

IMPACT OF LONG-TERM CULTIVATION ON THE STATUS OF CADMIUM IN CHERNOZEMIC SOILS

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By

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Dedicated to Yvonne, Dana, Danielle, and Daylon

ABSTRACT

Cadmium (Cd) from the soil can accumulate in our bodies via the consumption of our crops and cause serious health problems. While it has been documented that long-term cultivation affects physical and chemical properties of soil, little is known about its effect on the phytoavailability, solid-phase speciation, and profile distribution of soil Cd.

The objectives for this study were to determine the effect of long-term cultivation on: 1) a cadmium availability index (CAI) that reflects phytoavailable Cd for durum wheat, and related soil properties, 2) the solid-phase species of soil Cd and relationships between the CAI and the solid-phase species of soil Cd and related solid-phase soil component properties, and 3) the profile distribution of total soil Cd in the past, and the profile distribution of total soil Cd over the next 100 years.

One Orthic Chernozemic soil profile was investigated from a virgin and an adjacent long-term cultivated field at eight sites in the Brown, Dark Brown, and Black soil zones of Saskatchewan, Canada. Long-term cultivation significantly decreased the CAI. A decrease in total Cd, total Zn, and CEC, and an increase in aromaticity of the soil organic matter and soil pH all contributed to the decrease in the CAI. Both the virgin and cultivated soils had the same solid-phase Cd species with the same order of relative abundance: metal-organic complex-bound > easily reducible metal oxide-bound > H₂O₂ extractable organic-bound >

crystalline metal oxide-bound > exchangeable. However, metal-organic complex-bound Cd and H₂O₂ extractable organic-bound Cd decreased significantly with long-term cultivation. In the virgin soils two solid-phase Cd species correlated significantly with the CAI: exchangeable Cd ($r = 0.93$) and easily reducible metal oxide-bound Cd ($r = -0.88$). In the cultivated soils three solid-phase Cd species correlated significantly with the CAI: exchangeable Cd ($r = 0.95$), metal-organic complex-bound Cd ($r = 0.71$), and crystalline metal oxide-bound Cd ($r = 0.86$). For both the virgin and cultivated soils the concentration of A horizon Cd > C horizon Cd > B horizon Cd. In the past, A horizon Cd concentration decreased significantly with long-term cultivation. However, it is estimated that in 100 years, with the use of phosphate fertilizer made from Idaho ore, the total A horizon Cd content in these soils could be 3.5 times higher and reach a concentration of 1.18 mg Cd kg⁻¹ soil which is in the critical region where the phytoavailability of soil Cd could increase dramatically.

The present study has advanced the frontiers of knowledge on the effect of long-term cultivation on the Cd content and distribution in the soil profile, its phytoavailability index, solid-phase species, and the soil properties related to its phytoavailability. Extending research such as this to other major agricultural soil types and farming practices will assist in the development of innovative management strategies to curtail Cd contamination of the terrestrial food chain.

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1. INTRODUCTION

Cadmium is a trace heavy metal with no known biological function. In relatively low concentrations it appears to be harmless to soil microbes and plants. However, in high concentrations it is toxic to both (Woolhouse, 1983). For humans, relatively low concentrations of Cd in our food can accumulate in our bodies and cause kidney disease and eventual failure, and contribute to the bone diseases of osteoporosis and osteomalacia (Environmental Directorate, 1994). The main pathway for Cd to the human body is through our food (Jackson and Alloway, 1992), and the main pathway for Cd to our food is by uptake of Cd from the soil by our crops (Adriano, 1986).

Cadmium is found in a large variety of foods all over the world, and some countries around the world have adopted limits to the Cd content in their food (Jackson and Alloway, 1992). The United Nations is currently considering a maximum tolerance level of 0.1 mg kg^{-1} for Cd in cereal grains (Canadian Cadmium Workshop, 1997). If this is adopted it may have a detrimental effect on our durum wheat exports, since studies by the Canadian Grain Commission revealed that the average Cd content of recent export shipments of durum wheat was in excess of the proposed 0.1 mg kg^{-1} level (Canadian Cadmium Workshop, 1997). Considering that shipments of durum wheat from western Canada added up to over \$1.1 billion in the 1996/97 crop year (personal communication from G. C. Worden, Canadian

Wheat Board, 1999), keeping the current and future Cd content of our crops below the proposed 0.1 mg kg^{-1} level will not only benefit us physically but also economically.

There are three general sources of soil Cd: weathering of the parent material of the soil, atmospheric deposition of air-borne Cd onto soils, and soil amendments. Of the three, it is only the Cd input to the soil by soil amendments that can be easily controlled. Of the Cd containing soil amendments commonly used, phosphate fertilizers have the potential to put more Cd into agricultural soils than all of the other sources combined because: 1) their Cd concentration can be relatively high, ranging from $0.2\text{--}345 \text{ mg kg}^{-1}$ (Alloway and Steinnes, 1999), 2) they are commonly used on agricultural soil around the world, and 3) the amount of phosphate fertilizer applied annually to agricultural soils around the world should increase in the future because world demand for phosphate fertilizer is expected to increase from 37 499 000 tonnes in 1990 to 60 852 000 tonnes in 2025 (Banaante and Hellums, 1998).

Several soil factors have been identified as having an effect on or having the potential to affect the phytoavailability of soil Cd: 1) ionic strength of the soil solution (Garcia-Miragaya and Page, 1976; Spark et al., 1995; Temminghoff et al., 1995), 2) soil pH (MacLean, 1976; Jackson and Alloway, 1991; Temminghoff et al., 1995; Chlopecka et al., 1996; Yuan and Lavkulich, 1997), 3) the nature and concentration of the ligands in the soil solution (Lamy et al., 1993; McBride, 1994; Sakurai and Huang, 1995a,b; McLaughlin et al., 1996; Krishnamurti et al., 1997a), 4) CEC (Haghiri, 1974), 5) soil texture (Eriksson, 1989), 6) total soil Zn (Chaney et al., 1999), 7) total soil Cd (Merry et al., 1981; Chumbley and Unwin, 1982; Sillanpaa and Jansson, 1992), 8) the type and quantity of soil adsorption

sites (Maclean, 1976; Eriksson, 1988; Krishnamurti and Huang, 2001), and 9) the type and concentration of cations that compete with Cd for adsorption sites (Christensen, 1987; Ross, 1994).

Researchers have also attempted to link the phytoavailability of soil Cd with the chemical species of solid-phase Cd. Cadmium can form associations with many different solid-phase soil components resulting in many different chemical species of solid-phase Cd. The phytoavailability of the chemical species of solid-phase soil Cd is probably related to the strength with which Cd is bound to solid-phase soil components; stronger bonds between Cd and a solid-phase soil component will make it more difficult for Cd to be removed from the solid-phase and put into solution where it can be taken up by plants. Researchers have attempted to identify and quantify the different solid-phase species of soil Cd with sequential extractions schemes. The most recent and comprehensive scheme was developed by Krishnamurti et al.(1995a). The extraction scheme divides solid-phase soil Cd into the following eight different operationally defined species: exchangeable, carbonate-bound, metal-organic complex-bound, easily reducible metal oxide-bound, H₂O₂ extractable organic-bound, amorphous mineral colloid-bound, crystalline Fe oxide-bound, and residual. The researchers also demonstrated a positive relationship between the metal-organic complex-bound Cd and a cadmium availability index (CAI) which is highly correlated with the grain Cd concentration of durum wheat (Krishnamurti et al., 1995b).

Total soil Cd levels may increase with time, and this also may have an effect on the phytoavailability of soil Cd. Although it has been well documented that there is not any significant correlation between total soil Cd and the phytoavailability of soil Cd in

uncontaminated agricultural soils (Gavi et al., 1997), several studies have shown that a positive relationship exists between total soil Cd and plant uptake of Cd in soils that have unnaturally high levels of Cd (Merry et al., 1981; Chumbley and Unwin, 1982; Sillanpaa and Jansson, 1992). Unfortunately, unnaturally high levels of total soil Cd may eventually be reached in many agricultural soils because of the projected increase in phosphate fertilizer application (Banaante and Hellums, 1998) and because of the relatively high Cd concentrations in some phosphate fertilizers (Alloway and Steinnes, 1999). However, the addition of Cd to agricultural soils does not necessarily mean that the soil Cd concentration will increase to unnaturally high levels, and therefore increase the phytoavailability of soil Cd. There may be factors that have the potential to remove Cd from the soil, or to move it to a position in the soil profile where it will be relatively unavailable for plant uptake, at rates equal to the rates at which Cd is being added to agricultural soil.

To date, there has been limited published research which has investigated the effect of long-term cultivation on the profile distribution of total soil Cd, the solid-phase speciation of soil Cd, the phytoavailability of soil Cd, and most soil properties related to the phytoavailability and solid-phase speciation of soil Cd. Since cultivation does have a profound effect on the physical and chemical properties of soil (Blank and Fosberg, 1989), it is probable that long-term cultivation will also have a significant effect on soil Cd and all of the factors related to its phytoavailability. Research to find out how long-term cultivation has affected soil Cd and the factors related to its phytoavailability will advance the fundamental knowledge required to understand how the phytoavailability of soil Cd will change in the years to come. It is expected that this knowledge will enable us to understand

and possibly control soil Cd phytoavailability in the future.

Therefore, the objectives for this study were: 1) to determine the impact of long-term cultivation on a cadmium availability index and related soil properties, 2) to determine the effect of long-term cultivation on the solid-phase species of soil Cd and related soil properties and their relationships with the cadmium availability index, and 3) to determine how long-term cultivation in the past has affected the profile distribution of soil Cd in Orthic Chernozemic soils, and to provide a reasonable estimate of what the profile distribution of Cd would be for these soils in 100 years based on annual tilling, cropping and applications of low, medium, and high Cd content phosphate fertilizers.

2. LITERATURE REVIEW

2.1 Sources of Soil Cadmium

There are three general sources of soil Cd: weathering of the parent material of the soil, atmospheric deposition of air-borne Cd onto soils, and soil amendments. The soil's parent material is a natural source of soil Cd, while soil amendments containing Cd are anthropogenic in origin. Air-borne Cd can be from natural and anthropogenic sources.

2.1.1 Weathering of soil parent material

A major natural source of soil Cd comes from the weathering of the soil parent material. Cadmium concentrations in parent materials range from 0.005 mg kg⁻¹ in some schists to 240 mg kg⁻¹ in some marine black shales (Jackson and Alloway, 1992; Environmental Directorate, 1994). Although Cd is found in all three rock types, igneous, metamorphic, and sedimentary, it is the sedimentary rocks that generally contain the highest concentrations of Cd (Table 2.1).

2.1.2 Atmospheric deposition

Cadmium deposited from the atmosphere onto soil can come from a variety of natural and anthropogenic sources (Table 2.2). It is estimated that volcanism, the dominant

Table 2.1. Cadmium concentrations in some common rock types (Brewers et al., 1987).

Rock type	Cd (mg kg ⁻¹)	
	Range	Mean
Igneous:		
Granite	0.001-0.60	0.12
Granodiorite	0.016-0.10	0.07
Pitchstone	0.05-0.34	0.17
Basalt	0.006-0.60	0.22
Gabbro	0.08-0.20	0.11
Metamorphic:		
Eclogite	0.04-0.26	0.11
Garnet schist	-	1.00
Gneiss	0.12-0.16	0.14
Sedimentary:		
Bituminous shale	<0.3-11	0.80
Bentonite	<0.3-11	1.40
Marlstone	0.4-10	2.60
Limestone	-	0.35
Sandstone	-	0.01

natural source of atmospheric Cd, emits 520 Mg of Cd into the atmosphere annually. The dominant anthropogenic source of emission of Cd into the atmosphere is primary non-ferrous metal production which accounts for an estimated 4721 Mg of Cd emitted to the atmosphere

annually. The amount of Cd emitted to the atmosphere from all anthropogenic sources is estimated to be about one order of magnitude greater than that emitted from all natural sources.

Table 2.2. Estimated annual Cd emissions to the atmosphere (Cd, 1999).

Source	Annual emissions (Mg)
Natural:	
Volcanic eruptions	520
Vegetation	210
Windblown dusts	100
Forest fires	12
Seasalt sprays	1
Total natural emissions	843
Anthropogenic:	
Primary non-ferrous metal production	4721
Waste incineration	1350
Secondary non-ferrous metal production	595
Wood combustion	200
Phosphate fertilizers	118
Iron and steel production	72
Fossil fuel combustion	65
Industrial applications	53
Rubber tyre wear	10
Zinc mining	3
Total anthropogenic emissions	7187

2.1.3 Soil amendments

All soil amendments are anthropogenic in origin. The major agricultural soil amendment sources of Cd are farm yard manure, household and municipal solid waste compost, sewage sludge, and phosphorus fertilizer (Table 2.3). All of these soil amendments add Cd to agricultural soil but their impacts on the Cd levels in agricultural soils vary.

Table 2.3 Major agricultural soil amendment sources of Cd.

	Cd concentration (mg kg ⁻¹)	Reference
Farm yard manure	0.3-1.8	McGrath (1984); Kabata-Pendias and Pendias (1992)
Compost	0.26 - 11.7	Alloway and Steinnes (1999)
Sewage sludge	< 1 - 3650	Alloway (1990)
Phosphorus fertilizers	0.2 - 345	Alloway and Steinnes (1999)

Farm yard manure is commonly applied to many agricultural soils. The Cd in farm yard manure comes from the vegetation that is fed to the farm animals, and the Cd in the vegetation has been taken out of the soil by the plant. However, since most of the Cd ingested with the vegetation remains in the manure (Chaney et al., 1999) the concentration of Cd in manure is generally higher than the concentration of Cd in the vegetation consumed by the animals. Because the Cd in the farm yard manure comes indirectly from the soil in the first place, the overall net effect of manure application on total soil Cd is relatively

insignificant. However, localized increases in soil Cd concentration can occur with repeated applications of manure onto fields that were not the source of all of the Cd in the manure.

Household and municipal solid waste compost also contain Cd that had its origins in agricultural soil. Composts consist of food wastes that have been microbially degraded. The food wastes contain trace amounts of Cd, most of which originated from the soil (Adriano, 1986). The degradation process results in a compost with a much higher Cd concentration than the food wastes that went into it. Just like the farm yard manure, repeated applications of compost onto fields that were not the source of all of the Cd in the compost will result in localized increases in soil Cd concentration. However, the agricultural soils affected by compost application are in the minority since compost is applied mainly to soils around urban areas.

Sewage sludge is the solid residue formed during the treatment of sewage waste. The treatment process involves a digestion step so that the Cd in the sewage waste is concentrated. The Cd in sewage sludge comes from both industrial sewage and domestic sewage. The concentrations of heavy metals, including Cd, can be very high because of input from metal-using industries. In the past most of the sewage sludge was disposed of at sea or in landfills. However, since sewage sludges can be a useful source of nutrients such as P and N, and contain colloidal organic matter which can have a beneficial effect on soil structure, there has been a trend in recent years to apply sewage sludge to agricultural land (Alloway and Steinnes, 1999). Because of the relatively high concentrations of Cd in some sewage sludge (Table 2.3), regular applications of sewage sludge can result in large increases in the Cd concentrations of agricultural soils. However, the agricultural soils affected by

sewage sludge are in the minority since they are applied mainly to soils around urban areas (Brown and Jacobson, 1987).

While both compost and sewage sludge applications to agricultural soil are fairly localized, application of Cd contaminated phosphate fertilizer to the soil is not. Every year in major agricultural areas around the world farmers routinely apply Cd contaminated phosphate fertilizer (Table 2.3) to their soils. The Cd found in phosphate fertilizers has its origin in the rock phosphate from which the fertilizer is made. The Cd concentration in the rock phosphate ranges from 0.2 mg kg⁻¹ in the igneous rocks of the former USSR to 340 mg kg⁻¹ in the Western USA, and the mg of Cd per kg of P in these rocks ranges from 1 to at least 570 (McLaughlin et al., 1996) (Table 2.4). The mg of Cd per kg of P does not change when the rock is processed into superphosphate fertilizer, and although it does drop by 30 to 35 % when the ore is processed into higher analysis phosphate fertilizers (Potash & Phosphate Institute/Potash & Phosphate Institute of Canada, Foundation for Agronomic Research, 1998) there can still be as much as 532 mg Cd per kg of P.

2.2 Chemistry of Soil Cadmium

2.2.1 Properties of cadmium

Elemental Cd is a silvery white soft tarnishable metal. It has an atomic number of 48, atomic mass of 112.4, density of 8.6 g cm⁻³, a melting point of 320 ° C, and a boiling point of 765 ° C. It is relatively rare at 67th in order of elemental abundance (Alloway, 1995). There are eight stable isotopes of Cd found in nature: ¹⁰⁶Cd (1.22%), ¹⁰⁸Cd (0.88 %), ¹¹⁰Cd

Table 2.4. Cadmium contents in some phosphate rocks (McLaughlin et al., 1996).

Phosphate rock source	Cd (mg kg ⁻¹ rock)	Cd (mg kg ⁻¹ P)
USSR (Kola)	0.2	1
China (Yunan)	5	35
Mexico	8	57
Florida 72 %	9	63
Florida 68 %	16	115
Morocco (Boucraa)	38	240
North Carolina	47	311
Togo	51	320
Senegal	90	570
Western USA	60-340	NR ^a

^a Not reported.

(12.39 %), ¹¹¹Cd (12.75 %), ¹¹²Cd (24.07 %), ¹¹³Cd (12.26 %), ¹¹⁴Cd (28.86 %), and ¹¹⁶Cd (7.58 %). The abbreviated ground state electronic configuration of Cd is [Kr].4d¹⁰.5s². The pair of 5s electrons are quite distant from the nucleus and are therefore easily lost leaving a filled out d shell and a positive valence of two. Cadmium (II) is the most common valence of naturally occurring Cd and virtually the only valence of aqueous Cd (Baes and Mesmer, 1976). Because of the lack of multiple valences Cd only shows metallic properties. Cadmium has a preference for six-fold coordination (Cd, 1999) but complexes with 4 coordination are common (Helmke, 1999). Cadmium is classed as a soft Lewis acid, and therefore bonds preferentially with soft Lewis bases like chloride and sulphhydryl (McBride, 1994).

2.2.2 Soil solution cadmium

2.2.2.1 Total soil solution cadmium

The Cd concentration in soil solutions typically ranges from about 3 to 200 nM (Helmke, 1999). There are two general mechanisms that can control the amount of Cd in the soil solution: precipitation/dissolution and adsorption/desorption. Precipitation/dissolution can be a major influence on the concentration of Cd in the soil solution in four situations: 1) high concentrations of soil solution Cd, 2) acid and reducing soil conditions, which will result in the precipitation of Cd as CdS, 3) alkaline soil conditions with a $\text{pH} > 7.84$ and high concentrations of carbonates, which will result in the precipitation of Cd as CdCO_3 , and 4) in the diammonium phosphate fertilizer zone where the high concentrations of Cd and the high pH will result in the precipitation of Cd as $\text{Cd}_3(\text{PO}_4)_2$ (Levi-Minzi and Petruzzelli, 1984; Huang, 1987; Ross, 1994).

Since most agricultural soil solutions have a fairly low concentration of Cd, and the pH is usually in the mildly acidic to the mildly alkaline range, it is generally considered that precipitation/dissolution processes have only minor effects on the soil solution concentration of Cd (Holm et al., 1996). Therefore, adsorption/desorption processes appear to determine the amount of Cd in the soil solutions of most agricultural soils. However, research into the effect of precipitation and dissolution on the soil solution concentration of Cd uses bulk soil and assumes precipitation through homogeneous nucleation. In soil environments, heterogeneous nucleation is more likely than homogeneous nucleation because of the presence of mineral and organic surfaces that can catalyze nucleation (McBride, 2000). With

heterogeneous nucleation the energy barrier to nucleation is reduced or even removed especially if there are crystallographic similarities between the surface and the precipitate (McBride, 2000). For example, CaCO_3 seems to promote heterogeneous nucleation of CdCO_3 (McBride, 1989).

Conditions in the soil rhizosphere are much different than in the bulk soil. The concentration of Cd in the soil solution might be lower because of the uptake of Cd by plants and microbes, or it might be higher as a result of lower pH and the higher concentration of soluble complexing organic ligands. In these conditions it is not likely that the concentration of soil solution Cd is controlled by precipitation through homogeneous nucleation. The rhizosphere is a zone of intense microbial activity and precipitation of metals by heterogeneous nucleation onto microbial surfaces can result in the formation of distinct metallic minerals (Huang and Germida, 2001). Therefore, it is possible that precipitation may have more of an effect on the concentration of soil solution Cd than current research would indicate.

2.2.2.2 Chemical speciation of soil solution cadmium

Cadmium in the soil solution can be present in many different forms varying in size and charge. It is generally thought that the most common form of soil solution Cd is Cd^{2+} . Table 2.5 shows that this is not true for all soils.

The Cd^{2+} ion is found in a six coordinated complex with water molecules; $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ (Helmke, 1999). One or more of the water molecules can be replaced by one or more organic or inorganic ligands to form a different species of soil solution Cd. The hard,

Table 2.5. Total Cd concentrations and activities of Cd ²⁺ in soil solutions (Helmke, 1999).

Soil	Total Cd (nM)	Cd ²⁺ (nM)
Woburn Market Garden (sludge) nonrhizosphere ^a	60	54
Woburn Market Garden (sludge) rhizosphere ^a	19	15
Entisols ^b	32	14
Mollisols ^b	18	8
Inceptisols ^b	14	6
Mollisols ^c	8.5	2.9
Mollisols ^c	4.9	3.2
Mollisols (sludge) ^c	78	4.4
Mollisols (sludge) ^c	40	3.7
Alfisols ^d	2.52	0.8
Alfisols ^d	13	0.9
Oxisols ^d	18	7.4
Mollisols ^d	8.1	0.3
Ultisols ^c	213	18
Oxisols ^c	7	2.7
Oxisols ^c	4	3.6
Oxisols ^c	3	0.1
Entisols ^c	2.36	0.7
Mollisols ^f	1.7	0.49
Mollisols (sludge) ^f	9.84	1.91
Aridsols ^f	0.4	0.2
Aridsols (sludge) ^f	57	6.1

^a Holm et al. (1995); ^b Hirsch and Banin (1990); ^c Helmke et al. (1997); ^d Naidu (personal communication to Helmke, 1999); ^e Santos (personal communication to Helmke, 1999);

^f Salem and Helmke (1998).

soft Lewis acid and base concept is frequently used to determine what ligands Cd has a preference to form complexes with; soft Lewis acids tend to form complexes with soft Lewis bases and hard Lewis acids tend to form complexes with hard Lewis bases. Cadmium is a soft Lewis acid with a Misono softness parameter of 3.04 and therefore will form relatively stable soluble complexes with soft Lewis bases like sulphhydryls, thiols, and with borderline Lewis bases like aromatic amines, bromide, and chloride (McBride, 1994; Helmke, 1999).

Accordingly, Cd would not be expected to form relatively stable soluble complexes with hard Lewis bases like hydroxyl, sulphate, nitrate, orthophosphate, carbonate, or carboxyl. However, Cd does form complexes with relatively high stability constants with sulphate, a hard Lewis base, and some low-molecular-weight organic acids (LMWOAs) which only have the hard Lewis base carboxylic functional group (Table 2.6).

Analytical procedures have only been used to quantify the free hydrated Cd^{2+} ion in the soil solution. Many methods using species-specific instrumental techniques sometimes coupled with well-defined chemical separation procedures have been developed but do not have the sensitivity required to measure the levels of the free hydrated Cd^{2+} ion in uncontaminated soil solutions (Helmke, 1999). However, one method developed by Fitch and Helmke (1989) which uses a cation exchange membrane and the principles of Donnan equilibrium has been proven to measure accurately the levels of the free hydrated Cd^{2+} ion in uncontaminated soil solutions.

The measurement of other chemical species of soil solution Cd, other than the free hydrated Cd^{2+} ion, has not been accomplished. Instead, researchers have concentrated on computer models such as MINTEQA2 (Allison and Brown, 1995), GEOCHEM-PC (Parker

Table 2.6. Log stability constants (K) of selected Cd complexes common in soil solutions.

Ligand	Complex	Log K
Cl ⁻	CdCl ⁻	1.98 ^a
	CdCl ₂ ⁰	2.60 ^a
	CdCl ₃ ⁻	2.40 ^a
	CdCl ₄ ²⁻	2.50 ^a
Br ⁻	CdBr ⁻	2.15 ^a
I ⁻	CdI ⁻	2.28 ^a
SO ₄ ²⁻	CdSO ₄ ⁰	2.45 ^a
NO ₃ ⁻	CdNO ₃ ⁻	0.31 ^a
	Cd(NO ₃) ₂ ⁰	0.00 ^a
H ₂ PO ₄ ⁻	CdHPO ₄ ⁰	-4.00 ^a
HCO ₃ ⁻	CdHCO ₃ ⁻	-5.73 ^a
	CdCO ₃ ⁰	-14.06 ^a
OH ⁻	CdOH ⁻	-10.10 ^a
	Cd(OH) ₂ ⁰	-20.30 ^a
Citrate	Cd-Citrate	5.36 ^b
Acetate	Cd-Acetate	1.93 ^b
Oxalate	Cd-Oxalate	3.89 ^b
Succinate	Cd-Succinate	2.72 ^b
Formate	Cd-Formate	1.04 ^b

^a Lindsay (1979). ^b Martel and Smith (1974-1989).

et al., 1995), and SOILCHEM (Sposito and Coves, 1995) to estimate the different chemical species of Cd found in soil solutions. The models use stability constants for the different possible metal-ligand complexes, the concentrations of the elements and ligands in the soil

solution, and other data such as pH to estimate the concentrations of the different chemical species.

However, the results from these models can be suspect if the soil solutions contain soil humic substances, because of the wide range of stability constants (log K 2-8) reported for Cd and humic substance complexes (Helmke, 1999). Picking the correct stability constant for the soil solution may be a problem. Another problem is that these stability constants may not be representative of the actual stability constants found in soil solutions because they were determined using Cd concentrations several orders of magnitude greater than that found in uncontaminated soil solutions (Helmke, 1999). Because of these problems, there is generally not good agreement between the activity of the free hydrated Cd ²⁺ ion that is estimated with the computer model and that measured in soil solutions which contain humic substances (Helmke, 1999).

2.2.3 Solid-phase soil cadmium

Cadmium in the solid phase can be in the form of Cd minerals, associated with other minerals, or adsorbed to minerals and organic matter.

2.2.3.1 Cadmium in minerals

Cadmium ores are not common but Cd is commonly found substituting for zinc in the zinc ore sphalerite and for calcium in the phosphate ore apatite (Cd, 1999). However, three discrete Cd minerals can be found in soils depending on the soil conditions (Lindsay, 1979). Cadmium sulfide can form in strongly anaerobic soils with sulfide present, for

example rice paddy soils (Christensen and Huang, 1999). Cadmium carbonate can form in soils on calcareous knolls and other places with a $\text{pH} > 7.84$ and high concentrations of carbonates (Ross, 1994). Also, $\text{Cd}_3(\text{PO}_4)_2$ can form in the fertilizer zone of diammonium phosphate fertilizer because of the high pH and high concentration of phosphate ion (Levi-Minzi and Petruzzelli, 1984).

2.2.3.2 Physically adsorbed cadmium

Cadmium can be adsorbed physically with a range of binding strengths to various soil colloids. It can be weakly adsorbed physically through electrostatic attraction to layer silicate clays, smectites and vermiculite, and organic matter as the positively charged Cd^{2+} ion is attracted to the permanent negative charge of the layer silicate clay surface and the weak negative field of organic matter at near neutral pH (McBride, 1994). Slightly stronger adsorption of Cd can occur at pH-dependent adsorption sites at the edges of silica, allophane, and layer silicate clays (Figure 2.1), including kaolinite which possesses no permanent negative charge (McBride, 1994). The bonding of Cd here is fairly specific but largely electrostatic because the 1^- charge that Si^{4+} donates to the O^{2-} causes the electron density to move relatively close to the Si^{4+} increasing the distance between the electron density and the Cd^{2+} ion, and therefore decreasing the attraction. Only a very small percentage of soil Cd^{2+} is found adsorbed electrostatically because of competition from cations like Ca^{2+} and Mg^{2+} that have very high soil solution concentrations compared to Cd^{2+} , and because cations with a larger ionic radius than that of Cd^{2+} , like K^+ , Na^+ , and Ba^{2+} , will be preferentially adsorbed over Cd^{2+} (McBride, 1994).

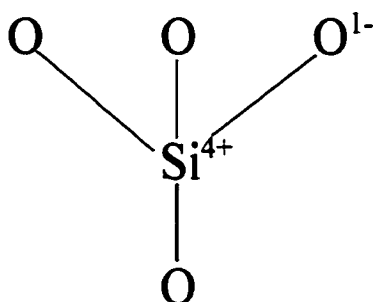


Figure 2.1 pH-dependent charge with a terminal O^{1-} on the edges of silica, allophane, and layer silicate clays (McBride, 1994).

2.2.3.3 Chemically adsorbed cadmium

Cadmium can also be adsorbed even more strongly by chemical adsorption onto allophane, metal oxides, and the edges of layer silicate clays. The Cd in this case displaces the H^+ and binds directly to the $O^{1.5-}$ (Figure 2.2).

The strength with which Cd is bound to metal oxides depends on the metal of the adsorbent. The higher the valence:coordination number ratio of the adsorbent metal the lower the strength of adsorption of trace metals (McBride, 2000). The valence:coordination number ratios indicate that Fe and Al oxides will bind Cd with approximately the same binding strength and will both bind Cd stronger than Mn oxides will (Table 2.7). Since Mn is octahedrally coordinated to six O atoms and has a valence of +4 (McKenzie, 1989) (Figure 2.3) it donates a +0.67 charge to each O atom while Fe and Al, because of their +3 valence, donate only a +0.5 charge to each O atom. This creates a greater pull on the electrons between the O and Mn which results in a larger distance between Cd and the

electrons in the Mn oxides. The larger distance combined with a larger neutralizing effect on the O 's negative charge by Mn results in a weaker bond with Cd.

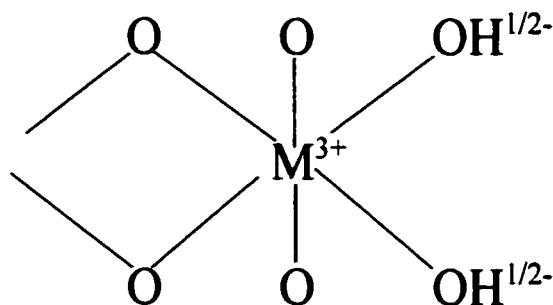


Figure 2.2 pH-dependent charge with a terminal OH ^{1/2-} on iron oxides, allophane, and the edges of Al hydroxide (Gibbsite) and layer silicate clays (McBride, 1994).

Table 2.7 Valence:coordination number ratios (V/C) of oxide surface OH groups.

Oxide	Valence	Coordination	Coordination number	V/C
> Si - OH	+4 ^a	tetrahedral ^a	4 ^a	1
> Mn - OH	+4 ^b	octahedral ^b	6 ^b	0.67
> Fe - OH	+3 ^a	octahedral ^a	6 ^a	0.5
> Al - OH	+3 ^a	octahedral ^a	6 ^a	0.5

^a McBride (1994); ^b McKenzie (1989).

Although Mn oxides should bind Cd and other trace metals less strongly than Fe and Al oxides, some studies demonstrate that Mn oxides are better at scavenging trace metals including Cd, and bind them strongly (McKenzie, 1989; Welch and Norvell, 1999). This

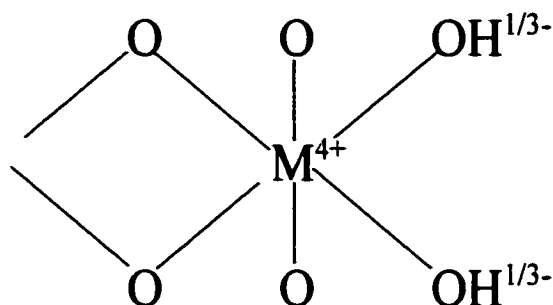


Figure 2.3 Deduced pH-dependent charge on Mn oxides as a result of octahedral coordination and a valence of +4.

should not be the case since, as discussed in the previous paragraph, the valence:coordination number ratio for Mn oxides indicates that they should bind Cd less strongly than Fe and Al oxides bind Cd. However, the structure of many Mn oxides may be the reason for their ability to scavenge and strongly bind trace metals including Cd. Some Mn oxides form tunnels out of single, double, or multiple chains of MnO_6 octahedra linked by the corners (Figure 2.4). These tunnels contain water molecules and an assortment of cations such as K^+ , Na^+ , and Pb^{2+} (McKenzie, 1989). It is possible that the cations which inhabit these tunnels may be bound by more than one coordination point and therefore, be bound more strongly than they would be if they were adsorbed to an outside surface point. Therefore, any Cd residing in these tunnels may be bound much more strongly than the valence:coordination number ratio of Mn oxides would indicate.

Another mineral that Cd can be chemically adsorbed to is CaCO_3 . The Cd^{2+} ion is less soluble than Ca^{2+} possibly because Cd^{2+} is a soft Lewis acid while Ca^{2+} is a hard Lewis

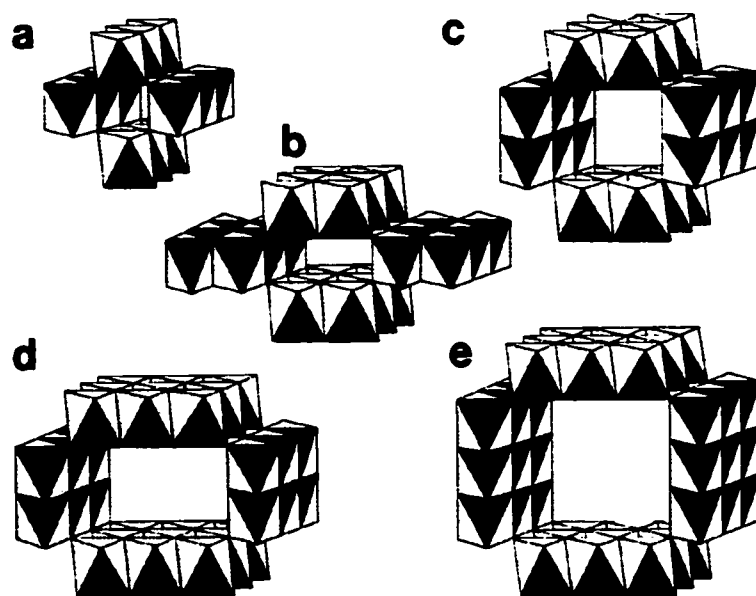


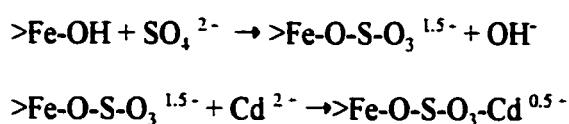
Figure 2.4 Manganese oxides' tunnel structures: a) pyrolusite, b) ramsdellite, c) hollandite, d) romanechite, e) todorokite (McKenzie, 1989).

acid and H_2O is a relatively hard Lewis base (Sullivan, 1977). Because Cd^{2+} is less soluble it will replace Ca^{2+} at the mineral surface. This reaction is considered adsorption and not precipitation because it will proceed to a degree determined by the surface area of the mineral and will occur even when the suspension is undersaturated with respect to solid CaCO_3 (McBride, 2000).

Soil organic matter can also strongly chemically adsorb Cd. However, the determined stability constants between Cd and soil organic matter may not reflect the actual strength of bonding between Cd and soil organic matter. Soil organic matter contains different functional groups with a range of affinity for Cd. They include carboxylic, phenolic, amine, carbonyl, and sulphhydryl, with the carboxylic and phenolic groups classed as harder Lewis bases than

amine which is harder than sulphhydryl (McBride, 1994). Cadmium is a soft Lewis acid and therefore will preferentially complex with the soft Lewis base sulphhydryl. Recent studies determining the stability constants between Cd and humic substances give log K stability constants of 2.9 (Manunza et al., 1995) and 3.4 (Bolton et al., 1996). However, these studies used concentrations of Cd several orders of magnitude greater than that found in uncontaminated soil (Helmke, 1999) and therefore measured an average stability constant between Cd and all of the humic substance functional groups including the more abundant carboxylic and phenolic groups. Cadmium at normal soil concentrations would not be expected to bind with carboxylic and phenolic functional groups. Therefore, it is likely that the log stability constant between Cd and humic substances at normal soil Cd concentrations would be much higher than 2.9 and 3.4 since a larger proportion of the soil Cd would be bound to softer Lewis bases like amine and sulphhydryl.

Finally, Cd can also be specifically adsorbed onto a variable charge mineral or organic surface forming a ternary complex (McBride, 2000). For example, an anion such as SO_4^{2-} can displace the hydroxyl group on the surface of Fe oxide and then bind Cd to itself forming a ternary complex:



Ternary complexes only seem to form between multivalent cations, especially transition and heavy metals, and anions with at least two metal coordinating ligand positions

(McBride, 2000). Therefore, organic ligands such as citrate, which has three carboxylic functional groups could also form a ternary complex with Cd. Furthermore, it seems possible for citrate to bind with Cd in solution and then form a ternary complex with a soil colloid. Either way, the presence of solution ligands which can form ternary complexes usually result in a lowering of the metal solution concentration (McBride, 1994).

2.2.3.4 Identification of solid-phase cadmium species

Sequential extraction schemes have been used in the past in an effort to quantify different solid-phase species of soil Cd. The most recent scheme was developed by Krishnamurti et al. (1995a). It partitioned soil Cd into the following operationally defined solid-phase species: exchangeable, carbonate-bound, metal-organic complex-bound, easily reducible metal oxide-bound, H_2O_2 extractable organic-bound, amorphous mineral colloid-bound, crystalline Fe oxide-bound, and residual. The mean concentration in mg kg^{-1} of each solid-phase Cd species for the 16 Canadian soils used in the study was: metal-organic complex-bound = 0.107, carbonate-bound = 0.052, residual = 0.042, H_2O_2 extractable organic-bound = 0.035, crystalline Fe oxide-bound = 0.016, easily reducible metal oxide-bound = 0.010, amorphous mineral colloid-bound = 0.002, and exchangeable = not detectable. However, there are several problems with sequential extraction schemes. One problem is that the species remaining to be extracted may be altered with each extraction step. Another problem is that the species extracted may actually be several different species. For example, in the scheme of Krishnamurti et al. (1995a), the metal-organic complex-bound Cd is extracted with Na-pyrophosphate which dissolves all soil organic matter except humin,

the most resistant organic fraction (Schnitzer, 1982), as well as very fine hydrous amorphous Fe oxides (Bascomb, 1968). Therefore, the Cd that is brought into solution is likely not just one chemical species because the potential is there for it to be bound to Fe oxides and any of the different organic functional groups.

A better way to determine the solid-phase speciation of soil Cd is with X-ray Absorption Spectroscopy (XAS) based on synchrotron light source. To date research published using this technique to determine Cd speciation is fragmentary. However, it has been determined that the Cd-Fe (III) oxide complex is inner-sphere monodentate (Spadini et al., 1994) and that the majority of Cd atoms in apatite did not form discrete $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})_2$ domains but were randomly placed in the apatitic framework (Sery et al., 1996). Although it has not yet been attempted, researchers believe that with the use of the third generation synchrotron, high quality data on trace metal speciation in soils can now be obtained with metal concentrations as low as 1 to 10 mg kg^{-1} or less (Frenkel and Korshin, 2001). The Cd concentration of most uncontaminated soils is $<1 \text{ mg kg}^{-1}$ (Jackson and Alloway, 1992).

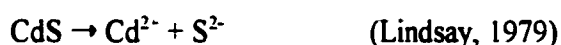
2.2.4 Transformation of soil cadmium

Soil environmental changes can occur over long periods of time with climate change and also during a growing season as a result of weather changes and farming practices. Because of this, the chemical species of any particular atom of Cd in the soil can also be changed. Cadmium can change from a mineral species to a soil solution species and *vice versa*, from an adsorbed species to a soil solution species and *vice versa*, and from an

adsorbed species to a mineral species.

2.2.4.1 Precipitation and dissolution of soil cadmium

The Cd in discrete Cd minerals, greenockite (CdS), otavite (CdCO₃), and cadmium phosphate (Cd₃(PO₄)₂), and the minerals containing Cd, apatite (Ca₅(PO₄)₃(OH,F)) and sphalerite (ZnS), can be released into the soil solution as a result of chemical weathering. There are a variety of chemical weathering processes which can change Cd from a mineral species to a solution species: solution, hydrolysis, oxidation, and acidification. In solution weathering the ionic components of the compound are separated by attraction to the polar ends of the water molecule and then move into solution (The Concise Oxford Dictionary of Earth Sciences, 1990). For example:



However, solution weathering by itself plays a minor role in the transformation of mineral Cd to soil solution Cd because the Cd minerals are relatively insoluble (Table 2.8).

Hydrolysis weathering involves a reaction between a water molecule and a mineral which splits the mineral into two or more products. The products react at the points of cleavage with the H⁺ or OH⁻ derived from the water molecule (The Concise Oxford Dictionary of Earth Sciences, 1990). For example:

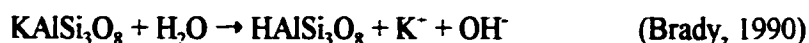


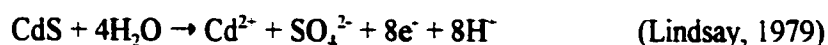
Table 2.8. Solubility product constants of Cd minerals.

Cadmium mineral	Log K
CdS	- 27.9 ^a
CdCO ₃	- 12.9 ^b
Cd ₃ (PO ₄) ₂	- 32.6 ^a

^a Martell and Smith (1974-1989). ^b Stipp et al. (1993).

There does not seem to be any information in the literature on the likelihood of hydrolysis of Cd minerals, however, for minerals in general it is thought that the effect of hydrolysis is relatively small (Summerfield, 1991).

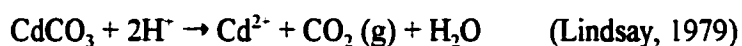
Oxidation weathering results in the loss of one or more electrons by an atom (McBride, 1994). Oxidation weathering of CdS does occur in soil environments that change from strongly anaerobic to aerobic conditions. For example, these conditions will occur in rice paddy soils that are flooded for a large part of the growing season. Cadmium sulphide will exist during the flooded conditions but will become oxidized and release Cd²⁺ into the soil solution when the fields drain. The following equation describes the reaction:



With the return of the flooding during the next growing season much of the hydrated soil solution species of Cd²⁺ will again be transformed into the mineral species CdS.

The last weathering process, acidification, has the greatest effect on the

transformation of mineral Cd to soil solution Cd. This process is dependent on the pH surrounding the mineral, since in order for it to occur a H^+ must be available to displace the Cd^{2+} ion from the mineral. For example:



A change in the H^+ activity can come from a variety of sources: 1) acid producing fertilizers such as elemental S or monoammonium phosphate, 2) carbonic acid produced from soil solution CO_2 which comes from the dissolution of atmospheric CO_2 in rain and the respiration of plant roots and soil microbes, and 3) low molecular weight organic acids (LMWOAs) and phytometallophores exuded by plant roots.

The initial soil solution Cd species produced by most of the weathering processes is the hydrated Cd^{2+} ion. However, the soil solution Cd species produced will react with organic ligands such as LMWOAs and phytometallophores and inorganic ligands such as Cl^- to form Cd-ligand complexes (Samurai and Huang, 1995a,b; Krishnamurti et al., 1997a).

Increasing the soil solution pH can result in the re-precipitation of Cd^{2+} as $CdCO_3$ or $Cd_3(PO_4)_2$. An increase in pH can occur with the application of lime or a base producing fertilizer like diammonium phosphate. However, much of the Cd^{2+} that comes out of solution with an increase in pH should become an adsorbed species since precipitation is a relatively slow process compared to adsorption (McBride, 1994) and in general, the amount of negative adsorption sites in the soil will increase as the pH increases.

It is possible that Cd^{2+} can also co-precipitate with Ca^{2+} to form a solid solution

(McBride, 2000). It has been demonstrated that in suspensions of calcite some Cd is removed from solution fairly rapidly followed by the slow removal of more Cd (McBride, 1980; Papadopoulos and Rowell, 1988). It is thought that Cd initially chemisorbs onto calcite surfaces with the following fast reaction:



Then, more Cd is slowly removed from the soil solution as a result of recrystallization as a thin calcite surface layer in the form of a $\text{Cd}^{2+}/\text{Ca}^{2+}$ solid solution on the calcite surface (McBride, 2000). However, at the present time there is a lack of evidence that this occurs in natural environments (Christensen and Huang, 1999).

2.2.4.2 Adsorbed species to mineral species

Cadmium chemically adsorbed to mineral surfaces can over time diffuse into the adsorbent mineral. Bruemmer et al. (1988) demonstrated that Cd can diffuse into goethite over time, and Stipp et al. (1992) demonstrated the same phenomena with Cd adsorbed to calcite. Stipp et al. (1992) used x-ray photoelectron spectroscopy (XPS) to show that adsorbed Cd moved into the bulk calcite at a rate of nanometres per week. Because there were no microfractures in the calcite, they suggested that it was probably solid-state diffusion of Cd along defects. Once adsorbed Cd has become a mineral species it can only become a soil solution species again if the mineral is exposed to the previously discussed weathering processes.

2.2.4.3 Adsorbed species to a different adsorbed species

With time and/or with changes in the environment surrounding the adsorbed Cd, the adsorbed Cd species may change to a more strongly or more weakly adsorbed species. It is possible that soil solution Cd may initially form relatively weak bonds with a soil particle and then over time gradually move to a site with a higher activation energy and become very strongly bound (McBride, 2000). For example, Cd that is weakly adsorbed through electrostatic attraction to the surface of layer silicate minerals and organic matter and to the pH-dependent sites on the edges of silica, allophane, and layer silicate clays may gradually move to sites such as metal oxides and organic matter functional groups which chemically bind Cd.

As well, changes in the strength with which Cd is bound can occur with Cd that is adsorbed chemically to oxides and organic matter. It has been noted that the speed at which Cd is adsorbed to oxides and organic matter is not consistent with adsorption to sites that would form relatively strong coordination complexes with Cd (McBride, 2000). Cd forms strong complexes with relatively weak acids like $\text{Fe-OH}^{0.5-}$ and the sulphhydryl organic functional group which both have relatively high activation energies, so if Cd was initially adsorbed to these sites the adsorption process would be slower than that observed. It has been suggested that Cd first forms coordination complexes at sites with low activation energies and then gradually becomes more strongly bound by displacing H^+ from sites with high activation energy (McBride, 2000). For example, Cd may initially come in contact with carboxylic functional groups because they are more plentiful than any of the other organic functional groups. The coordination bond formed would be relatively weak because

carboxylic acid is the strongest acid of the organic matter functional groups and therefore has the lowest activation energy. Over time Cd would displace a H^+ from a functional group with a higher activation energy and become more strongly bound (McBride, 2000). However, McBride (2000) does not address the fact that the same process cannot be happening with Fe oxides since they only possess one type of functional group. It is possible that with Fe oxides Cd is first electrostatically adsorbed to $>Fe-OH^{0.5-}$ and then over time displaces the H^+ to form a coordination complex:



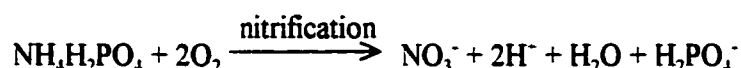
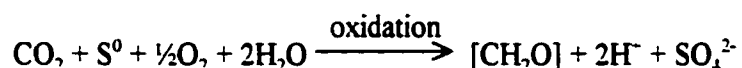
It is possible that these changes in the adsorbed species of Cd can also be affected by changes in soil pH because of competition between H^+ and Cd for the coordination sites on metal oxides and organic matter. An increase in pH should weaken the strength of the bond between H^+ and the coordinating functional group allowing Cd to move more easily from the organic functional groups that are relatively strong acids to the functional groups that are relatively weak acids. A decrease in pH should have the opposite effect.

2.2.4.4 Adsorbed species to solution species

Cadmium can change from an adsorbed species to a soil solution species in response to a variety of changes in the soil environmental conditions including a decrease in the soil pH, an increase in the ionic strength of the soil solution, and a change in the kinds of soil solution ligands.

A decrease in the soil pH results in the movement of some adsorbed Cd into the soil solution (Garcia-Miragaya and Page, 1978; Christensen, 1984; Bolton and Evans, 1996; Yuan and Lavkulich, 1997). The increased amount of H^+ will compete with Cd for adsorption sites on organic matter, metal oxides, and clay minerals. Soil pH can decrease slowly with a gradual change towards a more humid climate, and a decrease in soil pH has also been observed to occur in soils that have received repeated treatments with sewage sludge (Brady, 1990). Apparently the pH of the sludge treated soils decreased as a result of the formation of organic and inorganic acids during the decomposition of the organic matter (Brady, 1990).

Seasonal changes in the soil pH can occur with applications of acid producing fertilizers like elemental S and monoammonium phosphate ($NH_4H_2PO_4$) (Tisdale et al., 1993):



As well, it is possible that a seasonal decrease in pH will occur in the bulk soil that is changed to rhizosphere soil with the growth of crops. Plant roots can lower the pH of rhizosphere soil because they exude organic acids and produce CO_2 during respiration and because of root-cell efflux of H^+ (Welch and Norvell, 1999). In the rhizosphere it is likely that much of the adsorbed Cd moving into the soil solution will become complexed with soluble organic ligands from the LMWOAs and the phytometallophores released by the plant

root since many of the organic ligands from LMWOAs can form Cd complexes with relatively strong stability constants (Table 2.6) and the log stability constant of the Cd-phytometallophore complex is believed to be around 14.7 (Welch and Norvell, 1999).

Increases in soil pH with applications of lime can also move Cd from an adsorbed species to a soil solution species. Normally increasing the soil pH would result in less competition from H^+ for adsorption sites which would result in the movement of Cd from the soil solution to adsorption sites. However, because humic acid exists in the solid phase in acid conditions and dissolves as the pH increases (Oades, 1989), any Cd bound to humic acid that dissolves will become soil solution Cd as the pH is raised. Cadmium can be bound to humic substances at a pH as low as 3 (Bolton and Evans, 1996)

Seasonal applications of fertilizers can increase the ionic strength of the soil solution because most fertilizers consist of soluble salts. Generally, an increase in ionic strength of the soil solution will result in the movement of more ions, including Cd, from the soil adsorption sites into solution (Garcia-Miragaya and Page, 1976; Spark et al., 1995; Temminghoff et al., 1995). An increase in ionic strength results in greater inter-ionic forces affecting the movement of the ions in solution, which in turn will result in smaller activity coefficients for the dissolved cations. A smaller activity coefficient will cause a shift in the exchange surface-soil solution equilibrium which will result in the desorption of ions. The amount of Cd moved into the soil solution in this manner is partially dependent on the ions causing the increase in ionic strength. The increase in soil solution Cd will be greater if Cd-ligand complexes are formed and not significantly adsorbed, or if there is strong competition for the adsorption sites from the cations partially responsible for the increased ionic strength (Spark et al.,

1995). Not all species of adsorbed Cd are affected equally by an increase in ionic strength. For example, Cd physically adsorbed to the surface of a layer silicate clay such as bentonite will be affected more than Cd adsorbed to kaolinite which will in turn be affected more than Cd chemically adsorbed to goethite (Zachara et al., 1992).

A change in the kinds of soil solution ligands can occur seasonally with the application of fertilizers and with the formation of rhizosphere soil as the crops grow. Fertilizers can add ligands such as SO_4^{2-} and Cl^- , and plant roots can exude LMWOAs and phytometallophores, all of which can form relatively stable soluble complexes with Cd (Table 2.6). After the stable soluble Cd complexes are formed there will be less Cd^{2+} in solution so more Cd^{2+} will move from adsorption sites into the soil solution to re-establish a new equilibrium. As well, soil solution ligands that can form relatively stable complexes with Cd can remove Cd from adsorption sites that Cd has less of an attraction to. The result in both cases is more Cd in the soil solution. For example, Cl^- , LMWOAs, and soluble fulvic acids have all been shown to form relatively stable soluble complexes with Cd resulting in more Cd in the soil solution (Lamy et al., 1993; Samurai and Huang, 1995a,b; Krishnamurti et al., 1997a).

The amount of Cd that is removed from the adsorption sites and put into solution by the ligands depends both on the amount of the ligand in the soil solution and on the strength of the bond between Cd and the ligand (Krishnamurti et al., 1997a); a ligand that forms a complex with Cd with a relatively weak stability constant will only be able to remove Cd from adsorption sites with a weak attraction for Cd, while a ligand that forms a complex with Cd that has a relatively strong stability constant will be able to remove Cd from adsorption

sites with a much wider range of adsorption strengths.

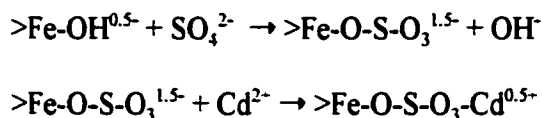
2.2.4.5 Solution species to adsorbed species

Cadmium can change from a soil solution species to an adsorbed species in response to a variety of changes in the soil environmental conditions including changes in the soil pH, the nature and amount of adsorption sites in the soil, and the kinds and concentration of soil solution ligands.

An increase in the soil pH with the application of lime will result in less H^+ to compete with Cd for adsorption sites and therefore should result in the changing of some solution Cd to adsorbed Cd. However, if there is a substantial amount of dissolved humic acid with Cd bound to it, a decrease in pH would precipitate the humic acid and also result in the change of some Cd from a solution species to an adsorbed species.

If the amount of adsorption sites in the soil increases it is probable that some soil solution Cd will become adsorbed Cd. An increase in the soil adsorption sites does happen with the addition of solid organic matter such as crop residues and manure. As the organic matter decomposes Cd from the soil solution may form insoluble organic complexes with the organic matter (Jones and Johnston, 1989).

Finally, a change in the concentration of certain types of ligands in the soil solution can result in the movement of soil solution Cd to adsorbed Cd. Application of fertilizers that contain the anions HPO_4^{2-} and SO_4^{2-} can remove Cd from the soil solution by forming a ternary complex onto a variable charge mineral or organic surface (McBride, 2000). For example:



Also, with the seasonal growth of crops there is an increase in the organic ligands in the soil that becomes rhizosphere soil because roots exude LMWOAs (Szmigielska et al., 1995; 1996). Organic ligands such as citrate and oxalate can also form ternary complexes with Cd. Furthermore, since they have more than one functional group, they could bind with Cd in solution and then form a ternary complex with a soil colloid (McBride, 2000).

2.3 Mass Movement of Soil Cadmium

This section examines the factors that influence the movement of Cd into a soil, throughout the soil's profile, and out of a soil (Figure 2.5). Not every soil will be affected by all of the factors, but all agricultural soil will have at least one factor adding Cd to the soil, one factor removing Cd from the soil, and one factor moving Cd throughout the soil profile.

2.3.1 Movement of cadmium into the soil

Cadmium can enter the soil profile of agricultural soils with the deposition of eroded soil, accidentally, by atmospheric deposition of air-borne Cd, and with the application of a variety of soil amendments (Figure 2.5).

Much of the soil that is eroded from hilltops and slopes in a drainage basin can end up deposited in depressions within the same basin (Martz and de Jong, 1987). The Cd in the

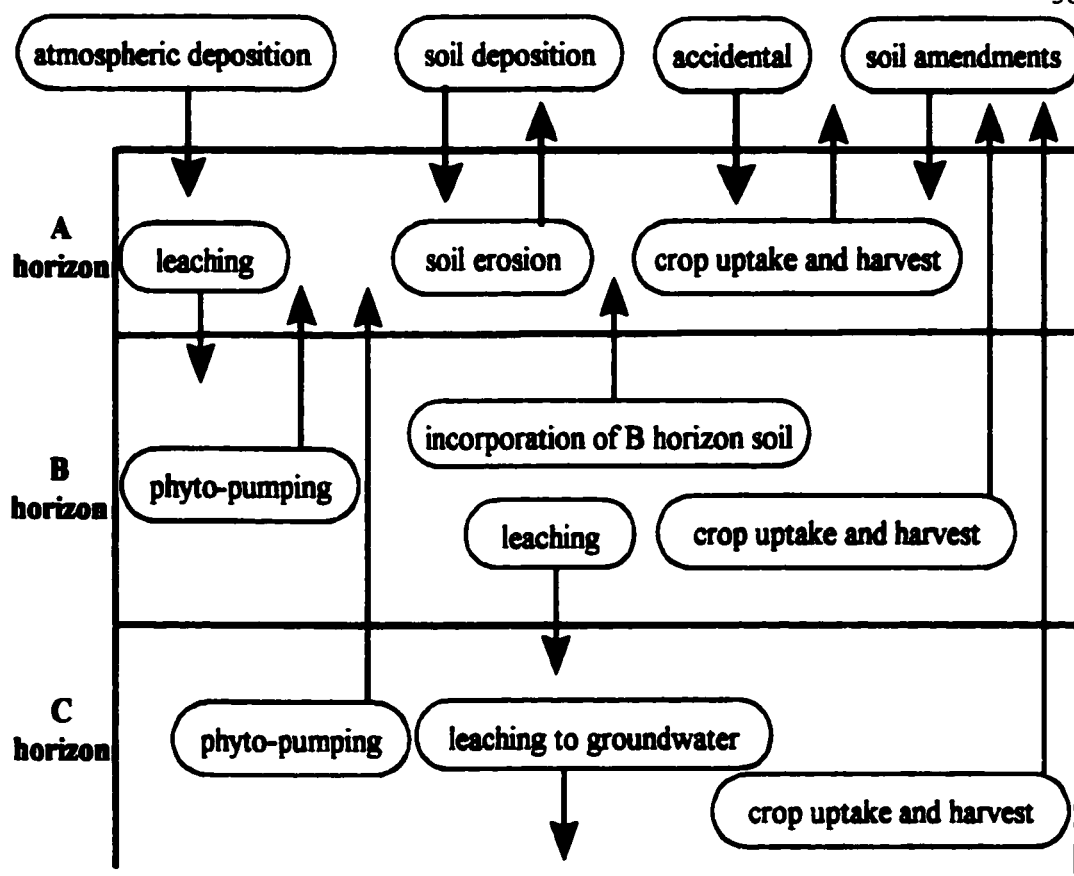


Figure 2.5. Factors involved in the movement of Cd into, throughout, and out of an agricultural soil profile.

deposited soil will become part of the soil profile in the depression. While it is logical that Cd addition to the soil profile as a result of soil deposition can occur, there does not appear to be any information in the literature on this subject. However, the rates of soil deposition have been estimated for different landforms in Saskatchewan, Canada (Martz and de Jong, 1987). The use of these rates and a knowledge of the Cd concentration in the deposited soil would allow for the calculation of the rate of Cd addition to the A horizon as a result of soil deposition. However, it would be difficult to know the exact Cd concentration of the soil deposited.

Accidental input of Cd to soils can occur at industrial plants such as electroplating plants, chemical plants, plastics manufacturers, and non-ferrous smelters (Alloway and Steinnes, 1999). Spillages or leakage of soluble forms of Cd have been found to increase the Cd concentration of soils to as high as 120 mg kg^{-1} (Alloway and Steinnes, 1999). Accidental input of Cd into the soil can also occur as a result of corrosion of galvanised metal from fencing materials and buildings and movement of the corrosion products into the soil with rainfall (Alloway and Steinnes, 1999). There does not seem to be any information in the literature as to the extent of accidental input of Cd.

There have been some studies quantifying atmospheric deposition of air-borne Cd to soil (Table 2.9). The rates of deposition range from $0.006 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Greenland to $13.56 \text{ mg m}^{-2} \text{ yr}^{-1}$ near a smelter. The deposition of atmospheric Cd is very wide ranging because of transport by winds. However, in general, the rate of atmospheric deposition of Cd increases with increasing physical proximity to large industry.

Cadmium containing soil amendments which are added to agricultural soils include farm yard manure, household and municipal compost, sewage sludge, and phosphate fertilizers. Because farm yard manure and household and municipal compost consist of soil and organic matter that came directly or indirectly from plants, their Cd content comes from the soil in the first place. Therefore, the overall net effect of their application on total soil Cd may be relatively insignificant. However, since they both can contain Cd concentrations that are generally higher than uncontaminated soils (Table 2.3), localized increases in soil Cd concentration can occur with repeated applications of manure and compost onto fields that were not the source of all of the Cd in the manure and compost. There do not seem to be any

Table 2.9. Estimates of atmospheric deposition of Cd in different regions.

Region	Cd deposition ($\text{mg m}^{-2} \text{yr}^{-1}$)	Reference
Greenland	0.006	Jackson and Alloway (1992)
Rural Europe	0.06-2.5	Jackson and Alloway (1992)
Central Saskatchewan	0.038	Shewchuk (1982)
Rural USA	<0.11	US EPA (1979)
Sweden	0.32	Bergkvist et al. (1989)
Great Lakes	0.45-0.49	Sweet et al. (1998)
London England	0.4-1.25	Harrison et al. (1975)
New York City	4.44	Jackson and Alloway (1992)
Adjacent to smelter	13.56	Jackson and Alloway (1992)

studies in the literature that deal with the rate of addition of Cd to soil with applications of farm yard manure and compost.

Sewage sludge can contain relatively large concentrations of Cd (Table 2.3). However, there has been a marked reduction in the average concentration of Cd in sewage sludge since industry has started to reclaim trace metals from their waste products. For example, the average sewage sludge Cd concentration in the United Kingdom decreased from 1983 to 1991 by 66 % to 3.2 mg kg^{-1} (Alloway and Steinnes, 1999). It was estimated that the rate of addition of Cd in sewage sludge to agricultural soils in the United Kingdom in 1986 was $0.096 \text{ mg m}^{-2} \text{yr}^{-1}$ and in Denmark in 1983 it was $0.012 \text{ mg m}^{-2} \text{yr}^{-1}$ (Jackson and Alloway, 1992). These numbers are far below the annual loading limits set by many countries

(Table 2.10).

Table 2.10. Maximum Cd concentrations in sewage sludge and sludge treated soils, and maximum annual loading limit of some countries (McGrath et al., 1994).

Country	Year	Maximum mg Cd kg ⁻¹ sludge DM ^a	Maximum mg Cd kg ⁻¹ sludge treated soil	Loading limit (mg Cd m ⁻² yr ⁻¹)
France	1988	20	2.0	15
Germany	1992	10	1.5	15
Spain	1990	20	1.0	15
Denmark	1990	1.2	0.5	0.8
Denmark	1995	0.8	-	-
Finland	1995	1.5	0.5	0.15
Sweden	1995	2.0	0.5	0.2
United Kingdom	1989	-	3.0	15
USA	1993	85	20	190

^a Dry matter.

However, these estimated rates of Cd addition do not adequately reflect the rate of addition of sewage sludge Cd to agricultural soils today because: 1) sewage sludge production will increase as the world human population increases, and 2) the practice of disposal at sea was banned for European countries as of 1998 (Alloway and Steinnes, 1999). Much of the sludge that was previously disposed of at sea is now being applied to agricultural soil.

Phosphate fertilizers put more Cd into agricultural soils than all of the other sources

combined because of: 1) their relatively high Cd concentration (Table 2.3), and 2) their widespread use on agricultural soil. The mean annual inputs to agricultural soils of phosphate fertilizer Cd for various countries are shown in Table 2.11.

Since the values in Table 2.11 are mean values, some soils could have a much higher annual input rate than the mean value. For example, in California phosphate fertilizers with a Cd concentration of 174 mg kg^{-1} had an annual input rate of $10 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$ (Mortvedt, 1987). The rates should increase in the future because world demand for phosphate fertilizer is expected to increase from the 37 499 Mg used in 1990 to 60 852 Mg in 2025 (Table 2.12).

Table 2.11. Estimated national mean annual inputs of Cd into agricultural soils as a result of phosphate fertilizer application (Alloway and Steinnes, 1999).

Country		Cd ($\text{mg m}^{-2} \text{ yr}^{-1}$)	Source
Germany		0.35-0.43	Kloke et al. (1984)
Sweden	1971-1975	0.33	Bergback et al. (1994)
Sweden	1986-1990	0.09	Bergback et al. (1994)
UK		0.43	Hutton and Symon (1986)
EC countries, average		0.25	Biberacher and Shah (1990)
USA		0.03-0.12	Mortvedt (1987)
Australia		0.16	Sumner and McLaughlin (1995)
New Zealand		0.89	Bramley (1990)

Table 2.12. Projected increase in demand for phosphate fertilizer (Banaante and Hellums, 1998).

Region	Projected increase in P_2O_5 demand from 1990 to 2025 (Mg)	Projected P_2O_5 demand in 2025 ^a (Mg)
North America	1672	6272
Western Europe	-1258	3842
Eastern Europe	235	2535
Eurasia	-1382	6818
Sub-Saharan Africa	765	1165
South Africa	374	674
North Africa	765	1165
Central America	622	1122
South America	2628	4528
West Asia	2263	3763
South Asia	6064	9764
East Asia	10125	17625
Oceania	480	1580
World	23353	60852

^a Assuming constant exponential rate of growth in world population.

2.3.2 Movement of cadmium throughout the soil profile

Cadmium can be moved throughout the soil profile as a result of phyto-pumping, leaching, and incorporation of B horizon soil into the A horizon (Figure 2.5). Phyto-pumping is the movement of Cd from the sub-horizons to the surface horizon via plants. Plant roots

in the B and C horizons will take up Cd from the these horizons and move it to the above-ground part of the plant. When the plant dies the Cd in the above-ground part of the plant, including the Cd that came from the lower horizons, will be incorporated into the A horizon. The only published data on this subject appears to be by Christensen and Tjell (1984). They developed the following equation which predicts the amount of Cd that will be taken up from either the topsoil or subsoil:

$$(\text{Cd uptake from topsoil/Cd uptake from the subsoil}) = (T_t/T_s) \times (S_t/S_s) \times (K_{ds}/K_{dt})$$

Where:

T_t = % transpired water that comes from the topsoil.

T_s = % transpired water that comes from the subsoil.

S_t = Soil Cd concentration in the topsoil.

S_s = Soil Cd concentration in the subsoil.

K_{ds} = Cd distribution coefficient (solid-phase Cd to solute Cd) for the subsoil.

K_{dt} = Cd distribution coefficient (solid-phase Cd to solute Cd) for the topsoil.

The S_t and S_s values can be determined for the soils in question, and the average ratio of K_{ds}/K_{dt} for soils with > 10% clay was determined by Christensen and Tjell to be 1. There does not seem to be any published data on the values of T_t and T_s . However, it is thought that, for a semi-arid climate, approximately 75% of the water transpired by wheat should come from the A horizon (personal communication from E. de Jong, 2001).

Leaching is the movement of soil materials in solution by water to a lower part of the soil profile (Figure 2.5). There does not seem to be any published studies on the rate of leaching of Cd to lower positions in the soil profile. However, there have been many studies on the movement of Cd into the soil profile following applications of sewage sludge (McGrath, 1987; Davis et al., 1988) and phosphate fertilizer (Williams and David, 1976; Mulla et al., 1980). While most of the studies reported that Cd remained in the top 15 cm of the soil profile, some of the sludge treated soils reported movement of Cd to a depth of 30 cm (McGrath, 1987). However, the use of the above types of studies to investigate the rate at which Cd is leached from the A horizon to the B horizon is inappropriate since, in a strict sense, the above studies are not investigating leaching. They are really investigating the net movement of Cd into the soil profile as a result of two processes which are working at odds with each other: 1) phyto-pumping of Cd to the A horizon, and 2) leaching of Cd from the A horizon to the B horizon.

Another type of Cd leaching study uses soil columns which in effect eliminates the phyto-pumping of Cd to the A horizon. Some soil column studies have been carried out using soil columns treated with sewage sludge and inorganic Cd salts, or columns containing soils that had been contaminated in the field (McGrath, 1987). The columns were leached with water in amounts equivalent to up to 10 years of rainfall but the researchers found no movement of Cd through the soil column. This would seem to indicate that Cd does not leach. However, there is a problem in relating these types of studies to the actual leaching of Cd in the field; removing the plants that cause the movement of Cd from the B horizon to the A horizon also eliminates the plant root organic acids that can increase the amount of

Cd leached by moving Cd from the soil particles into the soil solution.

It is likely that a relatively high average annual rainfall and a relatively light soil texture will increase the probability of the movement of Cd down the soil profile. Although none of the previously mentioned field studies reported the average annual rainfall received by the soils, some of the studies did report the soil texture. The results showed that Cd moved further down the soil profile in the lighter textured soils (sandy loam versus loam) (Mulla et al., 1980; Davis et al., 1988).

None of the above studies can offer a rate at which Cd would be leached from the A horizon to the B horizon. However, because Saskatchewan prairie soils endure a semi-arid climate with an average annual precipitation of <400 mm, with much of that precipitation from snowfall, leaching of Cd from the A horizon to the B horizon probably does not occur to any significant degree for most prairie soils. One exception would be soils that exist in depressions, because of the increased water that would flow through them relative to other Saskatchewan prairie soils.

Finally, B horizon Cd can become A horizon Cd if soil is eroded from the A horizon. The plough layer always tends to remain relatively uniform and represents the thickness of the A horizon in many cultivated soils. Therefore, with erosion of soil from the surface of the A horizon, the plough layer of cultivated soils will move deeper into the soil profile. As it moves deeper into the soil profile the plough layer will incorporate B horizon soil into the A horizon.

2.3.3 Movement of cadmium out of the soil

There are three main ways that Cd can be removed from the profile of agricultural soils: crop uptake and removal with harvest, leaching to the groundwater, and soil erosion, which includes wind erosion of soil particles and water erosion of dissolved and particulate soil components (Figure 2.5).

Soil can be removed from the surface of the A horizon by wind or water erosion. If this soil contains Cd, the erosion of the soil will effectively remove Cd from the A horizon. Soil erosion does not occur on all soils. For example, Martz and de Jong (1987) studied the erosion of soil in a drainage basin in southern Saskatchewan and found that net erosion occurred on level, crest, midslope, swale, and tributary landforms, while net deposition of soil occurred on depression and the main channel landforms. The study used ^{137}Cs which allowed for an estimation of the net rate of soil erosion over a 23 year period. Although there have been no studies calculating the rate of erosion of soil Cd, an estimate can be obtained if the landform and A horizon Cd concentration are both known.

There have been some estimates published on the leaching of Cd out of the soil profile to the groundwater (Bowen, 1975; Tjell et al., 1983; De Boo, 1990). The values range from 0.05-0.5 mg Cd m⁻² yr⁻¹ out of the soil profile to the groundwater. These values were estimated for soils in the Netherlands, Denmark, and Britain, all of which have relatively humid climates. To my knowledge there is no published literature on the rates of leaching of Cd out of the soil profile in semi-arid regions such as southern Saskatchewan. However, as discussed in section 2.3.2, leaching of soil Cd is unlikely to occur in the Saskatchewan prairies except possibly in soils found in depressions.

Crops take Cd from the soil and this Cd is then effectively removed from the soil when the crop is harvested. The unharvested part of the plant remains at the site and any Cd in it will be incorporated back into the soil. The amount of Cd removed from the soil by crop uptake and harvest can be estimated if the average Cd concentration for the harvested crop and the average yield per hectare of the crop are known. There have been numerous studies on the Cd concentration of many harvested crops (Grant et al., 1999), and statistics on the average yield and Cd concentration of a particular crop over a period of years can be obtained from government agencies. However, because the crop yield and Cd concentration are affected by many factors, including soil type (Cieslinski et al., 1996) and climate (Grant et al., 1999), the statistical data on the average yield and crop Cd concentration must match the region for which the rate of Cd removal from the soil with crop uptake and harvest is estimated.

Another factor that must be considered is that the Cd that is removed from the soil by the plant comes from both the surface soil and the subsoil (Figure 2.5). The fraction of total Cd removed by the plant from the subsoil will vary according to the type of plant. In general, plants like flax with long tap roots should take up a higher fraction of their Cd from the subsoil than plants like durum wheat that have relatively shallow fibrous roots. The only study in the literature that deals with uptake by plants from different positions in the soil profile is the study on Cd and wheat by Christensen and Tjell (1984) that was discussed in section 2.3.2. Their study estimated that for wheat growing in loamy soils approximately 83 % of the Cd taken up comes from the A horizon.

2.4 Phytoavailability of Soil Cadmium

2.4.1 Chemical extractions as indicators of phytoavailability

Several methods have been used in an attempt to predict plant available soil Cd (Table 2.13). DTPA buffered to a pH of 5.3 and AAAC-EDTA at an initial pH of 4.65 are suitable for extracting Cd from acidic soils (Krishnamurti et al., 1995b). However, problems can occur with the use of acidic extractants. For example, Sillanpaa and Jansson (1992) noted that the amount of Cd extracted with AAAC-EDTA at an initial pH of 4.65 increased as the soil pH increased from 4.0 to 7.5 while the plant (wheat and maize) concentration of Cd decreased through the same pH range.

Table 2.13. Extractants used for predicting plant available soil Cd.

Extractant	Reference
ABDTPA (pH 7.6)	Soltanpour and Schwab (1977)
DTPA (pH 5.3)	Norvell (1984)
AAAC-EDTA	Lakanen and Ervio (1971)
0.05 M CaCl ₂	Sauerbeck and Styperek (1984)
M NH ₄ NO ₃	Symeonides and McRae (1977)
M NH ₄ OAc	John et al. (1972)
M MgCl ₂	Krishnamurti et al. (1995b)
M Mg(NO ₃) ₂	Krishnamurti et al. (1995b)
M NH ₄ Cl	Krishnamurti et al. (1995b)
Chelating resin membrane	Lee and Zheng (1993)

There can also be problems with the use of an extractant with a relatively high pH such as DTPA buffered to a pH of 7.3. MacLean (1976) found that in soils spiked with Cd, plant uptake of Cd decreased with increasing soil organic matter but DTPA extractable Cd increased with increasing soil organic matter. The pHs of the soils were 5.9 and 6.8 so it is possible that some soil organic matter that had Cd complexed to it dissolved because of the higher pH of the DTPA.

Fairly good results were achieved using the chelating resin membrane as an indicator of phytoavailable Cd. It was used with soils that had a pH range of 4.3 to 8.0 and had a correlation coefficient of 0.97 with the Cd content of 35-day old wheat seedlings (Lee and Zheng, 1993). However, this high correlation may not reflect field conditions for most agricultural soils because: 1) the wheat was grown in a phytotron, 2) 50 g of quartz sand was added to 90 g of each soil, and 3) the soils were from heavily contaminated land or were uncontaminated soil that was spiked with Cd to concentrations of 0, 10, 20, 30, 40, and 50 mg kg⁻¹.

Krishnamurti et al. (1995b) used all of the methods in Table 2.13 except for DTPA (pH 5.3), AAAC-EDTA, and the chelating resin membrane to extract Cd from 11 different agricultural soils with a pH range of 6.0 to 7.8 and Cd concentrations ranging from 0.107 to 0.456 mg kg⁻¹. They then correlated the results with the Cd concentration of durum wheat grain grown on the different soils. They found that M NH₄Cl extractable Cd had the best correlation with durum wheat grain Cd ($r = 0.94$).

2.4.2 Influences on soil cadmium phytoavailability

For soil Cd to be phytoavailable it must enter the soil solution, and it must be in a form in the soil solution that is taken up by plants. Therefore, the kinetics and mechanisms that control the amount of Cd in the soil solution and its plant availability once there, must be understood.

2.4.2.1 The amount of soil solution cadmium

There are two general mechanisms that can control the amount of Cd in the soil solution: precipitation/dissolution and adsorption/desorption. However, the amount of total soil Cd can also have an effect on the amount of soil solution Cd.

2.4.2.1.1 Precipitation and dissolution

The following was previously discussed in more detail in section 2.2.2.1. Precipitation/dissolution can be a major influence on the concentration of Cd in the soil solution in some situations but in general it is considered that precipitation/dissolution processes do not control the soil solution concentration of Cd in most agricultural soils. However, research into the effect of precipitation and dissolution on the soil solution Cd concentration uses bulk soil and assumes precipitation through homogeneous nucleation. In soil environments, heterogeneous nucleation, which reduces or removes the energy barrier to nucleation, is more likely than homogeneous nucleation because of the presence of mineral and organic surfaces that can catalyze nucleation. Also, conditions in the soil rhizosphere are much different than in the bulk soil. The rhizosphere is a zone of intense microbial activity

and precipitation of metals by heterogeneous nucleation onto microbial surfaces can result in the formation of distinct metallic minerals (Huang and Germida, 2001). Therefore, it is possible that precipitation/dissolution may have more of an effect on the concentration of soil solution Cd than current research would indicate.

2.4.2.1.2 Adsorption and desorption

The following factors can influence adsorption and desorption of soil Cd: 1) a change in the ionic strength of the soil solution (Garcia-Miragaya and Page, 1976; Spark et al., 1995; Temminghoff et al., 1995), 2) a change in the kind of soil solution ligands (Lamy et al., 1993; McBride, 1994; Samuray and Huang, 1995a,b; Krishnamurti et al., 1997a), 3) a change in the concentration of cations that can compete successfully with Cd for adsorption sites (Christensen, 1987; Ross, 1994), 4) a change in the type and quantity of adsorption sites (Maclean, 1976; Eriksson, 1988), and 5) a change in the soil pH (MacLean, 1976; Jackson and Alloway, 1991; Temminghoff et al., 1995; Chlopecka et al., 1996; Yuan and Lavkulich, 1997).

Change in the ionic strength of the soil solution

The ionic strength of the soil solution can change with the application of fertilizer salts and with the formation of a rhizosphere. An increase in ionic strength results in greater inter-ionic forces affecting the movement of the ions in solution, which in turn will result in smaller activity coefficients for the dissolved cations. A smaller activity coefficient should cause a shift in the exchange surface-soil solution equilibrium which will result in the

desorption of ions. However, whether there will be a change in the amount of soil solution Cd as a result of an increase in ionic strength is partially dependent on the ions causing the increase in ionic strength. An increase in ionic strength will have the following possible results on the soil solution concentration of a metal cation: 1) decreased due to the formation of metal-ligand complexes which are then specifically adsorbed, 2) not changed if the ions that are causing the increase in the ionic strength do not interact with the adsorption surface or the metal cation, and 3) increased if metal-ligand complexes are formed and not significantly adsorbed, or if there is strong competition for the adsorption sites from the cations partially responsible for the increased ionic strength (Spark et al., 1995). Whether any one of the above three results occur will depend on the specific combination of metal cation and ions causing the increase in ionic strength. Spark et al. (1995) have shown that increasing the ionic strength with either KNO_3 or NaCl will result in an increase in solution Cd concentration.

Change in soil solution ligands

Applications of fertilizer salts and the formation of a rhizosphere can also change the kinds and amount of organic and inorganic ligands present in the soil solution, which can then result in a change in soil solution Cd. In general, if the soil solution ligands form relatively stable soluble complexes with soil solution Cd^{2+} the amount of soil solution Cd will increase, however, in some instances some ligands can result in the movement of Cd from the soil solution to the solid phase.

If the soil solution ligands form relatively stable soluble complexes with soil solution

Cd^{2+} , more Cd^{2+} will move from adsorption sites into the soil solution to re-establish a new equilibrium. As well, soil solution ligands that can form relatively stable complexes with Cd can remove Cd from adsorption sites that Cd has less of an attraction to. The result in both cases is more Cd in the soil solution. For example, Cl^- , LMWOAs, and soluble fulvic acids have all been shown to form relatively stable soluble complexes with Cd that resulted in more Cd in the soil solution (Lamy et al., 1993; Samurai and Huang, 1995a,b; Krishnamurti et al., 1997a). The amount of Cd that is removed from the adsorption sites and put into solution by the ligands depends both on the amount of the ligand in the soil solution and on the strength of the bond between Cd and the ligand; a ligand that forms a complex with Cd with a relatively low stability constant will only be able to remove Cd from adsorption sites with a weak attraction for Cd, while a ligand that forms a complex with Cd that has a relatively high stability constant will be able to remove Cd from adsorption sites with a much wider range of adsorption strengths.

A change in the ligands in the soil solution can also result in the movement of Cd from the solution to the solid phase. Application of fertilizers that contain the anions HPO_4^{2-} and SO_4^{2-} can remove Cd from the soil solution by forming a ternary complex with Cd and a variable charge mineral or organic surface (McBride, 2000). Also, with the seasonal growth of crops there is an increase in the organic ligands in the soil that becomes rhizosphere soil because roots and rhizosphere microbes produce LMWOAs. It is possible that some of the organic ligands that have two or more coordinating ligand positions, such as citrate and oxalate, can also form ternary complexes with Cd. Furthermore, since they have more than one functional group, they could bind with Cd in solution and then form a

ternary complex with a soil colloid (McBride, 2000).

Whether organic ligands will form ternary complexes with Cd seems to depend on the pH of the soil solution. Boily and Fein (1996) found that citrate increased the adsorption of Cd to α -Al₂O₃ in the pH range of 3.5 to 7.2 but inhibited adsorption of Cd at pH > 7.2. Also, Naidu and Harter (1998) found that at pH < 6 the amount of Cd adsorbed by soil was greater with citrate and oxalate solutions than with nitrate and acetate solutions, but at pH > 6 the reverse was found. Naidu and Harter (1998) also found that while all of the different concentrations of oxalate and citrate solutions that they used did extract Cd from the soil, increasing concentrations of oxalate and citrate resulted in a decrease in the amount of Cd extracted at pH < 6 and an increase at pH > 6. The results of the above two studies do suggest that ternary complexes between Cd, organic ligands, and soil colloids do occur and that their formation is relatively dependent on a low pH. However, the formation of ternary complexes should also be relatively dependent on the ratio of citrate or oxalate to Cd in the soil solution. If there is enough Cd in the soil solution all of the organic ligand functional groups might become occupied with Cd leaving no functional groups available to form ternary complexes with soil colloids.

Change in the concentration of cations competing with Cd for adsorption sites

It has been shown that Cu²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cr²⁺, and Zn²⁺ all tend to compete successfully with Cd for adsorption sites in mineral soils (Christensen, 1987; Ross, 1994). A change in the concentrations of these cations will to some degree affect the soil solution concentration of Cd. As the concentration of these competing cations increases the number

of sites that will be available to chemically adsorb Cd will decrease and vice versa. Cations competing with Cd for adsorption sites can increase or decrease over time. They can increase if significant amounts of phosphate fertilizers are applied to the soil, since phosphate fertilizers contain many heavy metals as impurities (Mermut et al., 1996; Raven and Leoppert, 1997). However, the amount of competing cations in the soil may decrease if they are taken up by plants at a faster rate than Cd; for example, crops take up much higher quantities of Zn than Cd (Hamon et al., 1997).

Change in the type and quantity of adsorption sites

The different types of soil adsorption sites can also affect the amount of Cd in the soil solution; the strength of the bonds between Cd and the adsorption site affects the ease with which Cd can be moved from the site and put into solution. Some research has been done on the relationship between Cd and the different soil adsorption sites. It has been shown that Cd-humate stability constants are relatively high and approximately range from a log K of 5-7 at a pH ranging from 5.0 to 6.0 (Takamatsu and Yoshida, 1978). It has also been shown that metal oxides specifically adsorb Cd (Hsu, 1989; Schwertmann and Taylor, 1989), although the only stability constant in the literature for a metal oxide-Cd complex is a log K of 0.47 for the hydrous ferric oxide-Cd complex (Dzombak and Morel, 1990).

A change in the amount of soil adsorption sites can occur. Over time weathering processes can break down primary minerals. Some of the weathering products will be adsorbed by soil colloids, some will be taken up by plants, and it is possible that in some soils some will be leached from the soil. However, some of the weathering products will be

transformed to metal oxides and metal-organic complexes, which can act as sites of adsorption of Cd. As well, a change in the amount of another soil colloid can also occur. Soil organic matter will decrease when a virgin soil undergoes cultivation (Blank and Fosberg, 1989), and it will increase with applications of farm yard manure (Jones et al., 1987). Any increase in metal oxides, metal-organic complexes, and organic matter content of the soil should decrease the amount of soil solution Cd because it will increase the amount of chemical adsorption sites in the soil.

Change in the soil pH

A change in the soil pH can occur with the application of acid-producing or base-producing fertilizers or lime, with the growth of a rhizosphere, and with a gradual change in climate. An increase or decrease in the pH will affect the number of adsorption sites available for Cd. As the pH of the soil decreases, H^+ will displace Cd from adsorption sites on organic matter, metal oxides, and clay minerals to the soil solution. Conversely, as the pH of the soil increases the H^+ will move from these adsorption sites forming water molecules with OH^- , thereby freeing up adsorption sites for other cations including Cd^{2+} .

2.4.2.1.3 Total soil cadmium

The amount of total soil Cd can also influence the amount of Cd in the soil solution. If the amount of Cd in the soil exceeds the ability of the soil to chemically adsorb it, the surplus will then become physically adsorbed. Since this surplus soil Cd is physically adsorbed, bound by electrostatic attraction, it is much less strongly bound than chemically

adsorbed Cd which is bound with covalent bonds. Because of the relatively weak bonds of the surplus Cd, there will be a shift in the equilibrium between adsorbed Cd and soil solution Cd which will allow more Cd in the soil solution. This reasoning is backed up by several studies which show a positive relationship between total soil Cd and plant uptake of Cd on agricultural soils with unnaturally high total Cd levels (McLaughlin et al., 1996). For example, a study by Merry et al. (1981) showed that, on soils that were contaminated with Cd from a lead-zinc smelter, the amount of Cd taken up by the wheat closely corresponded to the amount of total Cd in the soils.

2.4.2.2 The species of soil solution cadmium

While Cd must enter the soil solution to be phytoavailable, not all soil solution Cd is phytoavailable. It is the species of Cd in the soil solution which determines whether or not soil solution Cd will be taken up by plants. For example, Cd^{2+} is easily taken up by plants but soluble humic acid-Cd complexes are not (Tyler and McBride, 1982). Also, there has been some research which suggests that Cd-Cl (Smolders and McLaughlin, 1996a; b), Cd-SO₄ (McLaughlin et al., 1998), and Cd-phytometallophore complexes (Welch and Norvell, 1999) are taken up by plants.

2.4.2.3 The species of solid-phase cadmium

In general an increase in the strength of the bonds between Cd and a soil colloid will result in a decrease in the phytoavailability of soil Cd. However, determining the different chemical species of Cd in the soil has been a problem. Sequential extractions, which

operationally define the chemical species of Cd, have been developed and used. The most recent scheme is by Krishnamurti et al. (1995a). They reported that Cd is found in differing amounts in eight different operationally defined soil particulate fractions: exchangeable, carbonate-bound, metal-organic complex-bound, easily reducible metal oxide-bound, H_2O_2 extractable organic-bound, amorphous mineral colloid-bound, crystalline Fe oxide-bound, and residual. Although the phytoavailability of the Cd in each of the eight different fractions has still not been determined, some correlational evidence suggests that some of the metal-organic complex-bound Cd is relatively phytoavailable (Krishnamurti et al., 1997b). Future use of XAS based on synchrotron light source should help determine the different chemical species of soil solid-phase Cd and this will then help give insight into the phytoavailability of the different species.

2.4.2.4 Farm management practices

The following farming practices have been identified as having an affect on the phytoavailability of soil Cd: crop selection, crop rotation, tillage system, irrigation, and soil amendments (Grant et al., 1999).

The amount of phytoavailable Cd in the soil is to a certain degree dependent on the crop that is grown because different species and cultivars can differ greatly in the amount of Cd that they accumulate in their tissue (Table 2.14). Kuboi et al. (1986) classified Leguminosae as low Cd accumulators, Gramineae, Liliaceae, Cucurbitaceae and Umbelliferae as moderate Cd accumulators, and Chenopodiaceae, Cruciferae, Solanaceae and Compositae as high Cd accumulators. Table 2.14 also shows that the average Cd

concentration of cultivars within a species can be quite different.

Table 2.14. Examples of the range of Cd concentrations found within cultivars of different species (Grant et al., 1999).

Species	Cultivar	Cd (mg kg ⁻¹)
Durum wheat	Arcola	0.077
	Kyle	0.157
Spring wheat	Genesis	0.038
	Katepwa	0.055
Potatoes	Russet Burbank	0.15
	Kennebec	0.24

It is logical to assume that some of the differences in the amount of Cd taken up by different species and cultivars is a result of differences in the environment at the soil-root interface of different species and cultivars. Although very little research has been done on this subject, Cieslinski et al. (1998) demonstrated that there were significantly higher amounts of LMWOAs in the rhizosphere of a high Cd accumulating cultivar of durum wheat than there were in a low Cd accumulator. The extra LMWOAs may be partially responsible for the difference in the amount of Cd taken up by each cultivar.

The crop rotation that is used can also affect the phytoavailability of soil Cd. Cadmium concentrations in wheat grown after lupins were higher than in wheat grown after

cereals (Oliver et al., 1993). The authors of this study suggest that the higher Cd concentrations in the wheat following the lupins may have been the result of preferential growth of the wheat roots in acidified zones associated with lupin roots. Another study showed that Cd concentrations in wheat grown after flax were 30% higher than wheat grown after fallow, lentils, or spring wheat (Selles et al., 1996). In this case it is possible that, since flax straw and roots can have a relatively high concentration of Cd (up to $\sim 1.3 \text{ mg kg}^{-1}$) (Cieslinski et al., 1996), the degradation of the flax tissue leads to relatively high concentrations of Cd in the soil solution.

Seemingly conflicting results have been achieved with the effect of zero-till on the bioavailability of soil Cd. The research of Brown (1997) showed that the concentration of Cd in wheat grown in a wheat/wheat rotation decreased as a result of zero-tillage. However, the research of Oliver et al. (1993) showed an increase in the amount of Cd taken up by wheat grown in a zero-till system. It is probable that the results of Brown reflect the true effects of zero-till, because Oliver et al. used a lupin/wheat rotation which could have affected the results. As discussed previously, Oliver et al. suggest that the higher Cd concentrations in the wheat following the lupins may have been the result of preferential growth of the wheat roots in acidified zones associated with lupin roots.

Irrigation of crops may also affect the bioavailability of soil Cd. Unpublished data of M. J. McLaughlin showed that there was a significantly higher potato tuber concentration of Cd for years that irrigation had to be used (Grant et al., 1999). Because the irrigation water was relatively saline, these effects could have been partially from the increase in the ionic strength of the soil solution. However, McLaughlin attributes most of the effect to the

formation of Cd-Cl complexes since the salinity was caused mainly by NaCl salts in the irrigation water. Related to irrigation is the practice of growing rice in flooded fields. Research by Zhang et al. (1988) has shown that the Cd concentration of rice in paddy soils that were kept waterlogged for as long as possible was 0.145 mg kg^{-1} while that in rice grown in the same soils that were drained was 0.278 mg kg^{-1} . The reduced environment of the waterlogged soil kept most of the soil Cd in the rather insoluble form of CdS and thus not available for plant uptake.

Depending on the soil amendment, it can lead to an increase or a decrease in the bioavailability of soil Cd. Many studies have shown that the use of N fertilizers can lead to an increase in the plant concentration of Cd (Williams and David, 1973; Eriksson, 1990; Oliver et al., 1993; Grant et al., 1996). The increase in Cd uptake is thought to be due to a combination of effects: increase in ionic strength of the soil solution, ion-exchange reactions, and soil acidification (Grant et al., 1999). Banding of phosphate fertilizers, superphosphate and monoammonium phosphate, resulted in more Cd uptake by crops than broadcasting of the same fertilizers (Sparrow et al., 1992; Grant and Bailey, 1997). Applications of KCl resulted in an higher Cd content in potato tubers (Sparrow et al., 1994). The authors suggest that this is the result of the formation of Cd-Cl complexes because an equivalent amount of K as K_2SO_4 did not have the same effect.

Applications of lime are used to increase the pH of acid soils. Since many studies have demonstrated that increasing the soil pH will lead to a greater adsorption of soil Cd (Garcia-Miragaya and Page, 1978; Christensen, 1984; Bolton and Evans, 1996; Yuan and Lavkulich, 1997), it is likely that applications of lime to increase the pH will reduce the plant

uptake of Cd. Many studies have demonstrated that this is indeed the case (Williams and David, 1976; Street et al., 1977; Page et al., 1981; Eriksson, 1989). However, some studies have demonstrated an increase in plant uptake of Cd with applications of lime (Andersson and Siman, 1991; Singh and Myhr, 1998; Maier et al., 1997). McLaughlin et al. (1996) suggest that the soils in these studies had a relatively low pH dependent charge so that any increased adsorption of Cd due to the increase in pH was more than offset by competition for adsorption sites by the high concentration of Ca^{2+} .

Organic matter in the form of farm yard manure is routinely applied to some agricultural soils. This may affect the bioavailability of soil Cd in two ways: 1) it will add extra organic functional group adsorption sites to the soil which can form strong coordination complexes with Cd, therefore reducing its bioavailability, and 2) it can lower the pH of the soil with the creation of organic acids as the organic matter is degraded by soil microbes, and therefore lower the number of available adsorption sites for Cd. Studies which added peat, farmyard manure, and humic acid to the soil resulted in a decreased uptake of Cd by plants (Ram and Verloo, 1985; Eriksson, 1988). Archived wheat and soil samples (1877 to 1984) from Rothamsted Experimental Station in the United Kingdom were analysed for Cd concentration (Jones et al., 1987; Jones and Johnston, 1989). The researchers found that while the soil Cd concentrations of phosphate-treated soils and manure-treated soils both increased over time, the wheat Cd concentrations from the manure treated soils decreased over time while those from the phosphate treated plots increased with time. The manure treated plots actually received more Cd over the years than the phosphate treated plots. Also, while the organic matter content of the phosphate treated soils remained

approximately the same, that of the manure treated soils increased to about 2.5 times the original content. It appears that the increase in organic matter adsorption sites resulted in a decrease in the plant uptake of Cd.

3. EXPERIMENTS, RESULTS AND DISCUSSION

3.1 Sampling

Eight sites in the agricultural region of southern Saskatchewan, Canada were chosen for this study (Figure 3.1.1). Each site consisted of a field subjected to long-term cultivation and an adjacent field of virgin prairie. One Orthic Chernozemic soil profile was investigated from both the virgin and the adjacent cultivated fields at each site. Pertinent information about the sites is shown in Table 3.1.1. The following controls were in place to ensure that any differences between the virgin and cultivated soils were the result of long-term cultivation only:

- The fields containing the cultivated and virgin sampling sites were separated by only a fence or a road.
- The virgin sampling sites were at least 64 metres from any roads or cultivated fields to reduce the chance of aerial fallout contamination originating from roads or cultivated fields.
- The angle, aspect, length, and elevation of the slope that contained the sampling spots for the cultivated and virgin soils were similar.
- The parent materials of the cultivated and virgin sampling sites were the same, as determined by physical proximity, large scale soil maps, visual inspection of the soil

profiles, and similarity of the bulk density, pH, and Cd concentration of the virgin and cultivated C horizons.

SOIL ZONES:

- I Brown
- II Dark Brown
- III Black
- IV Dark Gray
- V Gray

Sampling Sites : ① to ⑧

N
↑
↓
S

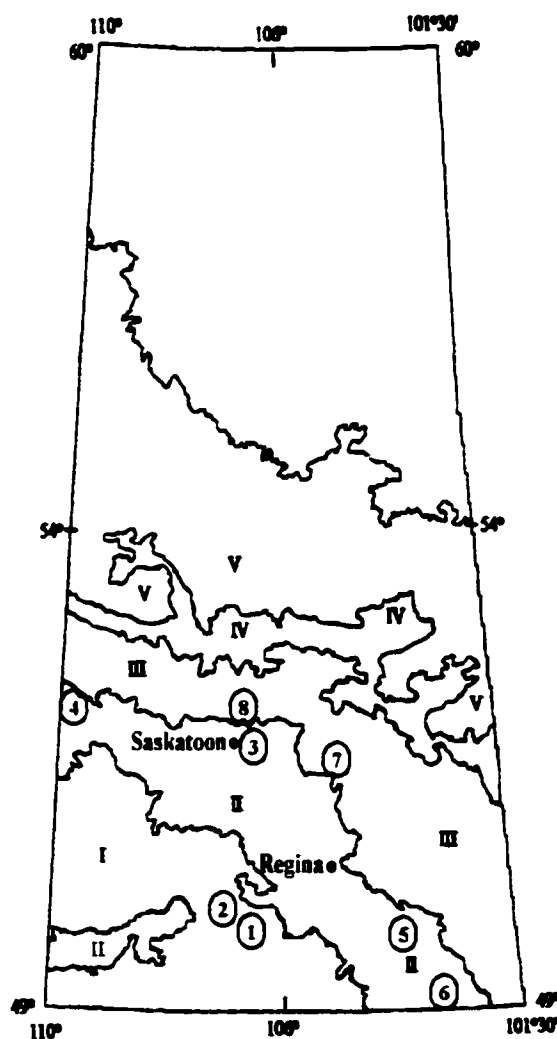


Figure 3.1.1. Map of Saskatchewan showing the distribution of the eight sampling sites.

Table 3.1.1. Background information on the eight sampling sites.

Site	Location	Soil association	Soil zone	Parent material	Cultivation (years)	P fertilizer (years)
1	106° 21' 12" W long. 49° 35' 0" N lat.	Ardill	Brown	glacial till	50+ ^z	1
2	107° 4' 41" W long. 50° 1' 22" N lat.	Ardill	Brown	glacial till	31	NA ^y
3	106° 32' 0" W long. 52° 9' 19" N lat.	Elstow	Dark Brown	silty glacio-lacustrine	53+	16+
4	109° 59' 29" W long. 52° 29' 48" N lat.	Elstow	Dark Brown	silty glacio-lacustrine	85	NA
5	103° 32' 57" W long. 49° 38' 47" N lat.	Amulet	Dark Brown	glacial till	48+	5
6	102° 50' 55" W long. 49° 2' 30" N lat.	Weyburn	Dark Brown	glacial till	94	1
7	104° 55' 19" W long. 51° 50' 16" N lat.	Oxbow	Black	glacial till	50+	NA
8	106° 53' 40" W long. 52° 26' 0" N lat.	Oxbow	Black	glacial till	53+	10

^z “+” means at least this many years and possibly more.

^y “NA” means that the number of years is not available.

Soil samples and bulk density samples were taken from each of the genetic horizons from each virgin and cultivated soil profile and the genetic horizons were measured for thickness. As well, one composite A horizon soil sample, consisting of ten sub-samples from within a five metre radius of the profile sampling spot, was taken from each virgin and cultivated field.

3.2 Impact of Long-term Cultivation on the Cadmium Availability Index and Related Soil Properties

3.2.1 Background

Cadmium is a trace heavy metal that when found in relatively low concentrations in human food can lead to the accumulation of Cd in the human body at levels which may cause serious health problems (Environmental Directorate, 1994). Soils with relatively low concentrations of Cd can still result in agricultural products that contain enough Cd to pose a serious health threat to the consumer (Jackson and Alloway, 1992). Research on the phytoavailability of soil Cd is needed to gain the knowledge required to lower the concentration of Cd in agricultural products.

The following factors have been identified as having an effect on or having the potential to affect the phytoavailability of soil Cd: ionic strength of the soil solution (Garcia-Miragaya and Page, 1976; Spark et al., 1995; Temminghoff et al., 1995), soil pH (MacLean, 1976; Jackson and Alloway, 1991; Temminghoff et al., 1995; Chlopecka et al., 1996; Yuan and Lavkulich, 1997), the nature and concentration of the ligands in the soil solution (Lamy et al., 1993; McBride, 1994; Samuray and Huang, 1995a,b; McLaughlin et al., 1996; Krishnamurti et al., 1997a), CEC (Haghiri, 1974), soil texture (Eriksson, 1989), total soil Zn (Chaney et al., 1999), total soil Cd (Merry et al., 1981; Chumbley and Unwin, 1982; Sillanpaa and Jansson, 1992), the type and concentration of cations that compete with Cd for adsorption sites (Christensen, 1987; Ross, 1994), and the type and quantity of adsorption

sites (Maclean, 1976; Eriksson, 1988; Krishnamurti and Huang, 2001).

There does not seem to have been many published studies on the effect of long-term cultivation on the phytoavailability of soil Cd and soil properties related to the phytoavailability of soil Cd. There has been one study that investigated the differences in total soil Cd, extractable Cd with the use of several different chemical extractants, and plant tissue Cd between newly cultivated (< 4 years) and long-term cultivated (> 30 years) soils (He and Singh, 1993). However, that study is not comparable to the present study for two reasons: 1) the soils had already been cultivated for up to four years and the effects of cultivation had likely already begun, and 2) no attempt was made to verify that the Cd content of the parent materials of the paired newly cultivated and long-term cultivated soils was similar.

There have been studies dealing with the change in plant Cd, total soil Cd, and soil pH over long periods of fertilization (Jones et al., 1987; Mortvedt, 1987; Jones and Johnston, 1989; Herrero and Martin, 1993; Nicholson and Jones, 1994; Jeng and Singh, 1995; Gavi et al., 1997; Hamon et al., 1998). However, all of these studies took place on soils that had already been long-term cultivated prior to the start of the study and any effects noted were the result of long-term fertilization and not long-term cultivation. One study, which was not investigating soil Cd, did investigate the effect of long-term cultivation on some soil properties which are related to the phytoavailability of soil Cd. Blank and Fosberg (1989) found a statistically significant decrease in organic C as a result of long-term cultivation. They also found an increase in soil pH and ionic strength, but the increases were not statistically significant. Therefore, the objective for this study was to determine the

impact of long-term cultivation on the CAI of A horizon soil and related soil properties.

3.2.2 Materials and methods

One composite A horizon soil sample, consisting of ten sub-samples within a five metre radius, was taken from both virgin and the adjacent cultivated fields at each of the eight sites. All 16 samples were air dried, crushed to <2 mm using a marble roller and polyethylene sieve, and homogenized. The soil saturated paste pH (McLean, 1982), Cl⁻ concentration (Adriano and Doner, 1982), ionic strength of the soil solution (Griffin and Jurinak, 1973), CEC (Peech et al., 1962), particle size distribution (Gee and Bauder, 1986), and Cd Availability Index (CAI) (Krishnamurti et al., 1995b) were determined for each soil sample. A sub-sample of each soil sample was crushed further to <0.15 mm with an agate mortar and pestle and a stainless steel sieve, and analyzed for total organic and inorganic C (Wang and Anderson, 1998), total Zn (Wei et al., 1997), and total Cd (Krishnamurti et al., 1994). All of the above analyses were determined in duplicate for each sample. The nature of the soil organic matter was determined with ¹³C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance spectroscopy (¹³C CPMAS NMR), recorded on an Avance/DRX360 spectrometer (manufactured by Bruker Analytik, Rheinstetten/Karlsruhe, Germany) with a rotor size of 7 mm, a frequency of 90.56 MHz, a spinning rate of 5000 hertz, a relaxation decay of 1 second, and a contact time of 1.5 milliseconds. Because it has been shown that the solid state NMR rotor produces peak area in the aromatic range, the ¹³C NMR spectra of the soils were corrected by subtracting the free induction decays (FIDs) of the rotor spectra from the FIDs of the soil spectra (Condon and Newman, 1998). For all of

the results, the first uncertain decimal place was dropped and the number of significant figures was determined by the method used by Gillespie et al. (1989). All of the results are presented on an oven dried weight basis (overnight at 105° C).

3.2.3 Results and discussion

3.2.3.1 Impact on related soil properties

Results of the analyses by site for the virgin and cultivated soils are presented in Table 3.2.1, and the mean virgin and cultivated values are in Table 3.2.2. Long-term cultivation resulted in a large significant decrease in the mean total soil organic matter (Table 3.2.2). The majority of the decrease is attributed to cultivation-enhanced microbial degradation of the soil organic matter. However, some of the decrease was possibly due to erosion. Baldock et al. (1997) suggest the use of the alkyl C/O-alkyl C weight ratio (0-45 ppm/45-110 ppm) as an indicator of the extent of the degradation of organic matter; an increase in this ratio would indicate that degradation has occurred since the alkyl region of aliphatic C is often associated with residues such as cutin, suberin, and microbial biomass that are fairly resistant to degradation. However, there was no significant change in the mean alkyl C/O-alkyl C ratio with long-term cultivation for the soils in the present study (Table 3.2.2). These results could mean that no degradation of soil organic matter occurred, however that is not likely the case since almost half of the soil organic C disappeared with long-term cultivation (Table 3.2.2). Rather it is likely that there was no change in the ratio because of selective stabilisation of normally easily decomposable organic matter against

microbial attack by adsorption onto mineral surfaces (Baldock et al., 1997).

Table 3.2.1. A horizon data for the individual virgin (V) and cultivated (C) sites.

		Site							
		1	2	3	4	5	6	7	8
Thickness (m)	V	0.13	0.10	0.12	0.10	0.9	0.11	0.12	0.9
	C	0.12	0.11	0.13	0.11	0.10	0.11	0.11	0.10
Sand (g kg ⁻¹)	V	280	313	173	351	298	365	499	404
	C	350	336	254	386	421	424	526	368
Silt (g kg ⁻¹)	V	440	397	485	380	396	373	298	382
	C	400	353	428	356	303	317	290	418
Clay (g kg ⁻¹)	V	270	290	342	269	306	263	203	214
	C	240	311	318	262	277	260	183	214
Texture	V	L-CL	CL	CL	CL	CL	CL	L	L
	C	L	CL	CL	CL	CL	CL	L	L
CEC (cmol kg ⁻¹)	V	23.0	27.0	33.1	26.9	31.7	26.9	30.0	28.2
	C	19.2	26.2	28.8	26.0	23.6	20.7	23.7	26.6
pH	V	6.8	6.3	6.2	6.0	6.2	7.0	6.6	6.2
	C	7.3	6.8	6.0	6.8	6.4	6.6	7.7	6.3
Ionic strength	V	0.0050	0.0045	0.0037	0.0044	0.0046	0.0091	0.0044	0.0046
	C	0.0059	0.0117	0.0145	0.0117	0.0071	0.0054	0.0061	0.0059
Cl ⁻ (mg L ⁻¹)	V	20.1	9.3	11.0	30.6	15.6	10.6	13.3	15.5
	C	10.5	5.8	9.6	6.3	10.1	11.5	10.9	8.4
Inorganic C (g kg ⁻¹)	V	nd ^a	nd	nd	nd	nd	nd	nd	nd
	C	nd	nd	nd	nd	nd	nd	nd	nd
Organic C (g kg ⁻¹)	V	35.4	45.7	54.4	39.6	49.9	41.4	54.4	54.3
	C	14.9	24.1	27.6	20.5	18.0	15.4	27.9	35.2

Table 3.2.1 continued

		Site							
		1	2	3	4	5	6	7	8
Aromaticity ^y (%)	V	23.1	20.3	22.2	20.9	26.1	22.9	23.1	20.0
	C	32.0	26.5	25.9	27.9	26.9	28.3	32.7	25.1
Alkyl C:O-alkyl C (wt.)	V	0.425	0.437	0.397	0.421	0.376	0.400	0.394	0.393
	C	0.419	0.414	0.407	0.391	0.374	0.408	0.339	0.411
Total Zn (mg kg ⁻¹)	V	68.7	82.0	99.8	82.4	79.9	80.0	70.6	83.6
	C	61.2	68.5	84.2	62.7	62.1	62.0	52.2	77.8
Total Cd (mg kg ⁻¹)	V	0.326	0.387	0.511	0.383	0.400	0.360	0.399	0.417
	C	0.275	0.331	0.435	0.298	0.248	0.204	0.287	0.399
Zn:Cd (wt.)	V	211	212	195	215	200	223	177	201
	C	222	207	194	219	250	305	182	195
CAF ^x (mg kg ⁻¹)	V	0.072	0.104	0.129	0.124	0.103	0.041	0.071	0.088
	C	0.045	0.061	0.142	0.076	0.063	0.043	0.022	0.092

^z Not detectable.

^y % Aromaticity = [aromatic peak area (110-160 ppm) / {total peak area - COOH peak area (160-190 ppm)}] x 100 (Stevenson, 1994). Aromatic peak area = (peak area from 110 to 160 ppm) - (carboxylic side band peak area). Total peak area = (peak area from 0 to 190 ppm) - (carboxylic side band peak area).

^x Cadmium availability index.

Although there was no change in the alkyl C/O-alkyl C weight ratio, there was a dramatic increase in the % aromaticity of the soil organic matter as a result of long-term cultivation (Figure 3.2.1, Table 3.2.2). This is possibly the result of cultivation enhanced microbial degradation of the aliphatic C (0-110 ppm) relative to the aromatic C (110-160

Table 3.2.2. Effects of long-term cultivation on the mean values of selected A horizon soil properties.

	Virgin soils	Cultivated soils
CAI ^z (mg kg ⁻¹)	0.091	0.068 ^{y*}
Total Cd (mg kg ⁻¹)	0.398	0.308 ^{y***}
Total Zn (mg kg ⁻¹)	80.9	66.3 ^{y***}
Zn:Cd (wt.)	204	221 ^x
pH ^w (saturated paste)	6.4	6.7 ^{y*}
Ionic strength	0.0050	0.0085 ^{y***}
Chloride (mg L ⁻¹)	15.8	9.1 ^{y***}
CEC (cmol kg ⁻¹)	28.4	24.4 ^{y***}
Clay (g kg ⁻¹)	270	258 ^x
Silt (g kg ⁻¹)	394	359 ^x
Sand (g kg ⁻¹)	335	383 ^x
Total inorganic C (g kg ⁻¹)	nd ^v	nd
Total organic C (g kg ⁻¹)	46.8	22.9 ^{y****}
Aromaticity ^u (%)	22.3	28.2 ^{y****}
Alkyl C:O-alkyl C (wt.)	0.405	0.395 ^x

^z Cadmium availability index.

^y Significantly different from the virgin value at * $\alpha = 0.10$, *** $\alpha = 0.025$, **** $\alpha = 0.005$.

^x No significant difference from the virgin soils at $\alpha = 0.10$.

^w Mean pH calculated with pH values (not with actual H⁺ activities).

^v Not detectable.

^u % Aromaticity = [aromatic peak area (110-160 ppm) / {total peak area - COOH peak area (160-190 ppm)}] x 100 (Stevenson, 1994). Aromatic peak area = (peak area from 110 to 160 ppm) - (carboxylic side band peak area). Total peak area = (peak area from 0 to 190 ppm) - (carboxylic side band peak area).

ppm), since in general double bonded C is considered more refractory than single bonded C. However, Baldock et al. (1997) have shown that degradation of organic matter does not always result in an increase in aromaticity, possibly because of the presence of lignin-degrading fungi. The increase in aromaticity may also have come from crop residue burning during the years of cultivation (Golchin et al., 1997a, b; Schmidt et al., 1999; Skjemstad et al., 1996; 1999a, b). Crop residue burning would increase the amount of charcoal in the soil, and charcoal gives a large peak in the aromatic range of the ^{13}C NMR spectra (Skjemstad et al. 1999a). Significant amounts of charcoal have been found in Black Chernozemic soils in Saskatchewan (Ponomarenko and Anderson, 2001). It is possible that both enhanced microbial degradation and crop residue burning contributed to the increase in aromaticity. These results validate the research of Lessa et al. (1996) which showed that the aromaticity of the soil organic matter of a cultivated Chernozemic soil from the Black soil zone of Saskatchewan was much higher than that in an equivalent virgin soil. Also, the results of the present study extend the research of Lessa et al. (1996) since this study not only used soils from the Black soil zone, but also used soils from the Dark Brown and Brown soil zones of Saskatchewan (Table 3.1.1).

The mean soil pH is higher in the cultivated soils than the virgin soils although the difference is only statistically significant at $\alpha = 0.10$ (Table 3.2.2). Blank and Fosberg (1989) also found an increase in pH with long-term cultivation although there was no statistical significance established. It is expected that the pH would increase with long-term cultivation because the significant decrease in organic C (Table 3.2.2) equals a decrease in organic matter including humic and fulvic acids and other acid producing organics. The lack of a

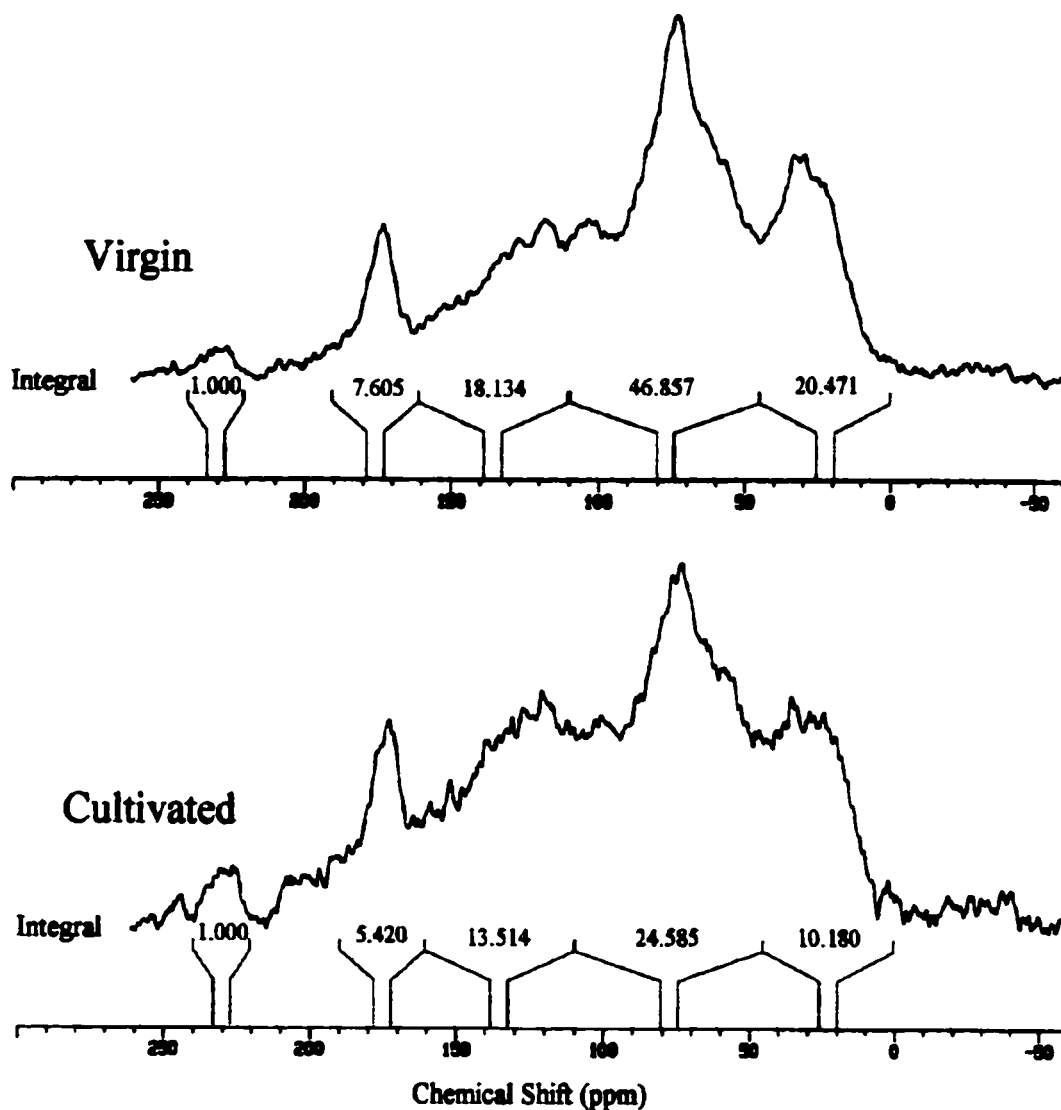


Figure 3.2.1. ^{13}C CPMAS NMR spectra of virgin and cultivated soils at site # 2. Alkyl C ranges from 0 to 45 ppm, O-alkyl C from 45 to 110 ppm, aliphatic C from 0 to 110 ppm, aromatic C from 110 to 160 ppm, and carboxylic C from 160 to 190 ppm (Baldock et al., 1997; Malcolm, 1989). The peak at 230 ppm is a carboxylic side band. A similar change in the distribution of ^{13}C due to long-term cultivation was observed in the NMR spectra of the soils from all eight sites.

better statistical significance is related to the two sites, 3 and 6, where the pH decreased with long-term cultivation (Table 3.2.1). It is possible that the decrease in pH at these sites is related to the application of acid producing fertilizers.

The mean ionic strength, which is also related to the application of fertilizers and the decomposition of the soil organic matter, increased significantly with long-term cultivation (Table 3.2.2). Research by Blank and Fosberg (1989) also found an increase in ionic strength with long-term cultivation, although the increase was not statistically significant. An increase in ionic strength was an expected result since the application of fertilizers can increase the ionic strength by adding soluble salts. Also, more ions should move from the soil adsorption sites into the soil solution as the soil organic matter decreases with cultivation.

Both the mean chloride and the mean zinc content of the soil decreased significantly with long-term cultivation (Table 3.2.2). Most of the decrease is probably related to the removal of these elements from the cultivated soils by crop uptake and crop harvest, although the increased rate of erosion that comes with cultivation may also play a part in the decrease. There was no statistically significant change in the mean Zn:Cd weight ratio with long-term cultivation (Table 3.2.2). The ratio before cultivation was 204:1 and after cultivation was 221:1. Both of these Zn:Cd ratios will result in a plant Zn:Cd ratio that significantly reduces the detrimental effects of Cd in our food (McKenna et al., 1992, 1993).

There was no statistically significant change in the mean concentration of sand, silt, and clay with long-term cultivation which suggests that the effects of erosion on the soil separates were minor (Table 3.2.2). However, the mean CEC did decrease significantly

(Table 3.2.2) which is almost certainly related to the decrease in the soil organic matter that occurred with long-term cultivation.

The mean total Cd in the cultivated soils was significantly lower than that in the virgin soils (Tables 3.2.2). Some of the change in the total Cd is due to the removal of Cd from the cultivated soil by crop uptake and harvest. However, other factors may have had an effect on the concentration of total soil Cd. The application of phosphate fertilizers may have added Cd to the cultivated soils, although the number of years of P fertilizer application was far less than the number of years of crop harvest (Table 3.1.1). Also, erosion may have removed some Cd from the cultivated soils, especially from those soils that were under cultivation before the drought of the 1930's. As well, the rate of phyto-pumping of Cd from the lower horizons to the surface horizon in the cultivated soils was probably different from that in the virgin soils because of the difference in vegetation during the years of cultivation. Finally, some of the virgin sites will have lost some Cd from the soil as a result of periodic cattle grazing; some of the Cd in the virgin vegetation that is eaten by the cattle will remain in the tissue of the cattle and will be removed from the site when the cattle are removed from the site. Although there is not any data on the extent of cattle grazing that has occurred, some Cd has probably been removed from the virgin soils in this manner. The cumulative effects of all of the above factors have resulted in the differences found in total soil Cd between the virgin and cultivated soils used in this study.

3.2.3.2 Impact on the cadmium availability index

The mean CAI of the cultivated soils was also lower than that of the virgin soils

although the difference is only statistically significant at $\alpha = 0.10$ (Table 3.2.2). Since past research has demonstrated that soil pH can have a large effect on the plant availability of soil Cd (MacLean, 1976; Jackson and Alloway, 1991; Temminghoff et al., 1995; Chlopecka et al., 1996; Yuan and Lavkulich, 1997), the decrease in the CAI is partially attributed to the increase in the mean soil pH that occurred with long-term cultivation (Table 3.2.2). However, the decrease in the CAI may also be related to the change in the nature of the soil organic matter. Krishnamurti and Huang (2001) found that, of two soils subjected to long-term cultivation, there was less phytoavailable Cd in the soil with the higher humic acid:fulvic acid ratio. This is probably because humic acid has a much higher stability constant with Cd than fulvic acid does (Takamatsu and Yoshida, 1978; Sposito et al., 1981). Also, humic acid generally has higher aromaticity than fulvic acid (Mahieu et al., 1999), so the significantly higher aromaticity of the organic matter in the cultivated soils (Table 3.2.2) could mean that the organic matter of the cultivated soils had a higher humic acid:fulvic acid ratio than the virgin soils. Therefore, the increase in aromaticity in the cultivated soils could be partially responsible for the decrease in the CAI. The decrease in the CAI might also be a result of the decrease in the mean CEC (Table 3.2.2), which should result in less Cd present in the exchangeable form.

3.2.3.3 Relationships between the cadmium availability index and the measured soil properties

Simple correlations were performed between the CAI and related soil properties for both the virgin and the cultivated soils. The results are shown in Table 3.2.3. Total soil Cd

had a significant positive correlation with the CAI in the cultivated soils ($r = 0.81$, $P = 1.59 \times 10^{-2}$). This significant positive correlation suggests that the amount of Cd in the soil does have an effect on the availability of Cd even in non-contaminated cultivated soils. The significant positive correlations between total Zn and the CAI in both the virgin ($r = 0.63$, $P = 9.17 \times 10^{-2}$) and cultivated ($r = 0.93$, $P = 7.60 \times 10^{-4}$) soils could result from Zn out-competing Cd for adsorption sites; the Zn in the soil can compete with Cd for adsorption sites so a decrease in the Zn content could result in more available adsorption sites that can bind Cd strongly thereby reducing the CAI. Soil pH had significant negative correlations with the CAI in both the virgin ($r = -0.92$, $P = 1.30 \times 10^{-3}$) and the cultivated ($r = -0.84$, $P = 8.98 \times 10^{-3}$) soils, which was expected since many studies have determined that soil pH is the dominant factor affecting the phytoavailability of soil Cd. The Zn:Cd ratio, while a factor in the uptake of Cd by plants, does not seem to have any relationship with the CAI in either the virgin or the cultivated soils. Ionic strength has a significant negative correlation with the CAI in the virgin soils ($r = -0.79$, $P = 2.03 \times 10^{-2}$) but has a significant positive correlation in the cultivated soils ($r = 0.70$, $P = 5.19 \times 10^{-2}$). These opposite results may have been caused by the different types of ions in the soil solutions of the virgin and cultivated soils. In the cultivated soils the ions causing an increase in ionic strength may have cations that compete with Cd for adsorption sites and anions that form strong soil solution complexes with Cd that are not adsorbed, while in the virgin soils the ions causing an increase in ionic strength could consist of anions that form complexes with Cd which are then strongly adsorbed. Total Cl^- had no significant correlation with the CAI in both the virgin and cultivated soils. It might be that the levels of Cl^- are not high enough to have any noticeable

effect.

The soil CEC had a significant positive correlation with the CAI in the cultivated soils ($r = 0.76$, $P = 2.92 \times 10^{-2}$). It is possible that an increase in the CEC could mean that a higher proportion of the soil Cd could end up on the exchange surfaces and therefore more of the Cd in the soil would be phytoavailable Cd. The correlation coefficient is also positive between the CAI and the CEC in the virgin soils but the level of statistical significance is

Table 3.2.3. Correlations between the A horizon cadmium availability index (mg kg^{-1}) and related soil properties.

	Virgin soils		Cultivated soils	
	r	P	r	P
Total Cd (mg kg^{-1})	0.62	1.01×10^{-1}	0.81	1.59×10^{-2}
Total Zn (mg kg^{-1})	0.63	9.17×10^{-2}	0.93	7.60×10^{-4}
Zn:Cd (wt.)	0.15	7.30×10^{-1}	0.30	4.67×10^{-1}
pH (saturated paste)	-0.92	1.30×10^{-3}	-0.84	8.98×10^{-3}
Ionic strength	-0.79	2.03×10^{-2}	0.70	5.19×10^{-2}
Total chloride (mg L^{-1})	0.31	4.59×10^{-1}	-0.29	4.83×10^{-1}
CEC (cmol kg^{-1})	0.46	2.57×10^{-1}	0.76	2.92×10^{-2}
Total clay (mg kg^{-1})	0.55	1.63×10^{-1}	0.57	1.40×10^{-1}
Total silt (mg kg^{-1})	0.45	2.68×10^{-1}	0.71	4.66×10^{-2}
Total sand (mg kg^{-1})	-0.51	1.91×10^{-1}	-0.82	1.31×10^{-2}
Total organic C (g kg^{-1})	0.26	5.37×10^{-1}	0.43	2.85×10^{-1}
Aromaticity (%)	-0.21	6.17×10^{-1}	-0.73	3.88×10^{-2}

low. The only significant correlations between the clay, silt, and sand fractions and the CAI was a significant positive correlation with silt ($r = 0.71$, $P = 4.66 \times 10^{-2}$) and a significant negative correlation with sand ($r = -0.82$, $P = 1.31 \times 10^{-2}$) in the cultivated soils. However, the general trend in both the virgin and cultivated soils is that the CAI increases with an increase in the finer fractions of the soil (clay and silt) and decreases with an increase in the sand fraction of the soil. These results are a reflection of the CEC results; the CEC and the CAI should both increase as the finer fractions increase, and decrease as the sand fraction increases. No significant correlation was found between total soil organic C and the CAI in both the virgin and the cultivated soils. This result is not unexpected since total soil organic C represents all of the soil organic fractions, including both those that bond relatively strongly with Cd and those that have relatively weak bonds with Cd. Since different soils may contain approximately the same concentration of soil organic matter but differ greatly in the relative amounts of the different sub-fractions of soil organic matter (based on bond strength with Cd), a correlation between total soil organic C and phytoavailable soil Cd will not likely occur. However, in the cultivated soils aromaticity seems to have a significant negative correlation with the CAI ($r = -0.73$, $P = 3.88 \times 10^{-2}$). It is expected that an increase in aromaticity should result in a decrease in phytoavailability since humic acid, which is more aromatic than fulvic acid, binds more strongly to Cd than fulvic acid does. The correlation coefficient is also negative between the CAI and the aromaticity in the virgin soils but the level of statistical significance is low.

3.2.4 Summary and conclusions

Long-term cultivation resulted in a significant decrease in the mean concentration of total soil Cd, Zn, and Cl^- . The decrease is attributed to crop uptake and harvest and soil erosion. The mean Zn:Cd weight ratio did not significantly change and remains at a level that offers some protection from the detrimental effects of Cd in our food. The soil organic matter also decreased with long-term cultivation. The majority of the decrease is attributed to the cultivation-enhanced microbial degradation of the soil organic matter. However, some of the decrease was possibly due to erosion. As the soil organic matter decreased with long-term cultivation the mean % aromaticity of the organic matter increased significantly. The mean soil CEC decreased significantly with long-term cultivation. The decrease is attributed to the significant decrease in the soil organic matter. The mean ionic strength of the soil solution increased significantly with long-term cultivation. The increase is attributed to the combined effects of the addition of soluble salts with applications of fertilizer and the decrease in the CEC. The mean soil pH also increased significantly with long-term cultivation. The increase is attributed to the decrease of humic and fulvic acids and other organics as the soil organic matter decreased. None of the other soil properties related to the phytoavailability of soil Cd showed a significant change with long-term cultivation.

Long-term cultivation significantly decreased the mean CAI. A decrease in total soil Cd, total soil Zn, and the soil CEC contributed to the decrease in the CAI; the results show a positive correlation between these three soil properties and the CAI in both the virgin and the cultivated soils although the level of statistical significance between the CEC and the CAI in the virgin soils was low. An increase in the aromaticity of the soil organic matter and the

soil pH also contributed to the decrease in the mean CAI with long-term cultivation; pH and aromaticity were both negatively correlated with the CAI in both the virgin and cultivated soils, although the level of statistical significance between the aromaticity and the CAI in the virgin soils was low.

While studies by other researchers have demonstrated that all of the soil properties investigated in the present study do have an effect on the phytoavailability of soil Cd, the present study has determined that for the cultivated soils in this study, only total soil Cd, total soil Zn, CEC, aromaticity of the soil organic matter, and soil pH have a significant effect on the CAI. As well, this study has shown that these soil properties change with long-term cultivation and their changes are related to changes in the CAI. The information obtained in this study will add to the body of knowledge required in order to predict how the phytoavailability of soil Cd will change in the future.

3.3 Impact of Long-term Cultivation on the Solid-Phase Species of Soil Cadmium

3.3.1 Background

The phytoavailability of soil Cd should be related to the strength with which Cd is bound to solid-phase soil components; the stronger the bonds between Cd and a soil component, the less phytoavailable the Cd. Cadmium can form associations with many different solid-phase soil components resulting in many different solid-phase species of Cd. Researchers have attempted to identify and quantify the different solid-phase species of soil Cd with sequential extraction schemes. The most recent and comprehensive scheme was developed by Krishnamurti et al. (1995a). The extraction scheme divides solid-phase soil Cd into the following eight different operationally defined species: exchangeable, carbonate-bound, metal-organic complex-bound, easily reducible metal oxide-bound, H_2O_2 extractable organic-bound, amorphous mineral colloid-bound, crystalline Fe oxide-bound, and residual. The research of Krishnamurti et al. (1995a) also demonstrated a positive relationship between the metal-organic complex-bound Cd and the CAI (1M NH_4Cl extractable Cd). However, relationships between the CAI and amount of the different solid-phase soil components that solid-phase Cd was associated with were not determined.

There does not seem to be any published research on the effect of long-term cultivation on the different solid-phase species of soil Cd and their relationships with bioavailable soil Cd. The objectives of this study were: 1) to determine the effect of long-term cultivation on the solid-phase species of soil Cd, and 2) to uncover relationships

between the cadmium availability index and the solid-phase species of soil Cd and related solid-phase soil component properties.

3.3.2 Materials and methods

One composite A horizon soil sample, consisting of ten sub-samples within a five metre radius, was taken from both the virgin and cultivated fields at each of the eight sites. All 16 samples were air dried, crushed to <2 mm using a marble roller and polyethylene sieve, and homogenized. The <2 mm soil was then analysed in duplicate for the CAI as per the method of Krishnamurti et al. (1995b). As well, sub-samples of each of the <2 mm soil samples were analysed in duplicate for the distribution of solid-phase Cd and the Mn, Fe, and Al content in the relevant sequential fractions with the sequential extraction scheme of Krishnamurti et al. (1995a) (Table 3.3.1). The extraction for carbonate-bound Cd was not done because none of the soils contained inorganic C (Table 3.2.1). A sub-sample of each of the <2 mm soil samples was then crushed further to <0.15 mm with an agate mortar and pestle and a stainless steel sieve, and digested in duplicate and analysed for total Cd (Krishnamurti et al., 1994). The mean amount of total Cd from the total Cd digestion was compared with the mean total amount of Cd sequentially extracted. For all of the results, the first uncertain decimal place was dropped and the number of significant figures was determined by the method used by Gillespie et al. (1989). All of the results are presented on an oven dried weight basis (overnight at 105° C).

Table 3.3.1. Sequential extraction scheme of Krishnamurti et al. (1995a).

Step	Species	Reagent ^z	Shaking time and temp. (°C)	Source
1	Exchangeable	10 ml of 1 M Mg(NO ₃) ₂ (pH 7)	4 h at 25 °C	Shuman, 1985
2	Carbonate-bound	25 ml of 1 M CH ₃ CO ₂ Na (pH 5)	6 h at 25 °C	Tessier et al., 1979
3	Metal-organic complex-bound	30 ml of 0.1 M Na ₄ P ₂ O ₇ ·10H ₂ O (pH 10)	20 h at 25 °C	McKeague, 1967
4	Easily reducible metal oxide-bound	20 ml of 0.1 M NH ₂ OH·HCl in 0.01 M HNO ₃	30 min at 25 °C	Shuman, 1985
5	H ₂ O ₂ extractable organic-bound	5 ml of 30% H ₂ O ₂ (pH 2), 3 ml of 0.02 M HNO ₃ ;	2 h at 85 °C	Tessier et al., 1979
		then add 3 ml of 30% H ₂ O ₂ (pH 2);	2 h at 85 °C	
		cool, add 10 ml of 2 M Mg(NO ₃) ₂ in 20% HNO ₃	30 min at 25 °C	
6	Amorphous mineral colloid-bound	10 ml of 0.2 M (NH ₄) ₂ C ₂ O ₄ (pH 3)	4 h at 25 °C (dark)	Shuman, 1985
7	Crystalline Fe oxide-bound	25 ml of 0.2 M (NH ₄) ₂ C ₂ O ₄ (pH 3) in 0.1 M ascorbic acid	30 min at 95 °C	Shuman, 1985
8	Residual	Residual of step 7 was digested with HF-HClO ₄		Tessier et al., 1979

^z The volume of the reagents was for 1 g of soil sample (<2 mm); after each treatment the extract was collected by centrifugation for 10 min at 12000 g, the residue was washed once with 10 ml of deionised distilled water, centrifuged for 10 min. at 12000 g, and the supernatants were combined and made up to a known volume.

3.3.3 Results and discussion

3.3.3.1 Impact on the solid-phase species of soil cadmium

The results by site are shown in Table 3.3.2 and the means of the eight sites are in Table 3.3.3. The mean amount of total Cd sequentially extracted showed good agreement with the mean amount of Cd as determined by total digestion. For the virgin soils the mean total amount of sequential Cd expressed as a % of mean total digested Cd is 98.2 ± 2.2 % SE and for the cultivated soils it is 100.4 ± 1.7 % SE (Table 3.3.3). The mean relative abundance of the different solid-phase Cd species for both the virgin and the cultivated soils followed the order: metal-organic complex-bound > easily reducible metal oxide-bound > H_2O_2 extractable organic-bound > crystalline metal oxide-bound > exchangeable > amorphous mineral colloid-bound (Table 3.3.3). These results are the same as Krishnamurti et al.'s (1995a) results in that the metal-organic complex-bound Cd species was the most abundant species among the solid-phase Cd species. However, the results were bound to differ in certain aspects since the present study used only Orthic Chernozemic soils from the Brown, Dark Brown, and Black soil zones while Krishnamurti et al. (1995a) used Chernozemic soils not only from those three soil zones but also from the Dark Grey soil zone, and also used some Luvisolic soils. The results differed in the following ways: 1) Krishnamurti et al. (1995a) detected carbonate-bound Cd in all of their soils, while the present study left out the carbonate-bound Cd extraction step because it was assumed that there was no carbonate-bound Cd in the soils since there was no detectable inorganic C in any of the soils (Table 3.2.1), 2) while Krishnamurti et al. (1995a) found residual Cd in all of their soils, no detectable amount of residual Cd species was found in the soils in the

Table 3.3.2. Impact of long-term cultivation on the solid-phase soil Cd species and cadmium availability index for the individual virgin (V) and cultivated (C) sites.

		Site							
		1	2	3	4	5	6	7	8
Cadmium availability index									
(mg kg ⁻¹):	V	0.072	0.104	0.129	0.124	0.103	0.041	0.071	0.088
	C	0.045	0.061	0.142	0.076	0.063	0.043	0.022	0.092
Exchangeable Cd (mg kg⁻¹):									
	V	0.010	0.016	0.021	0.026	0.014	0.006	0.011	0.016
	C	0.004	0.008	0.029	0.015	0.014	0.009	0.004	0.015
Metal-organic complex-bound									
Cd (mg kg ⁻¹):	V	0.181	0.208	0.319	0.232	0.240	0.182	0.273	0.261
	C	0.161	0.189	0.267	0.164	0.127	0.112	0.179	0.288
Easily reducible metal oxide-bound Cd (mg kg⁻¹):									
	V	0.068	0.058	0.054	0.061	0.059	0.078	0.062	0.067
	C	0.056	0.070	0.062	0.057	0.048	0.048	0.069	0.075
H₂O₂ organic-bound Cd (mg kg⁻¹):									
	V	0.033	0.053	0.080	0.041	0.068	0.054	0.078	0.068
	C	0.033	0.042	0.039	0.036	0.024	0.021	0.033	0.038
Amorphous mineral colloid-bound Cd (mg kg⁻¹):									
	V	nd ^a	nd	nd	nd	nd	0.001	nd	nd
	C	nd	nd	nd	nd	0.003	0.001	nd	nd
Crystalline metal oxide-bound Cd (mg kg⁻¹):									
	V	0.018	0.019	0.019	0.017	0.012	0.009	0.013	0.022
	C	0.019	0.018	0.027	0.018	0.015	0.017	0.013	0.018

Table 3.3.2 continued

		Site							
		1	2	3	4	5	6	7	8
Residual Cd (mg kg ⁻¹):									
	V	nd	nd	nd	nd	nd	nd	nd	nd
	C	nd	nd	nd	nd	nd	nd	nd	nd
Total sequentially extracted									
Cd (mg kg ⁻¹):	V	0.310	0.355	0.494	0.377	0.392	0.329	0.437	0.435
	C	0.274	0.326	0.427	0.290	0.228	0.206	0.298	0.434
Total digested Cd (mg kg ⁻¹):									
	V	0.326	0.387	0.511	0.383	0.400	0.360	0.399	0.417
	C	0.275	0.331	0.435	0.298	0.248	0.204	0.287	0.399
Total sequential Cd as % of									
total digested Cd:	V	95.1	91.7	96.5	98.5	98.2	91.6	109.4	104.3
	C	99.6	98.5	98.2	101.2	91.9	101.1	103.9	108.7

^z Not detectable.

present study, 3) the mean amounts of exchangeable Cd for both the virgin and cultivated soils in this study, 0.015 and 0.012 mg kg⁻¹ respectively, were two orders of magnitude greater than the mean amount detected by Krishnamurti et al. (1995a) (<0.001 mg kg⁻¹), and 4) the mean amount of easily reducible metal oxide-bound Cd in the present study was greater than both the H₂O₂ extractable organic-bound Cd and the crystalline metal oxide-bound Cd, while Krishnamurti et al. (1995a) found that it was less than both of these species in their soils.

Only two of the solid-phase Cd species had a significant change in their concentration with long-term cultivation (Table 3.3.3). Both the metal-organic complex-bound Cd and the

Table 3.3.3. Mean impact of long-term cultivation on the solid-phase soil Cd species and the cadmium availability index.

	Virgin soils	Cultivated soils
Exchangeable Cd (mg kg ⁻¹)	0.015	0.012 ^z
Metal-organic complex-bound Cd (mg kg ⁻¹)	0.237	0.186 ^{y**}
Easily reducible metal oxide-bound Cd (mg kg ⁻¹)	0.064	0.061 ^z
H ₂ O ₂ extractable organic-bound Cd (mg kg ⁻¹)	0.059	0.033 ^{y****}
Amorphous mineral colloid-bound Cd (mg kg ⁻¹)	nd ^x	nd
Crystalline metal oxide-bound Cd (mg kg ⁻¹)	0.016	0.018 ^z
Residual Cd (mg kg ⁻¹)	nd	nd
Total sequentially extracted Cd (mg kg ⁻¹)	0.391	0.310 ^{y***}
Total digested Cd (mg kg ⁻¹)	0.398	0.308 ^{y***}
Total sequential Cd as a % of total digested Cd	98.2 ± 2.2 ^w	100.4 ± 1.7
Cadmium availability index (mg kg ⁻¹)	0.091	0.068 ^{y*}

^z No significant difference from the virgin soils at $\alpha = 0.10$.

^y Significantly different from virgin soils at * $\alpha = 0.10$, ** $\alpha = 0.05$, *** $\alpha = 0.025$, **** $\alpha = 0.005$.

^x Not detectable.

^w Standard error.

H₂O₂ extractable organic-bound Cd decreased significantly with long-term cultivation. This is not surprising since by definition both of these Cd fractions contain organic matter and the soil organic matter as represented by total organic C showed a greater than 50 % decrease

with long-term cultivation (Table 3.2.2).

3.3.3.2 Impact on the solid-phase species of soil iron, aluminum, and manganese

The amounts of solid-phase Fe, Al, and Mn for each of the eight sites are shown in Table 3.3.4 and the means of the eight sites are shown in Table 3.3.5. The mean concentration of Mn in the metal-organic complex, easily reducible metal oxide, and H_2O_2 extractable organic fractions of the soil decreased significantly with long-term cultivation. However, there was a slight significant increase in the concentration of Mn in the amorphous mineral colloid and crystalline metal oxide fractions. The mean concentrations of both Fe and Al in the metal-organic complex and easily reducible metal oxide fractions increased significantly as a result of long-term cultivation, but decreased significantly in the H_2O_2 extractable organic fraction. The mean amount of Fe and Al in the amorphous mineral colloid and crystalline metal oxide fractions increased as a result of long-term cultivation for the soils in this study, but the increase was not statistically significant.

It is possible that increased weathering of the soil particles as a result of cultivation will result in the breakdown of primary minerals and the subsequent release into solution of metals such as Mn, Fe, and Al. The released metals would become associated with the different solid-phase soil fractions that are operationally defined by the sequential extraction scheme. However, while increased weathering as a result of long-term cultivation should increase the metal content of most of the solid-phase fractions, an increase in the metal content of the H_2O_2 extractable organic fraction would not be expected since this fraction itself degrades with cultivation (Table 3.2.2) and would therefore release metals into solution

Table 3.3.4. Impact of long-term cultivation on the Mn, Al, and Fe in the sequentially extracted fractions, and the cadmium availability index of the whole soil for the individual virgin (V) and cultivated (C) sites.

		Site							
		1	2	3	4	5	6	7	8
Metal-organic complex-									
bound Mn (mg kg ⁻¹):	V	102.0	117.0	193.0	136.0	160.0	170.0	195.0	162.0
	C	90.9	93.7	85.5	71.8	58.7	63.6	126.0	137.0
Easily reducible metal oxide-									
bound Mn (mg kg ⁻¹):	V	113.0	136.0	134.0	119.0	145.0	207.0	161.0	124.0
	C	138.0	134.0	102.0	112.0	122.0	142.0	143.0	108.0
H₂O₂ extractable organic-									
bound Mn (mg kg ⁻¹):	V	138.0	204.0	179.0	134.0	191.0	171.0	209.0	175.0
	C	118.0	137.0	138.0	119.0	115.0	126.0	98.8	140.0
Amorphous mineral colloid-									
bound Mn (mg kg ⁻¹):	V	5.35	9.81	8.51	12.20	13.20	10.50	6.97	10.50
	C	6.50	9.35	13.70	16.80	14.80	11.00	7.34	17.40
Crystalline metal oxide-									
bound Mn (mg kg ⁻¹):	V	26.8	29.5	27.9	28.6	24.8	20.0	18.4	25.1
	C	34.7	27.9	32.2	29.6	28.7	29.9	24.2	26.4
Metal-organic complex-									
bound Al (mg kg ⁻¹):	V	2050	2500	2680	3270	2740	1530	1020	1410
	C	2060	2780	4990	3330	3630	3410	1140	2180
Easily reducible metal oxide-									
bound Al (mg kg ⁻¹):	V	160	188	148	172	153	164	170	189
	C	206	206	201	229	235	222	172	159

Table 3.3.4 continued

		Site							
		1	2	3	4	5	6	7	8
H ₂ O ₂ extractable organic-									
bound Al (mg kg ⁻¹):	V	2450	2140	2250	1800	2110	1660	1320	1670
	C	1500	1880	1850	1910	1620	1460	1050	1500
Amorphous mineral colloid-									
bound Al (mg kg ⁻¹):	V	309	360	402	361	617	455	261	388
	C	306	483	494	601	551	337	243	396
Crystalline metal oxide-									
bound Al (mg kg ⁻¹):	V	2200	2180	2210	1950	1880	1820	1230	1680
	C	2080	2290	2240	2150	1840	1930	1450	1730
Metal-organic complex-									
bound Fe (mg kg ⁻¹):	V	1690	2070	2140	2230	2270	1490	1130	1390
	C	1430	2260	3360	2680	3030	2720	1120	2030
Easily reducible metal oxide-									
bound Fe (mg kg ⁻¹):	V	36.5	42.0	43.2	41.0	40.8	47.0	65.3	56.8
	C	57.3	53.8	48.1	57.8	72.6	80.6	52.1	44.0
H ₂ O ₂ extractable organic-									
bound Fe (mg kg ⁻¹):	V	1550	1820	1980	1390	1800	1510	1570	1850
	C	1110	1540	1260	1300	1150	1040	1070	1850
Amorphous mineral colloid-									
bound Fe (mg kg ⁻¹):	V	1150	1360	1760	1470	1690	1370	1120	1930
	C	1270	1870	1990	1960	1820	1520	1200	1660
Crystalline metal oxide-									
bound Fe (mg kg ⁻¹):	V	6940	7080	6920	6230	6440	5550	4500	6460
	C	6970	7020	7400	7080	6780	6620	5500	6100

Table 3.3.4 continued

		Site							
		1	2	3	4	5	6	7	8
Cadmium availability index									
(mg kg ⁻¹):	V	0.072	0.104	0.129	0.124	0.103	0.041	0.071	0.088
	C	0.045	0.061	0.142	0.076	0.063	0.043	0.022	0.092

as it degrades. This reasoning seems to hold true for Fe and Al, since their mean content increases for all of the solid-phase fractions of the soil except for the H₂O₂ extractable organic fraction (Table 3.3.5). According to this reasoning the Mn content of the solid-phase fractions should follow the same pattern. However, the mean Mn content not only decreased with long-term cultivation in the H₂O₂ extractable organic fraction, but also decreased in the metal-organic complex and easily reducible metal oxide fractions (Table 3.3.5). It is possible that the Mn decrease in these fractions is due to uptake by crops. Both Fe and Mn are required nutrients for plants and the average concentration of plant tissue Fe is 100 mg kg⁻¹ and that of Mn is 50 mg kg⁻¹ (Tisdale et al., 1993). Therefore, it would seem that Fe would be more susceptible to depletion in some of the solid-phase fractions than Mn. However, the soil content of Mn ranges from 20 to 3000 mg kg⁻¹ while that of Fe ranges from 7000 mg kg⁻¹ to 550000 mg kg⁻¹ (Tisdale et al., 1993). Therefore, weathering of the soil primary minerals may release more Fe and less Mn than is removed by crops. This reasoning is backed up by the fact that the total free Mn in this study decreased significantly with long-term cultivation while the total Fe and Al increased, although not significantly (Table 3.3.5).

Table 3.3.5. Mean impact of long-term cultivation on the concentrations of the Mn, Al, and Fe in the sequentially extracted fractions, and the cadmium availability index of the whole soil.

		Virgin soils (mg kg ⁻¹)	Cultivated soils (mg kg ⁻¹)
Metal-organic complex-bound:	Mn	154.0	91.0 ^{z****}
	Al	2150	2940 ^z
	Fe	1800	2330 ^z
Easily reducible metal oxide-bound:	Mn	142	125 ^z
	Al	168	204 ^{z****}
	Fe	46.7	58.3 ^{z**}
H ₂ O ₂ extractable organic-bound:	Mn	175	124 ^{z****}
	Al	1930	1590 ^{z**}
	Fe	1680	1290 ^{z****}
Amorphous mineral colloid-bound:	Mn	9.63	12.10 ^z
	Al	394	426 ^y
	Fe	1480	1660 ^y
Crystalline metal oxide-bound:	Mn	25.1	29.2 ^{z***}
	Al	1900	1960 ^y
	Fe	6260	6690 ^y
Total from all fractions:	Mn	506.4	381.3 ^{z****}
	Al	6531	7126 ^y
	Fe	11276	12025 ^y
CAI of the whole soil		0.091	0.068 ^z

^z Significantly different from virgin soils at * $\alpha = 0.10$, ** $\alpha = 0.05$, *** $\alpha = 0.025$, **** $\alpha = 0.005$.

^y No significant difference from the virgin soils at $\alpha = 0.10$.

The only study in the literature that addresses the change due to long-term cultivation in Mn, Fe, and Al of different solid-phase fractions of the soil, excluding primary minerals, is the work done by Blank and Fosberg (1989). They used ammonium oxalate and dithionite-citrate-bicarbonate (DCB) to extract Mn, Fe, and Al from virgin and adjacent cultivated soils. They reported that long-term cultivation decreased Mn and Al and increased Fe in both the ammonium oxalate-extractable and the DCB-extractable fractions of A horizon soil. Blank and Fosberg (1989) were working on the assumption that ammonium oxalate extracts amorphous metal oxides and that DCB extracts crystalline metal oxides. However, it has been shown that ammonium oxalate will extract not only amorphous metal oxides but will also extract some crystalline metal oxides and metal-organic complexes, and that DCB extracts amorphous and varying proportions of crystalline metal oxides and some metal-organic complexes (McKeague et al., 1971). Since they used the two extractants separately on whole soil samples, it is certain that the ammonium oxalate removed more than just amorphous metal oxides, and the DCB removed more than just crystalline metal oxides. Therefore, their results cannot be meaningfully compared with the data obtained in this present study.

3.3.3.3 Relationships between the solid-phase species of soil cadmium, iron, aluminum, and manganese, and the cadmium availability index

Table 3.3.6 shows the results of correlation analysis between the CAI and the solid-phase Cd species. In the virgin soils only two of the solid-phase species are statistically significantly correlated with the CAI: exchangeable Cd ($r = 0.93$, $P = 9.64 \times 10^{-4}$) and easily

reducible metal oxide-bound Cd ($r = -0.88$, $P = 4.10 \times 10^{-3}$). Exchangeable Cd should be related to phytoavailable Cd since it is loosely bound by electrostatic attraction, and the negative correlation between easily reducible metal oxide-bound Cd and the CAI suggests that this species of Cd is bound so strongly to the metal oxides in this fraction that it is not phytoavailable. Although not statistically significant, the correlations between the CAI and the metal-organic complex-bound Cd ($r = 0.58$, $P = 1.36 \times 10^{-1}$) and the crystalline metal oxide-bound Cd ($r = 0.55$, $P = 1.62 \times 10^{-1}$) suggests that some phytoavailable Cd exists as these solid-phase species in the virgin soils.

In the cultivated soils three species of Cd show a statistically significant positive correlation with the CAI: exchangeable Cd ($r = 0.95$, $P = 2.31 \times 10^{-4}$), metal-organic complex-bound Cd ($r = 0.71$, $P = 4.93 \times 10^{-2}$), and crystalline metal oxide-bound Cd ($r = 0.86$, $P = 5.78 \times 10^{-3}$) (Table 3.3.6). The positive correlation between the CAI and exchangeable Cd is expected, but it is not so easy to explain the increase with long-term cultivation in the positive correlations between the CAI and the metal-organic complex-bound Cd and the crystalline metal oxide-bound Cd. However, each of these two species of Cd can be bound to different metal oxides: Mn, Al, and Fe oxides (Table 3.3.5). It is possible that the Cd in these fractions is relatively strongly bound to Mn oxides as a result of multiple coordination in the tunnel structures of many Mn oxides. As well, the Cd in these fractions might be relatively weakly bound to Fe and Al oxides, since the valence:coordination number ratio indicates that both Fe and Al oxides should bind Cd with approximately the same strength (section 2.2.3.3) and the log stability constant of the Cd-Fe oxide complex is relatively small at 0.47 (Dzombak and Morel, 1990). If Cd is bound strongly to Mn oxides and weakly to Fe and Al oxides, then the increase with long-term cultivation in the positive correlation coefficient between the metal-organic complex-bound Cd and the CAI would

make sense since there is a decrease in Mn and an increase in Al and Fe in this fraction with long-term cultivation (Table 3.3.5). This reasoning also offers an explanation for the increase with long-term cultivation in the positive correlation coefficient between the CAI and crystalline metal oxide-bound Cd since there is a relatively large increase in Fe and Al and only a very small increase in Mn in this fraction (Table 3.3.5).

Table 3.3.6. Correlations between the cadmium availability index (mg kg^{-1}) and the solid-phase soil Cd species (mg kg^{-1}).

Correlation	Virgin soils		Cultivated soils	
	r	P	r	P
CAI ^z and:				
Exchangeable Cd	0.93	9.64×10^{-4}	0.95	2.31×10^{-4}
Metal-organic complex-bound Cd	0.58	1.36×10^{-1}	0.71	4.93×10^{-2}
Easily reducible metal oxide-bound Cd	-0.88	4.10×10^{-3}	0.18	6.61×10^{-1}
H ₂ O ₂ extractable organic-bound Cd	0.16	7.05×10^{-1}	0.45	2.62×10^{-1}
Crystalline metal oxide-bound Cd	0.55	1.62×10^{-1}	0.86	5.78×10^{-3}

^z Cadmium availability index.

Another interesting change with long-term cultivation is the disappearance of the negative correlation between the CAI and easily reducible metal oxide-bound Cd (Table 3.3.6). However, again, if it is assumed that Cd is bound relatively strongly to Mn oxides and relatively weakly to Al and Fe oxides, then the disappearance of the negative correlation makes sense because the Mn in this fraction decreased and Al and Fe in this fraction increased with long-term cultivation (Table 3.3.5).

The interpretation of the data so far suggests that Cd bound to Mn oxides is relatively non-phytoavailable and that the Cd bound to Al and Fe oxides is relatively phytoavailable. However, in order to establish a firm relationship between phytoavailable Cd and Mn, Al, and Fe oxides, the amount of phytoavailable Cd and the amount of Fe, Al, and Mn within each sequential fraction must be known. The amount of phytoavailable Cd in each sequential fraction is not known, however, there is an indicator of the relative phytoavailability of the Cd in each sequential fraction. The indicator is the correlation coefficient between the CAI and the amount of Cd in each of the sequential fractions (Table 3.3.6). For example, the correlation coefficient between the CAI and the Cd in the easily reducible metal oxide-bound fraction in the virgin soils is -0.88 which suggests that the Cd within this fraction is relatively non-phytoavailable while that for the crystalline metal oxide-bound fraction in the cultivated soils is 0.86 which suggests that the Cd in this fraction is relatively phytoavailable. Performing a correlation between the indicator of the relative phytoavailability of the Cd within each of the eight sequential fractions that contain Cd, Fe, Al, and Mn (metal-organic complex, easily reducible metal oxide, H_2O_2 extractable organic, and crystalline metal oxide fractions of both the virgin and cultivated soils) and the Fe, Al, and Mn within each of the eight fractions could give more information on the effect of Fe, Al, and Mn on the phytoavailability of Cd.

The results of the correlation analysis (Table 3.3.7) further strengthen the suggestion that Cd associated with Mn is relatively non-phytoavailable while that associated with Fe and Al is relatively phytoavailable. The negative correlation coefficient with Mn, although not statistically significant, suggests that the relative phytoavailability of Cd decreases as the Mn

content increases, and the significant positive correlation coefficients with Fe and Al indicate that the relative phytoavailability of Cd increases as the Fe and Al content increases.

Table 3.3.7. Correlations between the indicator of the relative phytoavailability of each solid-phase Cd species and the mean value of Mn, Fe, and Al associated with each solid-phase Cd species.

Correlation	r	P
Relative phytoavailability indicator ^z of Cd species and associated Mn ^y	-0.50	2.07 x 10 ⁻¹
Relative phytoavailability indicator of Cd species and associated Fe	0.63	9.59 x 10 ⁻²
Relative phytoavailability indicator of Cd species and associated Al	0.77	2.66 x 10 ⁻²
Relative phytoavailability indicator of Cd species and associated Fe + Al	0.74	3.51 x 10 ⁻²

^z The correlation coefficient between the CAI and the amount of operationally defined solid-phase Cd species (mg kg⁻¹).

^y The amount of metal (mg kg⁻¹) extracted with the operationally defined solid-phase Cd species.

3.3.4 Summary and conclusions

The species of solid-phase Cd found in both the virgin and cultivated Orthic Chernozemic soils used in this study and the order of their mean relative abundance were: metal-organic complex-bound > easily reducible metal oxide-bound > H₂O₂ extractable organic-bound > crystalline metal oxide-bound > exchangeable > amorphous mineral colloid-

bound and residual. The only solid-phase Cd species that changed significantly with long-term cultivation were the metal-organic complex-bound Cd and the H_2O_2 extractable organic-bound Cd, both of which significantly decreased. This is attributed to the fact that both of these species contain organic matter, and the organic matter of the soils decreased by more than half during the years of cultivation. In the virgin soils the CAI had a significant positive correlation with exchangeable Cd ($r = 0.93$, $P = 9.64 \times 10^{-4}$), a significant negative correlation with easily reducible metal oxide-bound Cd ($r = -0.88$, $P = 4.10 \times 10^{-3}$), and a slight positive relationship with metal-organic complex-bound Cd and crystalline metal oxide-bound Cd. In the cultivated soils the CAI had a significant positive correlation with exchangeable Cd ($r = 0.95$, $P = 2.31 \times 10^{-4}$), metal-organic complex-bound Cd ($r = 0.71$, $P = 4.93 \times 10^{-2}$), and crystalline metal oxide-bound Cd ($r = 0.86$, $P = 5.78 \times 10^{-3}$). The above results combined with the quantity of Mn, Fe, and Al associated with each solid-phase Cd species suggests that solid-phase Cd bound to Mn oxides may be relatively less phytoavailable than the solid-phase Cd bound to Al and Fe oxides.

3.4 Impact of Long-term Cultivation on the Past and Future Profile Distribution of Soil Cadmium

3.4.1 Background

Typically, uncontaminated soils have Cd concentrations of $< 1 \text{ mg kg}^{-1}$ (Jackson and Alloway, 1992). Although it is well known that there is not any significant correlation between total soil Cd and phytoavailable soil Cd in uncontaminated agricultural soils (Gavi et al., 1997), several studies have shown that a positive relationship exists between total soil Cd and plant uptake of Cd in soils that have unnaturally high levels of Cd (Merry et al., 1981; Chumbley and Unwin, 1982; Sillanpaa and Jansson, 1992). Since some phosphate fertilizers currently being used in the Canadian prairies have relatively high concentrations of Cd, for example monoammonium phosphate fertilizer derived from Idaho phosphate ore has $144 \text{ mg Cd kg}^{-1}$ fertilizer (Krishnamurti et al., 1996), it is possible that the Cd content in the A horizons of agricultural soils that have applications of high Cd content phosphate fertilizers may eventually increase to levels which will result in large increases in phytoavailable soil Cd in the A horizon. It has been estimated that approximately 83 % of the soil Cd taken up by grain comes from the A horizon (Christensen and Tjell, 1984) so a large increase in A horizon Cd could result in a large increase in the concentration of Cd in our grain crops.

However, many factors other than phosphate fertilizer application can affect the amount of total Cd in the A horizons of soils (Figure 2.5): 1) Cd can be phyto-pumped from

the lower horizons to the surface horizon, 2) Cd can be leached from the surface horizon to lower horizons, 3) Cd can be removed from the surface horizon by soil erosion, 4) Cd can be added to the surface horizon with the incorporation of B horizon soil into the A horizon as the plough layer moves deeper into the soil profile after soil has been eroded from the surface of the A horizon, 5) Cd can be removed from the A and B horizons by crop uptake and harvest, and 6) Cd can be added to the A horizon through atmospheric deposition. Of the factors that add Cd to Canadian prairie soils, the addition of Cd with phosphate fertilizer application is the only factor that can be manipulated in the farming practices to reduce the amount of Cd entering Canadian prairie soil. Whether or not control needs to be exercised on this factor is dependent on whether or not the combined effect of all five factors results in a net increase in the amount of A horizon Cd.

There have been no published studies on the effect of long-term cultivation on the profile distribution of soil Cd. Studies estimating the rate of change in soil Cd in surface soils only have been done for soil in the Netherlands (De Boo, 1990), southern Australia (Merry and Tiller, 1991), and Norway (Jeng and Singh, 1995). However, all of these studies neglected the effects of soil erosion, incorporation of B horizon soil into the A horizon as the plough layer moves deeper into the soil profile as a result of erosion, and phyto-pumping of Cd from the B horizon to the A horizon (Figure 2.5). Also, these studies used current average application rates of phosphate fertilizer and Cd contents of phosphate fertilizer used in the country or region. They did not consider that both of these factors may be much higher in some parts of the agricultural regions studied or that in general both of these factors may increase over time. Therefore, there were two objectives for this study: 1) to determine how

long-term cultivation in the past has affected the profile distribution of soil Cd in Orthic Chernozemic soils in southern Saskatchewan, Canada, and 2) to provide an estimate of what the profile distribution of Cd would be for these soils in 100 years based on a durum wheat system under annual cropping and applications of low, medium, and high Cd-bearing phosphate fertilizers.

3.4.2 Materials and methods

3.4.2.1 Past change in the cadmium soil profile distribution

The bulk density samples were taken in triplicate from each genetic horizon at each site, and then weighed after drying overnight in an oven at 105 ° C. All of the other samples were air dried, crushed to <2 mm using a marble roller and polyethylene sieve, and then homogenized. The pH of each sample was determined in duplicate with the saturated paste method (McLean, 1982). A sub-sample of each soil sample was then crushed further to <0.15 mm with an agate mortar and pestle and passed through a stainless steel sieve, and analysed in duplicate for total Cd by the method of Krishnamurti et al. (1994). For all of the results, the first uncertain decimal place was dropped and the number of significant figures were determined by the method used by Gillespie et al. (1989). All of the results are presented on an oven-dried weight basis (overnight at 105 ° C).

The difference between the amount of Cd in the cultivated horizons and that in the virgin horizons was taken as representing the past effects of long-term cultivation. The amount of Cd in each horizon (mg m^{-2} of horizon) was calculated with the following

equation:

$$HCd = D_b \times HT \times [Cd] \quad (3.1)$$

Where:

HCd = Mass of Cd in the horizon ($mg\ m^{-2}$).

D_b = Bulk density of the horizon ($kg\ m^{-3}$).

HT = Horizon thickness (m).

$[Cd]$ = Horizon Cd concentration ($mg\ kg^{-1}$).

3.4.2.2 Future change in the cadmium soil profile distribution

The future change in the cadmium soil profile distribution was estimated for each of the eight cultivated soils used in this study, and then the means of the eight values were calculated. It is assumed that these Orthic Chernozemic soils will undergo annual tilling, cropping of durum wheat, and applications of phosphate fertilizer with three different concentrations of Cd. The following factors were considered (Figure 2.5): 1) addition of Cd to the A horizon with phosphate fertilizer application, 2) removal of Cd from the A and B horizons by crop uptake and harvest, 3) movement of Cd from the lower horizons to the A horizon by phyto-pumping, 4) movement of Cd from the A horizon to the lower horizons by leaching, 5) atmospheric deposition of Cd onto the A horizon, 6) removal of Cd from the A horizon with the erosion of topsoil, and 7) addition of Cd to the A horizon with the incorporation of the upper part of the B horizon as the plough layer moves deeper into the soil profile as a result of soil erosion.

3.4.2.2.1 A horizon cadmium in 100 years

To estimate the amount of A horizon Cd that the cultivated soils in this study would contain in 100 years, it was necessary to determine the rates of change in A horizon Cd as a result of each of the factors which can influence the amount of A horizon Cd. The rate equations for each of the factors are in Table 3.4.1. With the use of the equations and a computer spreadsheet program, an estimate for the amount of A horizon Cd (mg Cd m^{-2}) that the soils in this study would contain in 100 years was obtained by calculating the A horizon Cd content for each year in sequence:

$$A_n = (A_{n-1} + R6) - (A_{n-1} \times FE) \quad (3.2)$$

Where:

A_n = The amount of A horizon Cd (mg Cd m^{-2}) for any year (n =year) from the year of sampling (1997, = year 0) to 100 years after the year of sampling.

A_{n-1} = The amount of A horizon Cd (mg Cd m^{-2}) in the previous year.

$R6$ = Rate of change in the A horizon Cd ($\pm \text{mg Cd m}^{-2} \text{ year}^{-1}$) due to 6 of the 7 factors that affect the Cd content of the A horizon as determined by Equations 3.4 to 3.9 (Table 3.4.1); the effect of the 7th factor, soil erosion, is taken into account with FE.

FE = Mean fraction of A horizon Cd removed each year with soil erosion, which is assumed to be equal to the mean fraction of A horizon soil eroded each year (Table 3.4.2).

After the 100 year A horizon Cd content (mg Cd m^{-2}) was determined the 100 year A horizon Cd concentration (mg kg^{-1}) was calculated with the following equation:

$$[\text{ACd}]_{100} = A_{100} / (D_b \times \text{HT}) \quad (3.3)$$

Where:

$[\text{ACd}]_{100}$ = A horizon Cd concentration (mg kg^{-1}) in 100 years.

A_{100} = Estimated mass of A horizon Cd (mg m^{-2}) in 100 years (Equation 3.2).

D_b = Bulk density of the A horizon (kg m^{-3}). It is assumed to be the same as the 1997 value.

HT = A horizon thickness (m). It is assumed to be the same as the 1997 value.

The present study used $45 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1} \text{ yr}^{-1}$ (Equation 3.4, Table 3.4.1) which is the maximum recommended application rate of P for Saskatchewan (Guide to Farm Practice in Saskatchewan, 1987) and assumed Cd concentrations of 18.2, 109.1 and $261.8 \text{ mg Cd kg}^{-1} \text{ P}_2\text{O}_5$, which corresponds to the use of monoammonium phosphate fertilizers derived from the phosphate ores from Florida (Alloway and Steinnes, 1999), Togo (Potash & Phosphate Institute/Potash & Phosphate Institute of Canada, Foundation for Agronomic Research, 1998), and Idaho (Krishnamurti et al., 1996), respectively. The seven year average (1991-1997) concentration of Cd in the durum wheat grain produced in Saskatchewan (0.111 mg kg^{-1}) (personal communication from E. Gawalko, Canadian Grain Commission, 1999) and the 10 year average (1987-1996) durum wheat yield in Saskatchewan ($1880 \text{ kg ha}^{-1} \text{ yr}^{-1}$)

Table 3.4.1. Equations used for estimating the rates of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) in a durum wheat/Chernozemic soil system under annual cropping due to the individual factors involved.

Factor	Equation ²	Equation
Phosphate fertilizer application	$\text{RF} = (\text{A} \times \text{B})/\text{C}$	3.4
Durum crop uptake and harvest	$\text{RC} = (\text{D} \times \text{E} \times \text{F})/\text{C}$	3.5
Phyto-pumping from B to A horizon	$\text{RP} = (\text{D} \times \text{E} \times \text{G} \times \text{H})/\text{C}$	3.6
Atmospheric deposition	$\text{RA} = (\text{I} + \text{J})/2$	3.7
Leaching from A to B horizon	$\text{RL} = \text{RP}/2$	3.8
Incorporation of B horizon into A horizon	$\text{RI} = [\text{K} - \text{L} - (\text{M} \times 100)]/100$	3.9
Soil erosion	$\text{RE} = (\text{O} - \text{P} - \text{Q})/100$	3.10

² Explanation of symbols:

RF = The rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) due to phosphate fertilizer application.

RC = The rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) as a result of crop uptake and harvest of durum grain.

RP = Rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) due to phyto-pumping.

RA = Rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) due to atmospheric deposition.

RL = Rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) due to leaching from the A horizon.

RI = Rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) due to incorporation of B horizon soil, which is equal to the rate of change in B horizon Cd as a result

of incorporation of B horizon into the A horizon.

RE = The rate of change in A horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) as a result of soil erosion.

A = The Cd concentration in the phosphate fertilizer ($\text{mg Cd kg}^{-1} \text{ P}_2\text{O}_5$).

B = The phosphate fertilizer application rate ($\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \text{ yr}^{-1}$).

C = The m^2 of soil surface in one hectare ($10000 \text{ m}^2 \text{ ha}^{-1}$).

D = The Cd concentration of the durum grain (mg kg^{-1}).

E = The durum wheat yield ($\text{kg ha}^{-1} \text{ yr}^{-1}$).

F = The fraction of grain Cd that comes from the A horizon.

G = Ratio of Cd in durum straw to Cd in durum grain.

H = The fraction of the straw Cd that comes from the B horizon.

I = The rate of atmospheric deposition of Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) in Greenland.

J = The lowest rate of atmospheric deposition of Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) in rural Europe.

K = The amount of B horizon Cd (mg Cd m^{-2}) in 1997 (Table 3.4.5).

L = The estimated amount of B horizon Cd (mg Cd m^{-2}) in 2097 (Equation 3.11, section 3.4.2.2.2).

M = The rate of change in B horizon Cd ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) as a result of crop uptake (straw and grain) and leaching (Equation 3.12, section 3.4.2.2.2).

O = A horizon Cd (mg Cd m^{-2}) at the start of the 100 year period (Table 3.4.5).

P = A horizon Cd in 100 years (mg Cd m^{-2}) (from Equation 3.2).

Q = Net change in A horizon Cd in 100 years that is attributed to all of the factors involved except soil erosion ($\pm \text{mg Cd m}^{-2}$).

Table 3.4.2. Estimated rates of soil erosion ($\text{kg m}^{-2} \text{yr}^{-1}$) and fraction of A horizon soil removed each year for the cultivated soils.

Site	Mass of Ap-horizon soil (kg m^{-2})	Rate of soil erosion ($\text{kg m}^{-2} \text{yr}^{-1}$) ^z	Fraction of A horizon eroded/year
1	136.8 ^y	0.13 ^x	0.0010
2	134.2	0.13	0.0010
3	140.4	0.30 ^w	0.0021
4	123.2	0.13	0.0011
5	130.0	0.13	0.0010
6	133.1	0.30	0.0022
7	132.0	0.13	0.0010
8	109.0	0.30	0.0027
mean	128.7	0.19	0.0015

^z The rates of erosion are arbitrarily set at 1/3 of those determined by Martz and de Jong (1987) because the model in this study is assuming a continuous cropping system under annual tillage which should have much less erosion than the soils investigated by Martz and de Jong (1987) which were under a crop/fallow system.

^y Taken to four significant figures only for the purpose of calculating the fraction eroded.

^x 0.13 $\text{kg m}^{-2} \text{yr}^{-1}$ represents the net rate of soil erosion for a mid-slope position.

^w 0.30 $\text{kg m}^{-2} \text{yr}^{-1}$ represents the net rate of soil erosion for level topography.

(Agricultural Statistics, 1997) were adopted for this study. The fraction of the grain and straw Cd that comes from the A horizon and the B horizon were set at 0.83 and 0.17, respectively (Christensen and Tjell, 1984). It was assumed that durum straw contains 3.05

times more Cd than durum grain (Brown, 1997).

The rate of change in the mass of A horizon Cd as a result of atmospheric deposition onto the surface of the A horizon ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) (Equation 3.7, Table 3.4.1) was arbitrarily assumed to be equal to the average value between the rate of deposition for Greenland ($0.006 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$) and the lowest recorded rate for rural Europe ($0.06 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$) (Jackson and Alloway, 1992), since Saskatchewan is closer to major industry than Greenland and farther from major industry than rural Europe. The average of the two values is $0.033 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$. The use of this figure is supported by some data from a study by Shewchuk (1982) who sampled the six month winter snowfall at eight sites in central Saskatchewan that were south of the precambrium shield to just north of the southern treeline. The average amount of Cd deposited was $0.0190 \text{ mg Cd m}^{-2}$ which when multiplied by two gives an approximate rate of atmospheric deposition of Cd of $0.038 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$. This rate is just slightly higher than the rate of $0.033 \text{ mg Cd m}^{-2} \text{ yr}^{-1}$ that is used in this study.

The rate of change in the mass of A horizon Cd as a result of leaching from the A horizon to the B horizon ($\text{mg Cd m}^{-2} \text{ yr}^{-1}$) was estimated by examining the factors that affect Cd distribution in the virgin soils, namely, atmospheric deposition, phyto-pumping, and leaching. It is reasonable to assume that atmospheric deposition of Cd onto southern Saskatchewan soils has been insignificant for most of the years since the end of the last glacial period, because point sources of Cd emissions to the atmosphere in or near Saskatchewan did not exist until the latter part of the 20th century. Therefore, the only factor, besides leaching, that has had a significant effect on the amount of A horizon Cd in the virgin soils in the past is phyto-pumping (Figure 2.5). Since for the soils in this study, the

concentration of A horizon Cd in the virgin soils is substantially higher than the concentration of B horizon Cd in the virgin soils (Table 3.4.5), the rate of change as a result of leaching has to be somewhere between zero and a rate less than the rate of change as a result of phyto-pumping. For the purposes of this calculation, the rate of change in A horizon Cd due to leaching (Equation 3.8, Table 3.4.1) was set at ½ the rate due to phyto-pumping.

3.4.2.2.2 B horizon cadmium in 100 years

An estimate for the amount of B horizon Cd that the cultivated soils in this study would contain in 100 years was determined with the following equation:

$$B_n = [B_{n-1} - M] - [B_{n-1} \{SE/(BS - (n-1)SE)\}] \quad (3.11)$$

Where:

B_n = The amount of B horizon Cd (mg Cd m^{-2}) for any year (n =year) from the year of sampling (1997, = year 0) to 100 years after the year of sampling.

B_{n-1} = The amount of B horizon Cd (mg Cd m^{-2}) in the previous year.

SE = The amount of soil (kg m^{-2}) incorporated into the A horizon from the B horizon each year. It is assumed to be the same as the amount of soil eroded from the A horizon each year (Table 3.4.2) since it is assumed that the plough layer, which is the cultivated A horizon, remains a constant thickness, and only moves deeper into the soil profile until the soil that was eroded from the A horizon is replaced by B horizon soil.

BS = The amount of B horizon soil (kg m^{-2}) for the year of sampling (1997), which is equal to horizon thickness x horizon bulk density (Table 3.4.5).

M = The change in the amount of B horizon Cd (mg Cd m^{-2}) each year as a result of crop uptake and leaching:

$$M = RL - (SB + GB) \quad (3.12)$$

Where:

RL = The change in the amount of B horizon Cd (mg Cd m^{-2}) each year as a result of leaching of Cd from the A horizon to the B horizon (Equation 3.8).

SB = The change in the amount of B horizon Cd (mg Cd m^{-2}) each year as a result of Cd uptake by straw (Equation 3.6).

GB = The change in the amount of B horizon Cd (mg Cd m^{-2}) each year as a result of Cd uptake by grain (Equation 3.5 x $(0.17/0.83)$).

After the 100 year B horizon Cd content (mg Cd m^{-2}) was determined, the 100 year B horizon Cd concentration (mg kg^{-1}) was calculated with the following equation:

$$[BCd]_{100} = B_{100}/(BHT \times Db) \quad (3.13)$$

Where:

$[BCd]_{100}$ = B horizon Cd concentration (mg kg^{-1}) in 100 years.

B_{100} = Estimated B horizon Cd content (mg Cd m^{-2}) in 100 years (Equation 3.11).

D_b = Bulk density of the B horizon (kg m^{-3}). It is assumed to be the same as the 1997 value.

BHT = B horizon thickness in 100 years which is calculated with the following equation:

$$\text{BHT} = (\text{SS} - \text{SR}) / D_b \quad (3.14)$$

Where:

SS = Mass of the B horizon soil (kg m^{-2}) in 1997.

SR = Mass of B horizon soil removed (kg m^{-2}) in 100 years calculated using the rates of erosion in Table 3.4.2.

D_b = Bulk density of the B horizon (kg m^{-3}). It is assumed to be the same as the 1997 value.

3.4.3 Results and discussion

3.4.3.1 Past change in the cadmium soil profile distribution

The results for the individual sites for selected soil profile properties and Cd soil profile properties are shown in Tables 3.4.3 and 3.4.4, respectively. For both the virgin and the cultivated soils, the mean concentration of A horizon Cd was higher than that of the unaltered parent material while the mean concentration of B horizon Cd was lower than that

of the unaltered parent material (Table 3.4.5). These changes in the concentration of Cd in the A and B horizons from the concentration of Cd in the unaltered parent material are attributed to the effects of phyto-pumping of Cd from the B horizons to the A horizons since the deposition of the parent materials.

The mean concentration of A horizon Cd decreased significantly as a result of long-term cultivation (Table 3.4.5). It appears that in the past the effects of soil erosion, leaching, and crop uptake and harvest on the concentration of A horizon Cd were greater than the effects of those factors that added Cd to the A horizon (Figure 2.5). While the Cd concentration in the A horizon has decreased as a result of long-term cultivation, there is no significant difference between the virgin and cultivated B horizon mean Cd concentrations (Table 3.4.5). However, it is probable that the concentration of Cd in the B horizons did actually decrease during the years of cultivation, since phyto-pumping of Cd from the B horizon to the A horizon would have continued during the years of cultivation in both the virgin and cultivated soils.

Long-term cultivation has resulted in a decrease although not statistically significant, in the mean mass of Cd in both the A and B horizons of the Orthic Chernozemic soils used in this study (Table 3.4.5). The lack of statistical significance for the decrease in solum Cd mass is apparently related to the fact that two of the cultivated sites had more Cd mass in their A horizons than their virgin counterparts (Table 3.4.4). Sites 3 and 8 show an increase in A horizon Cd mass with long-term cultivation. The increases are possibly the result of 16 years of phosphate fertilizer application at site 3 and 10 years of phosphate fertilizer application at site 8 (Table 3.1.1). If these two sites are excluded there is a statistically

Table 3.4.3. Selected soil profile properties of the individual virgin (V) and cultivated (C) sites.

Site	Horizon		pH		Thickness (m)		Bulk density (kg m ⁻³)		Soil (kg m ⁻²)	
	V	C	V	C	V	C	V	C	V	C
1	Ah	Ap	6.8	7.3	0.13	0.12	990	1140	130	140
	Bm	Bm	7.1	7.9	0.15	0.16	1250	1330	190	210
	Cca	Cca	7.8	8.1	0.24	0.24	1260	1170	300	280
	Ck1	Ck1	8.6	8.2	0.28	0.20	1310	1430	370	290
	Ck2	Ck2	8.4	8.4	nd ²	nd	1370	1470	nd	nd
2	Ah	Ap	6.3	6.8	0.10	0.11	960	1220	100	130
	Bm1	Bm1	6.5	6.7	0.16	0.17	1250	1330	200	230
	Bm2	Bm2	6.7	7.9	0.14	0.15	1290	1270	180	190
	Ck1	Ck1	7.9	8.0	0.22	0.26	1390	1380	310	360
	Ck2	Ck2	8.0	8.0	nd	nd	1540	1460	nd	nd
3	Ah	Ap	6.2	6.0	0.12	0.13	800	1080	100	140
	Bm1	Bm1	6.2	6.4	0.20	0.19	1190	1220	240	230
	Bm2	Bm2	6.7	7.2	0.20	0.12	1240	1170	250	140
	Ck1	Cca	8.0	8.3	0.27	0.17	1210	1170	330	200
	Ck2	Ck1	8.3	8.3	nd	nd	1290	1330	nd	nd
4	Ah	Ap	6.0	6.8	0.10	0.11	960	1120	100	120
	Bm1	Bm1	6.6	6.6	0.16	0.14	1210	1240	190	170
	Bm2	Bm2	7.2	7.0	0.17	0.14	1230	1230	210	170
	Ck1	Ck1	7.9	7.9	nd	nd	1300	1320	nd	nd
5	Ah	Ap	6.2	6.4	0.09	0.10	830	1300	70	130
	Bm	Bm	6.0	6.7	0.16	0.13	1380	1460	220	190

Table 3.4.3 continued

Site	Horizon		pH		Thickness (m)		Bulk density (kg m ⁻³)		Soil (kg m ⁻²)	
	V	C	V	C	V	C	V	C	V	C
6	Ck1	Ck1	7.8	7.9	0.26	0.28	1450	1320	380	370
	Ck2	Ck2	8.2	8.6	nd	nd	1640	1400	nd	nd
	Ah	Ap	7.0	6.6	0.11	0.11	990	1210	110	130
	Bm	Bm	7.1	7.6	0.20	0.12	1230	1380	250	170
	Ck1	Ck1	7.8	8.1	0.26	0.19	1290	1310	340	250
7	Ck2	Ck2	8.0	7.9	nd	nd	1380	1390	nd	nd
	Ah	Ap	6.6	7.7	0.12	0.11	1000	1200	120	130
	AB	AB	6.5	7.7	0.08	0.08	1370	1330	110	110
	Bm1	Bm1	6.8	7.8	0.13	0.11	1320	1380	170	150
	Bm2	Bm2	7.4	7.9	0.11	0.12	1310	1470	140	180
8	Ck1	Ck1	7.9	7.9	0.22	0.23	1390	1460	310	340
	Ck2	Ck2	7.9	7.9	nd	nd	1550	1550	nd	nd
	Ah	Ap	6.2	6.3	0.09	0.10	900	1090	80	110
	Bm	Bm	6.7	6.7	0.22	0.13	1290	1350	280	180
	Ck1	Ck1	7.9	7.7	0.20	0.16	1380	1540	280	250
	Ck2	Ck2	8.5	8.1	0.20	0.24	1410	1390	280	330
	Ck3	Ck3	8.5	8.4	nd	nd	1630	1680	nd	nd

^z Not determined.

significant difference between the mean A horizon Cd mass in the virgin soils and that in the cultivated soils. This decrease is attributed to the combined effects of crop uptake of Cd and soil erosion.

A decrease of the mean Cd mass in the B horizons as a result of long-term cultivation

Table 3.4.4. Cadmium soil profile properties for the individual virgin (V) and cultivated (C) sites.

Site	Horizon		Cd (mg kg ⁻¹)		Cd (mg m ⁻²)	
	V	C	V	C	V	C
1	Ah	Ap	0.338	0.316	44	43
	Bm	Bm	0.230	0.231	43	49
	Cca	Cca	0.253	0.258	76	72
	Ck1	Ck1	0.254	0.257	93	73
	Ck2	Ck2	0.258	0.256	nd ^z	nd
2	Ah	Ap	0.500	0.361	49	49
	Bm1	Bm1	0.189	0.216	38	49
	Bm2	Bm2	0.243	0.283	44	54
	Ck1	Ck1	0.277	0.242	85	87
	Ck2	Ck2	0.243	0.198	nd	nd
3	Ah	Ap	0.567	0.436	52	62
	Bm1	Bm1	0.243	0.194	58	45
	Bm2	Bm2	0.258	0.237	64	33
	Ck1	Cca	0.292	0.360	95	72
	Ck2	Ck1	0.269	0.299	nd	nd
4	Ah	Ap	0.412	0.308	41	38
	Bm1	Bm1	0.218	0.206	42	36
	Bm2	Bm2	0.187	0.170	39	29
	Ck1	Ck1	0.195	0.233	nd	nd
5	Ah	Ap	0.496	0.271	36	33
	Bm	Bm	0.104	0.167	23	32

Table 3.4.4 continued

Site	Horizon		Cd (mg kg ⁻¹)		Cd (mg m ⁻²)	
	V	C	V	C	V	C
6	Ck1	Ck1	0.247	0.262	93	97
	Ck2	Ck2	0.227	0.222	nd	nd
	Ah	Ap	0.314	0.227	34	30
	Bm	Bm	0.166	0.228	41	38
	Ck1	Ck1	0.226	0.259	76	64
7	Ck2	Ck2	0.213	0.215	nd	nd
	Ah	Ap	0.490	0.323	62	44
	AB	AB	0.243	0.266	27	28
	Bm1	Bm1	0.174	0.166	30	25
	Bm2	Bm2	0.171	0.151	25	27
8	Ck1	Ck1	0.235	0.193	72	65
	Ck2	Ck2	0.233	0.231	nd	nd
	Ah	Ap	0.458	0.410	37	45
	Bm	Bm	0.183	0.159	52	28
	Ck1	Ck1	0.226	0.184	63	45
	Ck2	Ck2	0.228	0.227	64	75
	Ck3	Ck3	0.237	0.226	nd	nd

^z Not determined.

(Table 3.4.5) is expected since soil erosion from the surface of the A horizon would indirectly move the plough layer (cultivated A horizon) deeper into the soil profile incorporating B horizon into the A horizon. The B horizon would become thinner with time and would contain less of everything per square metre of horizon including Cd. However,

Table 3.4.5. Effect of long-term cultivation on selected soil properties of the soil profiles
(mean values for the eight sites).

Soil property	Horizon	Virgin	Cultivated
pH ^z	A	6.4 ^{y****}	6.7 ^{y**** x*}
	B	6.7 ^{y****}	7.2 ^{y**** x**}
	Solum	6.6 ^{y****}	7.0 ^{y**** x*}
	Parent material	8.1	8.1
Thickness (m)	A	0.11	0.11 ^w
	B	0.26	0.22 ^w
	Solum	0.37	0.33 ^w
Bulk density (kg m ⁻³)	A	930 ^{y****}	1170 ^{y**** x****}
	B	1270 ^{y****}	1330 ^{y* x*}
	Solum	1170 ^{y****}	1270 ^{y**** x****}
	Parent material	1390	1390
Cd concentration (mg kg ⁻¹)	A	0.447 ^{y****}	0.332 ^{y**** x****}
	B	0.193 ^{y****}	0.202 ^{y**** w}
	Solum	0.251 ^v	0.242 ^{v w}
	Parent material	0.241	0.241
Cd mass (mg m ⁻²)	A	44	43 ^w
	B	66	59 ^w
	Solum	110	102 ^w

^z Mean pH calculated with pH values (not with actual H⁺ activities).

^y Significantly different from the parent material at * $\alpha = 0.10$, **** $\alpha = 0.005$.

^x Significantly different from the virgin value at * $\alpha = 0.10$, ** $\alpha = 0.05$, *** $\alpha = 0.01$,
**** $\alpha = 0.005$.

^w No significant difference from the virgin value at $\alpha = 0.10$.

^v No significant difference from the parent material at $\alpha = 0.10$.

the expected decrease in the thickness of the B horizon as an indirect result of soil erosion would be offset somewhat by soil formation processes. It has been estimated that soil formation worldwide occurs at a rate of $0.1 \text{ kg m}^{-2} \text{ yr}^{-1}$ (Gliessman, 1998). This rate is far below the estimated rates of erosion of 0.40 and $0.89 \text{ kg m}^{-2} \text{ yr}^{-1}$, respectively, for the types of landforms used in this study (Martz and de Jong, 1987). The mean Cd mass in the B horizons did decrease from 66 to 59 mg m^{-2} but the large variability in the B horizon thicknesses (Table 3.4.3) resulted in a large variability in the Cd masses in the B horizons (Table 3.4.4) which kept statistical significance from occurring.

3.4.3.2 Future change in the cadmium soil profile distribution

The calculated rates of change in the amount of A and B horizon Cd in Orthic Chernozemic soil under annual tilling, cropping of durum wheat, and applications of phosphate fertilizer as a result of all the factors involved are shown in Table 3.4.6 and in Figure 3.4.1. The data indicate that the dominant factor adding Cd to the A horizon is phosphate fertilizer application, while the dominant factor removing Cd from the A horizon is soil erosion. The predictions on the profile distribution of soil Cd in 100 years in tilled Orthic Chernozemic soils under annual cropping of durum wheat and applications of low, medium, and high Cd-bearing phosphate fertilizers are shown in Table 3.4.7. The model predicts that the Cd mass in the B horizon will decrease from 59 to 54 mg m^{-2} . Although the decrease is not statistically significant, it is expected since the B horizon soil mass will decrease as the plough layer moves deeper into the soil profile with soil erosion. The Cd concentration in the B horizon is predicted to increase slightly from 0.202 to 0.21 mg kg^{-1} ,

although the increase is not statistically significant. It is interesting to note that the predicted increase in the B horizon Cd concentration seems to be at odds with the predicted decrease in the B horizon Cd mass. However, the concentration is increasing because the soils form two groups with different rates of soil erosion and therefore different rates of B horizon incorporation (Table 3.4.2); the group with the highest rate of soil erosion/B horizon incorporation has the soils with the lowest mean concentration of B horizon Cd (Table 3.4.4). Therefore, with time, the mean concentration of B horizon Cd should increase because lower Cd concentration B horizon soil is being removed from the B horizon at a faster rate than the higher Cd concentration B horizon soil.

The model also predicts that with the application of any of the three phosphate fertilizers there will be a significant increase in both the concentration and the mass of A horizon Cd, although the level of significance with the concentration increase due to applications of Florida fertilizer is relatively low at $\alpha = 0.10$. The predicted increases in both the concentration and mass of Cd in the A horizon soil that has had applications of phosphate fertilizer made from the ore from Togo and Idaho are very large and highly significant (Table 3.4.7). With applications of a phosphate fertilizer made from the ore from Idaho, both the concentration and the total mass of A horizon Cd are predicted to be in 100 years about 3.5 times higher than in 1997. The Cd concentration of 1.18 mg kg^{-1} soil (Table 3.4.7) will have reached the commonly accepted critical region of 1.0 to $3.0 \text{ mg Cd kg}^{-1}$ soil (Tiller et al., 2000). Typically, when the concentration of soil Cd enters this region the crops grown on the soil have unacceptably high levels of Cd (Tiller et al., 2000).

Table 3.4.6. Calculated rates of change in A and B horizon Cd as a result of the various factors involved.

Factor		Rate of change (mg Cd m ⁻² yr ⁻¹)	
		A horizon	B horizon
Phosphate rock-derived fertilizers:	Idaho ^z	+1.180	na ^w
	Togo ^y	+0.491	na
	Florida ^x	+0.082	na
Phyto-pumping		+0.011	-0.011
Atmospheric deposition		+0.033	na
Incorporation of B horizon into A horizon		+0.039	-0.039
Durum grain harvest		-0.017	-0.004
Leaching		-0.005	+0.005
Soil erosion:			
with Idaho derived P fertilizer		-0.149	na
with Togo derived P fertilizer		-0.100	na
with Florida derived P fertilizer		-0.071	na

^z Fertilizer Cd concentration of 144 mg kg⁻¹ (Krishnamurti et al., 1996).

^y Fertilizer Cd concentration of 60 mg kg⁻¹ (Potash & Phosphate Institute/Potash & Phosphate Institute of Canada, Foundation for Agronomic Research, 1998).

^x Fertilizer Cd concentration of 10 mg kg⁻¹ (Alloway and Steinnes, 1999).

^w Not applicable.

There does not seem to have been any published research on the predicted future change in the profile distribution of soil Cd. However, some researchers have attempted to

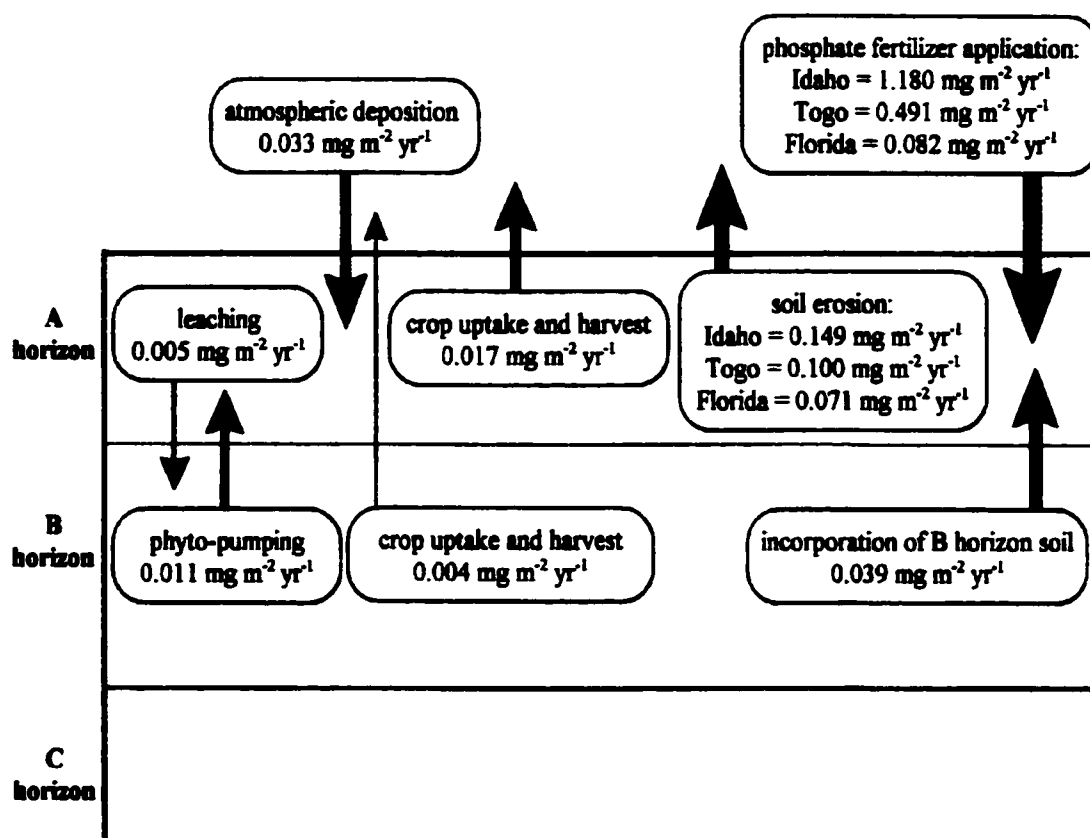


Figure 3.4.1. Flow chart depicting the estimated 100 year mean annual rates of Cd movement into, throughout, and out of a soil profile for all of the factors considered in this study.

predict the current annual rate of change of Cd in surface soil. Studies to predict the change in soil Cd in surface soils have been done for soil in the Netherlands (De Boo, 1990), southern Australia (Merry and Tiller, 1991), and Norway (Jeng and Singh, 1995). All of these studies took into account the effects of leaching, atmospheric deposition, crop uptake and harvest, and application of phosphate fertilizers on the rate of change in surface soil Cd. However, all of these studies neglected the effects of soil erosion, incorporation of B horizon

Table 3.4.7. Predicted 100 year change in the profile distribution of Cd of the Orthic Chernozemic soils studied based on a durum wheat system under annual cropping and applications of low, medium, and high Cd-bearing phosphate fertilizers.

Fertilizer ore source	Year	Cd concentration (mg kg ⁻¹)		Cd mass (mg m ⁻²)	
		A horizon	B horizon	A horizon	B horizon
	1997	0.332	0.202	43	59
Florida ^z	2097	0.39 ^y	0.21 ^x	50 ^w	54 ^x
Togo ^v	2097	0.68 ^u	0.21 ^x	88 ^u	54 ^x
Idaho ^t	2097	1.18 ^s	0.21 ^x	152 ^s	54 ^x

^z Fertilizer Cd concentration of 10 mg kg⁻¹ (Alloway and Steinnes, 1999).

^y Significantly different from the 1997 value at $\alpha = 0.10$.

^x No significant difference from the 1997 value at $\alpha = 0.10$.

^w Significantly different from the 1997 value at $\alpha = 0.05$.

^v Fertilizer Cd concentration of 60 mg kg⁻¹ (Potash & Phosphate Institute/Potash & Phosphate Institute of Canada, Foundation for Agronomic Research, 1998).

^u Significantly different from the Idaho, Florida, and 1997 values at $\alpha = 0.001$.

^t Fertilizer Cd concentration of 144 mg kg⁻¹ (Krishnamurti et al., 1996).

^s Significantly different from the Togo, Florida, and 1997 values at $\alpha = 0.001$.

soil into the A horizon as the plough layer moves deeper into the soil profile as a result of erosion, and phyto-pumping of Cd from the B horizon to the A horizon (Figure 2.5). Also,

these studies used the current average application rates of phosphate fertilizer and Cd contents of phosphate fertilizer used in the country or region. They did not consider that farmers in some parts of the agricultural regions may be applying phosphate fertilizer at much higher rates, or that they may be applying a phosphate fertilizer with a much higher than average Cd concentration, depending on the ore from which the fertilizer was made (Table 2.4). As well, the studies did not consider that the average concentration of Cd in phosphate fertilizer may increase over time as the world's supply of relatively low Cd concentration phosphate ore is consumed or that the amount of phosphate fertilizer used in the world is projected to increase dramatically in the future (Table 2.12).

3.4.4 Summary and conclusions

The mean profile distribution of total Cd was the same for both the virgin and cultivated soils; A horizon Cd > C horizon Cd > B horizon Cd. However, long-term cultivation in the past has resulted in a significant decrease in the concentration of total Cd in the A horizons of the Orthic Chernozemic soils. This is largely attributed to the fact that, in the past, more Cd was removed from the soil by crop uptake and harvest and soil erosion than was added to the soil with the application of phosphate fertilizers; phosphate fertilizer was not applied during the vast majority of years of cultivation at the sites studied (Table 3.1.1). However, with the increased use in the present and future of phosphate fertilizers with relatively high concentrations of Cd, the Cd concentration in the A horizons of these same soils will reach the critical levels that could dramatically increase the amount of phytoavailable Cd in them.

There are no published studies to date that have investigated the effect of long-term cultivation on the profile distribution of soil Cd. There are studies that estimate the rate of change in surface soil Cd at the time of the study (De Boo, 1990; Merry and Tiller, 1991; Jeng and Singh, 1995), but they do not examine all of the factors that can affect the movement of Cd into and out of the surface horizon. Also, these studies use the average phosphate fertilizer application rate and Cd content of the phosphate fertilizers being used at that time in the region studied and assume that this will remain constant in the future. Also, these studies fail to take into account that there may be areas within the region studied that use much more phosphate fertilizer and fertilizer with much higher Cd contents than the average. By looking at national or regional averages, these studies neglect areas that may become areas of very high surface soil Cd content which may then result in the production of food with unacceptably high Cd content.

The present study investigated the changes that have occurred in the profile distribution of soil Cd as a result of long-term cultivation for Orthic Chernozemic soils and estimates the changes in the profile distribution of Cd in these soils that will occur in the future for one specific farming system: tilled Orthic Chernozemic soils under annual tilling, cropping of durum wheat, and applications of phosphate fertilizer. It took into account all of the major factors that can influence the rate of change of Cd in the profile of Orthic Chernozemic soils in the Canadian prairies (Figure 2.5). Furthermore, the present study estimated the future change in the profile distribution of soil Cd with the use of phosphate fertilizers with three different levels of Cd, which reflects the fact that phosphate fertilizers being used today have a wide range of Cd concentrations (Table 2.3). With slight

modifications, the approaches used in the present study can be used with other types of soils, and other cropping and tillage systems to find out how the profile distribution of Cd in other types of soils has changed with long-term cultivation, and to estimate how it will change in the future. This type of information will give the fundamental knowledge required to prevent the Cd content of any of our soils from reaching levels that will significantly increase the amount of Cd taken up by our crops.

4. GENERAL DISCUSSION AND CONCLUSIONS

The Cd contents in some of our crops must be lowered because they have reached levels that pose a threat to our physical and economic health. Since the vast majority of Cd in our food has its origins in the soil, a thorough understanding of the mechanisms that control the transformation and phytoavailability of soil Cd is required to accomplish this task. Although understanding the mechanisms is essential, it must also be understood, as this research has shown, that the soil properties that affect soil Cd's phytoavailability and their effect on the phytoavailability of soil Cd can change over long periods of cultivation.

The present study has shown that long-term cultivation has resulted in a significant decrease in the CAI (Table 3.2.2) for Orthic Chernozemic soils in Saskatchewan. There has been one other study that investigated the effect of long-term cultivation on phytoavailable Cd. He and Singh (1993) extracted Cd from newly-cultivated (< 4 years) and long-term cultivated (> 30 years) soils with several different chemical extractants that had been used in the past as indicators of phytoavailability. They found that more Cd was removed by every extractant from the long-term cultivated soils than from the newly cultivated soils. These results would seem to indicate that the phytoavailability of soil Cd increases with long-term cultivation, which contrasts with the results of the present study. However, comparing the results of the two studies may not be appropriate for two reasons: 1) the soils in the present study had never been cultivated before, while the soils in the study by He and Singh (1993)

had already been cultivated for up to four years and the effects of cultivation had likely already begun, and 2) while there were strict controls in the present study to ensure that the differences found between the virgin and long-term cultivated soils were the result of cultivation only, He and Singh (1993) only ensured that the newly cultivated and long-term cultivated soils were from areas which were similar in geological and geographical conditions.

The present study investigated the impact of long-term cultivation on many of the soil properties that have been identified as having the potential to affect the phytoavailability of soil Cd (Table 3.2.2), and also investigated the relationship between the CAI and those soil properties (Table 3.2.3). The present study found that not all of the soil properties studied were related to the decrease in the CAI. The organic C and Cl^- content of the soil decreased significantly with long-term cultivation but no relationship was found between them and the CAI. Soil texture did not change significantly with long-term cultivation and again no relationship was found between it and the CAI. Ionic strength increased significantly with long-term cultivation and it was found that the ionic strength of the virgin and cultivated soils had different relationships with the CAI; the relationship was negative in the virgin soils and positive in the cultivated soils. The cultivated soils may have soil solution cations that compete with Cd for adsorption sites and ligands that form stable complexes with Cd which are not adsorbed by soil particles, while the virgin soils may have ligands in the soil solution that form metal-ligand complexes with Cd which are then strongly adsorbed.

Further, some of the soil properties were not only related to the CAI, but their changes as a result of long-term cultivation were also related to the decrease in the CAI.

Long-term cultivation significantly decreased total soil Cd, total soil Zn, and the soil CEC, and increased the aromaticity of the soil organic matter and soil pH (table 3.2.2). The decrease in the CAI was apparently partly due to the decrease in the total soil Cd, total soil Zn and the soil CEC. All three of these factors have a positive correlation with the CAI (Table 3.2.3), although the level of statistical significance between the CAI and the CEC was fairly low in the virgin soils. It is possible that a decrease in the Cd in the soil decreases all of the solid-phase Cd species including those that are relatively phytoavailable. Zinc will compete with Cd for adsorption sites (Christensen, 1987) so a decrease in soil Zn could result in more adsorption sites that can bind Cd relatively strongly which could then result in a decrease in the CAI. A decrease in the CEC will allow a relatively lower proportion of the soil Cd to be exchangeable Cd. The decrease in the CAI with long-term cultivation is also partly due to the increase in the aromaticity of the soil organic matter and soil pH, because it was found that the CAI had a negative relationship with the aromaticity of the soil organic matter and soil pH (Table 3.2.3). An increase in the aromaticity of the soil organic matter can be related to an increase in the humic acid:fulvic acid ratio since it has been shown that humic acid is generally more aromatic than fulvic acid (Mahieu et al., 1999). As well, it has been shown that humic acid binds Cd more strongly than fulvic acid (Takamatsu and Yoshida, 1978; Sposito et al., 1981) so an increase in aromaticity should mean an increase in the relative strength at which Cd is bound to the organic matter which in turn should result in a decrease in the CAI. An increase in the soil pH will result in the reactivation of pH-dependent adsorption sites on soil organic matter, metal oxides, and the edges of layer silicate clays. Therefore, an increase in soil pH usually, but not always (section 2.4.2.4),

results in more binding of Cd by soils and a decrease in the CAI.

As well, this part of the study shows that even though long-term cultivation resulted in a significant decrease in the concentration of total soil Zn, the decrease did not affect the soil Zn:Cd weight ratio, which remains at over 200:1 (Table 3.2.2) and offers some protection from the detrimental effects of Cd in our food (McKenna et al., 1992, 1993).

Krishnamurti et al. (1995a) developed a sequential extraction scheme which partitioned Cd into eight operationally defined solid-phase species and then related them to the CAI. The present study used the sequential extraction scheme of Krishnamurti et al. (1995a) to determine the change with long-term cultivation in the solid-phase species of soil Cd and their relationships with the phytoavailability of soil Cd. The results showed that the mean relative proportions of solid-phase soil Cd species did not change with long-term cultivation. The solid-phase Cd species found and the order of their relative abundance were: metal-organic complex-bound > easily reducible metal oxide-bound > H₂O₂ extractable organic-bound > crystalline metal oxide-bound > exchangeable. However, the data clearly showed that both the metal-organic complex-bound Cd and H₂O₂ extractable organic-bound Cd significantly decreased with long-term cultivation (Table 3.3.3). This is attributed to the fact that both of these species contain organics, and the organic matter of the soil decreased by more than half during the years of cultivation.

In the virgin soils the CAI had a significant positive correlation with exchangeable Cd ($r = 0.93$, $P = 9.64 \times 10^{-4}$), a significant negative correlation with easily reducible metal oxide-bound Cd ($r = -0.88$, $P = 4.10 \times 10^{-3}$), and a slight positive relationship with metal-organic complex-bound Cd and crystalline metal oxide-bound Cd (Table 3.3.6). In the

cultivated soils the CAI had a significant positive correlation with exchangeable Cd ($r = 0.95$, $P = 2.31 \times 10^{-4}$), metal-organic complex-bound Cd ($r = 0.71$, $P = 4.93 \times 10^{-2}$), and crystalline metal oxide-bound Cd ($r = 0.86$, $P = 5.78 \times 10^{-3}$) (Table 3.3.6). The above results (Table 3.3.6) combined with the quantity of Mn, Fe, and Al associated with each solid-phase Cd species (Table 3.3.5) suggests that Cd bound to Mn oxides may be relatively less phytoavailable than Cd bound to Al and Fe oxides.

One soil property that can dramatically increase the phytoavailability of soil Cd is total soil Cd. Although it has been well documented that, for uncontaminated agricultural soils, there is not any significant correlation between total soil Cd and the phytoavailability of soil Cd (Gavi et al., 1997), several studies have shown that, for agricultural soils that have unnaturally high levels of Cd, a positive relationship exists between total soil Cd and plant uptake of Cd (Merry et al., 1981; Chumbley and Unwin, 1982; Sillanpaa and Jansson, 1992). This is likely the result of a limited amount of chemisorption sites in any particular soil. Chemisorption sites bind Cd relatively strongly and therefore reduce the phytoavailability of soil Cd. If the amount of Cd in the soil exceeds the ability of the soil to chemically adsorb it, the surplus will then become relatively phytoavailable. Therefore, how long-term cultivation has affected the change in the amount of total soil Cd in the past should be determined and estimates should be made as to how long-term cultivation will change the amount of total soil Cd in the future.

There has been one published study which looked at the difference in total surface soil Cd between newly-cultivated and long-term cultivated soils (He and Singh, 1993). This study was discussed previously in this section in reference to phytoavailable Cd. As was

discussed previously it may not be strictly comparable to the present study. However, He and Singh (1993) found that for their Norwegian soils long-term cultivation resulted in an increase in total soil Cd from 0.048 to 0.062 mg kg⁻¹. In contrast the present study found that since the onset of cultivation in Saskatchewan, Canada, the mean concentration of A horizon Cd in Orthic Chernozemic soils has decreased significantly from 0.447 to 0.332 mg kg⁻¹ (Table 3.4.5). He and Singh (1993) suggest that the increase is the result of phosphate fertilizer applications, which for the soils in the present study, did not occur to any great extent (Table 3.1.1).

Some researchers have attempted to estimate the current annual rate of change of Cd in surface soil and then used these rates to estimate the Cd content of their surface soils at some point in the future (De Boo, 1990; Merry and Tiller, 1991; Jeng and Singh, 1995). However, all of these studies neglected several factors which can affect the profile distribution of soil Cd, and they assumed that the current average application rates of phosphate fertilizer and average Cd contents of phosphate fertilizer would not change in the future.

The present study took into account all of the factors that may significantly affect the total Cd content in the A horizon of Orthic Chernozemic soils, which are important agricultural soils in the durum wheat growing areas of the Canadian Prairies. As well, the present study took into account that phosphate fertilizers can have a wide range of Cd concentrations, depending on the source of the phosphate ore used to make the fertilizer. The model used monoammonium phosphate fertilizers made from the ores of Florida (10 mg Cd kg⁻¹), Togo (60 mg Cd kg⁻¹), and Idaho (144 mg Cd kg⁻¹).

The model predicts that with the application of any of the three phosphate fertilizers there will be a statistically significant increase in both the concentration and the mass of A horizon Cd (Table 3.4.7), although the level of significance with the increase in Cd concentration due to applications of Florida fertilizer is relatively low at $\alpha = 0.10$. The predicted 100 year increases in A horizon soil Cd concentration and mass as a result of applying phosphate fertilizer made from Togo and Idaho phosphate ores are very large and highly significant. If phosphate fertilizer made from Idaho ore is applied, both the concentration and the total mass of A horizon Cd are predicted to be about 3.5 times higher in 2097. The 100 year Cd concentration resulting from the use of phosphate fertilizer made from Idaho phosphate ore could reach 1.18 mg kg⁻¹ soil (Table 3.4.7) which is in the commonly accepted critical region of 1.0 to 3.0 mg Cd kg⁻¹ soil (Tiller et al., 2000). Typically, when the concentration of soil Cd enters this region the crops grown on the soil have unacceptably high levels of Cd (Tiller et al., 2000). The present research demonstrates that, with the use of fertilizers with relatively high concentrations of Cd, the Cd content in A horizon soil can eventually reach levels which could result in an increase in the phytoavailability of soil Cd.

However, knowing the net change over time in the total Cd content of A horizon soil is not enough. Because different species of crops can have different rooting systems, the relative amounts of Cd taken from different positions in the soil profile may be different for different crops. For example, crops like flax and sunflower have tap roots and therefore relatively more of their uptake from the soil may come from the deeper parts of the soil profile compared to crops like durum wheat that have relatively shallow fibrous roots.

Therefore, knowing the profile distribution of soil Cd, how it changes with long-term cultivation, and what proportion of Cd is taken from where in the soil profile by the different species of crops would aid in reducing the amount of Cd taken up by crops. For example, in a soil where the B horizon contains a higher Cd concentration than the A horizon, it may be wise to grow a shallow rooting crop like wheat because most of its uptake from the soil will come from the A horizon.

While the profile distribution of Cd has been determined for some soils (Kuo et al., 1983; McGrath, 1987; Krishnamurti et al., 1997b), there is no published research on the change in the profile distribution of soil Cd as a result of long-term cultivation. The present study has shown that the relative soil profile concentration of Cd did not change with long-term cultivation; A horizon Cd > C horizon Cd > B horizon Cd. However, it has also shown that, in the past, long-term cultivation with very little phosphate fertilizer use (Table 3.1.1) resulted in a significant decrease in the concentration of A horizon Cd (Table 3.4.5).

The model developed in this research predicts that in 100 years, regardless of the phosphate fertilizer used, the Cd mass in the B horizon will decrease from 59 to 54 mg m⁻² (Table 3.4.7). Although the estimated decrease is not statistically significant, a decrease is expected because the A horizon will move deeper into the soil profile because of erosion and at the same time incorporate some of the B horizon into itself. In contrast, the Cd concentration in the B horizon is predicted to increase in 100 years from 0.202 to 0.21 mg kg⁻¹. Although the increase is not statistically significant, it is interesting that the mass of B horizon Cd is predicted to decrease while the concentration is predicted to increase. However, it is likely that the predicted concentration increase is a result of the fact that the

soils used in this study form two groups of soils that are exposed to different rates of soil erosion (0.30 and $0.13 \text{ kg m}^{-2} \text{ yr}^{-1}$) and therefore have different rates of B horizon incorporation (Table 3.4.2); the group with the highest rate of soil erosion/B horizon incorporation has the soils with the lowest mean concentration of B horizon Cd (Table 3.4.4). Therefore, with time, the mean B horizon Cd concentration should increase because lower Cd concentration B horizon soil will be removed from the B horizon at a faster rate than the higher Cd concentration B horizon soil.

While the present study has demonstrated how the profile distribution of soil Cd has changed in the past as a result of long-term cultivation and how it is expected to change in the future, it has only done so for Orthic Chernozemic soils. The profile distribution of soil Cd and how long-term cultivation affects it is likely to be different for other types of soils. For example, Calcareous Chernozemic soils on the tops of knolls may not have an accumulation of Cd in the A horizon because of the relatively high rate of erosion. Conversely, Chernozemic soils in depressions may have an excessively high accumulation of Cd because of deposition of eroded soil and increased phyto-pumping of Cd from the lower horizons to the A horizon as a result of higher rates of vegetative mass production. On the other hand, the A horizon Cd might be lower in depressions because of a relatively higher rate of leaching and crop uptake. This type of speculation needs to be investigated with further research.

In summary, the present study shows that the Cd content and profile distribution in the soil, its phytoavailability index and solid-phase species, and the soil properties related to the phytoavailability of soil Cd change as a result of long-term cultivation. Long-term

cultivation in the past has decreased the CAI. This decrease in the CAI is a result of the effect that long-term cultivation has had on the chemical speciation of soil Cd and on other soil properties related to the CAI. In the future the phytoavailability of soil Cd may increase. The model developed in this study demonstrates that, with the use of phosphate fertilizer made from Idaho phosphate ore, the Cd content in the A horizon of agricultural soils in the future may reach levels which could increase phytoavailable Cd.

This study, however, was done only with Orthic Chernozemic soils. Many other soil/crop and management systems need to be included in studies such as this in the future. As well, the determination of the stability constants between Cd and all of the different soil solids would certainly aid in interpreting the phytoavailability of the different solid-phase Cd species. Future use of XAS based on synchrotron light source should provide fundamental understanding of the different chemical species of soil Cd at the molecular level and this will then help give insight into the phytoavailability of the different species.

Determining the Cd content and profile distribution in the soil, its phytoavailability index, solid-phase species, and the soil properties related to the phytoavailability of soil Cd and the effect of long-term cultivation is essential to advance the knowledge required in order to reduce Cd contamination of the food chain. However, since there are many different types of soils, each with widely differing chemical and physical properties, their interactions with soil Cd may also be different. Therefore, in order to develop innovative management strategies of soil resources to curtail Cd contamination of the terrestrial food chain, research such as this should be performed on all important representative agricultural soils under the influence of different farming practices.

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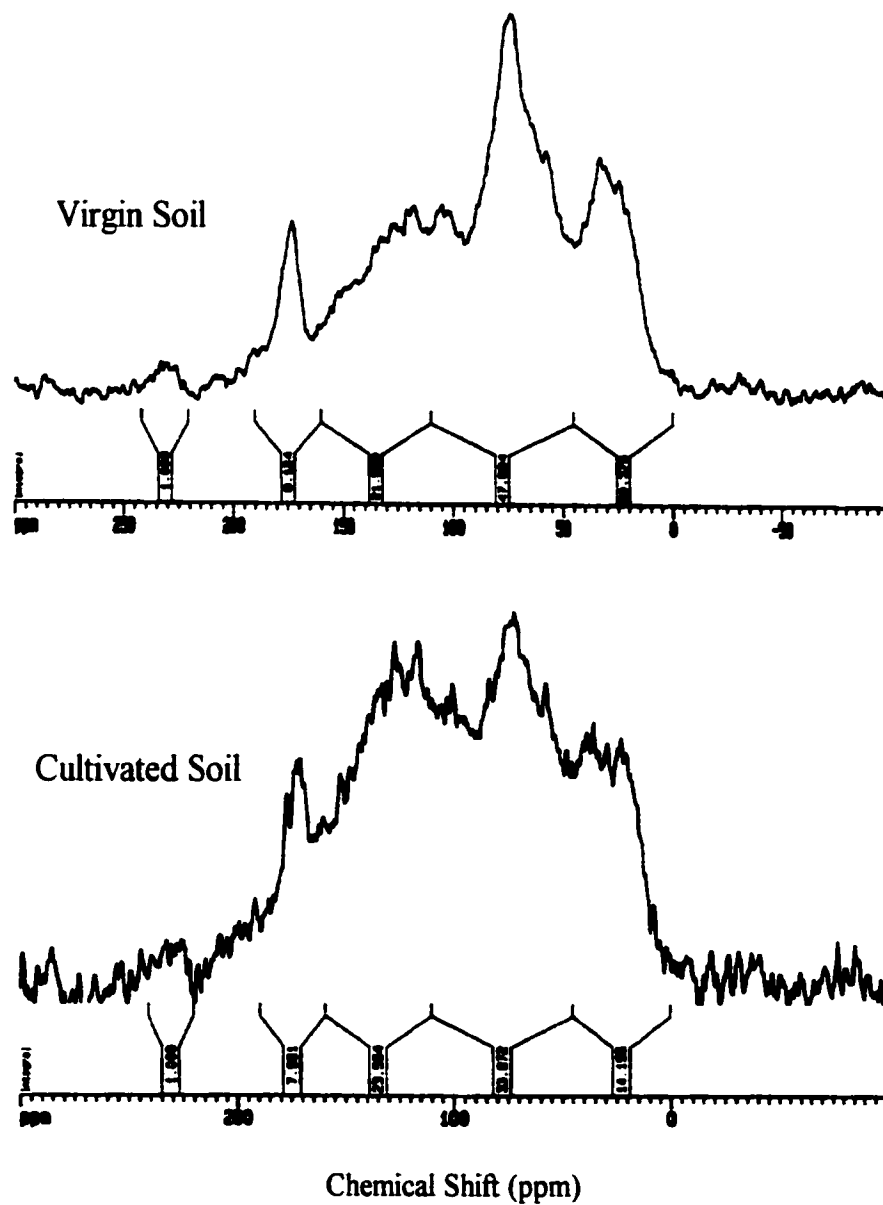
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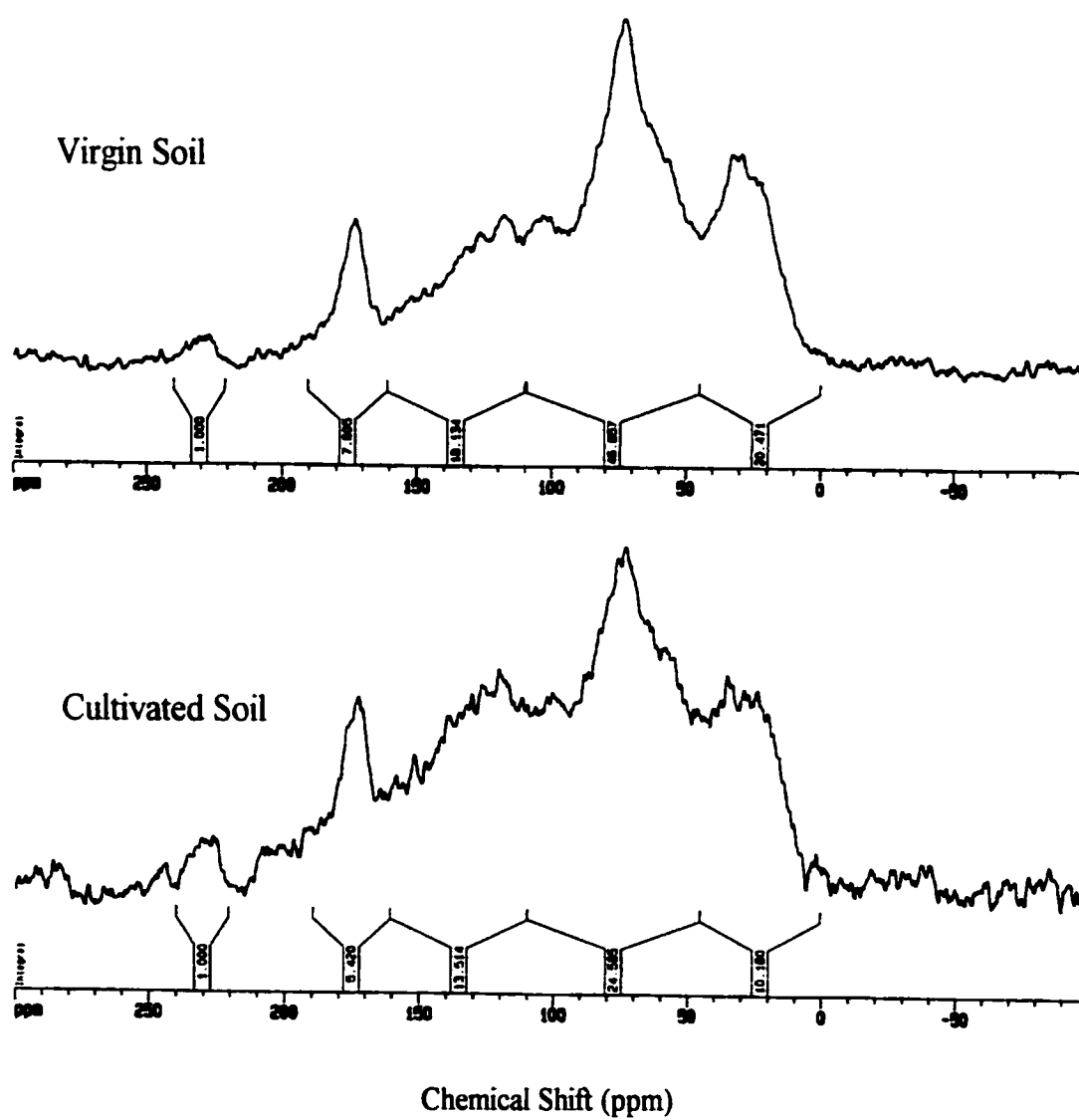
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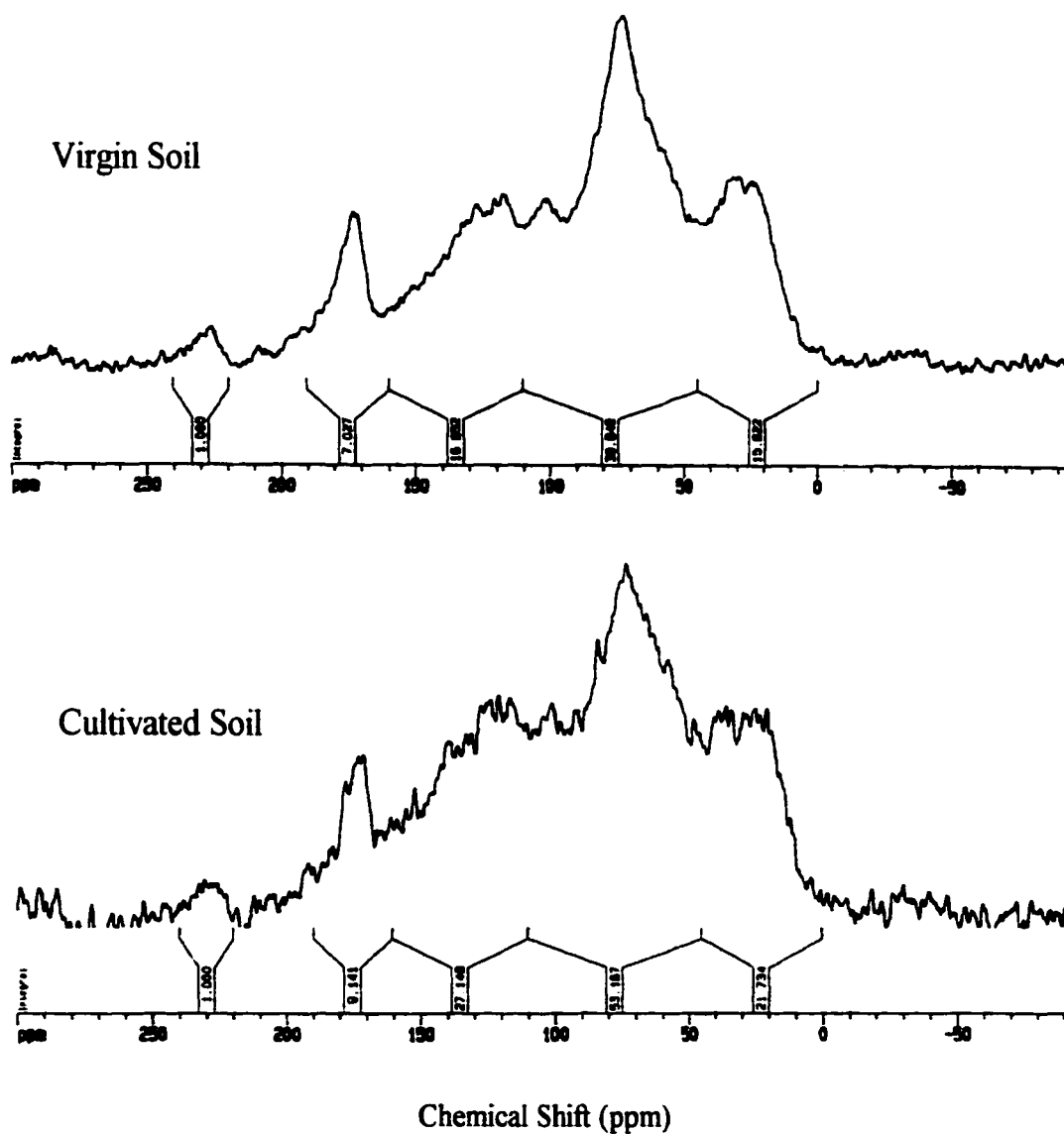
6. APPENDICES



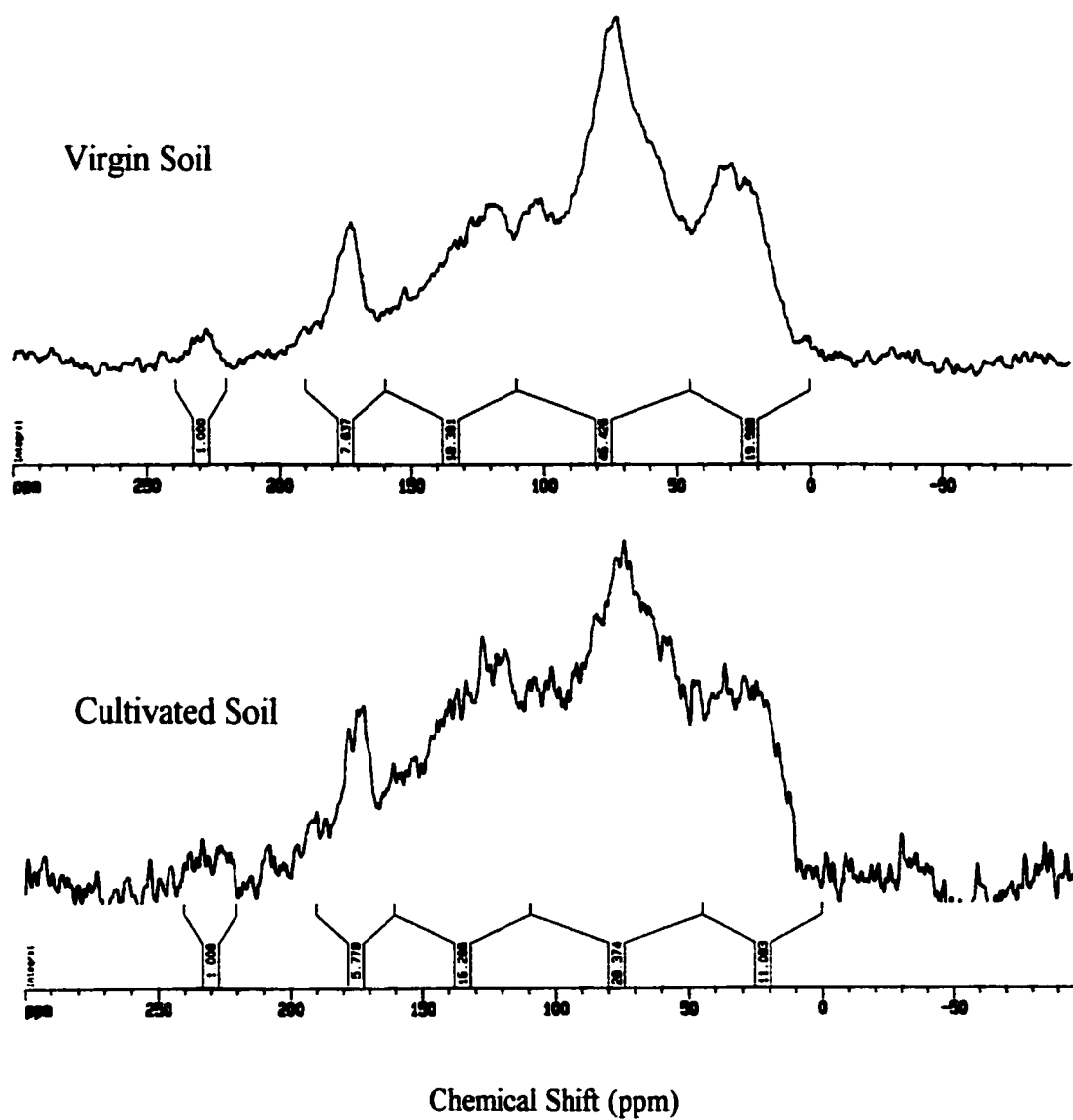
Appendix 6.1. ^{13}C NMR spectra for the virgin and cultivated soils at site number 1.



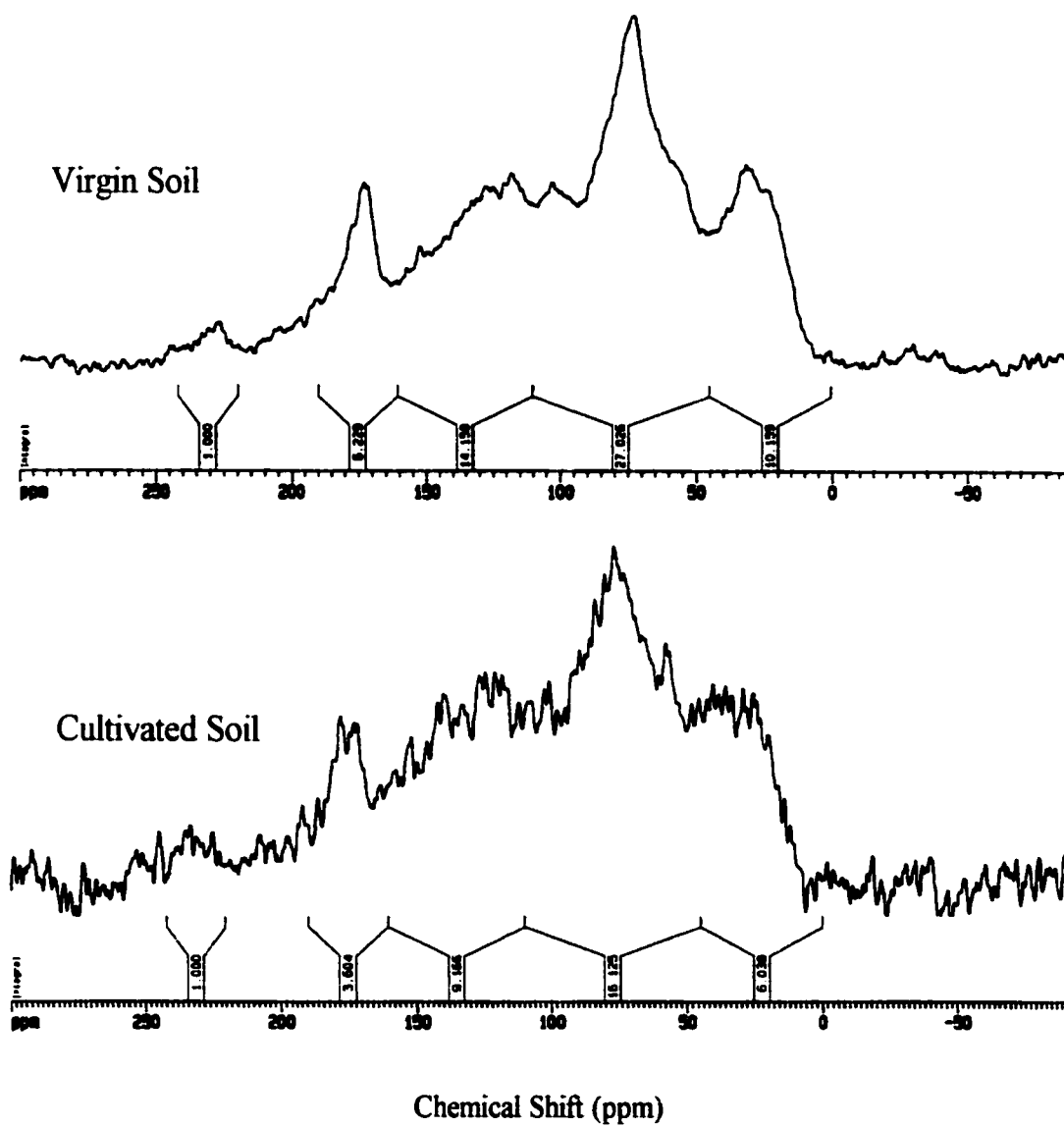
Appendix 6.2. ^{13}C NMR spectra for the virgin and cultivated soils at site number 2.



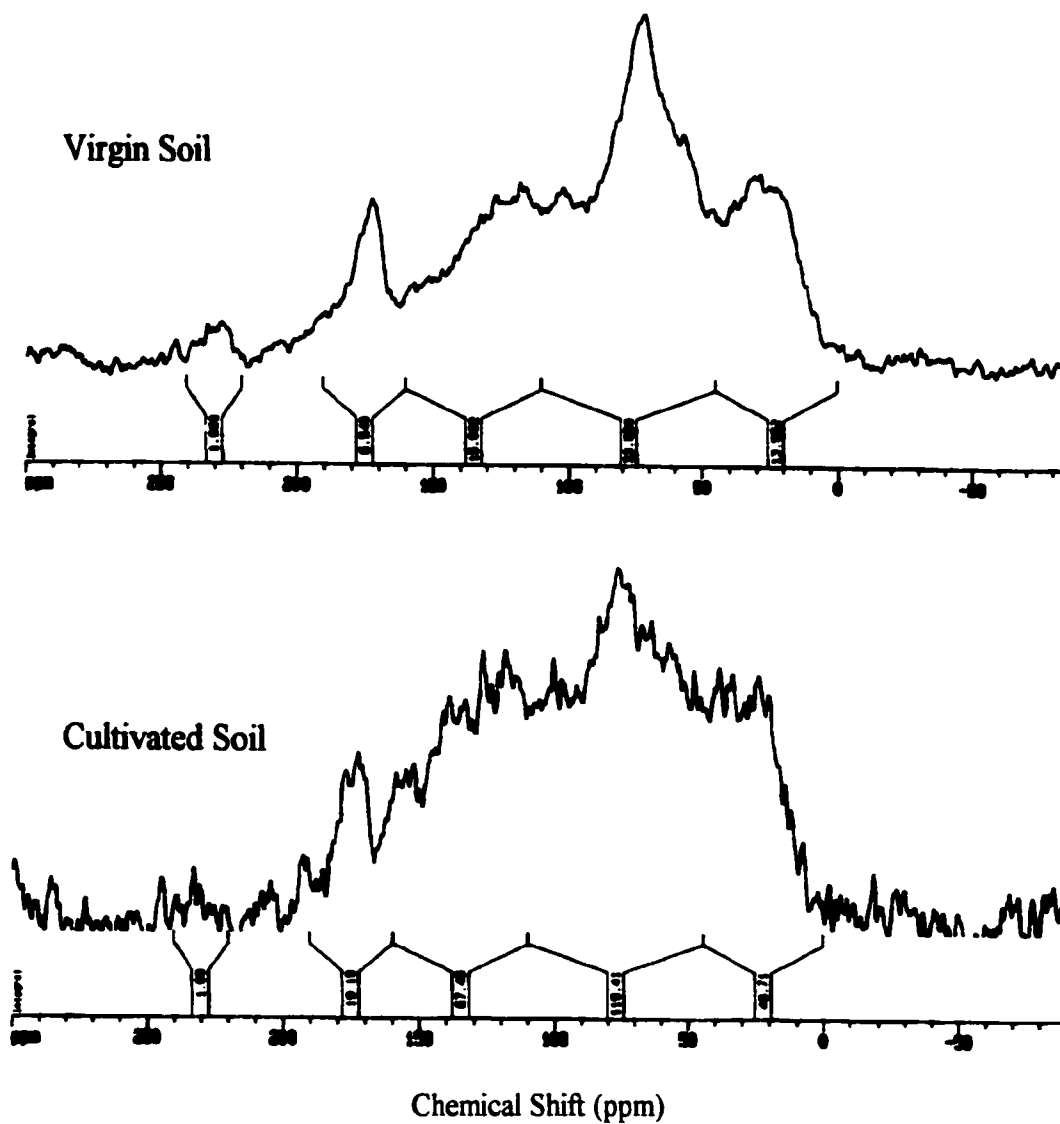
Appendix 6.3. ^{13}C NMR spectra for the virgin and cultivated soils at site number 3.



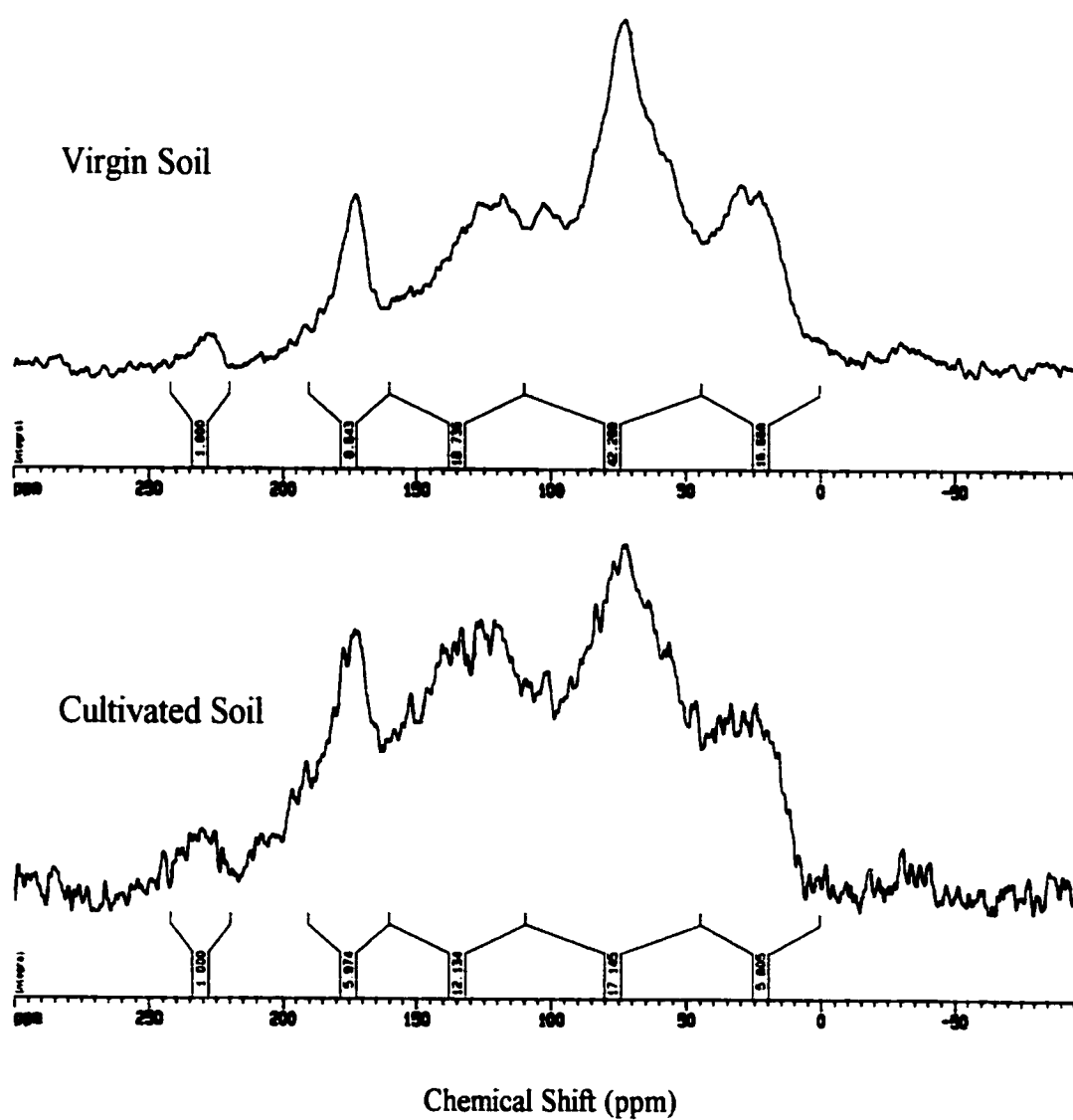
Appendix 6.4. ^{13}C NMR spectra for the virgin and cultivated soils at site number 4.



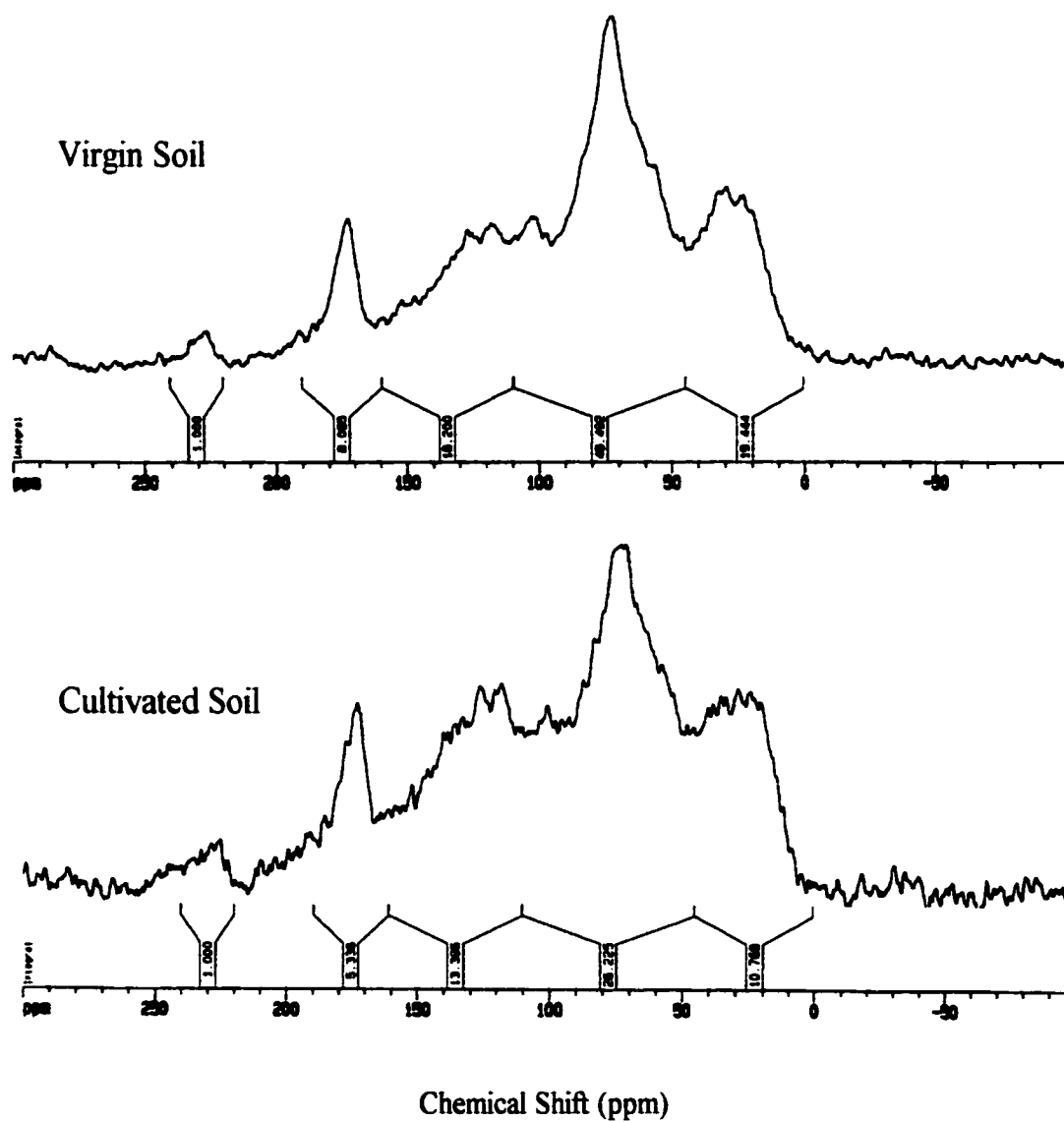
Appendix 6.5. ^{13}C NMR spectra for the virgin and cultivated soils at site number 5.



Appendix 6.6. ^{13}C NMR spectra for the virgin and cultivated soils at site number 6.



Appendix 6.7. ^{13}C NMR spectra for the virgin and cultivated soils at site number 7.



Appendix 6.8. ^{13}C NMR spectra for the virgin and cultivated soils at site number 8.