depth through the solum and then increasing in content closer toward the C horizon (parent material). Graphically, this could be represented as a sideways letter "U". Furthermore, the pedological redistribution of soil Cd within each profile, i.e., the curvature of the sideways "U" was intensified in going from Brown, Dark Brown, Black, and Dark Gray soil zones and Dark Gray Luvisol soils, respectively. Thus, the depletion of Cd from below the surface horizon is more prominent moving along the climatic gradient of the semiarid climate of the Brown soil zone to the subhumid to humid climate of the Dark Gray Luvisol soils. The soil Cd enrichment factor (Ap horizon / C horizon) for the Brown, Dark Brown, Black, Dark Gray and Dark Gray Luvisol soils (Table 3.5) were 1.38, 1.73, 2.04, 0.787, and 0.833, respectively.

This trend occurs even though the total soil Cd content of the unaltered parent material is generally decreasing along the same climosequence i.e., the mean Cd content in the C horizons were found to be in the order Brown: 0.266 mg Cd kg⁻¹, Dark Brown: 0.192 mg Cd kg⁻¹, Black: 0.102 mg Cd kg⁻¹, Dark Gray: 0.150 mg Cd kg⁻¹ (Table 3.5). This would also support the argument that surface soil Cd enrichment is a function of climate.

The method of expressing quantitative changes of Cd to the pedons during their development in this study has one main limitation. Analyses of the Cd profile distribution, and surface soil Cd enrichment were done attempting to ensure only uniform parent material for the entire depth of the control section were discussed. A more precise measure of the changes to the soils during their development would be to use a

Table 3.5 Soil cadmium^a enrichment factors from five Great Groups in the Prairie Ecozone.

Great Group	A horizon			C horizon			Mean	Pedons
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Cd Enrichment Factor	
	mg Cd kg ⁻¹						A / C	
Brown	0.368	0.232	0.521	0.266	0.256	0.275	1.38	2
Dark Brown	0.333	0.383	0.424	0.192	0.136	0.247	1.73	2
Black	0.208	0.100	0.317	0.102	0.096	0.108	2.04	2
Dark Gray	0.118	0.067	0.161	0.150	0.132	0.169	0.787	2
Gray Luvisol	0.384			0.461			0.833	1

^a all values are reported on an oven-dry basis

"Pedogenic Index" (St. Arnaud et al., 1988). This is a mass-balance method, which verifies the uniformity of the deposit. The pedogenic index is based on the premise that the total quartz content in a soil remains unchanged during soil development. A recalculation of the original composition of horizons using the parent material values for quartz and other constituents as representative of the original deposit can be used to express overall net changes to a soil property during soil development. The pedogenic indices method was not used for determining changes to soil Cd in the pedons, since a resistant mineral to weathering like quartz was not measured. The % sand and silt fraction could have been used as a rough estimate of a resistant mineral, with the assumption they represent quartz size particles. This was not done since the method used for determining the particle size fractions in this study did not remove the CaCO₃ from the soil. Therefore, erroneous pedogenic index values could result if % sand and silt fractions were used, since part of these fractions could include CaCO₃ size sand and silt particles.

A study by Dudas and Pawluk (1980) of Alberta soils from similar regions to the ones in this study found a similar trend for the soil Cd content in the surface mineral horizon moving along the climosequence from the Brown, Dark Brown, Black, and Gray Luvisol soil zones. They also reported that the Cd was depleted from the solum below the enriched surface horizons from the Black and Gray Luvisol soils.

Contrary to this study two previous studies on Manitoba soils have both reported that the C horizon was greater in soil Cd than the A horizon (Madden 1974; Mills and Zwarich 1975). The pedons from Manitoba in this study were generally found to have

a higher soil Cd content in the A horizon than any other horizon. The one exception in Manitoba was the Nayler soil Series. Madden (1974) reported a mean total soil Cd of 0.8 mg kg^{-1} in the A horizon and 1.1 mg kg^{-1} for the C horizon. The same author found that Zn content was higher in the A horizon than the C horizon.

The pedogenetic redistribution of total soil Cd in the pedons is to a large extent likely due to historic biopedological cycling (cheluviation) and to a smaller extent the addition of phosphatic fertilizers containing Cd impurities. To explain the nature of the historic biopedological cycling it is necessary to consider the rooting patterns of the native vegetation from the soil zones.

In the grassland ecosystem, most of the biomass is below the surface. The level of cycling among horizons in a pedon appears to follow a climatic gradient. The soil Cd at depth is brought up by the roots, plant residue is left to decay on the soil surface along with decaying plant roots where most of the root biomass is close to the surface. This results in the surface horizon having the greatest level of total soil Cd within the profile. The rooting depths of the native grass species in Saskatchewan have been found to follow the climatic gradient that occurs from the southwest in the subarid to semiarid climate of the Brown soil zone where rooting depth is greater than is observed moving towards the northeast in the subhumid climate of the Black soil zone (Coupland and Johnson 1965). Thus, if the native grass species of the prairie ecozone root deeper in the Brown soil zone they would be exploring a greater volume of soil. This may explain why the total soil Cd is vertically more uniformly distributed, i.e., the "sideways U" is not pronounced within the Brown and Dark Brown soil profiles. With a shallower rooting depth such as

in the Black soil zone, the roots of the native grasses would occupy a smaller volume of soil. The increase in precipitation from the Black soil zone (Table 3.2) would also result in a greater root density for grasses from this soil zone. In this type of ecosystem, the level of Cd removed from just below the surface horizon in the solum would be greater. The influence of climate on the type of vegetation and rooting depth can be used to explain, why the Cd enrichment factor increases moving from the Brown to the Black soil zone.

The Dark Gray soil zone is characterized as being a transition zone under Parkland prairie and Aspen Parkland vegetation in a subhumid climate. The Gray Luvisol soils in this study originally developed under an Aspen-Oak section of the Boreal Forest Region in a subhumid to humid climate. In ecosystems where trees are the dominant type of vegetation the above ground biomass is greater than the below ground biomass in contrast to the grassland ecosystem. Thus, a greater proportion of the total soil Cd becomes tied up in the above ground vegetation. It takes a long time for the Cd to be recycled back to the soil with the organic matter. In a Forest ecosystem, once the soil Cd has been taken up by the trees the Cd becomes incorporated into the noncycling fraction and is thus withdrawn from the geochemical cycle for the lifetime of the forest (Heinrichs and Mayer 1980). Once the land was cleared for cultivation and trees removed from the ecosystem the natural sequence of soil Cd biopedological cycling was broken. This results in much lower levels of total soil Cd from below the enriched surface horizon of the solum. Thus, in a forest ecosystem the Cd enrichment factor is much less than under the grassland ecosystem. As suggested earlier, phosphatic

fertilizers contribute to a smaller extent in the total soil Cd enrichment of the surface horizons.

The use of phosphatic fertilizers and the potential for the build up of Cd in soil was not studied directly. However, since 1960, phosphorus fertilization has added a total of about 38 g Cd ha⁻¹ to the plow layer of prairie soils (Roberts et al. 1995). Using as an example, the Ap horizon from the Chin soil Series, 3% or 0.0182 mg Cd kg⁻¹ soil (3.8×10^4 mg Cd ha⁻¹ / 2.08×10^6 kg ha⁻¹) is the contribution from phosphatic fertilizer to the total 0.615 mg Cd kg⁻¹ soil measured in this study. The Ck1 horizon Cd content was 0.296 mg Cd kg⁻¹ soil (Table 3.4), therefore, the Cd enrichment factor of 1.38 (Table 3.5) was mainly due to biopedological cycling.

There were four pedons that did not develop from uniform parent material were the Ardill Series, Niverville Series, Newstead Series, and the Pembina (2) Series soils. The Ardill soil Series profile consisted of three different parent materials. The upper till parent material of the Ardill soil Series is underlain by lacustrine parent material (IICk) which is underlain by till parent material (IIICk). The field description of the pedon (Appendix I) notes that shale fragments were observed from these horizons. The Ardill soil Series till includes Cretaceous shales and can be recognized by the presence of shale fragments (St. Arnaud 1976). The Judith River Formation is the underlying bedrock, to the areas where this soil Series is found. Support for this different parent material is also given by the difference in particle size distribution in the Ap, Bm, Bmk, and Cca horizons (Appendix I). The higher Cd content for the IICk and IIICk horizons is likely a reflection of the shale fragments. This type of pedon provides an example of why

collecting soil samples from the A horizon only may be an inadequate indication of the available Cd for crop uptake. In regions where shale outcrops are exposed or known to be close to the surface, soils derived from these materials may have to be described in detail to adequately determine the level of Cd available for crop uptake.

The Niverville soil Series has developed from lacustrine materials largely from Upper Cretaceous age shale materials. Based on textural group classification two different parent materials are present in the Niverville soil Series pedon. The Niverville soil Series has developed from clay loam lacustrine material over clay lacustrine material (Appendix I). The total soil Cd content was greatest in the Ap horizon of this pedon. The total soil Cd content of the lower horizons was lower than the Ap horizon, but increased with depth.

The Newstead Series and Pembina (2) Series soils have developed from medium and coarse textured parent materials. The Newstead soil Series has developed from medium textured glacio-fluvial outwash parent material over coarse textured parent material. This is indicated by the textural group change from medium texture in the first two surface horizons followed by coarse textured material in the two lower horizons. It is expected that at a depth lower than was sampled for the purposes of this study till parent material would be found below the 0.95 m maximum depth of this pedon. The difference textural groups for the horizons also corresponds to a difference in CaCO_3 content (Appendix I). The total soil Cd in the Newstead soil Series profile also greatest in the Ap horizon.

The Pembina (2) Series, sandy-skeletal substrate variant soil has developed from

moderately to very strongly calcareous, loamy mixed till with a sandy-skeletal substrate material of glacio-fluvial origin within a meter of the mineral surface. Evidence to support this soil series is also given by the changes in textural group between horizons. The upper four horizons are of medium texture overlying coarse textured material in the two lower horizons. The total soil Cd content for the Pembina (2) soil Series was also greatest in the Ap horizon. The Cd profile distribution then decreased with depth in the solum, and increased again in the IICk and IICk2 horizons.

The total soil Zn concentration in the pedons was often greatest in the surface horizon (Table 3.4). This was not as common as for Cd. The redistribution of Zn in the pedon was not as great as for Cd. The fact that soil Cd and Zn tended to accumulate to a greater degree in the organic carbon enriched surface horizons is contrary to the expected stability of metal-organic complexes for divalent cations of the Irving-Williams Rules (Brooks 1983). Some horizons displaying evidence of pervention did have a greater Zn content, but this was not consistent for all illuviated horizons.

The average crustal abundance ratio of Zn to Cd is 350, using 0.2 mg kg^{-1} for Cd and 70 mg kg^{-1} for Zn (Plant and Raiswell 1983). Generally the horizon with the highest total soil Zn to Cd ratio in a pedon had the lowest concentration of soil Cd (Table 3.4). The Whitewood soil Series was the exception, its highest total soil Zn to Cd ratio (1036) was the Bt1 horizon. However the Bt2 horizon which had a Zn to Cd ratio of 862 had the lowest total soil Cd concentration for the pedon. Conversely usually the horizon with the lowest total Zn to Cd ratio had the highest concentration of Cd. The exceptions to this were the Newstead Series, Nayler Series, and the Pembina (2) Series soils. The

IIcK1 horizon from the Newstead soil Series had the lowest soil Zn to Cd ratio yet the Cd concentration was greatest in the Ap horizon of this pedon. The Nayler soil Series was an exception because its lowest total soil Zn to Cd ratio was the Ap horizon. Instead it was the C horizon which had the highest total soil Cd concentration. The IIcK2 horizon from the Pembina (2) soil Series had the lowest soil Zn to Cd ratio even though the total soil Cd concentration was greatest in the Ap horizon. The lowest total soil Zn to Cd ratios were observed from soils in the Brown soil zone. The highest total soil Zn to Cd ratios were observed in the Black, Dark Gray, and Gray Luvisol soil zones. This trend may reflect the intensity of weathering going from the Brown to Gray Luvisol soil zone.

3.4.2 Lithosequence of total soil cadmium and other heavy metals

A lithosequence can be discussed for each of the Brown, Black, and Gray Luvisol soil zones by comparing soils derived of different parent material while the other state factors remain constant (i.e., $S_{Cd} = f(p_{cl, o, r, t, \dots})$). Three pedons developed from different parent materials were sampled from the Brown soil zone: Ardill Series, Maleb Series, and the Chin Series soils. The total soil Cd content of the different parent materials from the three soil zones is given in Table 3.6. The Ardill soil Series as described earlier is developed from three different parent materials. Two horizons from this pedon, IIcK derived from lacustrine parent material and IIIcK derived from mixed till parent material will be discussed under the assumption these two horizons have not been

Table 3.6 Lithosequence for different parent materials from three soil zones.

Soil Series	Parent Material	Horizon	Total soil Cd mg Cd kg⁻¹
Brown			
Maleb	mixed till	Ck	0.256
Chin	lacustrine	Ck1	0.296
Ardill	lacustrine	IICk	0.610
Ardill	mixed till	IICk	0.410
Black			
Niverville	lacustrine	IICk	0.293
Newstead	mixed till	IICk2	0.346
Mayfair	mixed till	Ck3	0.096
Beaverhills	mixed till	Ck	0.108
Gray Luvisol			
Nayler	shale till	C	0.461
Pembina (2)	mixed till	IICk2	0.351

modified. The Ardill soil Series IICk horizon had a total Cd content of 0.610 mg kg⁻¹, and the IIICk horizon 0.410 mg kg⁻¹. The Maleb soil Series pedon has developed from uniform mixed glacial till parent material. The Maleb soil Series parent material (Ck) had a total Cd content of 0.256 mg Cd kg⁻¹. The Chin soil Series is developed from lacustrine parent material overlying clay loam till. Pedological evidence for this parent material is given by the change in CaCO₃ content (257 g kg⁻¹) in the IICk horizon compared to 146 g kg⁻¹ in the overlying Ck1 horizon. The Chin soil Series parent material (Ck1) had a total Cd content of 0.296 mg Cd kg⁻¹. The lacustrine parent materials from the Ardill and the Chin soil Series' had the higher total soil Cd content from pedons in the Brown soil zone.

Different parent materials from the same climatic region representing the Black soils in the study had the following total soil Cd contents. The Mayfair soil Series parent material (Ck3) had a total soil Cd content of 0.096 mg Cd kg⁻¹. The Beaverhills soil Series parent material (Ck) had a total soil Cd content of 0.108 mg Cd kg⁻¹. The Niverville soil Series IICk horizon is derived from lacustrine parent material. This horizon had a total soil Cd content of 0.293 mg Cd kg⁻¹. The Newstead soil Series IICk2 horizon is derived from mixed till parent material. Its total soil Cd content was 0.346 mg Cd kg⁻¹. The lacustrine parent material from the Black soil zone was generally greater in total soil Cd content. Nevertheless, the mixed till parent material from the Newstead soil Series IICk2 horizon contained the largest total soil Cd content from the different parent materials in the Black soil zone. This is likely a result of the Upper Cretaceous shale rock contribution to the mixed till parent material from this region in

Manitoba.

Different parent materials from the same climatic region representing the Gray Luvisol soils in the study had the following total soil Cd contents. The Nayler soil Series parent material (C horizon) had a total soil Cd content of 0.461 mg Cd kg⁻¹. Large shale fragments were observed from the C horizon of the Nayler Series profile. Unfortunately, the Pembina (2) soil Series consists of two parent materials within its pedon. The Pembina (2) Series site (IIck2, 0.351 mg Cd kg⁻¹) was relatively close in proximity to the Nayler soil Series pedon site. The Pembina (2) soil Series has been described as being derived of mixed till material, this would include limestone, granite, and shale material. Elson (1967) reported that the Odanah shale forms a large portion of the glacial drift in the Tiger Hills region. Therefore the Pembina (2) soil Series would be expected to be lower in total soil Cd content in its parent material than the shale till derived Nayler soil Series and this was borne out by the results of this survey (Table 3.4). The shale till parent material contained a greater amount of total Cd than the mixed till parent material.

The Cd content of the different parent materials in the survey generally followed the order of lacustrine > shale till > mixed till. The location for the parent materials seems to also indicate the presence of regional geological influences. Parent material for the Ardill soil Series from near Mantario, Saskatchewan was higher in Cd than other pedons from the Brown soil zone. Parent materials for the Niverville and Newstead soil Series' from St. Jean and Virden, Manitoba, respectively were higher in Cd content than other soils from the Black soil zone. The parent material for the Nayler and Pembina (2)

soil Series' from Somerset and Altamont, Manitoba, respectively were higher in Cd than many of the other parent materials in the survey.

Climosequence analyses of total Cd for soils $S_{Cd} = f(cl)_{c, r, p, t, \dots}$ requires that the soils be derived of the same parent material but under different climatic conditions. What is called parent material really represents the mode of deposition from which the soil has developed. For example, soils described as mixed till have different soil Cd contents depending on the geochemistry of the source rock from which the soil has developed. It is known that most of the prairie ecozone are underlain by Upper Cretaceous period shales and that after the last glaciation these shale bedrock formations were incorporated into the till material from which much of the soils in the prairie ecozone have formed. Therefore, knowledge of the Cd content of these Upper Cretaceous age shales would be important in helping to identify regional differences in the total soil Cd content.

3.5 Summary and Conclusions

This survey of thirteen pedons from the prairie ecozone, demonstrated the pedogenic influences of two soil forming factors; climate, $S_{Cd} = f(cl)_{c, r, p, t, \dots}$ and parent material, $S_{Cd} = f(p)_{c, r, p, t, \dots}$ have on the horizontal and profile distribution of Cd.

Climate was found to influence the type of native vegetation found within the Chernozemic and Luvisolic soils. The profile distribution of Cd was found to be determined by the type of native vegetation. The amount of biopedological cycling was measured by the level of Cd enrichment to the surface horizon. The Cd enrichment

factor (Ap horizon/ C horizon) increased moving from the short prairie grasses in the Brown soil zone to the tall prairie grasses in the Black soil zone. The Cd enrichment factor decreased under grass / forest native vegetation of the Dark Gray and Dark Gray Luvisol soils.

The survey also determined that parent material is an important state factor in establishing the initial soil Cd content. Regional total soil Cd patterns were observed in the survey. In particular the rock source or underlying bedrock material is related to the these regional soil Cd patterns. As well the mode of deposition directly related to the level of Cd in the soil, i.e., lacustrine and shale till were found to have a higher total soil Cd content.

4. SOIL AND WHEAT GRAIN CADMIUM LEVELS FROM AN 80 KILOMETRE TRANSECT IN SOUTHERN MANITOBA

4.1 Abstract

Higher than Codex Alimentarius Commission (1995) proposed cadmium limits of 0.1 ppm (f.w.) were measured in wheat, *Triticum turgidum* and *Triticum aestivum* from a series of catenas along an 80 kilometre transect in southern Manitoba. The range in grain Cd was 0.027 to 0.301 ppm (f.w.). Total soil Cd content is often considered an important factor in causing an increase in Cd uptake by plants. This was a significant factor for the Bishop soil Series that contained 4.620 mg kg⁻¹ total soil Cd. The high total soil Cd from this soil also corresponded with a high clay content. Lithologically, total soil Cd was found to increase with clay content and showed an increase in grain Cd. Grain Cd of 0.301 ppm was measured at the Bishop soil Series site. Nevertheless, grain Cd contents > 0.100 ppm were also identified from sandy soils. The rock source of the soil parent material, specifically surface soil total Cd was positively correlated ($r = 0.54$) with grain Cd. The Zn / Cd ratio in the sub-soil, was negatively correlated ($r = -0.50$) with grain Cd. A low Zn / Cd ratio was also observed from the Bishop soil Series. Thus, total soil Cd and the Zn / Cd ratio are two important factors in southern Manitoba that account for the higher grain Cd from this region.

Total soil Cd and grain Cd was not found to be statistically related to

toposequence. There was, nevertheless, a trend for higher total soil Cd and grain Cd to occur at the crest-slope position.

4.2 Introduction

The study from the previous chapter examined soil profile development from a number of different vegetative ecosystems in terms of lithology within the prairie ecozone. Chapter 3 provided evidence for the *in situ* distribution of Cd from different soil zones in the prairie ecozone. Chapter 3 also highlighted the importance of parent material toward soil Cd content. The scope of the study in this chapter is focussed on one ecosystem. This chapter will examine the relationship between lithosequence toposequence and grain Cd content of wheat in the Red River Valley agro-ecosystem.

Codex Alimentarius Commission of the World Health Organization (FAO/WHO 1995) has proposed a grain cadmium (Cd) limit of 0.1 ppm (f.w.) for export. Germany currently has a guide value (Rechwert) limit of 0.1 ppm Cd (f.w.) for wheat. The European Union (1997) has proposed a cereal Cd limit of 0.2 ppm (f.w.).

The Canadian Grain Commission, Winnipeg, Grain Research Laboratory has established grain Cd levels of 0 - 0.05 ppm (f.w.) as representative for low grain Cd content, 0.05 - 0.1 ppm as medium and 0.1 - 0.2 ppm as high. The Morden area of Southern Manitoba has produced grain with high Cd levels (0.1 - 0.2 ppm f.w.) compared to other regions of the province for the years 1991 to 1994 (Canadian Grain Commission, Winnipeg, Grain Research Laboratory unpublished). Grain samples for

compared to other regions of the province for the years 1991 to 1994 (Canadian Grain Commission, Winnipeg, Grain Research Laboratory unpublished). Grain samples for analyses of heavy metals by the Canadian Grain Commission have been collected from grain elevators throughout the province. This method of collecting the grain samples does not identify the field from which the crop was grown.

The soil factors which can affect the availability of cadmium to plants are the rock source of the parent material, pH, organic matter, texture, and CEC. Page et al. (1987) found that the two most important factors governing the uptake of cadmium by crops were the soil pH and the concentration of Cd in the soil. Less important were soil temperature, content of hydrous oxides of iron and manganese in soils, redox potential in soil, and interactions with other metals. All soils contain Cd. The sources of Cd in the soil are both natural and anthropogenic. The rock source for the parent material from which the soil has developed will determine the natural background level of soil Cd. The anthropogenic sources of Cd are: long range transport of atmospheric pollutants, phosphatic fertilizers, sewage sludge, and farmyard manures.

Experimental laboratory research often shows that the level of Cd in potted soil is reflected in the Cd content of the grain (Williams and David 1977). How does this compare to field situations? There has not been any literature published on field research on the correlation between levels of soil Cd with grain Cd since 1977 (Dudas and Pawluk 1977).

Page et al. (1972) found that the concentration of Cd in the leaves of plants tested increased as the concentration of Cd added to the substrate solution increased.

Conversely, Dudas and Pawluk (1977) found that the contents of HCl extractable Cd in soil was not generally related to levels found in grain seeds. They suggested that the choice of HCl as an extractant may have been a factor in the poor relationship between soil Cd levels and grain seed Cd levels. Under similar soil conditions (pH, CEC, etc.), amounts of Cd absorbed by plants tend to increase as the concentration of Cd in the soil increases. There may be a positive linear or a positive curvilinear relationship between the increase of Cd concentration in plant tissues and in soil. This relationship is influenced by biological and environmental factors (Van Bruwaene et al. 1986). In pot experiments Eriksson (1990) found a positive correlation between total Cd contents in the soil (using HNO₃-digestible Cd) and Cd contents in grains of oats and winter wheat in the field. In winter wheat, total soil Cd content was the soil factor that had the greatest influence on grain Cd content.

Garrett (Geological Survey Canada, Ottawa, 1993, personal communication) reported a similarity between the regions of high bromide and the regions of elevated grain Cd in the prairie ecozone. This information suggested that Cl⁻ might share a similar pattern and as a result Cl analysis was included in this study. The Cl⁻ ion can serve as a ligand for Cd and form a number of complexes. Chloride salinity has been demonstrated to cause an increase in the solubility of Cd resulting in a greater concentration of plant Cd (Bingham et al. 1983). McLaughlin et al. (1994a) reported that the highest concentration of Cd in potato tubers was in a region of Australia where soils were neutral or alkaline (pH 6.0-7.5), but predominantly saline. The best relationship between tuber Cd concentrations and soil or plant factor was found with extractable Cl⁻

concentrations in the topsoil ($R^2 = 0.65$, $P < 0.001$).

As described in the previous chapter Jenny (1980) used a mathematical description to describe soil genesis. Thus, as an ecosystem property, soil properties (S) are a function of the five state factors. Jenny described this mathematically as $S = f(cl, \theta, r, p, t, \dots)$.

Soil genesis in the landscape is a relief dependent variable. A toposequence $S = f(r)_{cl, \theta, p, t, \dots}$ based on slope position within the fields sampled will be reflected in the soil series identified. The influence of topography on the toposequence soil series' will be identified by the degree of the sola development and soil properties, such as organic carbon, presence of free carbonates, and texture.

A lithosequence $S = f(p)_{cl, \theta, r, t, \dots}$ (really soil texture) can be studied if the parent material (geochemistry) of the rock source is known for the sola and all the other variables in the soil-forming equation are constant. Typically, shale rocks contain higher levels of Cd than other rock sources. A higher level of Cd in the source rock will likely increase the level of Cd found in the soil. Also the relative proportion of shale rock in the lacustrine material will influence the level of Cd in the soil.

The objectives of this study were to determine the pedogenic influences of two soil forming factors: relief, $S_{Cd} = f(r)_{cl, \theta, p, t, \dots}$ and parent material, $S_{Cd} = f(p)_{cl, \theta, r, t, \dots}$, on soil Cd levels in the Red River Valley. A series of catenas were used to measure in the influence of relief on the distribution of soil Cd. A lithosequence representative of different textures was used to measure the influence of parent material on soil Cd levels.

4.3 Materials and Methods

4.3.1 Soils

4.3.1.1 Study Area. Eleven field sites were selected across an 80-km transect from an agricultural region in southern Manitoba. All sites except one are located within the Manitoba Lowland region. Site 11 is located along the lower slope of the Manitoba Escarpment. The sites were located approximately 80 km from the nearest urban centre, and are considered nonpolluted agricultural soils. A map of the study area is given in Figure 4.1. Ten of the field sites were of lacustrine parent material, and one field site was a soil developed from residual parent material. The lithosequence forming the transect is based on different textural classes. Fourteen different soil series are represented in this study.

4.3.1.2 Field Methods. The soil samples were collected at least 25 m from the edge of the cropped field. A catenary function was observed in selecting sites for the study. A listing of the site numbers, the corresponding soil series and their slope position along with the Canadian and United States soil taxonomy classifications is provided in Table 4.1. Soil samples and mature wheat grain samples were collected at each field site from three slope positions: crest, mid-slope, and toe-slope. The slope gradient was $< 0.5\%$ for all sites except site #11. Site # 11 had a slope gradient of 12% and the slope positions were middle, lower, and toe. At each slope position, soil samples were

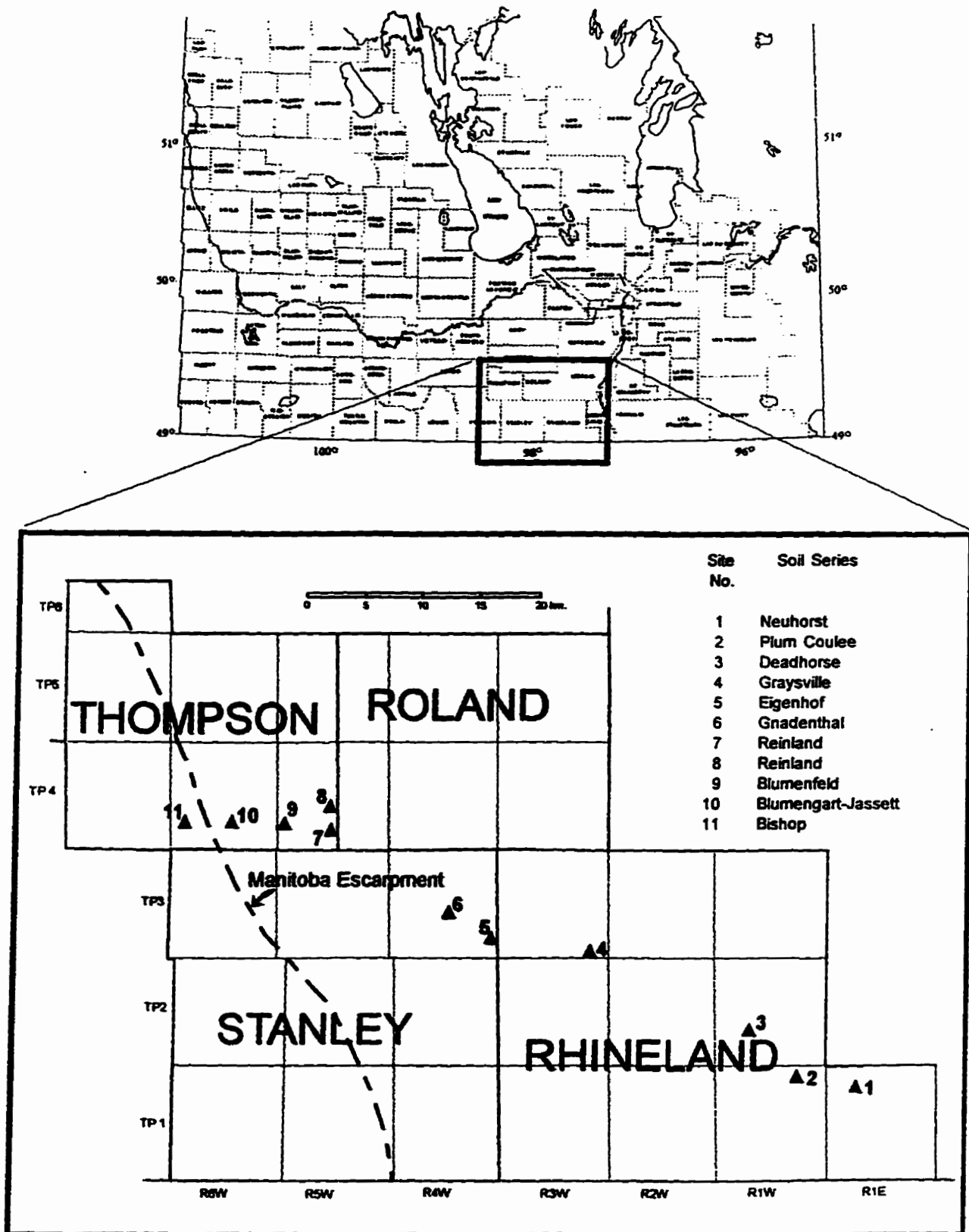


Figure 4.1 Location of fields from an 80 km transect for a survey of heavy metals in soil and wheat crops in southern Manitoba.

Table 4.1 Site number, location, legal description, slope position, soil Series, Canadian System of Soil Classification and United States Soil Taxonomy of sola.

Site Number	Location	Legal Description	Slope Position	Soil Series	Soil Subgroup	U.S. Soil Taxonomy
1	Sommerfeld	SW32-1-1E1	crest	Neuhorst	Gleyed Rego Black	Typic Pellustert
			mid	Neuhorst	Gleyed Rego Black	Typic Pellustert
			toe	Osborne	Rego Humic Gleysol	Typic Pellustert
2	New Bercthal	NE35-1-1W1	crest	Plum Coulee	Gleyed Black	Typic Pellustert
			mid	Plum Coulee	Gleyed Black	Typic Pellustert
			toe	Plum Coulee	Gleyed Black	Typic Pellustert
3	Altona	SE17-2-1W1	crest	Deadhorse	Gleyed Rego Black	Typic Pellustert
			mid	Neuhorst	Gleyed Rego Black	Typic Pellustert
			toe	Blumenfeld	Rego Humic Gleysol	Typic Pellustert
4	Plum Coulee	SW1-3-3W1	crest	Graysville	Gleyed Rego Black	Aquic Haploboroll
			mid	Graysville	Gleyed Rego Black	Aquic Haploboroll
			toe	Edkins	Rego Humic Gleysol	Aquic Haploboroll

Table 4.1 (continued)

Site Number	Location	Legal Description	Slope Position	Soil Series	Soil Subgroup	U.S. Soil Taxonomy
5	Greenfarm	NE12-3-4W1	crest	Winkler clay loam	Orthic Black	Typic Haploboroll
			mid	Eigenhof	Orthic Black	Typic Haploboroll
			toe	Eigenhof	Orthic Black	Typic Haploboroll
6	Winkler	NW15-3-4W1	crest	Gnadenthal	Gleyed Rego Black	Typic Pellustert
			mid	Gnadenthal	Gleyed Rego Black	Aquic Haploboroll
			toe	Gnadenthal	Gleyed Rego Black	Aquic Haploboroll
7	Rosebank	NE9-4-5W1	crest	Hochfeld	Orthic Black	Typic Haploboroll
			mid	Reinland	Gleyed Rego Black	Aquic Haploboroll
			toe	Reinland	Gleyed Rego Black	Aquic Haploboroll
8	Rosebank	SE16-4-5W1	crest	Hochfeld	Orthic Black	Typic Haploboroll
			mid	Reinland	Gleyed Rego Black	Aquic Haploboroll
			toe	Reinland	Gleyed Rego Black	Aquic Haploboroll

Table 4.1 (continued)

Site Number	Location	Legal Description	Slope Position	Soil Series	Soil Subgroup	U.S. Soil Taxonomy
9	Rosebank	NW7-4-5W1	crest	Jasset	Gleyed Black	Aquic Haploboroll
			mid	Blumenfeld	Rego Humic Gleysol	Typic Haplaquoll
			toe	Blumenfeld	Rego Humic Gleysol	Typic Haplaquoll
10	Miami	NE10-4-6W1	crest	Blumengart	Gleyed Regosol	Typic Pellustert
			mid	Hochfeld	Orthic Black	Typic Haploboroll
			toe	Jasset	Gleyed Black	Aquic Haploboroll
11	Miami	NE7-4-6W1	middle	Bishop	Gleyed Rego Black	Aquic Haploboroll
			lower	Bishop	Gleyed Rego Black	Aquic Haploboroll
			toe	Bishop	Gleyed Rego Black	Aquic Haploboroll

collected on a genetic horizon basis from the surface horizon and sub-surface horizon. Approximately 1 kg of soil was collected from the middle of each horizon. All soil samples were stored in plastic bags. The wheat grain samples were stored in cloth flour bags. Each solum was photographed and described in the field. Wheat grain samples were also collected from a number of other fields from the same region at the same time as the samples in this study (Dr. Russell Tkachuk, Canadian Grain Commission, Grain Research laboratory, Winnipeg, Manitoba). The Cd analyses from the grain samples collected in this study and by Dr. Tkachuk were subsequently used to form the sample set to statistically re-scale the grain Cd data to Canada Western Amber Durum (CWAD). This was done to achieve a larger sample set to produce more representative mean grain Cd value from the wheat classes studied and correlation analyses.

4.3.2 Analytical Procedures

Sample Preparation. Soil samples were air-dried then passed through a No. 10 plastic sieve with 2.0 mm size openings. Any soil aggregates which were too large to pass through were broken using a wooden rolling pin to allow all soil aggregates less than 2.00 mm to be collected. The hygroscopic water content was determined for the soil samples to allow all analytical determinations to be expressed on an oven-dry basis. Grain samples were air-dried then threshed. Grain samples were then prepared for analysis by the Canadian Grain Commission, Grain Research Laboratory, Winnipeg, Manitoba. All analytical determinations of soil samples were performed in triplicate.

The mean values of the particle size fractions, calcium carbonate, organic carbon, soil pH, exchangeable cations, cation exchange capacity(CEC), soil chloride, 0.01 M CaCl₂ extractable Cd, heavy metal contents of soil and wheat grain are reported.

Physical Analyses. Particle size fractions were determined using the pipette method (McKeague 1981).

Chemical Analyses. Inorganic carbon content was determined using the Bundy and Bremner (1972) titrimetric method. Organic carbon content was determined using a modified Mebius method (Yeomans and Bremner 1988). Soil pH was determined using 0.01 M CaCl₂ at 1:2 soil to solution ratio. Exchangeable cations and cation exchange capacity were determined using a modified version of the Hendershot and Duquette (1986) method of BaCl₂ saturation followed by MgCl₂ replacement. Soil chloride levels were determined by the mercury(II) thiocyanate method of Fixen et al. (1988) using a 1:2.5 soil to 0.01 M Ca(NO₃)₂ extracting solution ratio followed by colorimetric analysis. These analyses were conducted on the fine-earth fraction.

Representative subsamples of the fine-earth fraction were ground using an agate mortar and pestle then passed through a plastic mesh sieve with 150 μm diameter openings to prepare the soil for acid digestion before determination of total soil Cd. Soil samples of approximately 0.2 g were weighed into block digestion tubes. Two blanks and two standard reference soil samples were included with each set of 40 tubes. To each tube, 5 mL of HNO₃, and 2.5 mL of HClO₄ were added, samples were mixed and allowed to sit for 1 hour. The samples were then placed in a block digester and brought to 230° C where they were maintained for two hours. The samples were allowed to cool

and filtered through wetted #42 Whatman filter paper and brought to 25 mL using deionized water. Samples were stored in plastic scintillation vials for further analysis. About 10 mL of the sample was removed for analysis of Cu, Fe, Ni, Pb, and Zn on a Perkin-Elmer, 1100 B atomic absorption spectrophotometer, using flame directly. The remaining 15 mL of extract was treated with 0.05% dithizone at a pH of 4.5 to remove background interferences and concentrate the HNO_3 - HClO_4 digestible Cd. The samples were then analyzed using a Perkin-Elmer, 1100 B atomic absorption spectrophotometer with graphite furnace, with a detection limit of 0.250 ppb.

Four grams of soil were used for determination of CaCl_2 extractable Cd using a 1:10 soil to 0.01 M CaCl_2 solution ratio, and shaking for 1 hour. The samples were then centrifuged at 145 x g for 15 minutes and decanted into plastic scintillation vials (Novozamsky et al 1993). The extract was treated with 0.05% dithizone at pH 4.5 to remove background interferences and concentrate the extractable Cd. Analysis was conducted using a graphite furnace AAS.

From the 11 field sites a total of four different wheat classes were collected: Canada Western Hard Red Spring (CWRS), Canada Prairie Spring (CPS), Canada Western Amber Durum (CWAD), and Canada Western Extra Strong (CWES). Wheat grain Cd, Cu, and Zn analyses were conducted at the Canadian Grain Commission, Grain Research Laboratory, Winnipeg. Grain samples (100 g) were ground to a fine grind in a commercial grinder. From this, 0.5 g was weighed into a teflon digestion vessel. Next 6 mL of concentrated HNO_3 was added. Samples were then placed in the microwave digester CEM MDS - 2000, with pressure and temperature monitoring options for a 10

minute digestion period. Analysis of heavy metals in the wheat grain was also by atomic absorption spectrometer (Perkin Elmer 5100PC equipped with Perkin Elmer 5100 ZL graphite furnace fume extraction system, closed cooling system, AS 70 autosampler and EDL power supply) with a detection limit of 10 ppb. Analysis was performed in duplicate for Cd on a fresh weight (f.w.) basis. A mean grain Cd value was determined for each wheat class from both the sample set for this study and the sample set from a concurrent study by Dr. Russell Tkachuk in 1993 (only the mean wheat class values from Tkachuk personal communication are reported in this study). A re-scale factor was calculated by dividing the average Cd content for CWAD by the average Cd value for the wheat class to be re-scaled. Actual grain Cd values for CWRS, CWES, and CPS were re-scaled to CWAD by multiplying the re-scale factor by the actual grain Cd value to arrive at a re-scaled (to CWAD) grain Cd content. The re-scaled grain Cd values were used in the correlation analysis.

4.4 Results and Discussion

4.4.1 Pedologic Properties and Sola Development

The sand, silt, and clay content, textural class and group, and content of the sola are presented in Table 4.2. The calcium carbonate (CaCO_3), organic carbon (O.C.), pH, exchangeable cations, cation exchange capacity, % base saturation (% BS), and chloride content are presented for the sola in this study in Table 4.3. Topography, as a factor of

Table 4.2 Physical soil properties of sola. All values are reported on an oven dry basis.

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Sand	Silt %	Clay	Textural Class	Textural Group
1	Neuhorst	crest	Ap	0 - 0.15	36	22	42	C	C
			AC	0.15 - 0.50	48	17	35	SCL	FL
	Neuhorst	mid	Ap	0 - 0.18	35	25	40	CL	FL
			AC	0.18 - 0.51	24	28	48	CL	FL
	Osborne	toe	Ap	0 - 0.14	32	26	42	C	C
			Ck	0.14 - 0.50	6	27	67	HC	C
2	Plum Coulee	crest	Ap	0 - 0.15	21	29	50	C	C
			AC	0.15 - 0.50	14	23	63	HC	C
	Plum Coulee	mid	Ap	0 - 0.18	25	29	46	C	C
			Ah	0.18 - 0.36	25	21	54	C	C
	Plum Coulee	toe	Ap	0 - 0.13	37	25	38	CL	FL
			AC	0.13 - 0.20	33	24	43	C	C
3	Deadhorse	crest	Apk	0 - 0.12	43	24	33	CL	FL
			Ck	0.12 - 0.50	27	22	51	C	C
	Neuhorst	mid	Ap	0 - 0.11	40	24	36	CL	FL
			AC	0.11 - 0.24	43	22	35	CL	FL
	Blumenfeld	toe	Ap	0 - 0.15	35	24	41	C	C
			AC	0.15 - 0.21	36	26	38	CL	FL

Table 4.2 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Sand	Silt %	Clay	Textural Class	Textural Group
4	Graysville	crest	Apk	0 - 0.12	76	4	20	SCL	FL
			Bmk	0.12 - 0.39	83	1	16	VFSL	CoL
	Graysville	mid	Apk	0 - 0.12	77	4	19	VFSL	CoL
			Bmk	0.12 - 0.26	82	2	16	VFSL	CoL
	Edkins	toe	Apk	0 - 0.21	78	4	18	VFSL	CoL
			Bmk	0.21 - 0.34	76	4	20	VFSL	CoL
5	Winkler clay loam	crest	Ap	0 - 0.16	64	8	28	SCL	FL
			Bm	0.16 - 0.34	48	12	40	SC	C
	Eigenhof	mid	Ap	0 - 0.15	63	12	25	SCL	FL
			Ap	0.15 - 0.30	68	8	24	SCL	FL
	Eigenhof	toe	Ap	0 - 0.18	64	10	26	SCL	FL
			Bmk	0.18 - 0.42	73	5	22	SCL	FL
6	Gnadenthal	crest	Apk	0 - 0.17	51	13	36	SCL	FL
			AC	0.17 - 0.50	58	12	30	SCL	FL
	Gnadenthal	mid	Apk	0 - 0.17	66	10	24	SCL	FL
			AC	0.17 - 0.29	74	5	21	SCL	FL
	Gnadenthal	toe	Apk	0 - 0.18	78	5	17	FSL	CoL
			AC	0.18 - 0.46	82	3	15	VFSL	CoL

Table 4.2 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Sand	Silt %	Clay	Textural Class	Textural Group
7	Hochfeld	crest	Ap	0 - 0.41	90	0	10	VFS	CoL
			AB	0.41 - 0.48	91	0	9	VFS	CoL
			Bm	0.48 - 0.58	91	0	9	FS	S
	Reinland	mid	Apk	0 - 0.18	88	1	11	VFS	CoL
			AC	0.18 - 0.26	89	1	10	VFS	CoL
	Reinland	toe	Apk	0 - 0.20	86	1	13	LFS	S
			AC	0.20 - 0.46	81	2	17	VFSL	CoL
8	Hochfeld	crest	Ap	0 - 0.64	89	0	11	FS	S
			AB	0.64 - 0.81	90	0	10	VFS	CoL
			Bm	0.81 - 1.00	92	0	8	VFS	CoL
	Reinland	mid	Apk	0 - 0.25	86	1	13	LFS	S
			AC	0.25 - 0.62	87	1	12	LVFS	CoL
	Reinland	toe	Apk	0 - 0.23	81	3	16	FSL	CoL
			AC	0.23 - 0.61	82	3	15	VFSL	CoL

Table 4.2 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Sand	Silt	Clay	Textural	
					%			Class	Group
9	Jasset	crest	Apk	0 - 0.24	76	4	20	VFSL	CoL
			Ahk	0.24 - 0.39	72	6	22	SCL	FL
	Blumenfeld	mid	Apk	0 - 0.15	68	11	21	SCL	FL
			Bntj	0.15 - 0.26	69	28	3	VFSL	CoL
	Blumenfeld	toe	Apk	0 - 0.13	68	8	24	SCL	FL
			Bntj	0.13 - 0.29	64	28	8	VFSL	CoL
10	Blumengart	crest	Apk	0 - 0.10	41	23	36	CL	FL
			Ahk	0.10 - 0.20	36	22	42	C	C
	Hochfeld	mid	Ap	0 - 0.12	88	0	12	FS	S
			Bm	0.12 - 0.26	90	0	10	FS	S
	Jasset	toe	Ap	0 - 0.12	58	7	35	SCL	FL
			Bm	0.12 - 0.42	66	0	34	SCL	FL
11	Bishop	middle	Apk	0 - 0.06	11	28	61	HC	C
			Ahk	0.06 - 0.21	12	18	70	HC	C
	Bishop	lower	Apk	0 - 0.10	11	38	51	C	C
			AC	0.10 - 0.26	10	8	82	HC	C
	Bishop	toe	Ap	0 - 0.17	9	10	81	HC	C
			Ck	0.17 - 0.50	8	34	58	C	C

Table 4.3 Chemical soil properties of sola. All values are reported on an oven dry basis.

Site Number	Soil Series	Slope Position	Horizon	Sample Depth, cm	CaCO ₃ — g kg ⁻¹ —	O.C. —	0.01M CaCl ₂ pH	Exchangeable Cations				CEC	% BS	Cl mg kg ⁻¹
								Na	K	Mg	Ca			
1	Neuthorst	crest	Ap	0-15	7.0	39.0	7.7	1.2	6.8	10.1	21.1	46.0	85.4	23.0
			AC	15-50	138.0	12.0	7.9	3.0	2.6	14.4	13.0	26.3	125.1	42.5
	Osborne	toe	Ap	0-18	3.0	38.0	7.4	0.3	6.9	7.8	19.5	40.5	85.0	15.7
			AC	18-51	5.0	14.0	7.7	2.0	3.7	17.9	15.1	41.1	94.3	49.8
			Ap	0-14	7.0	35.0	7.6	0.1	11.0	8.2	25.9	43.3	104.4	9.70
AC	14-50	218.0	13.0	7.8	0.5	4.3	10.0	19.4	39.8	85.9	6.40			
2	Plum Coulee	crest	Ap	0-15	2.0	33.0	7.4	0.3	2.3	10.7	29.3	47.6	89.3	16.4
			AC	15-50	4.0	18.0	7.7	0.7	1.4	10.5	20.1	43.3	75.5	8.90
	Plum Coulee	toe	Ap	0-18	1.0	39.0	7.2	0.2	2.7	9.5	25.0	43.3	86.3	4.20
			Ah	18-36	2.0	20.0	7.3	0.7	1.7	8.7	18.3	40.9	71.9	40.4
			Ap	0-13	5.0	33.0	7.5	0.1	2.0	7.1	27.7	42.5	86.8	8.90
AC	13-20	9.0	16.0	7.7	0.3	1.0	9.3	23.9	30.8	112.3	149.0			
3	Deadhorse	crest	Apk	0-12	79.0	25.0	7.9	0.9	1.8	10.6	25.4	37.6	102.8	48.8
			Ck	12-50	226.0	7.0	7.9	0.3	0.7	12.7	20.0	27.9	120.9	30.2
	Blumenfeld	toe	Ap	0-11	25.0	28.0	7.9	1.4	1.3	16.0	18.8	41.6	90.3	282.0
			AC	11-24	86.0	17.0	7.9	1.7	0.7	17.7	14.9	30.6	114.1	396.0
			Ap	0-15	7.0	29.0	7.8	1.0	1.3	25.3	19.4	44.1	106.4	164.0
AC	15-21	25.0	18.0	7.9	1.5	0.8	24.0	13.0	38.3	102.7	335.0			

Table 4.3 (continued).

Site Number	Soil Series	Slope Position	Horizon	Sample Depth, cm	CaCO ₃ — g kg ⁻¹ —	O.C. — g kg ⁻¹ —	0.01M CaCl ₂ pH	Exchangeable Cations				Cl mg kg ⁻¹		
								Na	K	Mg Ca	CEC			
4	Graysville	crest	Apk	0-12	81.0	16.0	7.8	0.0	1.0	4.4	13.0	19.8	93.2	17.8
			Bmk	12-39	41.0	18.0	7.9	0.1	0.5	5.6	15.4	22.6	95.6	13.1
	Graysville	mid	Apk	0-12	73.0	20.0	7.9	0.0	0.8	4.5	14.4	19.8	99.6	3.7
			Bmk	12-26	48.0	17.0	8.0	0.1	0.5	7.0	15.1	21.9	103.8	13.4
	Edkins	toe	Apk	0-21	36.0	22.0	7.8	0.0	0.7	4.8	16.0	24.7	86.9	3.3
			Bmk	21-34	87.0	15.0	8.0	0.1	0.3	7.2	12.6	21.5	93.9	13.1
5	Winkler clay loam	crest	Ap	0-16	3.0	27.0	7.5	0.1	1.2	6.2	19.7	29.0	94.1	9.9
			Bm	16-34	2.0	18.0	7.7	0.2	0.7	7.4	14.3	26.3	85.9	21.2
	Eigenhof	mid	Ap	0-15	5.0	25.0	7.5	0.1	1.6	5.2	17.8	27.0	91.5	8.5
			Ap	15-30	2.0	21.0	7.7	0.1	0.7	4.7	15.0	23.1	88.4	8.3
	Eigenhof	toe	Ap	0-18	4.0	23.0	7.7	0.1	1.0	4.5	15.9	29.3	73.5	5.4
			Bmk	18-42	1.0	18.0	7.7	0.1	0.7	6.1	14.3	22.7	93.4	32.0
6	Gnadenenthal	crest	Apk	0-17	30.0	29.0	7.7	0.1	1.9	5.4	21.2	41.6	68.6	12.8
			AC	17-50	153.0	17.0	7.9	0.5	0.6	4.0	21.7	26.0	102.9	16.9
	Gnadenenthal	mid	Apk	0-17	45.0	22.0	7.8	0.0	1.3	4.6	17.4	24.2	96.2	3.5
			AC	17-29	130.0	10.0	8.0	0.1	0.5	5.0	12.7	17.6	103.9	11.1
Gnadenenthal	toe	Apk	0-18	23.0	19.0	7.8	0.0	0.9	2.9	14.6	16.0	115.5	2.6	
		AC	18-46	69.0	10.0	8.0	0.1	0.4	3.1	9.9	15.7	85.8	8.2	

Table 4.3 (continued).

Site Number	Soil Series	Slope Position	Horizon	Sample Depth, cm	CaCO ₃ — g kg ⁻¹ —	O.C.	0.01M CaCl ₂ pH	Exchangeable Cations					CEC	% BS	Cl mg kg ⁻¹
								Na	K	Mg	Ca	— cmol (+) kg ⁻¹ —			
7	Hochfeld	crest	Ap	0-41	6.0	15.0	7.7	0.0	0.7	0.9	10.1	13.3	88.3	0.50	
			AB	41-48	2.0	10.0	7.8	0.0	0.5	0.9	9.5	14.4	75.7	0.20	
			Bm	48-58	2.0	8.0	7.8	0.0	0.4	1.0	7.5	12.8	70.2	0.20	
	Reinland	mid	Apk	0-18	17.0	13.0	7.7	0.0	0.8	1.4	9.5	17.6	66.4	4.10	
			AC	18-26	10.0	7.0	7.8	0.0	0.5	1.5	7.0	9.6	95.0	2.90	
	Reinland	toe	Apk	0-20	39.0	14.0	7.8	0.0	0.7	2.1	11.5	18.6	76.8	1.90	
		AC	20-46	130.0	5.0	8.0	0.0	0.3	4.0	12.0	14.8	110.5	2.10		
8	Hochfeld	crest	Ap	0-64	11.0	16.0	7.6	0.0	0.6	1.6	12.0	18.3	77.3	0.40	
			AB	64-81	2.0	6.0	7.7	0.0	0.4	1.5	5.5	10.4	71.9	0.40	
			Bm	81-100	10.0	4.0	7.8	0.0	0.3	1.6	5.6	9.9	76.4	0.40	
	Reinland	mid	Apk	0-25	17.0	16.0	7.7	0.0	1.0	1.3	11.8	17.8	79.6	1.20	
			AC	25-62	78.0	6.0	7.9	0.0	0.4	1.3	9.5	12.2	91.0	0.40	
	Reinland	toe	Apk	0-23	42.0	17.0	7.9	0.0	0.7	4.2	12.3	18.5	93.3	1.60	
		AC	23-61	113.0	5.0	8.1	0.1	0.3	5.9	8.9	12.9	117.3	0.50		

Table 4.3 (continued).

Site Number	Soil Series	Slope Position	Horizon	Sample Depth, cm	CaCO ₃ — g kg ⁻¹ —	O.C.	0.01M CaCl ₂ pH	Exchangeable Cations					CEC	% BS	Cl mg kg ⁻¹
								Na	K	Mg	Ca	— cmol (+) kg ⁻¹ —			
9	Jasset	crest	Apk	0-24	8.0	35.0	7.6	0.1	2.0	3.2	21.3	31.1	85.5	2.5	
			Ahk	24-39	18.0	28.0	8.0	0.8	0.5	10.4	27.8	28.8	137.4	1.8	
	Blumenfeld	mid	Apk	0-15	23.0	35.0	7.9	0.2	1.9	7.8	28.0	34.6	109.7	8.5	
			Bntj	15-26	35.0	38.0	8.1	0.9	1.5	14.4	29.1	35.5	129.2	3.6	
	Blumenfeld	toe	Apk	0-13	17.0	37.0	7.7	0.3	3.3	5.7	21.4	34.8	88.0	22.2	
			Bntj	13-29	32.0	34.0	8.0	6.3	3.5	13.8	20.5	32.6	135.2	82.1	
10	Blumengart	crest	Apk	0-10	7.0	49.0	7.7	0.1	1.7	6.7	33.8	52.2	81.2	18.3	
			Ahk	10-20	4.0	43.0	7.7	0.3	1.1	8.0	36.1	53.0	85.8	25.2	
	Hochfeld	mid	Ap	0-12	2.0	16.0	7.5	0.0	0.8	1.3	10.3	16.8	74.2	1.4	
			Bm	12-26	4.0	7.0	7.7	0.0	0.5	1.3	9.1	11.0	99.6	9.8	
	Jasset	toe	Ap	0-12	2.0	47.0	7.1	0.0	2.7	4.6	27.5	43.5	80.1	7.4	
			Bm	12-42	1.0	24.0	7.3	0.1	1.1	4.1	19.5	32.3	76.6	1.2	
11	Bishop	middle	Apk	0-6	29.0	51.0	7.5	0.0	2.7	4.9	46.3	62.3	86.6	17.3	
			Ahk	6-21	46.0	33.0	7.6	0.1	1.7	6.3	38.7	57.1	82.0	5.1	
	Bishop	lower	Apk	0-10	20.0	50.0	7.6	0.0	2.1	5.8	40.5	64.1	75.6	11.9	
			AC	10-26	19.0	20.0	7.7	0.1	1.8	8.3	32.1	47.9	88.4	15.8	
	Bishop	toe	Ap	0-17	69.0	57.0	7.8	0.3	2.3	9.3	52.6	73.7	87.5	21.2	
			Ck	17-50	243.0	16.0	7.8	0.8	1.3	6.3	25.9	40.8	83.8	19.1	

soil genesis can in some cases depending on the slope gradient result in a decrease in sand content and an increase in organic carbon content moving from the crest to the toe-slope position in the landscape (Jenny 1980). Sites 3, 8, 9, and 11 displayed these characteristics in their toposequence. Site 4 displayed an increase in organic carbon at the toe-slope position although the sand content increased moving from the crest to the toe-slope position. At sites 1 and 7 there was a decrease in sand content at the toe-slope position however the organic carbon content did not increase at the toe-slope position. Sites 2, 5, and 10 displayed inconsistent sand and organic carbon patterns to be solely due to topography. Site 6 demonstrated the exact opposite of the type of trends that would be expected due to landscape position. Sites 7 and 8 possessed the greatest sand content from the sites in the transect. Both of these sites also had the most coarse textural group classification from the sola in the study. The clay content generally decreased moving along the transect towards the Manitoba Escarpment. The textural distribution from the transect represents the distribution pattern from the retreat of glacial ice in Manitoba. The more coarse textural materials were deposited at the deltas entering glacial Lake Agassiz. The finer textural materials were deposited further from the lake shore. Since the Manitoba escarpment represents the western shore of glacial Lake Agassiz it is understandable that the clay content decreases along the transect closer to the Manitoba Escarpment. However, the clay content was greatest at site 11 since this soil has developed from residual shale parent material. There were ten different textural classes for the surface soils and nine different textural classes for the sub-soils. There were four different textural groups for both the surface soils and sub-surface soils.

Generally, the soil chemical properties display evidence of the topographical influences on soil genesis. The series of catenas indicate that in the well drained mid-slope positions more leaching has occurred than in the lower landscape positions. The exchangeable cations were usually lower in the crest slope position. Generally, the exchangeable Na^+ content was $< 1.0 \text{ cmol (+) kg}^{-1}$ for the surface and sub-soil horizons. The sub-soil horizon at the toe-slope position from site 9 (Blumenfeld soil Series) had the greatest amount of exchangeable Na^+ ($6.3 \text{ cmol (+) kg}^{-1}$) of any soil in the study. This horizon was also designated Bntj based on the presence of salt crystals. The exchangeable K^+ in this soil horizon was also higher than in most soils in this study ($3.5 \text{ cmol (+) kg}^{-1}$). Exchangeable Mg^{2+} ranged in values from 0.9 to $25.3 \text{ cmol (+) kg}^{-1}$. The low end of the range for exchangeable Mg^{2+} occurred for the more coarse textured soils (Sites 7 and 8). The sites with the greater amount of exchangeable Mg^{2+} occurred at the three most easterly sites from the transect. In most cases the toe-slope position of the catena possessed the greater amount of exchangeable Mg^{2+} . Except for three toe-slope positions from the series of catenas (Site 3, 10, and 11), the exchangeable Mg^{2+} was always greater in the surface horizon. The exchangeable Ca^{2+} ranged from 5.5 to $52.6 \text{ cmol (+) kg}^{-1}$. Sites 7 and 8, the more coarse textured sites, contained the smallest exchangeable Ca^{2+} values from this range of values. The Bishop Series soils had the highest values for exchangeable Ca^{2+} . The exchangeable Ca^{2+} tended to be greater in the crest slope position from the series of catenas. The exchangeable Mg^{2+} content tended to decrease, while the exchangeable Ca^{2+} content tended to increase in a westerly direction along the transect. This difference is likely a reflection of the parent material

in southern Manitoba.

Generally, the poorly drained toe-slope positions have greater amount(s) of: calcium carbonate for both the surface and sub-surface horizons, CEC in the A horizon, and soil Cl in the sub-surface horizon. Sites 3, 7, 8, and 9 illustrate how topography effects hydrology and the impact this has on soil genesis. That is, in the crest position of the landscape the rate of surface water runoff will be greater. As a result there is less downward movement of water and thus less soil development. As the slope gradient decreases in the landscape the rate of surface water runoff is slow enough that the downward movement of water is sufficient to cause leaching. When there is no slope in the landscape the surface water may collect at this point in the landscape and the net downward movement at this point in the landscape will be limited by the depth of the water table from the surface. The other sites from the study do not consistently display this same topographic effect. The crest position for site 6 (Gnadenthal soil Series) indicates a higher CaCO_3 content for the sub-surface and decreasing down the catena (Table 4.3). This is evidence of better infiltration at the lower slope positions in this catena due to better downward movement of water. Likely due to a lower slope gradient at the mid and toe-slope positions of the catena.

The soils in this study were neutral to slightly basic in pH. The horizons with the higher soil pH were generally the sub-soil horizons in the toe slope position. Heavy metals like Cd are more bioavailable under low soil pH conditions.

The surface horizon with the lowest % base saturation was at site 7 a Hochfeld soil Series in the mid-slope position. This soil also possessed a high sand content of 882

g kg⁻¹. Generally the sola development in the catenas was more evident at the mid-slope position. At a number of the sites the mid-slope position possessed B horizons. Compared to the crest slope position which often had a sub-soil horizon which was still classified as an A horizon. Conversely, at the toe-slope position the sub-soil horizon was either an AC or Ck horizon.

The CEC was usually greater for the surface soil than for the sub-soil horizon. An arbitrary classification for CEC values in this study was used to categorize CEC values of ≤ 20 cmol(+) kg⁻¹ as low, $21 \geq 40$ cmol(+) kg⁻¹ as medium, and > 40 cmol(+) kg⁻¹ as high. Thus, 10 surface soils were low, 9 medium, and 14 high. In the sub-soils, 9 were low, 17 medium, and 7 high. If there are positively charged species of Cd in the soil solution then soils from the low CEC category (≤ 20 cmol(+) kg⁻¹) would possess a limited capacity for retaining these species. The toposequence effect on CEC was inconsistent. Typically, in a catena the lower slope positions would be expected to possess an increase in organic carbon and an accumulation of clay. Thus the CEC would be greater in the lower slope position of the catena. This was not always the case in this study. The effect of topography on the catenas in this study may have been less evident due to the low slope gradient to the catenas. All catenas except one had a slope gradient of $< 0.5\%$. Site 11 had a slope gradient of 12%. This site did display soil physical and chemical properties characteristic of a locations along a catena.

Soils in this study displayed an extremely large range in values for soil Cl. The surface soil Cl ranged from 0.4 to 282.1 mg kg⁻¹ and the sub-soil Cl ranged from 0.2 to 396.7 mg kg⁻¹. Generally, the lower soil Cl values were found in the more sandy soils.

Also, the sub-surface Cl was usually greater than the surface soil Cl. The soil Cl values for the surface horizon and in the sub-surface horizon were in most cases considerably higher than other Manitoba soils reported by Mohr (1992). Mohr (1992) reported soil Cl values for two Manitoba soils over a two year study. The soil Cl values from those Manitoba soils ranged from 2.0 to 6.0 mg kg⁻¹ in one year and 1.2 to 3.9 mg kg⁻¹ in the second year. The highest soil Cl values were observed from the catena at site 3. This site is situated in a field directly across the town of Altona's old sewage lagoon. The high soil Cl values for this site would suggest that the sewage lagoon liner is leaking. This would account for soil Cl values ranging from 30.2 to 396.7 mg kg⁻¹ at this site. Chloride anions are generally subject to negative adsorption when pH > 6 (Tan 1993). Therefore the amount of Cl in the bulk solution would be directly related to the CEC. Salt crystals were observed in the Ap horizons for Site 3 from the mid and toe-slope positions. Chloride can serve as a ligand for Cd and form a number of complexes which are phyto-available. The Cd²⁺ species in alkaline soils can react with the Cl⁻ ligand to form the following complexes: CdCl⁺, CdCl₂⁰, CdCl₃⁻, CdCl₄²⁻. Garcia-Miragaya and Page (1976) found that adsorption by montmorillonite surfaces was drastically reduced for the negatively charged or neutral Cd-Cl species. The clay fraction from soils in Manitoba are recognized as having montmorillonite as the predominant clay mineral (Forman and Brydon 1965; Brierley et al. 1996). Due to anomalously high Cl levels from Site 3, this site will not be used when discussing mean soil values and will be omitted from grain Cd analyses. In terms of the catena the landscape position was inconsistent for predicting where higher surface soil Cl values would be expected to be found.

Generally the higher surface soil Cl values from a catena were associated with the slope position which had the highest surface soil CEC value from a catena (Table 4.3). This trend was not as consistent for the sub-surface horizons.

The Cd and Zn contents of the soils in this study are given in Table 4.4. Appendix II contains the Cu, Ni, and Pb levels from the soils in this study. The total soil Cd content was usually greatest in the surface soil horizon compared to the sub-soil horizon. This is opposite to an earlier study of Manitoba agricultural soils by Mills and Zwarich (1975). The highest values of total soil Cd in the surface and sub-soil horizons (Site 11) is likely due to the soil developing from parent material that is derived from a particular shale member. The elevation at this site is 343 m (1125 ft.) this would place this site where the Pembina and Gammon Ferruginous members of the Pierre Shale Formation outcrop (Bannatyne 1970). Unpublished analytical results of a well core sample taken from Cretaceous Shales in Manitoba indicates that the Pembina and Gammon Ferruginous members are characterized by having 9 mg kg^{-1} Cd (E. Nielsen, Manitoba Energy and Mines, personal communication). These members appear to be geochemically enriched compared to most Cretaceous Shales. The values obtained from the Bishop soil Series are higher than any reported for total soil Cd in a non-polluted Canadian soil. A recent study in the United States of surface soils and subsurface soils found that the surface soils from the Northcentral U.S. region had a mean value of $0.36 \text{ mg Cd kg}^{-1}$ and the Northwestern U.S. had a mean value of $0.30 \text{ mg Cd kg}^{-1}$.

It is likely the chloride complex CdCl^+ and the free Cd^{2+} species are being extracted with the 0.01 M CaCl_2 extracting solution. The 0.01 M CaCl_2 extractable soil

Table 4.4 Distribution of Cd and Zn in the sola studied. All values are reported on an oven dry basis.

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cd \pm sd	Zn \pm sd	0.01M CaCl ₂	
							Cd	Zn / Cd
1	Neuhorst	crest	Ap	0 - 0.15	0.67 \pm 0.03	106.3 \pm 4.4	4.56 $\times 10^{-4}$	159
			AC	0.15 - 0.50	0.60 \pm 0.02	71.7 \pm 1.1	0.0	119
	Neuhorst	mid	Ap	0 - 0.18	0.70 \pm 0.10	112.3 \pm 8.6	6.67 $\times 10^{-4}$	160
			AC	0.18 - 0.51	0.77 \pm 0.04	141.2 \pm 47.0	1.96 $\times 10^{-4}$	183
	Osborne	toe	Ap	0 - 0.14	0.70 \pm 0.02	100.0 \pm 2.2	2.95 $\times 10^{-4}$	142
			Ck	0.14 - 0.50	0.83 \pm 0.01	96.1 \pm 7.8	1.03 $\times 10^{-4}$	115
2	Plum Coulee	crest	Ap	0 - 0.15	0.99 \pm 0.03	116.2 \pm 1.7	8.39 $\times 10^{-4}$	117
			AC	0.15 - 0.50	0.87 \pm 0.05	113.8 \pm 1.9	5.92 $\times 10^{-4}$	131
	Plum Coulee	mid	Ap	0 - 0.18	0.96 \pm 0.03	109.9 \pm 2.7	1.05 $\times 10^{-3}$	114
			Ah	0.18 - 0.36	1.06 \pm 0.10	108.7 \pm 4.0	8.83 $\times 10^{-4}$	102
	Plum Coulee	toe	Ap	0 - 0.13	0.89 \pm 0.02	100.1 \pm 3.6	1.24 $\times 10^{-3}$	113
			AC	0.13 - 0.20	0.63 \pm 0.06	95.4 \pm 3.1	1.01 $\times 10^{-3}$	152
3	Deadhorse	crest	Apk	0 - 0.12	0.33 \pm 0.15	80.7 \pm 3.6	4.46 $\times 10^{-4}$	247
			Ck	0.12 - 0.50	0.24 \pm 0.03	81.1 \pm 21.7	1.92 $\times 10^{-4}$	333
	Neuhorst	mid	Ap	0 - 0.11	0.51 \pm 0.03	83.1 \pm 1.7	4.88 $\times 10^{-4}$	164
			AC	0.11 - 0.24	0.49 \pm 0.03	75.5 \pm 2.1	1.04 $\times 10^{-4}$	154
	Blumenfeld	toe	Ap	0 - 0.15	0.57 \pm 0.03	94.9 \pm 5.5	4.99 $\times 10^{-3}$	166
			AC	0.15 - 0.21	0.58 \pm 0.04	81.8 \pm 0.6	4.53 $\times 10^{-4}$	141

sd = standard deviation

Table 4.4 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cd ± sd	Zn ± sd	0.01M CaCl ₂	
							Cd	Zn / Cd
							mg kg ⁻¹	
4	Graysville	crest	Apk	0 - 0.12	0.16 ± 0.02	44.9 ± 1.5	2.12 × 10 ⁻⁴	280
			Bmk	0.12 - 0.39	0.11 ± 0.0	44.0 ± 2.6	0.0	400
	Graysville	mid	Apk	0 - 0.12	0.18 ± 0.01	49.2 ± 2.0	2.12 × 10 ⁻⁴	279
			Bmk	0.12 - 0.26	0.12 ± 0.01	44.2 ± 1.9	1.00 × 10 ⁻⁴	358
	Edkins	toe	Apk	0 - 0.21	0.30 ± 0.02	43.7 ± 0.7	2.52 × 10 ⁻⁴	146
			Bmk	0.21 - 0.34	0.20 ± 0.01	38.9 ± 0.2	0.0	192
5	Winkler clay loam	crest	Ap	0 - 0.16	0.42 ± 0.03	57.2 ± 0.6	2.89 × 10 ⁻⁴	135
			Bm	0.16 - 0.34	0.33 ± 0.01	52.6 ± 1.7	2.72 × 10 ⁻⁴	158
	Eigenhof	mid	Ap	0 - 0.15	0.40 ± 0.02	56.0 ± 0.2	1.34 × 10 ⁻⁴	139
			Ap	0.15 - 0.30	0.33 ± 0.01	48.8 ± 1.2	1.08 × 10 ⁻⁴	146
	Eigenhof	toe	Ap	0 - 0.18	0.38 ± 0.02	52.0 ± 1.1	8.60 × 10 ⁻⁵	138
			Bmk	0.18 - 0.42	0.28 ± 0.01	44.3 ± 0.1	1.57 × 10 ⁻⁴	158
6	Gnadenenthal	crest	Apk	0 - 0.17	0.68 ± 0.02	74.0 ± 3.9	1.31 × 10 ⁻⁴	108
			AC	0.17 - 0.50	0.33 ± 0.02	41.2 ± 0.2	2.81 × 10 ⁻⁴	125
	Gnadenenthal	mid	Apk	0 - 0.17	0.42 ± 0.01	49.9 ± 0.7	6.87 × 10 ⁻⁴	119
			AC	0.17 - 0.29	0.29 ± 0.01	35.8 ± 0.2	6.00 × 10 ⁻⁴	124
	Gnadenenthal	toe	Apk	0 - 0.18	0.33 ± 0.05	1.3 ± 0.3	7.23 × 10 ⁻⁴	3.80
			AC	0.18 - 0.46	0.21 ± 0.05	1.3 ± 0.1	1.10 × 10 ⁻⁴	6.00

sd = standard deviation

Table 4.4 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cd \pm sd	Zn \pm sd	0.01M CaCl ₂	
							Cd	Zn / Cd
							mg kg ⁻¹	
7	Hochfeld	crest	Ap	0 - 0.41	0.14 \pm 0.1	2.3 \pm 0.1	0.0	16.0
			AB	0.41 - 0.48	0.25 \pm 0.14	2.3 \pm 0.6	2.80 $\times 10^{-4}$	9.50
	Reinland	mid	Bm	0.48 - 0.58	0.13 \pm 0.01	1.4 \pm 0.3	3.71 $\times 10^{-4}$	10.5
			Apk	0 - 0.18	0.26 \pm 0.10	1.9 \pm 0.6	1.12 $\times 10^{-4}$	7.40
	Reinland	toe	AC	0.18 - 0.26	0.11 \pm 0.04	2.4 \pm 0.4	3.25 $\times 10^{-3}$	20.9
			Apk	0 - 0.20	0.23 \pm 0.05	2.7 \pm 0.9	5.53 $\times 10^{-4}$	11.6
AC	0.20 - 0.46	0.17 \pm 0.03	2.1 \pm 0.2	0.0	12.2			
8	Hochfeld	crest	Ap	0 - 0.64	0.22 \pm 0.09	2.4 \pm 0.5	0.0	10.9
			AB	0.64 - 0.81	0.28 \pm 0.21	2.4 \pm 0.7	2.86 $\times 10^{-4}$	8.50
	Reinland	mid	Bm	0.81 - 1.00	0.12 \pm 0.04	5.4 \pm 3.3	1.19 $\times 10^{-4}$	43.8
			Apk	0 - 0.25	0.16 \pm 0.03	39.0 \pm 0.2	2.40 $\times 10^{-4}$	244
	Reinland	toe	AC	0.25 - 0.62	0.15 \pm 0.01	33.4 \pm 0.8	5.65 $\times 10^{-3}$	218
			Apk	0 - 0.23	0.24 \pm 0.02	40.2 \pm 1.0	2.38 $\times 10^{-4}$	167
AC	0.23 - 0.61	0.27 \pm 0.12	38.0 \pm 1.2	0.0	141			

sd = standard deviation

Table 4.4 (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cd ± sd	Zn ± sd	0.01M CaCl ₂	
							Cd	Zn / Cd
							mg kg ⁻¹	
9	Jasset	crest	Apk	0 - 0.24	0.52 ± 0.03	56.9 ± 1.4	5.61 × 10 ⁻⁴	109
	Blumenfeld	mid	Ahk	0.24 - 0.39	0.28 ± 0.02	45.3 ± 2.0	0.0	164
			Apk	0 - 0.15	0.40 ± 0.03	55.2 ± 0.5	1.37 × 10 ⁻⁴	139
	Blumenfeld	toe	Bntj	0.15 - 0.26	0.30 ± 0.03	48.7 ± 1.1	0.0	164
			Apk	0 - 0.13	0.47 ± 0.03	68.7 ± 0.9	5.61 × 10 ⁻⁴	146
			Bntj	0.13 - 0.29	0.42 ± 0.04	65.9 ± 2.6	8.86 × 10 ⁻⁵	158
10	Blumengart	crest	Apk	0 - 0.10	1.25 ± 0.09	99.5 ± 3.5	3.57 × 10 ⁻⁴	79.6
	Hochfeld	mid	Ahk	0.10 - 0.20	1.33 ± 0.06	100.4 ± 4.2	7.20 × 10 ⁻⁴	75.3
			Ap	0 - 0.12	0.29 ± 0.01	34.9 ± 0.3	2.91 × 10 ⁻⁴	122
	Jasset	toe	Bm	0.12 - 0.26	0.18 ± 0.02	32.3 ± 0.8	0.0	176
			Ap	0 - 0.12	0.83 ± 0.17	78.3 ± 2.1	7.76 × 10 ⁻⁴	94.8
			Bm	0.12 - 0.42	0.55 ± 0.02	70.5 ± 0.9	2.84 × 10 ⁻⁴	129
11	Bishop	middle	Apk	0 - 0.06	4.31 ± 0.92	174.8 ± 1.8	1.05 × 10 ⁻³	40.5
	Bishop	lower	Ahk	0.06 - 0.21	4.26 ± 0.21	152.5 ± 3.1	1.38 × 10 ⁻³	35.8
			Apk	0 - 0.10	4.62 ± 0.15	181.6 ± 1.2	4.31 × 10 ⁻⁴	39.3
	Bishop	toe	AC	0.10 - 0.26	3.56 ± 0.23	145.3 ± 3.3	0.0	40.8
			Ap	0 - 0.17	4.13 ± 0.98	203.0 ± 4.3	1.63 × 10 ⁻³	49.2
		Ck	0.17 - 0.50	4.35 ± 0.81	114.4 ± 5.2	0.0	26.3	

sd = standard deviation

Cd levels were considerably smaller ($< 4.99 \times 10^{-3} \text{ mg kg}^{-1}$) than the total soil Cd content and also slightly greater in the surface soil (Table 4.4). Site 3 had elevated soil Cl⁻ values due to contamination (Table 4.3). This site also had some of the higher CaCl₂ extractable soil Cd values (Table 4.4). Site 3 results will not be included later in discussions based on mean values, or when considering how soil factors relate to grain Cd content. The toe-slope position at site 11 possessed the largest CaCl₂ extractable soil Cd value ($4.99 \times 10^{-3} \text{ mg kg}^{-1}$). The extractable soil Cl content at site 11 (Table 4.3) were also some of the largest values observed from this study (Table 4.3). The high CaCl₂ extractable Cd from site 11 the Bishop soil Series was likely a result of both the high total soil Cd and soil Cl content from this site.

The total soil Zn content for the surface soil from the study area ranged from 1.3 to 203.0 mg kg⁻¹. Generally the Zn content was greater in the surface soils than in the sub-soils (Table 4.4). The Gnadenthal soil Series at the toe slope position is below the reported minimum range for Zn in Canadian soils of 10 - 200 mg kg⁻¹ by McKeague and Wolynetz (1979). This was also true for the catena from Site 7 and the Hochfeld soil Series which occupied the crest position at Site 8. These soils are representative of some of the more coarse textured soils from the study. Other coarse textured soils like the Graysville, Jasset, and the Blumenfeld soil Series' did not display such low Zn values (Table 4.4). The difference in Zn content among similar coarse textured soils likely reflects a difference in mineralogy of the parent material. These low Zn coarse textured soils could be considered Zn deficient agronomically.

Site 11 the Bishop soil Series generally had elevated levels for all heavy metals

measured. This site is strongly geochemically enriched since it is a residual soil developed from shale bedrock.

The Zn / Cd ratios for the soils in this study ranged from 3.8 to 400. The soils with the lower ratios were found in the two extremes of soil texture. The more coarse textured soils from the toe slope position at Site 6, Site 7 and the crest position from Site 8. Site 11 also had relatively low Zn / Cd ratios. The average crustal Zn / Cd ratio has been reported as 466 and 300 for shale (Krauskopf 1979). Tourtelot et al. (1964) reported finding Zn / Cd ratios as low as 10 to 30 in Pierre (black) shales. The low end range for Zn / Cd ratios has been reported as 113 (Connally et al. 1978). Soils in the study with a Zn / Cd ratio of < 119 often were associated with grain Cd contents. Nielsen (1995 personal communication) reported Zn levels in the Pembina and Gammon Ferruginous members of the Pierre Shale Formation of approximately 260 mg kg⁻¹.

The mean and median values for Cd, Zn, and 0.01 M CaCl₂-extractable Cd content of the soils in this study are presented in Table 4.5. The mean level of total soil Cd from the surface soil and sub-soil found in this study were within the range of what is considered normal background levels for soil of 1.0 mg kg⁻¹ (Plant and Raiswell 1983). The mean total soil Cd for the surface soils 0.876 mg kg⁻¹ is three times the mean value of 0.3 mg kg⁻¹ reported by Garrett (1994) for the Ap horizon in soils from the prairie ecozone. The median values in the surface and sub-surface soils were considerably smaller than the mean values. Statistically this indicates that the values found in this study's data set are skewed to the right. Site 11 which is geochemically enriched with heavy metals is responsible for this. Soil Zn and 0.01 M CaCl₂-extractable Cd show a similar pattern.

Table 4.5 Summary of mean and median Cd and Zn content^a for surface and sub-surface soil.

Element	mean	median
	—— mg kg ⁻¹ ——	
	Surface Soil	
Cd	0.876	0.422
Zn	70.5	56.5
0.01 M CaCl ₂ Cd	4.74 x 10 ⁻⁴	3.26 x 10 ⁻⁴
	Sub-Surface Soil	
Cd	0.781	0.313
Zn	61.1	47.0
0.01 M CaCl ₂ Cd	2.52 x 10 ⁻⁴	1.05 x 10 ⁻⁴

N = 30, ^a = all values reported on an oven-dry basis

4.4.2 Heavy Metal Content in samples of *Triticum turgidum* and *Triticum aestivum*

The actual grain cadmium, and the re-scaled grain Cd content are reported in Table 4.6. The wheat grain sampling in the study included two species: *Triticum turgidum* and *Triticum aestivum* variety *vulgari*. Four wheat classes were identified from the study. The *Triticum turgidum* samples represented one wheat class, Canada Western Amber Durum (CWAD) and included two varieties: Medora and Sceptre. The *Triticum aestivum* samples represented three wheat classes; Canada Western Red Spring (CWRS) and included two varieties: Neepawa and Roblin; Canada Prairie Spring (CPS) represented by the Biggar variety; and Canada Western Extra Strong (CWES) and was represented by the variety Glenlea. The four wheat classes from the study sites displayed distinctly different levels in their mean grain Cd content (Table 4.7). The level of grain Cd for the different wheat classes was in the order CWAD > CWES > CWRS > CPS. The mean grain Cd for the wheat classes from this study and from a concurrent study by the Canadian Grain Commission are reported in Table 4.7. The re-scale factors for the wheat classes are based on the sample pool from both studies to allow for a more representative mean value and thus a re-scale factor for the study area. Site 3 grain Cd data has been omitted from all sample pool calculations because this site was contaminated. Since the different wheat classes have differing capacities for the uptake of soil Cd, re-scaling the grain Cd content allowed statistical correlations to be carried out on the basis of one wheat class, CWAD. Canada Western Amber Durum was chosen for this purpose because of this wheat class's ability to accumulate more Cd than the

Table 4.6 Grain Cd^a content for the wheat classes from the study area.

Site Number	Soil Series	Slope Position	Wheat Variety	Wheat Class	Actual Cd	Re-scaled Cd
					———— ppm ————	
1	Neuhorst	crest	Glenlea	CWES	0.104	0.166
	Neuhorst	mid	Glenlea	CWES	0.070	0.112
	Osborne	toe	Glenlea	CWES	0.051	0.082
2	Plum Coulee	crest	Neepawa	CWRS	0.065	0.109
	Plum Coulee	mid	Neepawa	CWRS	0.072	0.122
	Plum Coulee	toe	Neepawa	CWRS	0.048	0.081
3	Deadhorse	crest	Neepawa	CWRS	0.026	NA
	Neuhorst	mid	Neepawa	CWRS	NS	NS
	Blumenfeld	toe	Neepawa	CWRS	0.205	NA
4	Graysville	crest	Biggar	CPS	0.019	0.027
	Graysville	mid	Biggar	CPS	0.021	0.030
	Edkins	toe	Biggar	CPS	0.028	0.041
5	Winkler clay loam	crest	Roblin	CWRS	0.024	0.040
	Eigenhof	mid	Roblin	CWRS	0.036	0.060
	Eigenhof	toe	Roblin	CWRS	0.032	0.053

NS = no sample, NA = not applicable (contaminated site)

^a = all values are reported on a f.w. basis

Table 4.6 (continued).

Site Number	Soil Series	Slope Position	Wheat Variety	Wheat Class	Actual Cd	Re-scaled Cd ppm
6	Gnadhenthal	crest	Sceptre	CWAD	0.091	0.091
	Gnadhenthal	mid	Sceptre	CWAD	0.080	0.080
	Gnadhenthal	toe	Sceptre	CWAD	0.152	0.152
7	Hochfeld	crest	Medora	CWAD	0.083	0.083
	Reinland	mid	Medora	CWAD	0.129	0.129
	Reinland	toe	Medora	CWAD	0.056	0.056
8	Hochfeld	crest	Sceptre	CWAD	0.056	0.056
	Reinland	mid	Sceptre	CWAD	0.119	0.119
	Reinland	toe	Sceptre	CWAD	0.064	0.064
9	Jasset	crest	Roblin	CWRS	0.038	0.064
	Blumenfeld	mid	Roblin	CWRS	0.033	0.056
	Blumenfeld	toe	Roblin	CWRS	0.070	0.118
10	Blumengart	crest	Biggar	CPS	0.064	0.095
	Hochfeld	mid	Biggar	CPS	0.026	0.038
	Jasset	toe	Biggar	CPS	0.095	0.140
11	Bishop	middle	Roblin	CWRS	0.178	0.301
	Bishop	lower	Roblin	CWRS	0.107	0.181
	Bishop	toe	Roblin	CWRS	0.054	0.091

Table 4.7 Grain Cd^a mean and ranges for the wheat classes from the study area and re-scale factors^b.

Wheat Class	n	Mean Cd	Range		Re-scale Factor
			ppm		
CWRS	12 ^c	0.063	0.024	0.205	
CPS	6 ^c	0.042	0.019	0.095	
CWAD	9 ^c	0.092	0.056	0.152	
CWES	3 ^c	0.075	0.051	0.104	
CWRS	86 ^d	0.049	0.014	0.204	1.69
CPS	11 ^d	0.056	0.018	0.154	1.48
CWAD	19 ^d	0.083	0.039	0.152	1.00
CWES	22 ^d	0.052	0.026	0.126	1.60

^a = all values are reported on a f.w. basis

^b = site 3 grain Cd data is omitted

^c = wheat class sample size from this study

^d = wheat class sample size from this study plus the Canadian Grain Commission

CWRS Re-scale Factor Sample Calculation:

$$\text{CWAD} / \text{CWRS} = 0.083 / 0.049 = 1.69$$

Re-scaling Actual Grain Cd to CWAD Sample Calculation:

eg. Site 2, crest position, CWRS

actual grain Cd = 0.065 ppm

re-scaled to CWAD = 0.065 x 1.69 = 0.110 ppm

other wheat classes and its tendency to take up Cd.

The mean grain Cd content for 30 of the 33 (site 3 omitted) samples re-scaled to CWAD was 0.094 ppm (range, 0.027 to 0.301 ppm). Wolnik et al. (1983) reported a mean grain Cd content in wheat of 0.043 (ppm, f.w.) from major U.S. growing areas. The higher grain Cd content from the transect are likely due to a number of factors in this area. The grain sample with 0.301 ppm Cd was from Site 11 along the lower slope of the Pembina Escarpment, Bishop soil Series (Table 4.6). The high grain Cd from this site reflects the very high total soil Cd content (Table 4.4).

An anomalously very high actual grain Cd (0.205 ppm) sample was obtained from the toe-slope position at Site 3. This site was contaminated with Cl (335.8 mg kg⁻¹, Table 4.3). McLaughlin et al. (1994a) have shown that high soil extractable Cl levels can increase Cd uptake in potatoes. This landscape position also had the highest 0.01 M CaCl₂-extractable soil Cd level recorded in this study.

Some high grain Cd values were also recorded at sites with relatively low total soil Cd and also low total soil Zn levels and low soil Zn / Cd ratios. The toe-slope position from Site 6, Site 7, and the crest position from Site 8 match this description (Table 4.4). Site 11 had high soil Zn levels but the ratio of Zn / Cd was relatively low. Fertilizing Zn deficient soils decreases Cd uptake (Oliver et al. 1994; McKenna et al. 1993; Choudhary et al. 1994). In 1991, the high end of the range for grain Cd from southern Manitoba was lower than the high end range from this study (Canadian Grain Commission, unpublished).

The Codex Alimentarius Commission of the World Health Organization

(FAO/WHO 1995) has proposed a limit of 0.1 ppm Cd (f.w.) for all agricultural produce intended for export trade. Eleven of the 30 grain samples had grain Cd concentrations > 0.1 ppm (f.w.) Cd. However, grain shipments for export are formed from a composite sample and can therefore be "diluted" through the marketing process to achieve the proposed 0.1 ppm grain Cd limit.

4.4.3 Toposequence of Total Soil Cadmium and other Heavy Metals

There was no statistically significant difference for total soil Cd based on catena position. This may have been due to the small sample size used in this study. Dudas and Pawluk (1977) reported finding no statistically significant difference in soil Cd for well drained and poorly drained soils from the Black Soil zone. The mean heavy metal content based on slope position for the surface soils and sub-surface is listed in Table 4.8. The catena results indicate that the total soil Cd content for the surface soil and sub-surface horizons was greatest in the crest position (Table 4.8). This is perhaps opposite to what would be expected in the landscape. A greater amount of total Cd would be expected at the toe-slope position for the following reasons: 1) erosional effects resulting in an accumulation of clay; 2) an increase in organic carbon in the toe-slope landscape position. An example of these processes in the landscape was observed in the catenas from sites 3, 8, 9, and 11 (Table 4.2). It was observed from the catenas (Table 4.4) that the total Cd content in the surface horizon tended to be greater at the crest position. However, in the sub-surface horizon the total Cd content tended to be greater at the toe-

Table 4.8 Mean soil Cd and Zn values^a, and grain Cd^b based on toposequence.

slope position	Cd ± sd	Total Zn ± sd	0.01 M CaCl ₂ Extractable Cd ± sd	Re-scaled Grain Cd ± sd
	mg kg ⁻¹			ppm
	Surface Soil			
crest	0.938 ± 1.239	73.4 ± 53.0	3.90 × 10 ⁻⁴ ± 3.48 × 10 ⁻⁴	0.103 ± 0.080
mid	0.839 ± 1.351	69.0 ± 51.5	3.96 × 10 ⁻⁴ ± 3.11 × 10 ⁻⁴	0.093 ± 0.048
toe	0.850 ± 1.176	69.0 ± 58.4	6.35 × 10 ⁻⁴ ± 4.84 × 10 ⁻⁴	0.081 ± 0.047
	Sub-Surface Soil			
crest	0.865 ± 1.249	62.6 ± 47.9	3.81 × 10 ⁻⁴ ± 4.27 × 10 ⁻⁴	
mid	0.688 ± 1.055	64.1 ± 49.4	1.98 × 10 ⁻⁴ ± 3.01 × 10 ⁻⁴	
toe	0.791 ± 1.270	56.7 ± 38.8	1.76 × 10 ⁻⁴ ± 3.08 × 10 ⁻⁴	

sd = standard deviation, N = 10

^a = all values are reported on an oven dry basis

^b = all values are reported on a f.w. basis

slope position. The mean total soil Cd was greater than the median value (not reported) for the surface and sub-surface horizons for each of slope positions of the catenas. This was reflected in the large standard deviation values from Table 4.8. This suggests that the distribution of surface soil total Cd is skewed to the right. This is a result of the extremely high total soil Cd from site 11.

An example of regional erosion and an accumulation of clay (Table 4.2) with an increase in total soil Cd content was observed for the Blumengart soil Series (Table 4.4). The Blumengart soil Series is described as being developed from fluvial deposits from the Manitoba Escarpment (Michalyna et al. 1988). The sedimentary materials originating from the Manitoba Escarpment may be geochemically enriched (Nielsen 1995 personal communication). Thus, soil types which describe: 1) those soils developed from erosional processes which originate from geochemically enriched shale; 2) residual soils developed from geochemically enriched shale material, may be useful to predict potentially high soil Cd levels.

The surface soil and sub-surface total Zn content was inconsistent in terms of which slope position from the catenas possessed the greatest amount (Table 4.4). Generally, the slope position that had the greatest surface soil total Zn content also had the greatest sub-soil total Zn content. The crest position of the catenas on average had the greatest Zn content the crest position for the surface soil horizon possessed the greatest content (Table 4.8). In the sub-surface soil the largest mean value for Zn was at the mid-slope position.

4.4.4 Toposequence of 0.01 M CaCl₂ Extractable Soil Cadmium

There was no statistically significant difference for 0.01 M CaCl₂ extractable soil Cd based on catena position. This may have been due to the small sample size used in this study. A summary of the toposequence results for 0.01 M CaCl₂ extractable soil Cd are given for the surface and sub-soils in Table 4.8 and 4.9 respectively. The surface soil 0.01 M CaCl₂ extractable soil Cd was greater in the toe-slope position (Table 4.8). The sub-soil 0.01 M CaCl₂ extractable soil Cd was greater in the crest position (Table 4.9).

4.4.5 Toposequence of Grain Cadmium and other Heavy Metals

There was no statistically significant difference for grain Cd based on catena position. This may have been due to the small sample size used in this study. The mean value for grain Cd based on slope position is provided in Table 4.8. The mean value for the mid-slope and toe-slope positions from this study were considerably higher than the average Cd content for wheat in well drained and poorly drained Black Soils (0.038 and 0.030 ppm, respectively) reported by Dudas and Pawluk (1977) for wheat in Alberta. The mean grain Cd for the toe-slope position was larger than compared to the other slope positions (Table 4.8). The lower standard deviation value for the mean grain Cd content from the mid-slope position indicates there was less variability from this slope position compared to the other slope positions.

4.4.6 Lithosequence of Total Soil Cadmium and other Heavy Metals

The mean values for total soil Cd, 0.01 M CaCl₂ extractable Cd, and re-scaled grain Cd are reported for the surface soils and sub-surface for the different textural classes and textural groups from the study area in Tables 4.9, 4.10, and 4.11, respectively. Total soil Cd in the surface soil and sub-surface displayed a trend for increasing Cd with increasing clay. A similar trend was also observed from the surface soil and sub-surface when the soils were separated into their textural groups. The clay and heavy clay textural classes of the surface soils from the study area display total soil Cd greater than what is reported as the normal background level for soils. The fine sand, very fine sand, loamy fine sand, and fine sandy loam textural classes possess total soil Cd values in the surface soil less than the mean value of 0.3 mg kg⁻¹ reported by Garrett (1994) for the Ap horizon in soils from the prairie ecozone. The mean value reported by Garrett (1994) was for all soils regardless of parent material or topographic position. The very fine sandy loam soils were similar to the reported mean for the Ap horizon in soils from the prairie ecozone by Garrett (1994). The sandy clay loam, clay loam, sandy clay, clay, and heavy clay textural classes of surface soils from this study all contained total soil Cd values greater than the prairie ecozone mean. The textural classes that were represented in both the surface soils and sub-surface horizons were generally greater in Cd content in the surface horizons.

Soil zinc exhibited a similar trend for increasing concentration with an increase in clay content in the surface soils and sub-surface when organized on the basis of

Table 4.9 Mean soil Cd and Zn values^a, and grain Cd^b for the surface soil textural classes from the study area.

Surface Soil Textural Class	n	Total Cd ±sd	0.01 M CaCl ₂ Extractable Cd ±sd mg kg ⁻¹	Total Zn ±sd	Re-scaled Grain Cd ±sd ppm
fine sand	2	0.253 ±0.047	1.45 x 10 ⁻⁴ ±2.06 x 10 ⁻⁴	18.6 ±23	0.047 ±0.012
very fine sand	2	0.202 ±0.082	5.62 x 10 ⁻⁵ ±7.94 x 10 ⁻⁵	2.1 ±0	0.106 ±0.032
loamy fine sand	2	0.197 ±0.052	3.96 x 10 ⁻⁴ ±2.21 x 10 ⁻⁴	20.8 ±26	0.087 ±0.044
fine sandy loam	2	0.287 ±0.066	4.81 x 10 ⁻⁴ ±3.43 x 10 ⁻⁴	20.7 ±28	0.108 ±0.063
very fine sandy loam	3	0.333 ±0.176	3.41 x 10 ⁻⁴ ±1.91 x 10 ⁻⁴	50.0 ±7	0.044 ±0.015
sandy clay loam	8	0.435 ±0.184	3.60 x 10 ⁻⁴ ±2.73 x 10 ⁻⁴	57.8 ±11	0.069 ±0.039
clay loam	3	0.947 ±0.278	7.53 x 10 ⁻⁴ ±4.46 x 10 ⁻⁴	104.0 ±7	0.096 ±0.016
sandy clay	1	0.683	1.31 x 10 ⁻⁴	74.0	0.091
clay	5	1.590 ±1.700	6.14 x 10 ⁻⁴ ±3.17 x 10 ⁻⁴	122.8 ±33	0.132 ±0.041
heavy clay	2	4.220 ±0.132	1.34 x 10 ⁻³ ±4.07 x 10 ⁻⁴	188.9 ±20	0.182 ±0.137

n = number of samples, sd = standard deviation

^a = all values are reported on an oven dry basis

^b = all values are reported on a f.w. basis

Table 4.10 Mean soil Cd and Zn values^a for the sub-soil textural classes from the study area.

Sub-Surface Textural Class	n	mg kg ⁻¹		
		Total Cd ±sd	0.01 M CaCl ₂ Extractable Cd ±sd	Total Zn ±sd
fine sand	1	0.183	0.00	32.3
very fine sand	3	0.214 ±0.089	1.99 x 10 ⁻⁴ ±1.44 x 10 ⁻⁴	2.4 ±0
loamy very fine sand	1	0.153	5.65 x 10 ⁻⁵	33.4
very fine sandy loam	8	0.225 ±0.101	3.74 x 10 ⁻⁵ ±5.20 x 10 ⁻⁵	35.4 ±23
sandy clay loam	7	0.380 ±0.136	2.04 x 10 ⁻⁴ ±2.10 x 10 ⁻⁴	51.1 ±14
clay loam	1	0.770	1.96 x 10 ⁻⁴	141.2
sandy clay	1	0.333	2.72 x 10 ⁻⁴	52.6
clay	4	1.845 ±1.697	6.54 x 10 ⁻⁴ ±4.52 x 10 ⁻⁴	104.7 ±8
heavy clay	4	2.381 ±1.791	5.20 x 10 ⁻⁴ ±6.31 x 10 ⁻⁴	126.9 ±27

n = number of samples, sd = standard deviation
^a = all values are reported on an oven dry basis

Table 4.11 Mean soil Cd and Zn values^a, and grain Cd^b for soil textural groups from the study area.

Textural Group	n	Total Cd ±sd	0.01 M CaCl ₂ Extractable Cd ±sd mg kg ⁻¹	Total Zn ±sd	Re-scaled Grain Cd ±sd ppm
Surface Soil					
sandy	4	0.225 ±0.052	2.71 x 10 ⁻⁴ ±2.27 x 10 ⁻⁴	19.7 ±20	0.067 ±0.035
coarse loamy	7	0.282 ±0.125	3.00 x 10 ⁻⁴ ±2.54 x 10 ⁻⁴	27.9 ±25	0.080 ±0.045
fine loamy	11	0.574 ±0.310	4.68 x 10 ⁻⁴ ±3.55 x 10 ⁻⁴	70.4 ±24	0.078 ±0.035
clayey	8	2.134 ±1.846	7.36 x 10 ⁻⁴ ±4.99 x 10 ⁻⁴	133.2 ±46	0.143 ±0.073
Sub-Surface Soil					
sandy	1	0.183	0.00	32.3	
coarse loamy	12	0.235 ±0.081	1.64 x 10 ⁻⁴ ±1.38 x 10 ⁻⁴	10.1 ±16	
fine loamy	8	0.428 ±0.187	2.03 x 10 ⁻⁴ ±1.94 x 10 ⁻⁴	62.3 ±34	
clayey	9	1.915 ±1.645	5.52 x 10 ⁻⁴ ±4.92 x 10 ⁻⁴	108.8 ±29	

n = number of samples, sd = standard deviation

^a = all values are reported on an oven dry basis

^b = all values are reported on a f.w. basis

textural class. A similar trend was observed when the soils were classified on the basis of textural groups. The concentration of Zn was usually greater in the surface soils for those textural classes and textural groups that were found in both the surface soils and in the sub-surface.

The concentration for Zn reported in this study for the surface soils on a textural class basis are similar to values reported for other Manitoba soils (Haluschak 1994).

4.4.7 Lithosequence of 0.01 M CaCl₂ Extractable Soil Cadmium

The 0.01 M CaCl₂-extractable soil Cd increased with increasing clay content in the surface soil and sub-surface when the soils were classified into their different textural classes and textural groups. The amount of 0.01 M CaCl₂-extractable soil Cd was generally greater in the surface soils from textural classes which were in both surface soils and sub-surface (Table 4.9 and 4.10). The amount of 0.01 M CaCl₂ extractable soil Cd was greater in the surface soils than the sub-surface when compared on the basis of textural groups (Table 4.11).

4.4.8 Lithosequence of Grain Cadmium and other Heavy Metals

The Cd content of the grain when expressed on a re-scaled basis and compared to sample sites from different textural classes (Table 4.9) and textural groups (Table 4.11) generally increased with increasing clay content. The fact that the grain Cd content

from soils of the textural classes; very fine sand and fine sandy loam, or the textural groups; sandy and coarse loamy had some of the highest grain Cd content and some of the lowest total soil Cd content suggests that the total soil Cd content is not the only important factor in the amount of Cd uptake by wheat. The lower CEC values for these soils may also reflect in a lower pH buffering capacity. Thus, a lowering of pH in the rhizosphere maybe significant enough to permit a large percentage of the low overall total soil Cd to be made more easily phyto-available.

4.4.9 Correlation of Soil Factors on Wheat Grain Cd

The frequency distribution patterns of the surface and sub-soil physical and chemical properties indicate, in most cases, a right handed skewness to the data set. This indicates statistically that the values are not normally distributed. Therefore a non-parametric test of correlation was used for statistical analyses. The Kendall and Spearman rank correlation was used to measure the correlation of selected soil properties and the re-scaled grain Cd content to CWAD from the study (Table 4.12 and 4.13). Site 3 was an anomaly in this study due to Cl contamination from an old sewage lagoon. Therefore, it was not included in any of the correlation analyses.

A number of surface soil parameters exhibited a significant positive correlation with wheat grain Cd. The results indicate that the surface soil total Cd ($r = 0.54$, $p \leq 0.01$) is a slightly better indicator of Cd uptake in wheat grain than 0.01 M CaCl₂-extractable Cd ($r = 0.46$, $p \leq 0.001$). Surface soil total Zn showed a significant positive

Table 4.12 Kendall and Spearman rank (non-parametric) correlation coefficient matrix for surface soil properties and grain Cd.

parameters	correlation coefficient (r)										
	Total soil Cd	Total soil Zn	Soil Zn / Cd	CaCl ₂	0.01M Cd	OC	CEC	Clay	Silt	Sand	Wheat grain Cd
Total soil Cd	1.00										
Total soil Zn	0.91***	1.00									
Soil Zn / Cd	-0.23	0.08	1.00								
0.01M CaCl ₂ Cd	0.68***	0.60***	-0.16	1.00							
OC	0.92***	0.91***	-0.01	0.60***	1.00						
CEC	0.92***	0.96***	-0.03	0.56**	0.93***	1.00					
Clay	0.91***	0.97***	0.03	0.60***	0.88***	0.94***	1.00				
Silt	0.86***	0.88***	0.03	0.49**	0.79***	0.85***	0.92***	1.00			
Sand	-0.91***	-0.96***	-0.01	-0.59***	-0.86***	-0.93***	-1.00***	-0.93***	1.00		
Wheat grain Cd	0.54**	0.41*	-0.37*	0.46*	0.48**	0.43*	0.42*	0.44*	-0.44**	1.00	

*, **, *** statistically significant at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$, respectively. N = 30

Table 4.13 Kendall and Spearman rank (non-parametric) correlation coefficient matrix for sub-surface soil properties and grain Cd.

parameters	correlation coefficient (r)									
	Total soil Cd	Total soil Zn	Soil Zn / Cd	0.01M CaCl ₂ Cd	OC	CEC	Clay	Silt	Sand	Wheat grain Cd
Total soil Cd	1.00									
Total soil Zn	0.88***	1.00								
Soil Zn / Cd	-0.29	0.06	1.00							
0.01M CaCl ₂ Cd	0.42*	0.27	-0.25	1.00						
OC	0.52**	0.64***	0.21	0.24	1.00					
CEC	0.88***	0.94***	-0.02	0.30	0.75***	1.00				
Clay	0.79***	0.81***	-0.17	0.35	0.34	0.76***	1.00			
Silt	0.74***	0.74***	0.01	0.16	0.48**	0.78***	0.53**	1.00		
Sand	-0.92***	-0.91***	0.13	-0.25	-0.52**	-0.91***	-0.88***	-0.83***	1.00	
Wheat grain Cd	0.51**	0.38*	-0.50**	0.28	0.11	0.39*	0.38*	0.24	-0.42*	1.00

*, **, *** statistically significant at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$, respectively. N = 30

correlation ($r = 0.41$, $p \leq 0.05$) with wheat grain Cd. This would be expected since Zn and Cd share similar properties and Cd can be taken up in place of Zn. This would reflect the situation where there was a high total soil Zn content and a concomitant higher total soil Cd content. Sites 1, 2, and 11 represent this situation. The ratio of surface soil Zn / Cd was found to be a significant negative correlation ($r = -0.37$, $p \leq 0.05$) with grain Cd. This suggests that Zn deficient soils are likely to result in higher grain Cd, eg. Sites 6, 7 and 8. Also soils which are not Zn deficient but have a low Zn / Cd ratio due to being geochemically enriched with Cd, eg. Site 11. Surface soil organic carbon, CEC, clay, and silt were also determined to have a significant positive correlation and sand a significant negative correlation with grain Cd. The correlation between clay and grain Cd would be expected since as described earlier the total soil Cd content increases with clay content (Table 4.9 and 4.11).

Few sub-surface parameters were significantly correlated with wheat grain Cd. A significant positive correlation ($r = 0.51$, $p \leq 0.01$) was determined for total sub-surface Cd with grain Cd. A significant negative correlation ($r = -0.50$, $p \leq 0.01$) was determined for the sub-surface Zn / Cd ratio with grain Cd. The correlation between sub-surface Zn and grain Cd was a significant positive relationship, but less than the correlation coefficient for the surface soil. A significant positive correlation was found for sub-surface CEC, and clay with grain Cd. A significant negative correlation occurred for sand with grain Cd. The fact that in the surface and sub-surface soil total Cd and Zn were positively correlated with the clay to being geochemically enriched with Cd would result in high grain Cd, this was the case for site 11, the Bishop soil Series.

From the results of this study it appears that a couple of factors are important in causing higher wheat grain Cd in the Red River Valley. The total soil Cd content, and the Zn / Cd ratio were the most important factors in causing higher wheat grain Cd levels from the transect.

4.5 Summary and Conclusions

The pedogenic influence of relief on soil Cd, $S_{Cd} = f(r)_{cl, s, p, t, \dots}$ was found to be greatest in the crest position from the toposequence for both the surface and sub-surface soils in the red River Valley. Wheat grain Cd content was also greater in the crest position from the catenas in this study.

A lithosequence, designed to determine the influence of parent material (measured on the basis of different soil textures) on soils Cd, $S_{Cd} = f(p)_{cl, s, r, t, \dots}$ found that soil Cd in the surface and sub-surface soil increased with increasing clay content. The lithosequence also indicated that wheat grain Cd content also increased with increasing clay content.

Statistical analyses of the relationship between soil properties to wheat grain Cd determined that total soil Cd and the Zn / Cd ratio in soil had the greatest significance to wheat grain Cd content.

5. GENERAL DISCUSSION

Chapter 3 established that lacustrine and shale till parent material are likely to possess high total soil Cd levels than mixed till parent material. The soils developed from lacustrine parent material in the Red River Valley were determined in Chapter 4 to contain a mean total surface soil Cd level (0.876 mg kg^{-1}) three times the mean for the Ap horizon in the prairie ecozone (0.3 mg kg^{-1} , Garrett 1994).

The soil Cd profile distribution for the pedons presented in Chapter 4 indicated that historic biopedological cycling results in the surface horizon containing the greatest amount of Cd. The profile distribution of Cd in Chapter 3 was similar to results from others (Pierce et al. 1982; Dudas and Pawluk 1980). Sola studied in Chapter 4 contained a greater amount of Cd in the surface horizon compared to the sub-surface horizon. This was similar to the findings of Holmgren et al. (1993). But contrary to earlier studies in Manitoba by Madden (1974) and also Mills and Zwarich (1975).

Results from Chapter 4 demonstrated that total soil Cd is a significant factor in determining the amount of grain Cd. Soils from the prairie ecozone with high levels of total soil Cd are likely able to produce higher grain Cd.

Chapter 4 also highlighted the importance of the sub-surface Zn / Cd ratio to grain Cd content from soils in southern Manitoba. This observation could have a significance to other soils from the prairie ecozone and their potential for producing grain with high

Cd content. From Chapter 4 it appears that soils across the prairie ecozone which possess Zn / Cd ratios < 119 may have the potential for producing high grain Cd. From the pedons described in Chapter 3 it would appear that only one surface soil horizon examined among the 13 pedons described may be susceptible to producing high grain Cd levels. The Maleb soil Series Ap horizon had a Zn / Cd ratio of 129. This is a value only slightly higher than 119 Zn / Cd ratio suggested as the critical value in Chapter 4. Other soils from Chapter 3 might be susceptible to producing high grain Cd but these soils have horizons with low Zn / Cd ratios below the Ap horizon. The IICk horizon from the Ardill soil Series has a Zn / Cd ratio of 127. This horizon was from 60 - 92 cm within the rooting zone for cereal crops. The Ck1 horizon from the Readymade soil Series has a Zn / Cd ratio of 115. This horizon was from 0.30 - 0.70 m also within the rooting zone of cereal crops. The IICk2 horizon from the Pembina(2) soil Series has a Zn / Cd ratio of 101. This horizon was at a depth of 0.95 - 1.30 m possibly below the rooting depth of a cereal crop.

6. SUMMARY AND CONCLUSIONS

A number of significant findings were observed from the studies which formed this thesis. Two soil forming factors: parent material and climate are important to prairie ecozone soils for: 1) the initial soil Cd content; 2) the biopedological redistribution of Cd. The type of rock source(s) from which parent material is derived is an important soil forming factor in determining the amount of total soil Cd present in the soils of the prairie ecozone. The Bishop soil Series developed from residual shale parent material, from the lower slope of the Manitoba Escarpment highlighted this fact. Climate is a soil forming factor that influences the type of vegetation associated with the soil zones across the prairie ecozone. The role vegetation plays on biopedological cycling and the pedogenesis of soil Cd was indicated by the type of total soil Cd profile distribution.

The fact that surface horizons generally contained the greatest amount of total soil Cd also highlights the importance of crop residues acting as a sink for Cd accumulation in the surface soil. The lack of an accumulation of total soil Cd in any Bt horizons from the pedons examined demonstrated that Cd is not a mobile element.

Concerns that the use of phosphatic fertilizers has the potential to increase accumulation of Cd in prairie ecozone soils are largely unfounded. The fact that the surface horizons in this study contained the higher levels of soil Cd is likely to a larger extent a result of biopedological cycling and not through the use of phosphatic fertilizers.

Two important factors were observed from an area of southern Manitoba noted for its annually high grain Cd content by the Canadian Grain Commission. The first factor was the rock source (geochemically Cd enriched shale) of the parent material, and secondly, the Zn / Cd ratio (< 119) were critical to producing the high levels of grain Cd observed. The Ardill soil Series higher total soil Cd in horizons below the surface horizon and the higher correlation coefficient for sub-surface Zn / Cd with grain Cd highlights the importance of soil sampling to the two foot depth for enviro-agronomic purposes.

Therefore, agronomically managing to reduce the level of Cd in crops can possibly be achieved through a number of approaches. Producers may be able to select for low grain Cd accumulators for regions which are enriched in natural soil Cd or which may have a soil Zn - Cd ratio susceptible to increasing Cd uptake. In Canada, breeding programs by Agriculture Agri-Foods Canada exist to develop durum and flax lines of low Cd accumulators.

A recommendation for future work would be to establish the soil Zn / Cd ratio in cases of excess, optimum, marginal, and deficient Zn conditions for crop production. These results can also be used to compile a data set in order to choose the best Zn / Cd ratio associated with the lowest plant uptake of Cd. These results suggest that follow up work should be initiated to establish Zn fertilizer rates for soils deficient in Zn or a low Zn / Cd ratio (< 119).

7. CONTRIBUTION TO KNOWLEDGE

Many of the results from this study confirm the observations made from other studies. The pedological soil Cd distribution over a broad regional basis from the climosequence among soil zones in the prairie ecozone provides evidence that native soil Cd is not affected by the same leaching processes that cause the translocation of clay separates.

The southern Manitoba region has likely been producing higher grain Cd levels than most prairie ecozone districts due to geochemically Cd enriched shale from the Manitoba Escarpment. Another factor is possibly the low Zn / Cd ratio for some of the region.

The results from this study may help others in their attempt at reducing grain Cd levels from the non-polluted agro-ecosystem. A means of achieving this could be to produce a soil Cd map. Soil types could be rated on the basis of important soil factors identified from these two studies. Agricultural producers could then use this "tool" in combination with variety selection, and fertility management practices to limit the level of Cd in their grain.

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9. APPENDICES

I Morphological Description Including Physical and Chemical Properties of Soils From A Survey of Soil Cadmium Across The Prairie Ecozone

The 13 pedons sampled for analysis in chapter three were described and named by Ross Malegus, Tee Boon Goh, Simon Brookes, Tony Brierley, and Leonard Kozak in the field. These soils were selected to provide background levels of Cd in agricultural soils from the prairie ecozone, from different parent materials and different climatic zones.

Preliminary potential sites were determined based on data supplied by the Canadian Grain Commission that indicated regions in the prairie ecozone with higher than normal grain Cd. Sites were selected based on similar surface soil textures (clay loam) from polygons off of the Soil Landscapes of Canada maps for Manitoba, Saskatchewan, and Alberta. Various local soils reports were then used to further help identify soils to be sampled for the study. In the Mantario area of Saskatchewan a well drained sandy clay loam soil which formed in clay loam glacial till modified by Upper Cretaceous clays and shales was selected (The Soils of Chesterfield Rural Municipality No. 261 Saskatchewan 1993). In the Bow Island area of Alberta two soils one a well drained clay loam soil which formed in non-saline or weakly saline till and the other a well drained loam soil which formed in glaciolacustrine parent material of the Winnifred upland and

Etzikom Plain respectively (McNeil et al. 1994). In the Vulcan area of Alberta a well drained clay loam soil which formed in medium textured till of the Majorville uplands (Walker and Pettapiece 1996). In the Major area of Saskatchewan a well drained clay loam soil which formed in slightly stony, loamy glacial till was sampled in the Rural Municipality of Prairiedale (No. 321 - Preliminary Soil Map and Report, Saskatchewan Soil Survey 1989). In the St. Jean area of Manitoba a soil developed from strongly calcareous, medium to moderately fine textured alluvial and lacustrine deposits overlying lacustrine clay within a meter of the surface under poor drainage was sampled on the Red River Plain (Ehrlich et al. 1953). This soil is described in the Soils of Winnipeg Region Study Area (Michalyna et al. 1975). In the Virden area of Manitoba the soil sampled was formed on thin, strongly calcareous, medium textured lacustrine sediments overlying strongly calcareous, medium to moderately fine textured glacial till. A coarse textured layer (1 to 15 cm) occurs at the contact. These soils have developed under moderately good drainage of the Oxbow Till Plain (Ehrlich et al. 1956). This soil is described in the Soils of the Boissevain - Melita Area (Eilers et al. 1978). In the Lloydminster area of Saskatchewan a sandy clay loam soil formed in well drained slightly stony, loamy glacial till was sampled in the Rural Municipality of Wilton (No. 472 - Preliminary Soil Map and Report, Saskatchewan Soil Survey 1986). In the Kitscoty area of Alberta a well drained clay loam soil formed in loamy glacial till was sampled (Wyatt et al. 1944). In the St. Walberg area of Saskatchewan a well drained loam soil developed on undifferentiated boulder clay was sampled on the Paradise Hill-Lloydminster Upland (Mitchell et al. 1950). In the Myrnamarea of Alberta a well drained loam soil developed

on dark grayish brown to olive brown till of the Myrnam Upland was sampled (Macyk et al. 1985). In the Somerset area of Manitoba a well drained clay loam soil developed on shale till of the Pembina Hills (Langman 1986) was sampled. In the Altamont area of Manitoba a well drained loam soil developed on mixed till, with a sandy-skeletal substrate of glacial-fluvial origin within a meter of the mineral surface was sampled in the Pembina Hills (Langman 1986).

SOIL ONE

Soil Series: **Ardill (ADA)**
Classification: **Orthic Brown**
Profile Location: **SE32-26-27W3, southwest Saskatchewan, near Mantario**
Date: **June 18, 1993**
Topography: **hummocky**
Slope Position: **mid**
Aspect: **northwest**
Drainage: **moderately well**
Parent Material 1: **clay loam glacial till modified by Upper Cretaceous clays and shales**
Parent Material 2: **lacustrine**
Parent Material 3: **mixed till**
Vegetation: **Crops-fields (managed) summerfallow**

Ap 0 - 0.10 m **Dark brown (10YR 3/3 m*), dark grayish brown (10YR 4.5/2 d**) sandy clay loam; cloddy; non calcareous; abrupt smooth boundary between 0.08 to 0.18 m:**

Bm 0.10 - 0.30 m **Dark Yellowish brown (10YR 3/4 m), brown (10YR 5/3 d) sandy clay; weak to moderate medium to coarse subangular blocky; non calcareous; clear wavy boundary between 0.08 to 0.20 m:**

- Bmk** 0.30 - 0.45 m Dark grayish brown (10YR 3.5/2 m), grayish brown (10YR 5/2 d) sandy clay loam; very weak medium prismatic; moderate calcareous; gradual smooth boundary between 0.06 to 0.16 m:
- Cca** 0.45 - 0.60 m Olive brown (2.5Y 4/4 m), grayish brown (2.5Y 5/2 d) clay loam; very weak medium prismatic; moderate calcareous; iron staining; few clay films; clear smooth boundary between 0.21 to 0.24 m:
- IIck** 0.60 - 0.92 m Very dark grayish brown (2.5Y 3/2 m), light brownish gray (2.5Y 6/2 d) clay; structureless massive; strong calcareous; clear smooth boundary between 0.24 to 0.30 m:
- IIIck** 0.92 - 1.15 m Grayish brown (2.5Y 5/2 d), heavy clay; structureless massive; observed shale fragments; moderate calcareous; rooting depth to 1.15 m.

*m - moist color

**d - dry color

Physical and chemical properties* for the Ardill Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations			CaCO ₃ B. D. g kg ⁻¹	Particle Size			Textural Class Group						
			Na	K	Ca		%BS	%S	%Si		%C					
AP	7.5	12.0	0.1	1.5	8.4	3.7	18.4	74.5	0.0	1.39	54	13	33	SCL	M	
Bm	0.10-0.30	7.5	10.0	0.1	1.2	9.0	4.4	18.1	81.1	1.0	1.56	50	13	37	SC	F
Bmk	0.30-0.45	7.8	7.0	0.1	0.8	8.2	4.7	15.7	88.1	68.0	1.49	47	22	31	SCL	M
Cca	0.45-0.60	8.0	6.0	0.3	0.8	9.5	6.5	20.6	82.8	99.0	1.63	35	25	40	CL	M
IIck	0.60-0.92	8.2	7.0	1.7	1.0	17.5	11.9	29.3	109.7	214.0	1.49	2	39	59	C	F
IIIck	0.92-1.15	8.2	6.0	3.7	4.7	14.2	17.5	30.7	130.7	125.0	1.41	12	23	65	HC	F

* = all values are reported on an oven dry basis

SOIL TWO

Soil Series: Maleb (MAB)
Classification: Orthic Brown
Profile Location: NE10-12-9W4, southeast Alberta, near Bow Island
Date: June 7, 1993
Topography: undulating
Slope Position: mid
Aspect: north
Drainage: moderately well
Parent Material: non-saline or weakly saline till
Vegetation: crops-fields (managed) immature

Ap 0 - 20 cm Dark yellowish brown (10YR 3/3.5 d**) clay loam; weak fine granular; non calcareous; wet non sticky; clear smooth boundary:

Ahe 20 - 30 cm Dark brown (10YR 4/3.5 m*), dark brown (10YR 4/3 d) loam; weak to moderate medium prismatic; non calcareous; wet slightly sticky; diffuse smooth boundary:

Bmk 30 - 46 cm Dark brown (10YR 3/3 m), brown (10YR 5/3 d) clay loam; very weak medium prismatic; weakly calcareous; wet sticky; diffuse smooth boundary:

Cca 46 - 57 cm Dark grayish brown (10YR 4/2 m), light gray (10YR 7/2 d) clay loam; structureless massive; moderate calcareous; gravelly 3% by

volume; wet slightly sticky; clear wavy boundary:

Ck 57 - 100 cm Grayish brown (2.5Y 5/2 m), light brownish gray (10YR 6/2 d) clay loam; structureless massive; gravelly 3% by volume; weakly calcareous; wet sticky.

***m** - moist color

****d** - dry color

Physical and chemical properties^a for the Maleb Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	Particle Size			Textural Class Group				
			— cmol(+)kg ⁻¹ —						CaCO ₃ B. D. g kg ⁻¹ Mg m ⁻³	%S	%Si		%C			
			Na	K	Ca	Mg										
Ap	0-0.20	6.9	20.0	1.2	2.0	10.0	6.0	18.0	106.7	3.0	1.15	39	35	26	CL	M
Ahe	0.20-0.30	6.0	16.0	0.2	1.3	11.1	3.9	14.6	112.5	0.0	1.05	44	31	25	L	M
Bmk	0.30-0.46	7.7	9.0	0.2	0.9	12.8	5.3	21.7	88.3	57.0	1.31	33	37	30	CL	M
Cca	0.46-0.57	7.9	7.0	0.3	1.1	12.9	4.6	19.7	95.9	136.0	1.37	45	21	34	CL	M
Ck	0.57-1.00	8.1	6.0	1.7	1.5	8.6	6.9	21.1	88.7	58.0	1.46	42	25	33	CL	M

^a = all values are reported on an oven dry basis

SOIL THREE

Soil Series: Chin (CHN)
Classification: Orthic Brown
Profile Location: NE31-11-10W4, southeast Alberta, near Bow Island
Date: June 7, 1993
Topography: level
Slope Position: mid
Aspect: north
Drainage: moderately well
Parent Material: glaciolacustrine
Vegetation crops-fields (managed) immature: irrigated

Ap 0 - 15 cm Dark grayish brown (10YR 4/2 d**) loam; moderate medium granular; non calcareous; moist friable; abrupt wavy boundary:

AB 15 - 24 cm Dark brown (10YR 4/3 d) loam; moderate medium platy; non calcareous; moist very friable; clear wavy boundary:

Btj 24 - 42 cm Dark brown (10YR 4/3 d) sandy clay loam; weak medium prismatic; non calcareous; moist friable to firm; gradual irregular boundary:

BC 42 - 57 cm Yellowish brown (10YR 5/4 d) sandy clay loam; weak fine to medium prismatic; non calcareous; moist loose; clear wavy boundary:

Ck1 57 - 70 cm Pale brown (10YR 6/3 d) clay loam; structureless massive;

moderate calcareous; moist loose; gradual smooth boundary:

IIck 70 - 100 cm Light gray (10YR 7/2 d) silty clay loam; structureless
massive; moist loose; strong calcareous.

****d** - dry color

Physical and chemical properties^a for the Chin Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ B. D.			Particle Size			Textural Class Group
			Na	K	Ca	Mg			g kg ⁻¹	Mg m ⁻³	%S	%Si	%C		
Ap	0-0.15	7.7	16.0	1.1	3.0	11.3	9.3	18.4	134.1	6.0	1.39	48	29	23	L M
AB	0.15-0.24	7.6	9.0	1.3	1.9	4.6	9.4	12.0	143.0	1.0	1.50	48	29	23	L M
Btj	0.24-0.42	7.6	8.0	2.0	1.4	4.0	11.5	11.1	171.0	1.0	1.41	53	22	25	SCL M
BC	0.42-0.57	7.5	6.0	2.1	0.9	3.0	12.1	6.2	294.6	1.0	1.50	58	20	22	SCL M
Ck1	0.57-0.70	8.1	6.0	2.4	0.6	14.3	13.9	17.2	181.8	146.0	1.58	33	39	28	CL M
IIck	0.70-1.00	8.2	6.0	1.8	0.6	24.1	13.4	20.7	193.0	257.0	1.38	17	46	37	SiCL M

^a = all values are reported on an oven dry basis

SOIL FOUR

Soil Series: Readymade (RDM)
Classification: Orthic Dark Brown
Profile Location: SE26-17-21W4, southeast Alberta, near Vulcan
Date: June 9, 1993
Topography: hummocky
Slope Position: mid
Aspect: northwest
Drainage: moderately well
Parent Material: medium textured till
Vegetation: crops-fields (managed) immature

Ap 0 -10 cm Very dark brown (10YR 2.5/2 m*), very dark grayish brown (10YR 3.5/2 d**) clay loam; cloddy; non calcareous; gravelly 1 % by volume; very fine roots, vertical, impeded and expeditious root distribution; abrupt smooth boundary between 7 to 12 cm:

Bm 10 - 30 cm Dark yellowish brown (10YR 3/4 m), dark grayish brown (10YR 4/2 d) sandy clay loam; weak medium angular blocky; non calcareous; gravelly 1 % by volume; very fine roots, vertical, impeded and expeditious root distribution; abrupt smooth boundary:

Ck1 30 - 70 cm Dark grayish brown (2.5Y 4/3 m), grayish brown (2.5Y 5/2
d) sandy clay loam; weak medium angular blocky; moderate calcareous;
gravelly 2% by volume; coarse roots, vertical, impeded and expanded root
distribution; diffuse irregular boundary between 64 to 87 cm:

Ck2 70 - 100 cm Dark grayish brown (2.5Y 4/2 m), grayish brown (2.5Y 5/2
d) sandy clay loam; weak medium angular blocky; gravelly 10%; medium
roots, vertical, impeded and expanded root distribution; rooting depth to 90 cm;
moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Readymade Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group	
			Na	K	Ca	Mg					%S	%Si	%C		
Ap	0-0.10	6.4	41.0	0.0	2.1	14.4	4.0	22.4	82.4	0.0	1.01	41	27	32	CL M
Bm	0.10-0.30	6.5	18.0	0.0	0.9	9.7	4.2	18.4	80.9	1.0	1.27	51	15	34	SCL M
Ck1	0.30-0.70	7.8	7.0	0.2	1.0	9.7	5.7	16.5	100.5	140.0	1.57	46	24	30	SCL M
Ck2	0.70-1.00	8.0	4.0	0.1	0.7	13.7	8.9	18.5	126.7	144.0	1.63	46	24	30	SCL M

^a = all values are reported on an oven dry basis

SOIL FIVE

Soil Series: Weyburn (WRA)
Classification: Orthic Dark Brown
Profile Location: NE16-33-26W3, southeast Saskatchewan, near Major
Date: June 18, 1993
Topography: hummocky
Slope Position: mid
Aspect: northwest
Drainage: moderately well
Parent Material: slightly stony, loamy glacial till
Vegetation: crops-fields (managed) summerfallow

Ap 0 - 13 cm Very dark brown (10YR 2/1.5 m*), dark brown (10YR 3.5/3 d**) clay loam; weak medium to coarse subangular blocky; non calcareous; abrupt smooth boundary between 12 to 14 cm:

Bm 13 - 26 cm Dark yellowish brown (10YR 3/4 m), dark brown (10YR 3.5/3 d) sandy clay; moderate coarse prismatic; non calcareous; gradual wavy boundary between 12 to 16.5 cm:

Cca 26 - 56 cm Dark grayish brown (2.5Y 4/2 m), light brownish gray (10YR 6/2 d) clay loam; weak to moderate coarse prismatic; strong calcareous; gradual smooth boundary between 26 to 32 cm:

Ck1 56 - 66 cm Very dark grayish brown (2.5Y 3.5/2 m), grayish brown (10YR 5.5/2 d) sandy clay loam; structureless massive; moderate calcareous; gradual smooth boundary between:

Ck2 66 - 110 cm Olive brown (2.5Y 4/4 m), light brownish gray (10YR 6/2 d) sandy clay loam; structureless massive; rooting depth to 110 cm; moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties* for the Weyburn Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations			O.C. cmol(+)kg ⁻¹	Ca Mg	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group	
			Na	K	CEC						%S	%Si	%C		
Ap	0-0.13	6.0	41.0	0.0	1.3	11.0	4.1	20.6	79.8	3.0	1.94	41	28	31	CL M
Bm	0.13-0.26	6.6	11.0	0.1	0.6	9.1	5.1	19.8	74.9	3.0	1.45	46	18	36	SC F
Cca	0.26-0.56	8.0	7.0	0.2	0.7	7.4	5.7	16.8	83.5	166.0	1.52	40	25	35	CL M
Ck1	0.56-0.66	8.2	4.0	0.6	0.9	8.1	8.1	17.9	98.9	141.0	1.62	47	22	31	SCL M
Ck2	0.66-1.10	8.2	4.0	0.8	0.6	7.8	9.9	19.3	99.4	129.0	1.55	47	25	28	SCL M

* = all values are reported on an oven dry basis

SOIL SIX

Soil Series: Niverville (NIV)
Classification: Gleyed Calcareous Rego Black
Profile Location: NE28-2-1E1, south central Manitoba, near St. Jean
Date: September 3, 1992
Topography: level
Slope Position: level
Aspect: level
Drainage: imperfect
Parent Material: lacustrine
Vegetation: crops-fields (managed) cropped

Apk 0 - 15 cm Black (10YR 2.5/1 d**) clay loam; moderate calcareous;
clear irregular boundary tonguing observed to 50 cm:

AC 15 - 32 cm Dark gray (10YR 4.5/1 d) clay loam; moderate calcareous;
gradual wavy boundary:

Cca 32 - 80 cm Light brownish gray (10YR 6.5/2 d) clay loam; very strong
calcareous:

IIck 80 - 100 cm Grayish brown (2.5Y 5/2 d) clay, strong calcareous.

**d - dry color

Physical and chemical properties^a for the Niverville Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ B. D. g kg ⁻¹ Mg m ⁻³	Particle Size			Textural Class Group			
			Na	K	Ca	Mg				%S	%Si	%C	Class	Group		
Apk	0-0.15	7.3	50.0	0.3	1.3	28.0	11.5	ND	ND	71.0	1.36	32	32	36	CL	M
AC	0.15-0.32	7.1	44.0	0.5	1.1	21.0	14.5	ND	ND	78.0	1.63	36	29	35	CL	M
Cca	0.32-0.80	7.2	28.0	0.4	0.6	15.7	10.4	ND	ND	328.0	1.30	27	42	31	CL	M
HCk	0.80-1.00	7.3	28.0	0.2	1.3	29.6	22.2	ND	ND	161.0	1.48	5	34	61	C	F

ND = not determined, ^a = all values are reported on an oven dry basis

SOIL SEVEN

Soil Series: Newstead (NWS)
Classification: Orthic Black
Profile Location: NE27-9-28W1, southwest Manitoba, near Virden
Date: October 17, 1992
Topography: undulating
Slope Position: upper
Aspect: east
Drainage: well
Parent Material: boulder till
Vegetation: crops-fields (managed) cropped

Ap 0 - 20 cm Black (10YR 2/1 m*), very dark gray (10YR 3/1 d**) loam; non calcareous; plentiful fine roots, vertical, impeded and exped distribution; clear wavy boundary between 15 to 23 cm:

Bm 20 - 40 cm Dark brown (10YR 3/3 m), dark grayish brown (10YR 4/2 d) clay loam; weakly calcareous; few fine roots, vertical, impeded and exped distribution; gradual wavy boundary between 15 to 25 cm:

IIcK1 40 - 65 cm Brown (10YR 5/3 m), grayish brown (10YR 5.5/2 d) sandy loam; strong calcareous; very few roots, vertical, impeded and exped distribution; gradual smooth boundary 25 to 30 cm:

HCk2 65 - 95 cm Dark yellowish brown (10YR 4/4 m), pale brown (10YR

6.5/3 d) sandy loam; strong calcareous.

***m - moist color**

****d - dry color**

Physical and chemical properties^a for the Newstead Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ B. D.			Particle Size			Textural Class Group	
			Na	K	Ca	Mg			g kg ⁻¹	Mg m ⁻³	%S	%Si	%C	Class	Group	
Ap	0-0.10	6.8	35.0	0.5	1.3	21.4	5.4	ND	ND	2.0	1.26	46	29	25	L	M
Bm	0.10-0.40	6.9	23.0	0.3	0.8	10.3	7.2	26.1	70.9	47.0	1.36	45	24	31	CL	M
IIck1	0.40-0.65	7.0	12.0	0.4	0.6	8.3	7.3	18.6	89.0	224.0	1.55	58	35	7	SL	C
IIck2	0.65-0.95	7.2	14.0	1.4	0.6	17.4	11.9	19.0	164.8	247.0	1.84	56	41	3	SL	C

ND = not determined, ^a = all values are reported on an oven dry basis

SOIL EIGHT

Soil Series: Mayfair (MFA)
Classification: Orthic Black
Profile Location: SW16-49-27W3, central Saskatchewan, near Lloydminster
Date: June 17, 1993
Topography: hummocky
Slope Position: mid
Aspect: southwest
Drainage: well
Parent Material: glacial till
Vegetation: crops-fields (managed) immature

Ap 0 - 10 cm Black (10YR 2/1 m*), very dark gray (10YR 3.5/1.5 d**) sandy clay loam; weak medium to coarse subangular blocky; non calcareous; abrupt wavy boundary between 8 to 11 cm:

Btj 10 - 28 cm Dark yellowish brown (10YR 3/4 m), brown (10YR 5/3 d) clay loam; weak to moderate very coarse subangular blocky; non calcareous; clear smooth boundary between 13 to 20 cm:

Bm 28 - 37 cm Dark yellowish brown (10YR 3.5/3.5 m), olive brown (2.5Y 4.5/4 d) clay loam; weak very coarse subangular blocky; non calcareous; abrupt wavy boundary between 7 to 11 cm:

- Ck1** 37 - 60 cm Olive brown (2.5Y 4/4 m), light brownish gray (2.5Y 6/2 d) clay loam; structureless massive; moderate calcareous; gradual smooth boundary between 19 to 23 cm:
- Ck2** 60 - 88 cm Olive brown (2.5Y 3.5/3 m), grayish brown (2.5Y 5.5/2 d) clay loam; structureless massive; moderate calcareous; diffuse smooth boundary:
- Ck3** 88 - 112 cm Very dark grayish brown (2.5Y 3.5/2 m), grayish brown (2.5Y 5.5/2 d) clay loam; structureless massive; rooting depth to 110 cm; moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Mayfair Profile.

Horizon Depth, m	pH (CaCl ₂)	O.C. g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ B. D.			Particle Size			Textural Class Group	
			Na	K	Ca	Mg			g kg ⁻¹	Mg m ⁻³	%S	%Si	%C	Class	Group	
Ap	0-0.10	7.2	28.0	0.0	1.0	13.5	4.9	24.4	79.8	1.0	1.29	47	24	29	SCL	M
Btj	0.10-0.28	7.3	10.0	0.1	0.7	7.1	7.0	18.4	81.1	0.0	1.48	43	23	34	CL	M
Bm	0.28-0.37	7.4	8.0	0.1	0.6	4.5	7.7	17.3	74.0	3.0	1.60	44	25	31	CL	M
Ck1	0.37-0.60	8.1	7.0	0.2	0.8	4.8	8.1	15.5	89.2	118.0	1.53	41	29	30	CL	M
Ck2	0.60-0.88	8.2	5.0	0.3	0.9	6.2	9.2	17.7	93.5	109.0	1.56	41	30	29	CL	M
Ck3	0.88-1.12	8.1	5.0	0.1	0.7	7.9	7.2	17.7	90.4	89.0	1.65	43	26	31	CL	M

^a = all values are reported on an oven dry basis

SOIL NINE

Soil Series: Beaverhills (BVH)
Classification: Orthic Black
Profile Location: NW7-50-3W4, central Alberta near Kitscoty
Date: June 12, 1993
Topography: hummocky
Slope Position: mid
Aspect: northwest
Drainage: well
Parent Material: glacial loam
Vegetation: crops-fields (managed) immature

Ap 0 - 14 cm Black (10YR 1/1 m*), black (10YR 2/1 d**) clay loam; moderate coarse subangular blocky; non calcareous; moist friable; abrupt smooth boundary between 14 to 16 cm:

AB 14 - 21 cm Black (10YR 2/2 m), very dark grayish brown (10YR 3/2 d) clay loam; moderate coarse subangular blocky; non calcareous; moist friable; gradual wavy boundary between 2 to 10 cm:

Bm 21 - 40 cm Dark yellowish brown (10YR 3/4 m), brown (10YR 5/3 d) sandy clay loam; moderate coarse subangular blocky; non calcareous; moist friable; abrupt smooth boundary between 20 to 26 cm:

Bt 40 - 62 cm Dark brown (10YR 3/3 m), brown (10YR 5/3 d) clay loam; strong coarse prismatic; common clay films, thick, on ped faces; non calcareous; moist firm; abrupt smooth boundary between 10 to 16 cm:

BC 62 - 70 cm Very dark grayish brown (2.5Y 3/2 m), brown (10YR 5/3 d) clay loam; moderate coarse angular blocky; moderate calcareous; moist friable:

Ck 70 - 110 cm Brown (10YR 5/3 d) clay loam; rooting depth to 90 cm; moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties* for the Beaverhills Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations			cmol(+)kg ⁻¹	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group		
			Na	K	Ca					Mg	%S	%Si		%C	
AP	5.0	47.0	0.1	1.0	12.2	3.7	23.1	73.8	0.0	1.03	42	25	33	CL M	
AB	0.14-0.21	5.2	23.0	0.1	0.4	7.7	4.6	18.4	69.9	0.0	1.39	34	35	31	CL M
Bm	0.21-0.40	5.1	10.0	0.2	0.6	4.5	5.6	15.8	68.8	0.0	1.44	47	22	31	SCL M
Bt	0.40-0.62	6.8	8.0	0.8	1.0	6.7	9.0	22.5	77.8	4.0	1.63	42	19	39	CL M
BC	0.62-0.70	7.8	6.0	1.0	0.7	8.5	8.4	24.3	76.5	63.0	1.49	37	24	39	CL M
Ck	0.70-1.10	8.0	7.0	1.3	1.0	8.1	8.7	23.5	80.9	80.0	1.49	38	26	36	CL M

* = all values are reported on an oven dry basis

SOIL TEN

Soil Series: Whitewood (WHA)
Classification: Orthic Dark Gray
Profile Location: SE6-52-23W3, central Saskatchewan, near St. Walberg
Date: June 16, 1993
Topography: hummocky
Slope Position: mid
Aspect: south
Drainage: well
Parent Material: loamy glacial till
Vegetation: crops-fields (managed) summerfallow

- Ap** 0 - 10 cm Dark Gray (10YR 4.5/1 d**) loam; weak to moderate very coarse subangular blocky; non calcareous; moist friable; abrupt smooth boundary:
- Bt1** 10 - 27 cm Dark yellowish brown (10YR 3/4 m*), light yellowish brown (10YR 6/4 d) clay loam; weak to moderate coarse subangular blocky; common clay films, on ped faces; non calcareous; moist firm; clear smooth boundary:
- Bt2** 27 - 47 cm Dark yellowish brown (10YR 3/4 m), light yellowish brown (10YR 6/4 d) sandy clay loam; moderate medium to coarse angular blocky; many clay films, on ped faces; non calcareous; moist firm; abrupt

smooth boundary between 20 to 25 cm:

Ck1 47 - 72 cm Very dark grayish brown (2.5Y 3.5/2 m), brown (10YR 5/3 d) sandy clay loam; weak to moderate medium to coarse subangular blocky; moderate calcareous; dry hard; gradual smooth boundary between 18 to 25 cm:

Ck2 72 - 100 cm Very dark grayish brown (2.5Y 3/2 m), pale brown (10YR 6/3 d) sandy clay loam; weak very coarse subangular blocky; dry hard; moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Whitewood Profile.

Horizon	Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group	
				Na	K	Ca	Mg					%S	%Si	%C	Class	Group
Ap	0-0.10	6.9	27.0	0.0	1.1	11.2	2.5	16.8	88.7	1.0	1.26	50	32	18	L	M
Bt1	0.10-0.27	6.8	8.0	0.0	0.8	6.8	4.1	18.9	62.2	0.0	1.60	42	20	38	CL	M
Bt2	0.27-0.47	6.7	6.0	0.0	0.7	7.4	3.8	18.5	64.4	1.0	1.63	52	16	32	SCL	M
Ck1	0.47-0.72	7.8	6.0	0.0	0.6	9.2	3.2	14.8	88.0	108.0	1.41	50	22	26	SCL	M
Ck2	0.72-1.00	7.8	5.0	0.0	0.6	10.3	3.8	16.4	90.0	135.0	1.40	46	26	28	SCL	M

^a = all values are reported on an oven dry basis

SOIL ELEVEN

Soil Series: Falun (FLU)
Classification: Orthic Dark Gray
Profile Location: NW5-55-9W4, central Alberta, near Myrnam
Date: June 11, 1993
Topography: hummocky
Slope Position: mid
Aspect: northwest
Drainage: well
Parent Material: dark grayish brown to olive brown till
Vegetation: crops-fields (managed) immature

Ap 0 - 20 cm Very dark grayish brown (10YR 3/2 m*), dark gray (10YR 4/1 d**) loam; weak coarse subangular blocky; non calcareous; moist friable; abrupt smooth boundary 18 to 20 cm:

AB 20 - 25 cm Dark yellowish brown (10YR 3/4 m), brown (10YR 5/3 d) clay loam; moderate coarse subangular blocky; non calcareous; moist friable; clear irregular boundary between 0 to 5 cm:

Btj1 25 - 49 cm Dark yellowish brown (10YR 3/6 m), brown (10YR 5/3 d) sandy clay loam; moderate coarse subangular blocky; many clay films, thin, on ped faces; non calcareous; moist friable; gradual wavy boundary between 20 to 34 cm:

Btj2 49 - 76 cm Dark yellowish brown (10YR 3/6 m), brown (10YR 5/3 d)
sandy clay loam; moderate coarse subangular blocky; many clay films,
very thin, on ped faces; non calcareous; moist friable; gradual wavy
boundary between 20 to 27 cm:

BC 76 - 100 cm Dark brown (10YR 3/3 m), brown (10YR 5/3 d) sandy clay
loam; weak coarse angular blocky; common clay films, very thin, on ped
faces; non calcareous; moist firm; gradual wavy boundary between 19 to
24 cm:

Ck 100 + cm Dark yellowish brown (10YR 4/4 m), brown (10YR 5/3 d)
clay loam; weak coarse angular blocky; few clay films, very thin, on ped
faces; moist firm; moderate calcareous.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Falun Profile.

Horizon Depth, m	pH (CaCl ₂)	O.C. g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group		
			Na	K	Ca	Mg					%S	%Si	%C	Class	Group	
Ap	0-0.20	6.3	12.0	0.0	0.7	6.4	1.6	13.4	65.5	1.0	1.29	48	28	24	L	M
AB	0.20-0.25	6.5	6.0	0.0	1.1	10.0	3.2	16.5	86.7	0.0	1.65	39	25	36	CL	M
Btj1	0.25-0.49	6.5	6.0	0.0	1.0	9.1	3.4	18.1	74.8	0.0	1.71	48	17	35	SCL	M
Btj2	0.49-0.76	6.5	4.0	0.1	0.9	9.1	3.8	17.9	77.4	1.0	1.77	51	20	29	SCL	M
BC	0.76-1.00	7.5	6.0	0.1	0.7	9.6	3.8	19.1	73.7	9.0	1.61	46	20	34	SCL	M
Ck	1.00+	7.7	4.0	0.1	0.9	9.5	3.2	18.6	73.2	101.0	1.23	40	27	33	CL	M

^a = all values are reported on an oven dry basis

SOIL TWELVE

Soil Series: Nayler (NYO)

Classification: Dark Gray Luvisol

Profile Location: W30-5-9W1, south central Manitoba, near Somerset

Date: October 1, 1992

Topography: hummocky

Slope Position: upper

Aspect: southeast

Drainage: well

Parent Material: shale till

Vegetation: crops-fields (managed) cropped

Ap 0 - 20 cm Very dark gray (10YR 3/1 m*), dark gray (10YR 4/1 d**) clay loam; weak very to fine granular; non calcareous; clear smooth boundary:

Ae 20 - 30 cm Dark grayish brown (2.5Y 4/2 m), light brownish gray (2.5Y 6/2 d) clay loam; very weak very fine platy; non calcareous; abrupt smooth boundary:

Bt 30 - 50 cm Olive brown (2.5Y 4/4 m), grayish brown (2.5Y 5/3 d) clay loam; moderate to strong medium subangular blocky; many clay films, thin, on voids and channels; non calcareous; gradual smooth boundary:

- BC** 50 - 70 cm Olive brown (2.5Y 4.5/4 m), light brownish gray (2.5Y 6/3
d) loam; weak to moderate fine to medium subangular blocky; non
calcareous; clear smooth boundary; horizontal shale band, 2% by volume:
- C** 70 - 100 cm Olive brown (2.5Y 6/4 m), light brownish gray (2.5Y 6/2
d) clay loam; weak fine subangular blocky; non calcareous; shale
fragments, 6% by volume.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Nayler Profile.

Horizon Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ g kg ⁻¹	B. D. Mg m ⁻³	Particle Size			Textural Class Group		
			Na	K	Ca	Mg					%S	%Si	%C	Class	Group	
Ap	0-0.20	5.8	58.0	0.4	1.1	24.6	5.3	ND	ND	0.0	0.93	30	38	32	CL	M
Ae	0.20-0.30	5.0	39.0	0.7	0.8	13.7	6.1	ND	ND	0.0	1.11	31	39	30	CL	M
Bt	0.30-0.50	4.7	32.0	0.7	0.8	14.1	7.4	ND	ND	2.0	1.14	30	39	31	CL	M
BC	0.50-0.70	4.6	29.0	0.9	0.8	14.2	7.5	ND	ND	0.0	0.96	33	40	27	L	M
C	0.70-1.00	4.6	27.0	0.8	0.5	14.0	7.2	ND	ND	1.0	0.90	29	40	31	CL	M

^a = all values are reported on an oven dry basis

SOIL THIRTEEN

Soil Series: Pembina, sandy-skeletal substrate variant (PBI(2))
Classification: Dark Gray Luvisol
Profile Location: SW32-5-8W1, south central Manitoba, near Altamont
Date: October 8, 1992
Topography: hummocky
Slope Position: upper
Aspect: southeast
Drainage: well
Parent Material: mixed till
Vegetation: crops-fields (managed) cropped

- Ap** 0 - 25 cm Very dark brown (10YR 2/2 m*), dark grayish brown (10YR 4/2.5 d**) loam; weak fine granular; weakly calcareous; plentiful roots, fine, vertical, impeded and exped distribution; abrupt wavy boundary between 24 to 28 cm:
- Ae** 25 - 30 cm Pale brown (10YR 6/3 m), yellowish brown (10YR 5.5/4 d) silty loam; fine platy; weakly calcareous; few roots, fine, vertical, impeded and exped distribution; gradual wavy boundary:
- Bt1** 30 - 37 cm Dark brown (10YR 3/3 m), brown (10YR 5/3 d) loam; moderate medium subangular blocky; few clay films, thin, on some voids; non calcareous; few roots, fine, vertical, impeded and exped distribution;

abrupt smooth boundary between 6 to 10 cm:

Bt2 37 - 67 cm Dark yellowish brown (10YR 4/6 m), dark yellowish brown (10YR 4/4 d) sandy clay loam; moderate to strong medium to coarse subangular blocky; many clay films, moderately thick, on ped faces; non calcareous; few roots, fine, vertical, impeded and exped distribution; abrupt smooth boundary:

IIck 67 - 95 cm Dark yellowish brown (10YR 4/4 m), dark brown (10YR 4/3 d) loamy sand; moderate medium to coarse angular blocky; common clay films, thin, on voids and channels; moderate calcareous; gravelly 10% by volume; very few roots, very fine, vertical, impeded and exped distribution; diffuse smooth boundary:

IIck2 95 - 130 cm Yellowish brown (10YR 5/4 m), yellowish brown (10YR 5/4 d) sand; fine granular; strong calcareous.

*m - moist color

**d - dry color

Physical and chemical properties^a for the Pembina (2) Profile.

Horizon	Depth, m	pH	O.C. (CaCl ₂) g kg ⁻¹	Exchangeable Cations				CEC	%BS	CaCO ₃ B. D.		Particle Size			Textural Class Group	
				Na	K	Ca	Mg			g kg ⁻¹	Mg m ⁻³	%S	%Si	%C		
Ap	0-0.25	6.2	47.0	0.5	0.8	17.3	3.2	ND	ND	20.0	1.36	45	35	21	L	M
Ae	0.25-0.30	6.4	45.0	0.5	0.5	13.1	2.7	ND	ND	10.0	1.45	32	54	14	SiL	M
Bt1	0.30-0.37	6.5	31.0	0.6	0.6	13.1	3.7	ND	ND	1.0	1.43	38	36	26	L	M
Bt2	0.37-0.67	6.6	28.0	0.5	0.7	12.3	5.3	ND	ND	1.0	1.48	36	14	26	SCL	M
IIck	0.67-0.95	6.6	15.0	0.6	0.7	11.8	5.0	ND	ND	98.0	1.47	73	13	4	LS	C
IIIck2	0.95-1.30	6.8	15.0	0.5	0.3	6.0	1.9	ND	ND	204.0	1.63	86	14	0	C	C

ND = not determined, ^a = all values are reported on an oven dry basis

II. Profile Distribution of Other Heavy Metals^a in the Pedons from the Prairie Ecozone.

Soil Series	Horizon	Depth m	Cu ±sd	Ni ±sd	Pb ±sd
			mg kg ⁻¹		
Ardill	Ap	0 - 0.10	5.5 ±6	15.4 ±4	12.1 ±0
	Bm	0.10 - 0.30	7.4 ±8	21.2 ±3	12.3 ±2
	Bmk	0.30 - 0.45	3.1 ±5	18.4 ±3	14.1 ±0
	Cca	0.45 - 0.60	13.4 ±18	24.8 ±3	13.1 ±7
	IIck	0.60 - 0.92	16.2 ±11	42.3 ±2	26.4 ±2
	IIIck	0.92 - 1.15	20.7 ±10	38.4 ±3	24.4 ±4
Maleb	Ap	0 - 0.20	13.6 ±10	20.2 ±8	11.5 ±8
	Ahe	0.20 - 0.30	8.3 ±4	14.9 ±1	12.5 ±5
	Bmk	0.30 - 0.46	12.8 ±7	27.2 ±1	18.7 ±0
	Cca	0.46 - 0.57	11.7 ±3	42.0 ±28	23.2 ±6
	Ck	0.57 - 1.00	11.9 ±3	27.7 ±1	18.6 ±1

sd = standard deviation, ^a all values reported on an oven dry basis

II. (continued)

Soil Series	Horizon	Depth m	Cu ± sd	Ni ± sd mg kg ⁻¹	Pb ± sd
Chin	Ap	0 - 0.15	15.7 ± 2	16.6 ± 0	17.7 ± 14
	AB	0.15 - 0.24	11.9 ± 3	18.4 ± 1	10.6 ± 10
	Btj	0.24 - 0.42	15.2 ± 7	18.9 ± 3	11.5 ± 11
	BC	0.42 - 0.57	11.5 ± 5	22.1 ± 2	23.0 ± 13
	Ck1	0.57 - 0.70	35.4 ± 35	28.8 ± 2	20.0 ± 10
	IIck	0.70 - 1.00	18.0 ± 5	31.1 ± 4	24.9 ± 13
Readymade	Ap	0 - 0.10	22.2 ± 9	17.4 ± 2	9.4 ± 5
	Bm	0.10 - 0.30	23.2 ± 9	27.6 ± 2	12.9 ± 6
	Ck1	0.30 - 0.70	18.3 ± 2	24.6 ± 8	13.8 ± 8
	Ck2	0.70 - 1.00	19.4 ± 8	28.6 ± 2	18.3 ± 5

sd = standard deviation

II. (continued)

Soil Series	Horizon	Depth m	Cu ±sd	Ni ±sd	Pb ±sd
			mg kg ⁻¹		
Weyburn	Ap	0 - 0.13	9.9 ±6	17.0 ±4	17.6 ±5
	Bm	0.13 - 0.26	18.0 ±15	20.6 ±6	19.2 ±4
	Cca	0.26 - 0.56	22.1 ±7	25.6 ±5	25.8 ±7
	Ck1	0.56 - 0.66	8.9 ±6	21.1 ±5	22.2 ±7
	Ck2	0.66 - 1.10	13.9 ±4	20.2 ±5	23.0 ±7
Niverville	Apk	0 - 0.15	31.5 ±15	75.4 ±57	ND
	AC	0.15 - 0.32	21.8 ±5	36.7 ±2	ND
	Cca	0.32 - 0.80	26.3 ±11	41.4 ±10	ND
	IIck	0.80 - 1.00	38.7 ±3	57.4 ±4	ND

ND = not determined, sd = standard deviation

II. (continued)

Soil Series	Horizon	Depth m	Cu \pm sd —————	Ni \pm sd mg kg ⁻¹	Pb \pm sd —————
Newstead	Ap	0 - 0.20	15.2 \pm 4	20.0 \pm 0	ND
	Bm	0.20 - 0.40	16.7 \pm 3	31.8 \pm 2	ND
	IIck1	0.40 - 0.65	15.6 \pm 6	31.8 \pm 2	ND
	IIck2	0.65 - 0.95	16.4 \pm 2	35.3 \pm 2	ND
Mayfair	Ap	0 - 0.10	36.5 \pm 8	24.3 \pm 6	6.9 \pm 10
	Btj	0.10 - 0.28	21.2 \pm 5	31.0 \pm 4	9.8 \pm 7
	Bm	0.28 - 0.37	20.7 \pm 14	35.3 \pm 6	14.3 \pm 2
	Ck1	0.37 - 0.60	17.3 \pm 11	36.3 \pm 15	19.2 \pm 1
	Ck2	0.60 - 0.88	15.2 \pm 11	27.2 \pm 2	20.4 \pm 1
	Ck3	0.88 - 1.12	27.8 \pm 34	25.2 \pm 3	19.2 \pm 4

ND = not determined, sd = standard deviation

II. (continued)

Soil Series	Horizon	Depth m	Cu ±sd —————	Ni ±sd mg kg ⁻¹	Pb ±sd —————
Beaverhills	Ap	0 - 0.14	14.8 ±6	16.9 ±2	12.5 ±10
	AB	0.14 - 0.21	16.7 ±5	19.0 ±2	10.7 ±10
	Bm	0.21 - 0.40	9.0 ±7	21.1 ±3	9.6 ±6
	Bt	0.40 - 0.62	25.8 ±9	34.6 ±3	10.1 ±9
	BC	0.62 - 0.70	24.7 ±10	38.1 ±7	15.3 ±5
	Ck	0.70 - 1.10	36.8 ±26	36.3 ±6	11.4 ±10
Whitewood	Ap	0 - 0.10	15.4 ±10	18.3 ±6	8.0 ±7
	Bt1	0.10 - 0.27	27.1 ±13	36.7 ±4	9.1 ±13
	Bt2	0.27 - 0.47	24.1 ±7	33.5 ±8	9.4 ±9
	Ck1	0.47 - 0.72	24.5 ±8	30.3 ±5	10.5 ±10
	Ck2	0.72 - 1.00	27.7 ±15	31.3 ±6	13.9 ±2

sd = standard deviation

II. (continued)

Soil Series	Horizon	Depth m	Cu ±sd	Ni ±sd mg kg ⁻¹	Pb ±sd
Falun	Ap	0 - 0.20	9.2 ±9	17.7 ±4	11.8 ±2
	AB	0.20 - 0.25	15.8 ±8	22.1 ±2	10.0 ±8
	Btj1	0.25 - 0.49	23.8 ±13	20.3 ±4	15.3 ±13
	Btj2	0.49 - 0.76	20.2 ±15	23.7 ±4	5.6 ±6
	BC	0.76 - 1.00	21.3 ±12	28.2 ±2	8.7 ±8
	Ck	1.00+	15.9 ±6	26.4 ±1	12.7 ±3
Nayler	Ap	0 - 0.20	24.1 ±15	41.8 ±14	ND
	Ae	0.20 - 0.30	15.4 ±4	31.8 ±4	ND
	Bt	0.30 - 0.50	11.2 ±2	33.4 ±7	ND
	BC	0.50 - 0.70	14.0 ±2	30.1 ±1	ND
	C	0.70 - 1.00	13.3 ±4	32.6 ±2	ND

ND = not determined, sd = standard deviation

II. (continued).

Soil Series	Horizon	Depth m	Cu ± sd —————	Ni ± sd mg kg ⁻¹	Pb ± sd —————
Pembina (2)	Ap	0 - 0.25	15.8 ± 1	26.2 ± 0	ND
	Ae	0.25 - 0.30	11.2 ± 2	21.9 ± 0	ND
	Bt1	0.30 - 0.37	10.6 ± 4	26.1 ± 3	ND
	Bt2	0.37 - 0.67	11.5 ± 3	24.6 ± 5	ND
	IIck	0.67 - 0.95	16.8 ± 3	43.5 ± 4	ND
	IIck2	0.95 - 1.30	9.2 ± 2	25.3 ± 5	ND

ND = not determined, sd = standard deviation

III. Distribution of Other Heavy Metals^a in the Sola.

Site Number	Soil Series	Slope Position	Horizon	Depth, m	mg kg ⁻¹		
					Cu±sd	Ni±sd	Pb±sd
1	Neuhorst	crest	Ap	0 - 0.15	25.1±5.7	26.8±0.3	19.1±2.2
			AC	0.15 - 0.50	16.7±1.2	25.9±0.3	12.2±0.9
	Neuhorst	mid	Ap	0 - 0.18	23.2±3.2	26.5±0.7	16.9±2.0
			AC	0.18 - 0.51	24.4±1.4	37.8±8.2	15.5±0.2
	Osborne	toe	Ap	0 - 0.14	27.2±0.4	28.1±0.8	14.9±0.4
			Ck	0.14 - 0.50	30.6±0.9	28.8±0.2	14.0±0.4
2	Plum Coulee	crest	Ap	0 - 0.15	22.2±4.1	34.8±0.3	17.6±0.9
			AC	0.15 - 0.50	24.4±5.7	41.6±1.1	16.9±0.5
	Plum Coulee	mid	Ap	0 - 0.18	23.5±1.1	29.7±0.6	15.9±0.3
			Ah	0.18 - 0.36	25.7±2.1	37.9±2.2	16.8±0.5
	Plum Coulee	toe	Ap	0 - 0.13	22.7±2.9	28.2±0.3	15.2±0.1
			AC	0.13 - 0.20	25.8±1.4	36.1±0.3	15.9±2.7
3	Deadhorse	crest	Apk	0 - 0.12	22.4±0.8	24.3±0.4	13.4±1.6
			Ck	0.12 - 0.50	22.5±2.7	25.7±3.8	12.5±4.7
	Neuhorst	mid	Ap	0 - 0.11	25.0±1.3	25.1±0.3	13.1±1.0
			AC	0.11 - 0.24	25.2±1.0	26.5±0.6	11.2±0.5
	Blumenfeld	toe	Ap	0 - 0.15	27.2±6.7	27.5±1.7	14.4±0.8
			AC	0.15 - 0.21	19.7±1.7	31.5±0.3	12.8±0.3

sd = standard deviation, ^a = all values are reported on an oven dry basis

III. (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	mg kg ⁻¹		
					Cu±sd	Ni±sd	Pb±sd
4	Graysville	crest	Apk	0 - 0.12	9.2±1.9	11.7±0.6	8.1±0.8
			Bmk	0.12 - 0.39	9.5±2.0	9.8±0.2	6.8±0.8
	Graysville	mid	Apk	0 - 0.12	10.1±0.9	10.4±0.6	7.6±0.9
			Bmk	0.12 - 0.26	11.6±2.4	10.4±0.5	6.3±0.7
	Edkins	toe	Apk	0 - 0.21	9.6±0.6	20.4±0.7	8.0±0.3
			Bmk	0.21 - 0.34	9.8±0.9	22.8±0.9	6.9±1.6
5	Winkler clay loam	crest	Ap	0 - 0.16	19.5±2.1	27.7±0.5	11.2±0.5
			Bm	0.16 - 0.34	20.7±4.3	32.3±4.4	10.0±0.6
	Eigenhof	mid	Ap	0 - 0.15	23.0±1.8	29.4±0.2	11.2±0.8
			Ap	0.15 - 0.30	20.3±1.5	27.5±1.5	9.0±0.2
	Eigenhof	toe	Ap	0 - 0.18	11.9±0.3	22.8±0.4	9.8±0.3
			Bmk	0.18 - 0.42	10.5±0.3	23.0±0.3	8.4±0.3
6	Gnadenthal	crest	Apk	0 - 0.17	17.0±0.4	29.2±1.3	13.3±0.5
			AC	0.17 - 0.50	11.6±0.4	26.0±0.1	7.4±0.1
	Gnadenthal	mid	Apk	0 - 0.17	12.4±0.7	23.7±0.7	9.4±0.5
			AC	0.17 - 0.29	10.1±0.5	22.6±0.9	6.4±0.2
	Gnadenthal	toe	Apk	0 - 0.18	11.0±0.9	21.3±0.8	7.3±0.8
			AC	0.18 - 0.46	8.6±0.3	23.9±0.7	3.3±0.4

sd = standard deviation

III. (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cu ± sd	Ni ± sd	Pb ± sd
mg kg ⁻¹							
7	Hochfeld crest		Ap	0 - 0.41	5.0 ± 0.9	16.8 ± 0.8	4.0 ± 0.2
			AB	0.41 - 0.48	5.8 ± 1.1	52.8 ± 59.0	4.1 ± 1.0
	Reinland mid		Bm	0.48 - 0.58	7.4 ± 1.6	19.3 ± 1.0	4.5 ± 0.6
			Apk	0 - 0.18	6.0 ± 1.7	20.2 ± 0.7	5.1 ± 0.4
	Reinland toe		AC	0.18 - 0.26	4.0 ± 0.6	16.3 ± 0.4	3.7 ± 0.5
			Apk	0 - 0.20	4.2 ± 0.9	17.9 ± 1.8	4.6 ± 0.5
			AC	0.20 - 0.46	5.0 ± 0.5	20.8 ± 0.8	3.7 ± 0.7
8	Hochfeld crest		Ap	0 - 0.64	4.7 ± 1.1	13.4 ± 0.1	4.9 ± 0.5
			AB	0.64 - 0.81	4.2 ± 0.5	16.1 ± 0.3	4.8 ± 0.5
	Reinland mid		Bm	0.81 - 1.00	2.5 ± 1.9	16.6 ± 0.1	4.9 ± 0.7
			Apk	0 - 0.25	8.7 ± 1.4	14.2 ± 0.1	7.7 ± 2.1
	Reinland toe		AC	0.25 - 0.62	6.2 ± 0.7	18.5 ± 1.6	6.0 ± 1.1
			Apk	0 - 0.23	7.1 ± 0.8	18.9 ± 0.5	6.6 ± 0.3
			AC	0.23 - 0.61	8.2 ± 1.3	44.7 ± 40.8	5.2 ± 0.9

sd = standard deviation

III. (continued).

Site Number	Soil Series	Slope Position	Horizon	Depth, m	Cu±sd	Ni±sd	Pb±sd
					mg kg ⁻¹		
9	Jasset	crest	Apk	0 - 0.24	12.0±0.4	17.7±0.5	10.0±0.4
			Ahk	0.24 - 0.39	11.0±0.9	17.9±2.2	5.9±1.5
	Blumenfeld	mid	Apk	0 - 0.15	10.0±0.1	17.7±0.7	8.8±0.4
			Bntj	0.15 - 0.26	9.9±1.1	19.0±1.2	7.0±0.5
	Blumenfeld	toe	Apk	0 - 0.13	19.4±0.4	22.8±0.7	13.2±0.3
			Bntj	0.13 - 0.29	17.4±1.2	24.0±1.4	11.0±0.6
10	Blumengart	crest	Apk	0 - 0.10	28.0±1.2	40.3±1.9	17.1±0.6
			Ahk	0.10 - 0.20	30.6±0.7	61.1±24.5	17.1±0.4
	Hochfeld	mid	Ap	0 - 0.12	11.9±3.8	19.1±1.3	8.1±0.2
			Bm	0.12 - 0.26	11.6±0.4	21.4±2.1	7.5±0.2
	Jasset	toe	Ap	0 - 0.12	21.6±0.2	25.9±0.5	15.8±0.3
			Bm	0.12 - 0.42	22.0±0.7	30.7±0.5	14.1±0.5
11	Bishop	middle	Apk	0 - 0.06	47.4±0.3	65.2±0.5	16.8±0.9
			Ahk	0.06 - 0.21	53.3±0.9	63.4±1.4	15.5±0.2
	Bishop	lower	Apk	0 - 0.10	52.7±1.6	63.7±0.7	16.2±0.2
			AC	0.10 - 0.26	62.9±1.8	85.2±14.4	17.6±1.1
	Bishop	toe	Ap	0 - 0.17	46.3±0.2	62.3±3.5	15.3±0.4
			Ck	0.17 - 0.50	46.6±0.3	77.6±4.5	13.7±0.2

sd = standard deviation

IV. Mean Values of Other Heavy Metals^a for the Surface and Sub-Surface Soil Based on Toposequence.

slope position	Cu±sd	Ni±sd	Pb±sd
	————— mg kg ⁻¹ —————		
	Surface Soil		
crest	19.0 ±12.8	28.3 ±16.0	12.2 ±5.4
mid	18.1 ±13.8	25.4 ±14.8	10.7 ±4.2
toe	18.1 ±12.4	26.7 ±13.1	11.1 ±4.2
	Sub-Surface Soil		
crest	18.8 ±14.7	34.7 ±19.2	10.1 ±5.1
mid	18.7 ±17.2	29.7 ±21.4	9.6 ±5.1
toe	18.4 ±13.0	33.2 ±17.2	9.3 ±5.3

sd = standard deviation, N = 10,

^a = all values are reported on an oven dry basis

V. Mean Values of Other Heavy Metals^a for the Surface Soil Textural Classes.

Surface Soil Textural Class	n	Total		
		Cu ±sd	Ni ±sd mg kg ⁻¹	Pb ±sd
fine sand	2	8.3 ±5	16.3 ±4	6.5 ±2
very fine sand	2	5.5 ±1	18.5 ±2	4.6 ±1
loamy fine sand	2	6.4 ±3	16.0 ±3	6.2 ±2
fine sandy loam	2	9.1 ±3	19.1 ±3	7.0 ±0
very fine sandy loam	3	10.6 ±1	16.1 ±5	8.5 ±1
sandy clay loam	8	15.9 ±6	22.7 ±6	10.9 ±3
clay loam	3	24.6 ±3	31.7 ±8	14.4 ±1
sandy clay	1	17.0	29.2	13.3
clay	5	30.1 ±12	36.6 ±15	16.7 ±2
heavy clay	2	46.9 ±1	63.7 ±2	16.0 ±1

n = number of samples, sd = standard deviation

^a = all values are reported on an oven dry basis

VI. Mean Values of Other Heavy Metals^a for the Sub-Surface Soil Textural Classes.

Sub-Surface Textural Class	n	Total		
		Cu \pm sd	Ni \pm sd	Pb \pm sd
		mg kg ⁻¹		
fine sand	1	11.6	21.4	7.5
very fine sand	3	4.7 \pm 1	28.4 \pm 21	4.2 \pm 1
loamy very fine sand	1	6.2	18.5	6.0
very fine sandy loam	8	10.0 \pm 4	21.9 \pm 11	6.3 \pm 2
sandy clay loam	7	14.6 \pm 5	24.8 \pm 4	9.0 \pm 3
clay loam	1	24.4	37.8	15.5
sandy clay	1	20.7	32.3	10.0
clay	4	32.2 \pm 9.9	53.2 \pm 20	15.9 \pm 2
heavy clay	4	42.8 \pm 18	54.7 \pm 25	16.0 \pm 2

n = number of samples, sd = standard deviation

^a = all values are reported on an oven dry basis

VII. Mean Values of Other Heavy Metals^a for the Surface and Sub-Surface Soil Textural Groups.

Textural Group	n	Cu ±sd	Total	
			Ni ±sd	Pb ±sd
		mg kg ⁻¹		
Surface Soil				
sandy	4	7.4 ±4	16.2 ±3	6.3 ±2
coarse loamy	7	8.7 ±3	17.7 ±4	7.0 ±2
fine loamy	11	18.3 ±6	25.2 ±7	12.4 ±3
clayey	8	32.7 ±14	42.5 ±18	16.1 ±2
Sub-Surface Soil				
sandy	1	11.6	21.4	7.5
coarse loamy	12	5.1 ±1	25.9 ±18	4.7 ±1
fine loamy	8	15.8 ±6	26.4 ±6	9.9 ±4
clayey	9	35.6 ±15	51.6 ±21	15.3 ±2

n = number of samples, sd = standard deviation

^a = all values are reported on an oven dry basis