THE UNIVERSITY OF MANITOBA

TRIVALENT AND HEXAVALENT CHROMIUM, THEIR REACTIONS WITH

MINERALS AND POTENTIAL PHYTOTOXICITY IN SOILS

by

MICHELE CHESLOCK-FITZGERALD

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

Department of Soil Science

Winnipeg, Manitoba

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ABSTRACT

The concentrations of total and extractable Cr were measured in pedons representing four of Manitoba's agricultural soils to illustrate the range of occurrence of Cr and to correlate these contents with various soil properties. The pedons analyzed were from four soil series and consisted of soils from the following subgroups, Gleyed Rego Black, Orthic Gray Luvisol, and Humic Rego Gleysol. The potential of the soil to oxidize Cr(III) to Cr(VI) was also evaluated to understand the probable causes of Cr toxicity in these soils. There was no significant variation in the total Cr contents from horizon to horizon within a pedon, except in the Bt horizon of the Luvisolic soil where an accumulation of Cr occurred. The average total Cr content of the pedons ranged from 13 and to 27 μg Cr g^{-1} soil. Differences in the total Cr content among soils were believed to be due to differences in the mineralogy and texture of the geological parent materials from which these soils were derived.

Most of the Cr present in the soil profiles was Cr(III) and only small amounts of Cr(VI) were measured. Organically bound Cr was present in the greatest amounts in the surface A horizons and decreased with depth due to the decrease in the content of organic matter. The greatest proportion of the total Cr in these soils was extracted by citrate-bicarbonate-dithionite (CBD) which removed the free iron oxides from soils. The amount of Cr extracted by CBD was significantly correlated with the total contents of Cr, Fe and Mn, as well as the clay content of the soil.

The Cr oxidizing potential of the soils was determined by

equilibrating 20 mL of 10^{-3} mol L^{-1} $CrCl_3 \cdot 6H_2O$ with approximately three grams of moist soil for 15 minutes, and then measuring the amount of Cr(VI) formed. The amounts of added Cr(III) oxidized to Cr(VI) were the greatest in the surface horizons and decreased with depth. The amount of Cr(III) oxidized to Cr(VI) and in solution was in the range between 0.11 and 10.12 μg g^{-1} soil.

A laboratory experiment was conducted to investigate the reactions of Cr(III) and Cr(VI) with common soil minerals. The soil minerals utilized were two oxides, haematite and birnessite, and two clay minerals, montmorillonite and vermiculite. The soil minerals differed in their capacities to adsorb Cr(III) and Cr(VI), indicating that Cr(III) and Cr(VI) are most likely adsorbed at different sites on the soil minerals. Much more Cr(III) was adsorbed by the soil minerals than Cr(VI). Evidence was also given to suggest that Cr(III) was strongly fixed in the interlamellar sheets of vermiculite. The pH range selected had little effect on the adsorption of Cr(III), since most of the Cr(III) added was adsorbed. In contrast, the adsorption of Cr(VI) decreased as the pH increased and this was attributed to the increased negative charge on the soil minerals as the pH increased.

Adsorbed Cr(III) could only be extracted from montmorillonite with solutions of KH_2PO_4 and $CaCl_2$. Some of the Cr(III) adsorbed by birnessite was oxidized to Cr(VI). Adsorbed Cr(VI) was extracted from all the soil minerals studied, especially by phosphate, and hence would be more mobile and available to plants than Cr(III). Since chloride extracted some Cr(VI) it was suggested that Cr(VI) may have been held by nonspecific and specific adsorption mechanisms.

Growth chamber experiments were conducted, using barley as a test crop, to determine the effects of Cr(III) and Cr(VI), manganese dioxide and fertilizer phosphorus on yield and quality. Most of the added Cr(III) was immobilized by the soil and thus did not have a significant effect on yield and nutrient concentrations in the plants. By comparison, Cr(VI) additions resulted in decreased yields, delayed maturity, reduced nutrient concentrations and death at rates exceeding 50 μg Cr(VI) g^{-1} soil. Chromium from phosphorus fertilizer, added at rates of 0.03 and 0.05 μg Cr g^{-1} soil, did not increase Cr toxicity. Instead the phosphorous enhanced the growth in the Cr(III) treatments and reduced the toxicity of Cr(VI) by biological dilution. The addition of 490 μg MnO_2 g^{-1} soil, despite its role as an oxidizing agent, did not produce symptoms of Cr(VI) toxicity when combined with Cr(III) treatments. Although the effect was not always significant, the addition of 490 μg MnO_2 g^{-1} soil improved grain and straw yields for both Cr(III) and Cr(VI) and this was attributed to better nutrition. The addition of 1900 μg MnO_2 g^{-1} to the Cr(III) treated soil increased the availability of Cr(III) slightly, but this was not accompanied by a decrease in yields. In contrast, the addition of 1900 μg MnO_2 g^{-1} to the Cr(VI) treated soil increased the toxicity of Cr(VI), and yields were significantly reduced, especially at the higher rates of Cr(VI).

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I. Introduction

There is a paucity in the literature regarding nonessential heavy metals in plant nutrition, such as chromium, and this is due to the preoccupation with essential nutrients for plant growth. However, an understanding of the fate and bioavailability of the nonessential elements is no less important.

It is believed that the chromium (Cr) concentration in agricultural soils is increasing because many fertilizers and sewage sludges applied to these soils contain Cr as an impurity. Little is known about the profile distribution of Cr in terms of the total content and extractable forms, despite the concerns over the build up of Cr in the soil profile. Thus, it is not known if the content of Cr in soils is increasing. Furthermore, since little is known about the different extractable fractions of Cr in soils, it is not known which fraction of the soil will increase when Cr is added. Therefore, pertinent data for the interpretation of possible contamination and toxicity is nonexistent.

Chromium is a potentially serious pollutant whose behaviour in soils can be very complex. When added to soils, Cr can undergo several reactions such as oxidation-reduction, adsorption-desorption, organic complexation and precipitation. Several studies have shown that the dynamics of Cr in soils are governed by the oxidation state of Cr, as well as many soil factors including the pH, Eh, organic matter content and the mineralogy of the soil (Bartlett and Kimble 1976a; Griffin et al. 1977; Bloomfield and Pruden 1980; Zachara et al. 1989). There is,

however, a need to further investigate the fate of added Cr, particularly the reactions with soil minerals, to obtain a greater understanding of the behaviour of Cr in soils and its potential availability and toxicity to plants.

Chromium is an essential element in human and animal nutrition (Adriano 1986), but it is not an essential element in plant nutrition (Huffman and Allaway 1973a). Thus, studies on Cr in relation to plants have focused on two areas. On the one hand, studies were conducted to examine methods of increasing the Cr content of edible portions of the plants (Welch and Cary 1975; Cary et al. 1977a). On the other hand, research was done to measure toxic thresholds for Cr in plants, in both solution and soil culture (Hewitt 1953; Turner and Rust 1971; Davis et al. 1978). There have been, however, a limited number of investigations to determine the conditions under which the plant availability and toxicity of Cr may be increased, specifically with respect to oxidation of added Cr and competing ions.

This project was undertaken to study the natural occurrence of Cr in Manitoba soils, in terms of the total content and extractable forms, and to measure the potential of these soils to oxidize trivalent (Cr(III)) to hexavalent Cr (Cr(VI)). These objectives were extended to examine the reactions of Cr(III) and Cr(VI) with common soil minerals, and to determine the effects of Cr, in combination with manganese oxides and fertilizer phosphorus, on plant yield and quality.

II. LITERATURE REVIEW

2.1 Occurrence of Chromium in Soils

Chromium (Cr) ranks twenty first among the elements in crustal abundance of the earth (Adriano 1986). There is more Cr in the earth's crust than other heavy metals such as Co, Cu, Zn, Mo, Pb, Ni, and Cd (Adriano 1986). The concentration of naturally occurring soil Cr is extremely variable and is dependent upon the amount and type of parent rocks. Thus the contents of Cr in soils range from as little as 5 μg g^{-1} to as high as 5.23% (Reisenauer 1982; Adriano 1986). A mean Cr content of 65 μg Cr g^{-1} soil has been calculated on a world-wide basis (Kabata-Pendias and Pendias 1984). For Canadian soils an arithmetic mean of 43 μg Cr g^{-1} (n=173) and a range of 10 to 100 μg Cr g^{-1} soil has been given (Kabata-Pendias and Pendias 1984; Adriano 1986).

The pattern of Cr distribution in soil profiles is inconsistent. Several researchers have reported that the parent material contains the greatest amount of Cr in the soil profile (Conner et al. 1957; Pierce et al. 1982), while others have found that the Cr concentration was the greatest in the surface horizons and declined with depth (Bleeker and Austin 1970); still others have reported that Cr was uniformly distributed throughout the soil profile (Whitby et al. 1978; Roberts 1980). Nevertheless, it is recognized that the Cr content of surface soils will increase because Cr will be introduced into soils by deposition from the atmosphere, use of sewage sludges for improvement of soil fertility, and application of fertilizers containing this element as an impurity (NRCC 1976; Kabata-Pendias and Pendias 1984; Watanabe

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1984; Adriano 1986; Otabbong 1989c).

Although Cr has the potential of occurring in many different oxidation states with valencies ranging from -2 to +6 (Volborth 1969; Cotton and Wilkinson 1972), naturally occurring Cr compounds have valencies of +3 (chromic) or +6 (chromate) (Kabata-Pendias and Pendias 1984). In soils, Cr is capable of existing in four forms, depending on the pH and Eh values of the soil: there are two trivalent forms, the Cr^{+3} (chromic) cation and the CrO_2^- anion and two hexavalent anion forms, $CrO_4^=$ (chromate) and $Cr_2O_7^=$ (dichromate) (Bartlett and Kimble 1976a). The complete pH-Eh diagram of these forms given by Bartlett and Kimble (1976a) displays that Cr(III) forms predominate almost throughout the Eh range normally found in soils, with the Cr^{+3} cation found at low pH and the CrO_2^- anion at high pH. Hexavalent Cr anions form only at high soil Eh values, with $Cr_2O_7^=$ found at low pH and $CrO_4^=$ at high pH.

It is generally recognized that the majority of soil Cr exists as the chromic, Cr^{3+}, cation, while the Cr(VI) anions are rare (Soane and Saunder 1959; Shewry and Peterson 1974; Bartlett and Kimble 1976a,b). Most of the Cr^{3+} found in soils is present in the mineral chromite, $FeCr_2O_4$, or in other spinel structures, substituting for Fe or Al (Soane and Saunder 1959; Allaway 1968; Shewry and Peterson 1976; Cary et al. 1977a; Reisenauer 1982; Kabata-Pendias and Pendias 1984). In general, Cr^{3+} closely resembles Fe^{3+} and Al^{3+} in ionic size and its reactions in soils parallel in many respects those of Fe and Al (Volborth 1969; Bartlett and Kimble 1976a; Cary et al. 1977b; Reisenauer 1982; Kabata-Pendias and Pendias 1984). Both Cr^{3+} and chromite are insoluble and chemically quite inert, and thus exhibit low mobility in soils and

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availability to plants (Volborth 1969; Cary et al. 1976a; Shewry and Peterson 1976; Reisenauer 1982; Kabata-Pendias and Pendias 1984). In contrast, the Cr(VI) anions which form naturally from the oxidation of Cr(III), are unstable and readily mobile in soils and available to plants (Allaway 1968; Bartlett and Kimble 1976b; Kabata-Pendias and Pendias 1984). Therefore, the existence of Cr in the Cr(VI) oxidation state poses the greatest environmental concern (Soane and Sander 1959; Bartlett and Kimble 1976a; Reisenauer 1982).

2.2 Fates of Chromium When Added to Soils

Chromium has several possible fates when added to soils. Cr can be oxidized or reduced, remain in solution as the free ion, become chelated by an organic ligand, be adsorbed on mineral and organic exchange complexes or on Fe and Mn oxides coating soil particles, or be precipitated as a sparingly soluble or highly insoluble compound(s) (Adriano 1986). To explore these fates and their extent, experiments have been conducted using a variety of extracting solutions on Cr treated soils (Shewry and Peterson 1976; Cary et al. 1977b; Grove and Ellis 1980a).

Upon addition to soils, soluble Cr(III) or Cr(VI) will be rapidly converted to insoluble forms (Shewry and Peterson 1976; Cary et al. 1977b). Even after only one day of either $^{51}CrCl_3$ or $K_2^{51}CrO_4$ addition to soils, Cary et al. (1977b) found trace amounts of Cr were in the water soluble form. As well, a very small portion of the added ^{51}Cr was present as soluble-organic complexes of Cr(III). It was further reported that most of the added Cr(VI) was quickly reduced to Cr(III),

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and little oxidation of Cr(III) to Cr(VI) took place (Cary et al. 1977b). The fate of the greatest portion of the added ^{51}Cr consisted of insoluble forms of Cr that had properties of mixed hydrous oxides of Cr(III) and Fe(III) (Cary et al. 1977b).

In a similar investigation, Grove and Ellis (1980a) studied the fates of $CrCl_3$, CrO_3, as well as sludge Cr in soils. (The sludge was obtained from the Grand Haven, Michigan municipal treatment facility and contained 12500 μg Cr g^{-1} and was added to the soil at a rate of 1400 μg Cr g^{-1} soil.) Measurements of soil pH after the addition of Cr indicated that the addition of Cr(III) reduced soil pH, while the addition of Cr(VI) initially lowered soil pH then raised it. The pH of the sludge amended soils was reported to be very high initially and then declined with time, but was always greater than that of the control soil. The various extractable Cr fractions, in general, were the same for the three sources of Cr. The Cr found in the water soluble, exchangeable (1 mol L^{-1} NH$_4$Cl) and organically bound fractions (0.1 mol L^{-1} CuSO$_4$) were negligible; with most of the added Cr extracted by 0.3 mol L^{-1} (NH$_4$)$_2$C$_2$O$_4$ and Na$_3$ citrate/ Na$_2$ dithionite/ Na bicarbonate representing the amorphous-precipitated and more crystalline-precipitated fractions, respectively. This means that the majority of Cr added to soils forms insoluble Cr compounds, and hence, should not be mobile in soils. It was also reported that Cr in the sludge exhibited the chemistry of Cr(III), and upon addition to soils, the sludge Cr changed very little in its chemical character, remaining largely in insoluble forms (Grove and Ellis 1980a).

Two reaction pathways have been proposed to explain the soil

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chemistry of added Cr(III) and Cr(VI) (Grove and Ellis 1980a).

$$\text{I.} \quad Cr^{3+} + 6H_2O \; \rightleftharpoons \; Cr(H_2O)_6^{3+} \; \rightleftharpoons \; [Cr(OH)_x (H_2O)_{6-x}]^{3-x} + xH^+ \; \rightleftharpoons \; \tfrac{1}{2} Cr_2O_3 \cdot zH_2O.$$

$$\text{II.} \quad CrO_3 + H_2O \; \rightleftharpoons \; H_2CrO_4 \; \rightleftharpoons \; 2H^+ + CrO_4^{2-}$$

$$\xrightarrow[3e-]{6H^+} \; Cr^{3+} + 4H_2O. \\ \quad\quad\quad \downarrow \\ \quad\quad\quad \text{I.}$$
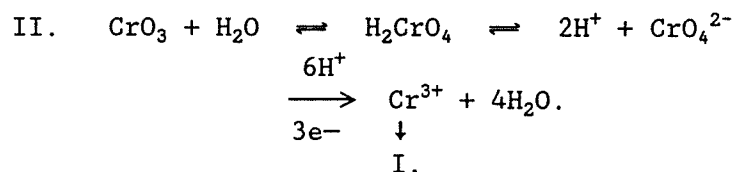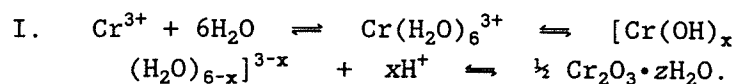
Reaction I accounts for the lower pH measured on the Cr(III) treated soils and the subsequent insolubility of the resulting Cr compounds. For reaction II, the hydrolysis and dissociation of the acid anhydride explains the initial lowering of soil pH relative to controls after Cr(VI) addition. The critical step in reaction path II is the reduction of Cr(VI) to Cr(III), since both protons and electrons must be present for this to occur. Once Cr(VI) is reduced to Cr(III), the reduced Cr enters reaction path I. Although the subsequent precipitation of Cr(III) generates protons, it does not meet the requirements for H^+ in the Cr(VI) reduction reaction, and thus the soil pH would rise above the control (Grove and Ellis 1980a).

2.2.1 Oxidation-Reduction Behaviour of Chromium in Soils

Oxidation of Cr(III) and reduction of Cr(VI) have been reported to occur under conditions prevalent in most soils.

Reduction of Cr(VI) has been extensively investigated by Bartlett and Kimble (1976b), Cary et al. (1977b), Bloomfield and Pruden (1980), and James and Bartlett (1983c). Hexavalent Cr can be reduced to Cr(III)

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in environments with a ready source of electrons according to (Artiole and Fuller 1979; Adriano 1986):

$$Cr_2O_7^= + 14\ H^+ + 6\ e^- \longrightarrow 2\ Cr^{+3} + 7\ H_2O.$$

In aerobic soils, easily oxidized organic compounds, such as citric and gallic acid, will act as reducing agents for Cr(VI); while under anaerobic conditions Fe^{2+} and S^{2-} may also be important (Bloomfield and Pruden 1980; James and Bartlett 1983c). Under both aeration regimes, low pH favours rapid reduction of Cr(VI) because the reaction consumes protons (Bartlett and Kimble 1976b; Cary et al. 1977b; Ottabong 1989b).

The biological or chemical conversion of soluble Cr(VI) to insoluble Cr(III) is of great significance because it is responsible for decreasing the mobility and plant availability of Cr(VI), and hence its potential for toxicity. Thus, with this reaction in mind, if Cr(VI) contamination occurred, by a chemical spill for example, it could be contained by the following suggested management strategy (Grove and Ellis 1980a; Kim and Zoltek 1977). First, acidification agents such as S and reducing agents such as leaf litter or acid compost could be incorporated into the soil to hasten Cr(VI) reduction, and after the reduction is complete, liming to further precipitate and crystallize Cr(III) compounds might be necessary.

The oxidation of Cr(III) is of great concern because this conversion to the more mobile Cr(VI) increases the potential of Cr toxicity. The key to this reaction is the presence in moist aerobic soils of oxidized Mn compounds which serve as electron acceptors in the

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oxidation. It is therefore prudent to know the soil's ability to oxidize Cr(III), prior to the disposal of Cr(III) wastes onto soils. Thus, tests have been developed to measure this ability. One test is to measure Mn reducible with hydroquinone, which measures the amount of oxidized Mn in the soil; another test, labelled as a quick test, consists of adding Cr(III) to a field moist soil sample and measuring the amount of Cr(VI) formed, thus directly determining the oxidation potential. It has been emphasized that soils should be studied in the field moist condition because drying of soil samples decreases the amount of oxidized Mn and hence, the ability to oxidize Cr decreases (Bartlett and James 1979, 1980).

The maximum reported amount of Cr oxidized by Bartlett and James (1979) was 24 μmol of Cr per gram of soil, for an unnamed series of Lithic Eutrochrepts from northern Vermont which contained 1200 μg Mn g^{-1} soil extracted by 1 mol L^{-1} HCl. Further, they found that average aerated soils may have the capacity to convert up to 10 μg Cr(III) g^{-1} soil to Cr(VI) (Bartlett and James 1979; NRCC 1985). Even Cr(III) present in wastes which have high levels of reducing compounds, such as tannery effluent and sewage sludge, will be oxidized when applied to soils, although the reaction is somewhat slower than for pure chemical forms (James and Bartlett 1983b). It has also been found that Cr(III) applied to alkaline soils remains reduced for considerable lengths of time (Sheppard et al. 1984). These examples should stress the need to determine the soil's ability to oxidize Cr prior to the disposal of Cr(III) wastes, since Cr(III), although chemically quite inert, presents a potential pollution problem if it is oxidized to Cr(VI).

2.2.2 Adsorption of Chromium in Soils

Adsorption of Cr by various soil components can reduce the potential for Cr toxicity by decreasing the mobility and plant availability of Cr in soils. Chromium adsorption has been investigated by several researchers and has been found to be dependent on several factors. These factors include, the oxidation state of Cr, the pH, competing ions, and the soil mineralogy, particularly the types of clay minerals and the presence of Fe and Al oxides (Bartlett and Kimble 1976b; Griffin et al. 1977; Bloomfield and Pruden 1980; James and Bartlett 1983c; Stollenwerk and Grove 1985; Ainsworth et al. 1989; Zachara et al. 1989).

In an investigation to determine the effects of oxidation state, pH, and complexing agent (represented by landfill leachate) on the adsorption of Cr by two clay minerals, montmorillonite and kaolinite, Griffin et al. (1977) observed that the adsorption of Cr from either the landfill leachate or Cr salt solutions by both clay minerals was highly dependent upon the pH of the clay suspensions and the physical-chemical properties of the clay minerals. The adsorption of Cr(III) by the clay minerals increased with pH (Griffin et al. 1977). However, above pH 5 Cr(III) should be immobile because it precipitates as $Cr(OH)_3$, given that the Ksp of $Cr(OH)_3$ is 6×10^{-31} (Peters et al. 1976). Nevertheless, below pH 4, Cr(III) was found to be strongly adsorbed and, therefore exhibits little mobility through soils or clay minerals regardless of pH. The adsorption of Cr(VI), in contrast, was markedly reduced as the pH of the clay suspensions was raised into the alkaline range and thus it would become very mobile at high pH (Griffin et al. 1977). Further,

the adsorption of Cr(VI) was lower (30 to 300 times less) than Cr(III),
even at very low pH values where Cr(VI) adsorption was highest (Griffin
et al. 1977). Therefore, Cr(VI) is the more mobile form of Cr in soils,
and the safe disposal of wastes containing Cr(VI) may require conversion
of Cr(VI) to Cr(III), to prevent pollution of water sources and to
decrease the mobility of Cr. It should be noted that more Cr(VI) was
adsorbed from the leachate solutions than from K_2CrO_4 solutions. These
results were attributed to the formation of polynuclear complexes,
either organic or inorganic in nature, that can be adsorbed by the clay.
It was also suggested that the high ionic strength of the leachate may
have contributed to the higher adsorption of Cr(VI) species by a
depression of the diffuse double layer surrounding the clay particles.
The clay minerals, because of differences in the probable number of
adsorption sites, based on structural differences and external surface
areas, do not adsorb Cr to the same extent: that is, montmorillonite,
in general, adsorbs two to three times more Cr than kaolinite, and thus,
reduces the mobility of Cr in soils better than kaolinite. Therefore,
soils, depending on their mineralogy, have different inherent capacities
to adsorb Cr, and these capacities should be determined prior to the
disposal of Cr containing wastes to estimate disposal guidelines which
will not result in Cr pollution and toxicity.

The predominant form of Cr(III) in soils is cationic (Bartlett and
Kimble 1976a) and it can be adsorbed onto many negatively charged
particles in soils such as clay minerals, organic matter, and metal
oxyhydroxides (NRCC 1985). Cation exchange has been accepted as the
principal mechanism for Cr(III) adsorption in soils and hence Cr(III) is

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subject to competition for exchange adsorption sites by other cations (Griffin et al. 1977). Griffin et al. (1977) reported that the adsorption of Cr(III) from the landfill leachate was 3 to 14% lower than Cr(III) from $Cr(NO_3)_3$ solutions. These results were attributed to the presence of cations in the leachate competing with cationic Cr(III) species for exchange sites, resulting in lower amounts adsorbed. Despite the fact that competing ions can reduce the amount of Cr(III) adsorbed, the extent to which this could be a potential problem is not known.

Considerably greater interest has been given to the adsorption characteristics of Cr(VI) than that of Cr(III) (Bartlett and Kimble 1976b; Bloomfield and Pruden 1980; James and Bartlett 1983c; Stollenwerk and Grove 1985; Ainsworth et al. 1989; Zachara et al. 1989). This is probably due to the fact that Cr(VI) is much more mobile in soils than Cr(III), and adsorption may be one method of reducing its mobility in soils (Bartlett and Kimble 1976b). Also, it has been reported that the removal of soluble Cr(VI) by the soil via reduction may be wrongly interpreted as adsorption, or vice versa (Bloomfield and Pruden 1980; James and Bartlett 1983c). Both forms of Cr(VI) in soils, namely, $Cr_2O_7^=$ and $CrO_4^=$, exist as anions and thus undergo anion adsorption in soils (Bartlett and Kimble 1976b; Griffin et al. 1977; James and Bartlett 1983c; Stollenwerk and Grove 1985). Further, it is believed that Cr(VI) as $CrO_4^=$, undergoes specific anion adsorption (Bartlett and Kimble 1976b; James and Bartlett 1983c). Specific anion adsorption occurs when anions coordinate directly with the metal ion of a mineral surface by ligand exchange (Hingston et al. 1967). Thus if Cr(VI)

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undergoes specific anion adsorption, it will be tightly bound compared with anions such as chloride, nitrate or sulphate, but it can be released by reaction with other specifically adsorbed anions such as phosphate, an important plant nutrient and major fertilizer (Bartlett and Kimble 1976b; Stollenwerk and Grove 1985).

Studies on the adsorption of Cr(VI) by various soils (James and Bartlett 1983c; Ottabong 1989b), clay minerals (Griffin et al. 1977), iron oxides (James and Bartlett 1983c; Ainsworth et al. 1989) and subsoils (Bloomfield and Pruden 1980; Zachara et al. 1989) have all shown that the adsorption of Cr(VI) increases as the pH decreases. This behaviour is characteristic of anion adsorption, and is the result of a greater positive net charge resulting from increasing H^+ activity (Stollenwerk and Grove 1985). The adsorption of Cr(VI) has been found to be depressed in the presence of SO_4^-, PO_4^- and dissolved inorganic carbon, which compete for adsorption sites (Bartlett and Kimble 1976a; Zachara et al. 1989). This gives evidence to suggest that Cr(VI) may undergo both specific and nonspecific anion adsorption (Stollenwerk and Grove 1985), but more importantly emphasizes the fact that P fertilizers commonly added to soils not only contain Cr as an impurity, but they also influence the mobility and plant availability of Cr in soils.

2.2.3 Organic Complexation of Chromium in Soils

Organic compounds in soils can markedly influence the mobility of Cr in soils under two sets of conditions: one is by the reduction of soluble Cr(VI) to Cr(III), and the other is by complexation of Cr(III). Trivalent Cr can be complexed in soils by a variety of organic components, such as citric acid, gallic acid, and acetic acid which may

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be present in organic waste materials added to soils, may form during their decomposition or that of other organic residues in soils, or may be formed from plant root exudates (Bartlett and Kimble 1976a; James and Bartlett 1983a,b). Organically complexed Cr(III) is more soluble than the free Cr(III) metal ion which, in general, will quickly become adsorbed and/or hydrolysed and precipitated in soils, in the absence of soluble complexing ligands (James and Bartlett 1983a). Therefore, if Cr(III) is organically complexed, it will be more mobile in soils than the free ion, and thus, presents a potential pollution problem (Bartlett and Kimble 1976a; James and Bartlett 1983a).

Free Cr(III) metal ions added to soils will precipitate in soils, even at very low concentrations, in a pH range between four and five (Bartlett and Kimble 1976a). However, it has been reported that if Cr(III) is complexed by citric acid, diethylenetriaminepentaacetic acid (DTPA), fulvic acids, or water soluble organic matter from air dried soil, complexing will allow the Cr(III) to remain soluble above pH 5.5 and will prevent its immediate removal by other reactions occurring in soils (Bartlett and Kimble 1976a; James and Bartlett 1983a). Similar effects have been reported in aluminum-montmorillonite systems where the presence of dissolved acetate and citrate anions hindered the hydrolysis, polymerization and eventual fixation of Al^{3+} by the clay (Goh et al. 1986). This ultimately led to an increase in aluminum toxicity. Whether or not the mobilization of Cr(III) by organic complexation reduces or enhances Cr toxicity would depend on the persistence and stability of the complexes in the solution phase. Although naturally occurring Cr(III) may be complexed by fulvic acids,

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this fraction does not represent a very large fraction of the total soil Cr (Bartlett and Kimble 1976a). However, these complexes can remain soluble in soils for at least one year (James and Bartlett 1983b). Thus, it is the addition of organic waste materials, such as manures, alfalfa meal and sewage sludges which will have the greatest effect on complexing Cr(III), thereby increasing its mobility in soils (Bartlett and Kimble 1976a; Gerritse et al. 1982; James and Bartlett 1983b). For sewage sludges, it is believed that the increased mobility in soils is due to a combination of complexation by dissolved organic compounds, high background concentrations and high ionic strengths of the soil solutions (Gerritse et al. 1982).

It is important to note that if Cr(III) is organically complexed it still may undergo reaction with Mn oxides, forming Cr(VI). The rate of Cr(VI) formation is however, slower, because complexing neutralizes the positive charge on Cr(III) and the reaction rate depends upon the rate of release of Cr^{+3} from the complex, either directly to the oxide or indirectly to hydroxyls and then to the oxide (James and Bartlett 1983b). Despite the fact that the rate of oxidation is slower, organically complexed Cr(III) is oxidized for longer periods of time, than free Cr^{+3} cations, most likely because the chelate complex is not precipitated in soils (James and Bartlett 1983b). It has further been reported that the binding of the organic ligand by Cr(III) prevents it from microbial attack and oxidative breakdown, and thus, once Cr(III) is released from the complex to Mn oxides, the free organic ligand can complex more Cr(III) (James and Bartlett 1983b). Therefore, chelation can increase the overall solubility of Cr in soils because it

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facilitates oxidation of Cr(III), and oxidation promotes further chelation.

There has been a very limited amount of research conducted to determine whether organic Cr(III) complexes are likely to be toxic to plants. One study reported, that the chelating agents EDTA and NTA increased the toxicity of $Cr_2(SO_4)_3$ in bush beans grown in soil (Wallace et al. 1976). Therefore, there is a possibility that organic complexation of Cr(III) can increase the toxicity of Cr(III), but more research is required to determine the extent to which Cr(III) complexes may be a problem and defined conditions under which toxicity is most likely to occur need to be developed.

2.3 Factors Influencing the Plant Availability of Chromium

Solution culture experiments have shown that Cr(III) and Cr(VI) are equally available for uptake by plant roots (Hunter and Vergnano 1953; Breeze 1973; Huffman and Allaway 1973b; McGrath 1982). Experiments using soil as a growth medium have demonstrated that many soil factors influence the mobilities in soil and availabilities of Cr(III) and Cr(VI) for plant uptake. The availability of Cr(III), as a cation, will decrease dramatically as the cation exchange capacity and pH of the soil increase, as a result of adsorption and precipitation reactions (Bartlett and Kimble 1976a; Griffin et al. 1977). In comparison, the availability of Cr(VI), an anion, is not significantly altered by these reactions; however, in this case increased levels of organic matter may reduce Cr(VI) to Cr(III), and then Cr(VI) will undergo subsequent reactions as Cr(III) which will drastically reduce

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its availability to plants (Cary et al. 1977b; Bloomfield and Pruden 1980; James and Bartlett 1983c). Organic complexation of Cr(III) can increase the availability of Cr(III) as its solubility in soils, and hence its plant availability in soils will increase (James and Bartlett 1983a,b). As well, the oxidation of Cr(III) to Cr(VI) can significantly increase the availability of Cr(III) in soils, since Cr(VI) is the more mobile oxidation state (James and Bartlett 1979).

2.4 Bioeffects of Chromium on Plants

2.4.1 Essentiality of Chromium in Plants

There is no evidence that Cr plays an essential role in plant metabolism (Allaway 1968; Zaccheo et al. 1982; NRCC 1985), despite the fact that many reports state that Cr had a stimulating effect on plant growth (Adriano 1986). The stimulating effects reported, in fact, have been difficult to explain because they were generally small, inconsistent and mostly inconclusive (Pratt 1966; Allaway 1968; Huffman and Allaway 1973a). Further, Huffman and Allaway (1973a) demonstrated that Cr was not an essential element for higher plant growth. Nevertheless, as they could not reduce the level of Cr in their solutions below 3.8×10^{-4} μM, and as a contamination of Cr entering their experiments from the atmosphere was detected, the question of essentiality of Cr at very low levels was not resolved.

2.4.2 Uptake, Translocation and Accumulation of Chromium by Plants

Solution culture experiments have demonstrated that both Cr(III) and Cr(VI) are taken up by plants (Breeze 1973; Huffman and Allaway

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1973b; McGrath 1982) and the uptake of Cr(III) is more rapid than Cr(VI) (Skeffington et al. 1976; Myttenaere and Mousny 1974). Further, it has been shown, through the use of metabolic inhibitor studies, that the two do not share a common uptake mechanism: that is, the uptake of Cr(III) as Cr^{+3} is a passive process while that of Cr(VI) as CrO_4^- is active (Skeffington et al. 1976). It is believed that CrO_4^- is transported across the plasmalemma via the "carrier" normally involved in the uptake of $SO_4^=$, since $SO_4^=$ has been shown to inhibit CrO_4^- uptake competitively (Shewry and Peterson 1974; Skeffington et al. 1976).

Once Cr is absorbed by plants, it remains primarily in the roots and it is poorly translocated to the shoots (Skeffington et al. 1976; Cary et al. 1977a; Parr and Taylor 1980; Schmitt and Weaver 1984; Johnson and Weaver 1986). Some researchers have found that the proportion of Cr translocated to the shoots is similar, regardless of the form of Cr supplied to the roots (McGrath 1982; Cary et al. 1977a), while others have reported that CrO_4^- is transported better than Cr^{+3} (Skeffington et al. 1976; Myttenaere and Mousny 1974). It is possible that the $CrO_4^=$ anion is more mobile in the plant tissues than Cr^{+3} because Cr^{+3} may be held up by ion exchange on the vessel walls, and this does not take place for CrO_4^- (Skeffington et al. 1976). Despite these findings, Cr, regardless of oxidation state, remains mainly in the roots. Solution culture experiments, conducted by Huffman and Allaway (1973b), using ^{51}Cr-labelled Cr(III) and Cr(VI), showed that mature bean roots contained about 92%, and wheat roots 95% of the total plant [51]Cr. Similar results were obtained for rice plants where more than 99% of the Cr absorbed by the plants remained in the roots (Myttenaere and Mousny

1974). These findings suggest that there is a very limited chance that Cr may accumulate in the above ground portions of plants to an extent that would ultimately be toxic to organisms which consume the plants.

The reason for the barrier in the translocation of Cr in plant tissues is unknown. It has been postulated that Cr may not be easily transported due to spatial localization in subcellular compartments such as vacuoles of root cells (Shewry and Peterson 1974). This hypothesis has not been completely accepted since others have found that the translocation of Cr in different plant species is associated with a single low molecular weight anionic complex and not associated with any subcellular organelles (Huffman and Allaway 1973b; Johnson and Weaver 1986). With respect to the limited translocation of Cr, it has been simply stated that the accumulation of Cr by plant roots is apparent and may be the result of precipitation of oxides or hydroxides of Cr on the surfaces of the plant roots and not within them (Cary et al. 1977a). This explanation appears quite logical since much of the Cr present and added to soils converts to insoluble forms.

The Cr content of the edible portions of plants has received substantial attention because of the known essentiality of Cr(III) in animal nutrition (Welch and Cary 1975; Cary et al. 1977a; Schmidt and Weaver 1984). In the literature, however, there are limited reports on the Cr contents of plants grown in uncontaminated soils. The concentration of Cr in plants, like most other elements, varies widely between plant species and within species for various tissues and stages of growth (Huffman and Allaway 1973b; Shewry and Peterson 1976; Schmidt and Weaver 1984). Cr present in plant materials is usually in the order

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of 0.02 to 0.2 μg g^{-1} (dry weight), and a decreasing gradient in the concentration of Cr exists from roots to leaves to seeds (Allaway 1968; Huffman and Allaway 1973b; Wallace et al. 1976; Kabata-Pendias and Pendias 1984). A survey of wheat seeds, collected in the United States, revealed, that the seeds contained between 3 and 43 ng Cr g^{-1} dry weight (Welch and Cary 1975). In a similar survey, the Cr and Fe concentrations of a number of vegetable crops were measured: the Cr contents of the vegetables were in the range between 0.02 and 0.80 μg g^{-1}, which is much greater than the Cr content of wheat seeds (Cary et al. 1977a). This survey also reported that the vegetables that accumulated more Fe, also accumulated more Cr (Cary et al. 1977a). There are plant species which can accumulate significant quantities of Cr. It should be noted that there are plants which accumulate large quantities of Cr in their tissues. These plants have been termed "accumulators" and characteristically are native to serpentine soils (Allaway 1968; Cary et al. 1977a). Although these plants collect considerable amounts of Cr, there are no food or feed crops identified as effective Cr accumulators; therefore, these plants are of little value in improving the Cr nutrition of animals (Allaway 1968).

Many attempts have been made to increase the Cr concentration in the edible portions of plants to improve the intake of Cr(III) by animals. Thus researchers have added Cr to soils (Cary et al. 1977a), injected Cr into the stems of plants (Johnson and Weaver 1986), sprayed [51]CrEDTA onto leaves (Myttenaere and Mousny 1976) and applied Cr to nutrient solutions containing chelates or no chelates (Cary et al. 1977a), in efforts to increase the Cr content of the edible tissues.

Although these experiments were somewhat successful, the results do not appear too promising in increasing the Cr intake of animals since the recovery by food crops, was very inefficient for the amounts of Cr added (Cary et al. 1977a) and, very little of the Cr contained in leaves is absorbed by the animals (Huffman and Allaway 1973b).

2.4.3 Toxicity of Chromium in Plants

The majority of reports which exist on Cr toxicity come from controlled experimental conditions in which varying levels of Cr have been added to nutrient solutions or soils. The occurrence of Cr toxicity in the field is rare: it has, in general, been restricted to serpentine soils which contain high levels of both total Cr and nickel (Ni) (Soane and Saunder 1959; Anderson et al. 1973). It should be emphasized, however, that the descriptions from serpentine sites can not be attributed solely to Cr toxicity. It is believed that either both Cr and Ni toxicities may have been occurring together on these sites, or that Ni may have been responsible for the bulk of the toxic effects and that presence of Cr aggravated Ni toxicity (Hunter and Vergnano 1953; Soane and Saunder 1959; Anderson et al. 1973).

Solution culture and soil experiments have demonstrated that the toxic thresholds for Cr(III) and Cr(VI) for different plant species depends upon the oxidation state of Cr and many soil factors such as pH, Eh, organic matter content, mineralogy and texture of soils. Nevertheless, it possible to make some generalizations with regards to toxic levels of Cr in nutrient solutions and in soils:

1. The toxic threshold for total Cr(III) or Cr(VI) in

solution culture is in the range of one to five μg g^{-1}
(Turner and Rust 1971; Breeze 1973; NRCC 1976; Wallace
et al. 1976; McGrath 1982).

2. The toxic threshold for total Cr(III) in soils changes
with the cation exchange capacity (CEC), pH, and
organic matter content of the soil. As the CEC
increases, the toxic threshold for Cr(III) increases
to five to ten μg g^{-1} for sand, and to 5000 μg g^{-1} for
compost, consisting mostly of organic matter (Breeze
1973; NRCC 1976). As well, by increasing acidity and
decreasing the organic matter content, Cr(III)
solubility increases and hence its plant availability
increases, thus decreasing its toxic threshold
(Bartlett and Kimble 1976a).

3. The toxic threshold for total Cr(VI) also increases to
five μg g^{-1} in a sandy soil (Soane and Saunder 1959)
and to 500 μg g^{-1} for compost (Breeze 1973; NRCC
1976), but in this case, the toxic threshold for
Cr(VI) is more affected by the extent that organic
matter reduces Cr(VI) to Cr(III). This conversion is
slower in alkaline than acid soils (Cary et al. 1977b)
and under anaerobic than aerobic conditions (Artiole
and Fuller 1979).

4. The toxic threshold for total Cr(VI) may be reached,
even if Cr(III) is added to soil, because the maximum
reported oxidation of Cr(III) to Cr(VI) by oxidized

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soil Mn was 1.2 mg g^{-1} (Bartlett and James 1979).

A range of Cr concentrations in plant tissues before symptoms and
when definite symptoms of Cr toxicity occur has been reported by many
researchers (Adriano 1986). For example, an upper critical level of Cr
(that is, the minimum concentration of Cr in actively growing tissues of
a plant at which yield is reduced) has been reported to be ten μg g^{-1}
in the leaves and shoots of barley (Davis et al. 1978). Although these
findings are significant, it was pointed out early by Hunter and
Vergnano (1953) and in many subsequent studies that while the toxic
effects of most heavy metals (for example Ni, Co, and Zn) are associated
with high concentrations of the element in the leaf tissue, this is not
the case with Cr (Soane and Saunder 1959; Turner and Rust 1971; Wallace
et al. 1976). This indicates that plants suffering from induced Cr
toxicity have essentially the same amount of Cr in leaves and stems as
that found in unaffected plants (Allaway 1968). Since the translocation
of Cr to the leaves is slight, the main toxic action of Cr has been
hypothesized by several researchers to occur in the roots where the Cr
concentration is the highest of all plant parts (Shewry and Peterson
1974; NRCC 1976; Wallace et al. 1976; Cary et al. 1977a; Dijkshoorn et
al. 1979). This means that there is little possibility of Cr
contamination of the food chain because plants would die before they
accumulated significant quantities of Cr in their tissues (Huffman and
Allaway 1973b; NRCC 1976; Cary et al. 1977a; Dijkshoorn et al. 1979).

The mechanism(s) involved as to the cause of Cr toxicity are
unknown, although several hypotheses have been provided. Cr has not

only been shown to repeatedly reduce yields in many plant species but also to interfere with the accumulation of a broad range of plant nutrients (Hewitt 1953; Turner and Rust 1971; Anderson et al. 1973; Skeffington et al. 1976; Barcelo et al. 1985). Since Cr may affect plant growth or elemental uptake either directly or indirectly, many of the explanations of Cr toxicity put forth have focused on the interactions between Cr and other elements either in soils or in plants. For example, several researchers have found that the solubilities of Fe and Mn have been modified when Cr was added to soils (Bartlett and James 1979; Grove and Ellis 1980b; Otabbong 1989b). The solubility of Mn has been shown to increase when Cr(III) is added to soils. This has been attributed to the lowering of soil pH resulting from the precipitation of Cr(III) thereby dissolving sparingly soluble compounds of Mn (Grove and Ellis 1980b). As well, Bartlett and James (1979) have shown that the amounts of soluble Mn(II) will increase when Cr(III) is oxidized to Cr(VI) by Mn oxides. In contrast to Mn, the solubility of Fe has been shown to decrease when Cr(III) is added to soils and it is suspected that this is due to a Cr-Fe coprecipitation reaction. Ottabong (1989b) also reported that the reduction of Cr(VI) by the oxidation of Mn(II) and Fe(II) may decrease the availability of these elements. Cr can also interfere with the uptake and translocation of many elements. Turner and Rust (1971) found Cr(VI) to interfere with Ca, K, P, Fe, Mg, and Mn uptake in nutrient culture and plant Ca, K, Mg, P, B, and Cu in soil culture. Because Cr(VI) inhibited H^+ exclusion and K^+ uptake by maize roots in nutrient solution, Zaccheo et al. (1982) concluded that the phytotoxicity of the Cr was due to the interference with H-K exchange.

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Further, Ross et al. (1981) reported that Cr(III) and Cr(VI) inhibited microbial activity and thus, may affect important soil microbial transformation such as nitrification.

The visual symptoms of Cr toxicity have been described for a number of plant species (Hunter and Vergnano 1953; Soane and Saunder 1959; Turner and Rust 1971; Anderson et al. 1973; Bartlett and James 1979; McGrath 1982). Because of the many possible conversions that Cr may undergo in soils and in plants, the individual toxicities of Cr(III) and Cr(VI) have not been distinguished (Skeffington et al. 1976; McGrath 1982; NRCC 1985). The most common symptoms of Cr toxicity described include chlorosis, stunted growth, a poorly developed root system and discoloured leaves. Some plant species may also exhibit brownish red leaves, containing small necrotic areas or purpling of basal leaves. It is believed that these symptoms reported for the leaves, are in general, subsequent to damage caused by Cr toxicity in the roots (Soane and Saunder 1959).

2.5 Chromium in Fertilizers and Sewage Sludges

Chromium can enter the environment from many sources via air emission, aqueous emission and land disposal (Adriano 1986; Schroeder 1987; Otabbong 1989c). It is the sources via land disposal particularly the use of fertilizers and sewage sludges which are of interest to agricultural soils in Manitoba.

Chromium can be found as an impurity in fertilizers, commonly added to soils, in the range of five to several thousand μg Cr g^{-1} (Watanabe 1984; Adriano 1986). The National Research Council of Canada

(NRCC 1976) reported the following values for Cr contents in various fertilizers in μg g^{-1}: Nitrogen Fertilizers <5 to 3000; Phosphorous Fertilizers 30 to 30 000; Superphosphates 60 to 250; Lime Meal <20 to 500; and Limestone <1 to 200. Studies conducted on the accumulation and bioavailability of this source of Cr indicate that there is little possibility that Cr originating from fertilizers will increase to toxic concentrations as a result of common applications of fertilizers and hence, should not be considered a source of man-induced contamination of cultivated soils (Frank et al. 1976; Goodroad and Caldwell 1979; Watanabe 1984). Although the Cr concentration may be somewhat higher in surface soils due to the application of Cr containing fertilizers, silicate and liming materials, it is inert and stable in soils, hardly mobilized and may be only moderately absorbed by plants (Goodroad and Caldwell 1979; Watanabe 1984). Plant studies have further demonstrated that Cr applied as a contaminant in fertilizers does not affect plant concentrations of Cr and in no way affects yields (Mortvedt and Giordano 1975; Goodroad and Caldwell 1979).

The application of sewage sludges to agricultural land has long been practised for purposes of improving the fertility and physical conditions of the soil, as well as, a means of avoiding pollution of surface waters (Lund et al. 1976; Zwarich and Mills 1979; Williams et al. 1985). Unfortunately it has been shown that sewage sludges introduce large amounts of heavy metals, including Cr, into agricultural soils which are considered harmful to plant or animal health (Cunningham et al. 1975a,b; Zwarich and Mills 1979; Gerritse et al. 1982; Chang et al. 1984a; Williams et al. 1985). Thus, numerous investigations have

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been conducted to determine the accumulation, movement and bioavailability of these heavy metals, as well as the risk of food chain contamination, from both a water quality and crop production point of view.

The concentrations of metals in sewage sludges varies greatly, even within a single treatment facility, and very markedly amongst different sources of sewage sludges (Lund et al. 1976; McGrath 1984). Thus, depending on the source, Cr in sewage sludges and other materials may range from trace to several thousand $\mu g\ g^{-1}$ (NRCC 1976; Adriano 1986). It is believed that the Cr present in sewage sludges exhibits the chemistry and immobility of Cr(III), and exists either as a precipitated Cr(III) compound(s), such as $Cr(OH)_3$, or as an organic complex with high molecular weight organic compounds (Grove and Ellis 1980a; James and Bartlett 1983b).

Although repeated annual applications of sewage sludges can significantly increase the Cr content of the amended soils (Cunningham et al. 1975a; McGrath 1984), Cr, as well as other heavy metals do not move to any great extent below the zone of incorporation in soils regardless of the physical and chemical properties of the soil, or of the physical characteristics of the sludge (either composted or liquid sludge) (Lund et al. 1976; Chang et al. 1984a,b; Williams et al. 1985; Dowdy et al. 1987). Further, it has also been reported that Cr is one of the least mobile of the heavy metals present in sludge-amended soils (Williams et al. 1985), and with time all of the metals in the sludge-amended soils change to less mobile and available forms (Cunningham et al. 1975b). These examples demonstrate that Cr present in sewage

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sludges and applied to soils poses little possibility of contaminating the food chain or ground water because of its insoluble and immobile behaviour.

Experiments using plants as indicators of the availability of Cr in sewage sludge-amended soils have shown that this source of Cr is relatively unavailable to plants or it is excluded by plants (Cunningham et al. 1975a,b; Zwarich and Mills 1979; Williams et al. 1980; Chang et al. 1984b). Some of these investigations have reported that no Cr is taken up by plants when sewage sludges are the source of Cr (Mortvedt and Giordano 1977; Zwarich and Mills 1979), while other studies have found that the Cr content of the tissues increases with sludge Cr content and the application rate (Cunningham et al. 1975a; Chang et al. 1984b). It must be emphasized, however, that although crops may absorb Cr, these amounts are insignificant (<1%) when compared to the amount of Cr introduced into the soil through land application of sludges (Chang et al. 1984b).

Although the majority of sewage sludge experiments have indicated that there is little possibility of food chain or water contamination by Cr, metal amended-sewage sludge investigations have demonstrated that realistic concentrations of Cr, as well as Cu and Cd, present in sludges, can detrimentally influence microbial populations in soils, many of which are active in the decomposition of sewage sludges (Zibilske and Wagner 1982). (The term metal amended-sewage sludge has been used by several authors to describe sewage sludge that has undergone equilibration with solutions containing varying amounts of heavy metals for different periods of time). Thus, Cr in sewage sludges

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may interfere with the capacity of soil microbial populations for nutrient recycling. Similar metal-amended sewage sludge experiments, however, showed that yields of plants increased as the sludge Cr concentration increased, because Cr inhibited the uptake or translocation of other toxic elements (Cunningham et al. 1975b). The reduction in uptake or translocation of other heavy metals by Cr was substantiated by tissue analysis which showed that with increasing sludge Cr tisssue concentrations of other metals (Cu, Zn, Ni, Cd and Mn) decreased (Cunningham et al. 1975b). Thus Cr in sewage sludges could be of some benefit but it is difficult to interpret the results of metal-amended sewage sludge experiments to the actual effect of sewage sludges because it is possible that the method of metal addition used in such experiments may result in different metal complexation reactions than those occurring in naturally contaminated sludge (Cunningham et al. 1975b; Zibilske and Wagner 1982). Similarly, reports from experiments with applications of reagent grade metals to soils can not be compared with sludge studies because the pure metals are much more soluble in soils and available to plants than the forms present in sewage sludges (Cunningham et al. 1975c; Mortvedt and Giordano 1975; Chang et al. 1984a). Therefore, caution must be used when attempting to use results of inorganic salt treatments, and metal amended sewage sludges to evaluate the phytotoxicity and toxic metal uptake from sewage sludge amended soils.

III. CHROMIUM IN MANITOBA SOILS

3.1 Introduction

Until the middle of the 1970s there was very little information available regarding the concentrations of heavy metals, such as Cr, in Canadian soils. Research however, was stimulated due to the concerns over the possibility of increasing concentrations in soils as a result of the use of fertilizers and sewage sludges which contain these elements as impurities and over the possibility of subsequent contamination of the food chain and water bodies. Consequently, background levels for many potentially harmful elements in some Canadian soils were established (Mills and Zwarich 1975; Frank et al. 1976; Dudas and Pawluk 1977; Whitby et al. 1978). These studies, in general, utilized only one or two extractants and analyzed only the surface horizons of the soils, and thus, there is little known about the profile distribution of these elements in terms of the total content and extractable forms. Further research to develop baseline levels of total and extractable forms of heavy metals within a soil profile are necessary in order to establish the fractions in soil that are dominated by heavy metals and to effectively interpret data for possible contamination.

This study was conducted to establish baseline levels of Cr in four of Manitoba's agricultural soils that exhibit a broad range of soil properties which occur in agricultural soils in the province. The soils were collected by horizon and analyzed for various soil properties, including total and extractable Cr.

Oxidation of added Cr(III) takes place in moist soils and Cr(VI) can be extracted from soil samples at least one year after Cr(III) addition (Bartlett and James 1979). Thus there is a concern about the oxidative behaviour of Cr(III) because Cr(VI) is much more mobile in soils and hence potentially toxic. Therefore, each horizon was analyzed in the field moist condition to determine its potential to oxidize added Cr(III) to Cr(VI).

3.2 Materials and Methods

3.2.1 Soils

Four pedons comprising soils from three Orders were sampled according to horizons. Table 3.1 displays the names of the soil series and subgroups given to the four pedons sampled. The pedons and their geographic characteristics, as well as descriptions of individual horizons are displayed in Appendix A.

Two soil samples were taken for analysis from each horizon. One sample was air dried in the laboratory, ground to pass a 2 mm sieve and its air-dried moisture content determined prior to further analysis. The second sample was immediately frozen so the sample would be kept in its field moist condition, until analysis. At the time of analysis, the frozen soil was thawed, and its moisture content was determined.

Table 3.1. Soil names and classification
of pedons used in this study.

Soil Series	Soil Subgroup
Almasippi	Gleyed Rego Black (Carbonated Phase)
Red River	Gleyed Rego Black
Waitville	Orthic Gray Luvisol
Osborne	Rego Humic Gleysol (Carbonated Phase)

3.2.2 Analytical Procedures

Each soil horizon was analyzed for chemical and physical
properties according to the procedures outlined below:

A. pH

Soil pH were determined on 1:1 water to soil, and 2:1 0.01 mol L^{-1}
$CaCl_2$ to soil pastes using a standard glass combination electrode. The
method was modified from McLean (1982).

B. Organic Matter Content

The organic matter contents were measured using the Walkley Black
method described by Allison (1965). The organic carbon was oxidized, in
acidic media, by $K_2Cr_2O_7$. An automatic titrator was used to back
titrate the excess K_2CrO_7 with $FeSO_4$, to an endpoint of 750 mV.

C. Calcium Carbonate Equivalent Content

The calcium carbonate equivalent content was determined by the
acid-neutralization method outlined by Allison and Moodie (1965). The
carbonates were decomposed with standardized HCl and the excess HCl was

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back titrated with standardized NaOH, to the phenolphthalein endpoint. The primary standard for NaOH was potassium hydrogen phthalate.

D. Soil Texture

The field textures were estimated by hand texturing. The percents of sand, silt, and clay were determined using the pipette method, after the removal of organic matter by oxidation with 30% H_2O_2 (Gee and Bauder 1986).

E. Total Chromium, Iron, and Manganese

The total contents of Cr, Fe, and Mn were determined by atomic absorption spectrometry following digestion of one gram of soil in concentrated HCl (McBride 1965).

F. Chromium Oxidation Quick Test

The ability to oxidize added Cr(III) to Cr(VI) was determined using a modification of the Cr oxidation quick test developed by Bartlett and James (1979). Approximately three grams of freshly thawed frozen soil were placed in a 50 mL centrifuge tube, along with 25 mL of 10^{-3} mol L^{-1} $CrCl_3 \cdot 6H_2O$. The suspensions were shaken for 15 minutes, and then centrifuged at 12 000 g for 30 minutes.

The Cr(VI) formed was sequestered by adding 1 mL of s-diphenyl carbazide reagent to 8 mL of supernatant and the complex produced was analyzed colorimetrically by measuring the absorbance at 540 nm. The s-diphenyl carbazide reagent was prepared according to Reisenauer (1982): 120 mL of 85% H_3PO_4 was diluted with 280 mL of distilled water, and added to 400 mg of s-diphenyl carbazide dissolved in 100 mL of 95% ethanol.

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G. Extractable Chromium, Iron, and Manganese

The contents of Cr, Fe, and Mn of the soils were estimated following extractions of individual samples with deionized water, 1 mol L^{-1} NH_4Cl, 0.1 mol L^{-1} HCl, DTPA, 0.01 mol L^{-1} KH_2PO_4, 2 mol L^{-1} HNO_3, 0.01 mol L^{-1} $Na_4P_2O_7$ and sodium citrate-bicarbonate-dithionite. These extractants were deemed to remove water soluble, exchangeable, acid-extractable, DTPA-extractable, readily available (Cr(VI)), and acid soluble Cr, Fe, and Mn, as well as Cr, Fe, and Mn associated with organic complexes and oxides, respectively. The supernatants collected from each extractant were analyzed for Cr, Fe, and Mn by atomic absorption spectroscopy, and for Cr(VI) using the s-diphenyl carbazide reagent when indicated.

1. Deionized Water

Ten grams of soil (oven dry equivalent) were shaken with 20 mL of deionized water for two hours, and then centrifuged for 20 minutes at 11 000 rpm. The procedure was repeated once and the supernatants were combined.

2. 1 mol L^{-1} NH_4Cl

Ten grams of soil (oven dry equivalent) were shaken with 20 mL of 1 mol L^{-1} NH_4Cl, for two hours and then centrifuged for 20 minutes at 11 000 rpm. The extraction was repeated once with 1 mol L^{-1} NH_4Cl, followed by two 20 mL washings with 60% acetone-water. The supernatants were combined. The acetone was added to promote flocculation of the residue.

3. 0.1 mol L^{-1} HCl

The method was described by Baker and Amacher (1982). Two

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grams of soil were treated with 20 mL of 0.1 mol L^{-1} HCl. The suspension was immediately centrifuged at 13 000 g for 25 minutes. The procedure was repeated five times and the supernatants were combined.

4. DTPA

The method followed was that according to Lindsay and Norvell (1976). Ten grams of soil were shaken for 2 hours with 20 mL of the DTPA extracting solution. The suspension was then centrifuged for 20 minutes at 13 000 g.

5. 0.01 mol L^{-1} KH_2PO_4

The procedure followed was described by Reisenauer (1982) and Bartlett and James (1979); however, air dried soil were used. Three grams of air dry soil were shaken for 5 minutes with 25 mL of 0.01 mol L^{-1} KH_2PO_4 and centrifuged at 13 000 g for 25 minutes.

6. 2 mol L^{-1} HNO_3

The procedure employed was described by Hafez et al (1979) and Reisenauer (1982). Twenty-five mL of 2 mol L^{-1} HNO_3 and 2.5 g of soil were shaken for two hours and then centrifuged at 13 000 g for 20 minutes.

7. 0.1 mol L^{-1} $Na_4P_2O_7$

The method followed was modified from Bascomb (1968) and McKeague (1967). Two grams of soil were brought into suspension with 35 mL of 0.1 mol L^{-1} $Na_4P_2O_7$. The suspensions remained in contact for 22 hours, followed by shaking for four hours and then centrifuged at 13 000 g for 30 minutes.

8. Sodium citrate-bicarbonate-dithionite (CBD)

The free iron oxides were removed from the soil according to the method of (Mehra and Jackson 1960). The extractant used consisted of a buffer (sodium bicarbonate), a reductant (sodium dithionite) and a chelating agent (sodium citrate).

Once the procedure was completed, the residue remaining was washed four times with 20 mL each time with 75% acetone-water, to ensure all of the Cr, Fe and Mn extracted were removed from solution.

3.3 Results and Discussion

3.3.1 Properties of Soils Sampled and Analyzed

Table 3.2 displays the variation in pH, organic matter content, calcium carbonate equivalent content and particle size distribution in the horizons of the four pedons under study. The surface horizons of the Red River Series and Waitville Series soils were slightly acidic. The organic matter contents in the surface horizons of the pedons varied between 1.12% in the Waitville Series soil and 10.19% in the Osborne Series soil. Organic Matter decreased with depth within all pedons. All of the soils were formed from parent materials containing carbonates. The Almasippi Series soil was developed from a sandy parent material and of the four pedons under study contained the greatest amount of sand. Both the Osborne and Red River Series soils developed from clay parent materials. The Red River Series soil, however, contained much more clay than the Osborne Series soil. The Waitville Series soil developed from boulder till parent material which resulted

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Table 3.2. Comparison of soil properties among pedons studied.

Soil Series	Horizon	pH Water	pH CaCl$_2$	%Organic Matter	%Calcium Carbonate	%Sand	%Silt	%Clay
Almasippi	Ah	8.2	7.8	4.9	12.5	74	11	15
	AC	8.3	7.6	0.5	7.1	93	0	7
	Ck1	8.5	7.6	0.2	7.6	96	0	4
	Ck2	8.5	7.7	0.2	11.9	97	0	3
Red River	Ap	7.0	6.6	6.4	0.0	12	20	68
	Ck1	8.1	7.7	2.2	12.5	7	29	64
	Ck2	7.9	7.8	1.4	12.6	4	34	62
Waitville	Ae	6.2	5.5	1.1	0.0	66	9	25
	Bt	6.6	6.0	1.4	0.0	42	7	51
	BC	8.0	7.3	1.1	24.7	59	18	23
	Ck	8.1	7.5	0.6	24.7	55	15	30
Osborne	Apk	7.8	7.4	10.2	6.9	31	24	45
	Ahk1	8.0	7.6	6.2	5.8	26	19	55
	Ahk2	8.1	7.9	2.8	2.8	25	20	55
	Ckg1	8.1	8.0	1.0	12.0	19	26	55
	Ckg2	8.2	7.8	1.0	12.6	15	25	60

in a medium textured soil. It is evident from the Ae and Bt horizons of this soil that the soil is strongly leached and has undergone eluviation of clay, as well as some organic matter.

The Almasippi Series and Red River Series soils are grassland soils which have developed under imperfect drainage. Both of these soils were classified in the Chernozemic soil order as Gleyed Rego Blacks. The Waitville Series soil developed under forest vegetation and good drainage and was classified in the Luvisolic soil order as an Orthic Gray Luvisol. The Osborne Series soil is also a grassland soil but it developed under poor drainage. It was classified in the Gleysolic soil order as a Rego Humic Gleysol.

3.3.2 Total Chromium, Iron, and Manganese

The total contents of Cr, Fe, and Mn in the concentrated hydrochloric acid digest, are presented in Table 3.3 by soil and by horizon. The profile averages for total Cr range from 13 in the Almasippi Series soil to 27 μg Cr g^{-1} soil in the Waitville Series soil. Among the individual horizons within the soils, the range of Cr concentrations was from 6 μg Cr g^{-1} in the Ck1 horizon of the Almasippi soil to 36 μg Cr g^{-1} in the Bt horizon of the Waitville soil. These results show that the naturally occurring amounts of Cr in Manitoba's agricultural soils fall into the lower portion of the range given for Canadian soils which is between 20 and 125 μg Cr g^{-1} soil (Adriano 1986). The total Cr contents in each soil profile are distributed quite uniformly with the exception of the Waitville Series soil. Similar results of uniformity have been reported from other regions in Canada: Whitby et al. (1978) found (Ap=53; B=55; and C=49 μg Cr g^{-1} soil) for

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Table 3.3.   Distribution of chromium, iron and manganese in the
             pedons analyzed in this study.

Soil Series	Horizon	Total Cr (μg g^{-1})	Total Fe (μg g^{-1})	Total Mn (μg g^{-1})
Almasippi	Ah	17 ±3	8276 ±25	406 ±3
	AC	13 ±2	8948 ±179	227 ±15
	Ck1	6 ±1	8208 ±71	140 ±1
	Ck2	15 ±3	11758 ±158	192 ±5
Red River	Ap	22 ±2	24142 ±184	784 ±14
	Ck1	26 ±2	27553 ±30	674 ±28
	Ck2	26 ±4	28518 ±219	658 ±16
Waitville	Ae	11 ±1	13462 ±2298	813 ±140
	Bt	36 ±2	34300 ±1289	930 ±22
	BC	10 ±3	17435 ±772	534 ±33
	Ck	7 ±1	11507 ±319	620 ±8
Osborne	Apk	22 ±4	18631 ±519	365 ±8
	Ahk1	26 ±2	20295 ±487	238 ±2
	Ahk2	13 ±3	15916 ±110	202 ±3
	Ckg1	26 ±4	25362 ±185	575 ±10
	Ckg2	26 ±2	27995 ±315	734 ±14

some agricultural soils in Ontario, and Roberts (1980) obtained a range between 750 - 1530 μg Cr g^{-1} soil for young soils in Newfoundland derived from serpentine parent materials which contained only C horizons. In other countries, Cr contents have been found to be higher in the parent material than in the surface horizons (Conner et al. 1957; Pierce et al. 1982) or higher in the surface horizons than in the parent material (Bleeker and Austin 1970).

The Bt horizon of the Waitville Series soil displayed a significant accumulation of total Cr (Table 3.3), compared to the other horizons in that soil. Thus, Cr is concentrated in the clay fraction and is subject to illuviation in the Bt horizon with the clay. The results obtained for the other soils, further show that soils which contain greater amounts of clay, namely the Red River and Osborne Series soils, have higher total Cr contents than soils with lower clay contents, such as the Almasippi Series soil. Correlation analysis of these results (Table 3.5) indeed reveals that the total Cr content is negatively correlated with the amount of sand, and positively correlated with the contents of silt and clay within the soils. Several authors have reported that the majority of Cr in soils is associated with the clay fraction (Conner et al. 1957; Bartlett and Kimble 1976a; Whitby et al. 1978; MacLean and Langille 1980) or have stated that sandy soils contain lower amounts of total Cr than clay soils (Frank et al. 1976).

The total Fe contents ranged from 8208 μg g^{-1} in the Ck1 horizon of the Almasippi Series soil to 34285 μg g^{-1} in the Bt horizon of the Waitville Series soil (Table 3.3). In each soil, except the Waitville soil, the amount of Fe increased with depth in the soil profiles. In

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the Waitville soil, there was a significant accumulation of Fe in the Bt horizon due to the illuviation of Fe with the clay; there was also an enrichment of Fe in the BC horizon. It is of interest to note further that in contrast to the other soils, the Ae horizon of this soil, which has undergone eluviation, contains somewhat more Fe than the Ck horizon.

The total contents of Mn in the soils varied between 140 μg g^{-1} in the Ck1 horizon of the Almasippi soil and 930 μg g^{-1} in the Bt horizon of the Waitville soil (Table 3.3). The Mn concentrations in the Almasippi, Red River and Waitville soils decreased with depth in a soil profile, while the contents increased with depth in the Osborne soil. In the Waitville soil, there was also an accumulation of Mn in the Bt due to illuviation with the clay.

Total Cr was significantly correlated with the total contents of Fe and Mn, despite the fact that it was uniformly distributed within the soils. This means that the amounts of these elements in the soils is dependent on the mineralogy of the parent material of these soils. Furthermore, the total contents for both Fe and Mn, as well as Cr, are significantly correlated with the texture of the soil (Table 3.5), which is a property inherited from the parent material of a soil.

3.3.3 Extractable Chromium

Table 3.4 displays the amounts of Cr extracted from the soils with various extractants. The Mn and Fe extracted were also analyzed. These results are presented in Appendix B.

The amounts of water soluble Cr from all soils were below detection limits which means that there was very little or no Cr in the soil solution (Table 3.4). It is likely that if Cr was not adsorbed or

Table 3.4. Amounts of chromium released from soil by various extractants ($\mu g\ g^{-1}$).*

Soil Series	Horizon	DTPA	1 mol L^{-1} NH_4Cl	0.01 mol L^{-1} HCl	2 mol L^{-1} HNO_3	CBD	0.1 mol L^{-1} $Na_4P_2O_7$	0.01 mol L^{-1} KH_2PO_4
Almasippi	Ah	1.14	0.27	0.51	4.28	4.23	0.41	0.12
	AC	1.26	0.27	1.01	1.71	3.85	0.22	0.00
	Ck1	1.22	0.17	1.26	2.70	4.16	0.14	0.10
	Ck2	1.38	0.22	1.00	3.57	4.54	0.09	0.15
Red River	Ap	1.56	0.16	0.27	4.63	6.40	2.87	0.15
	Ck1	1.57	0.11	0.27	6.66	6.00	0.83	0.19
	Ck2	1.75	0.16	1.05	6.65	5.56	0.18	0.14
Waitville	Ae	0.75	0.00	2.52	1.65	5.89	0.97	0.35
	Bt	0.87	0.00	0.00	3.88	10.32	1.62	0.15
	BC	0.87	0.00	0.00	6.64	6.30	0.67	0.14
	Ck	0.85	0.00	0.00	7.26	5.52	0.35	0.22
Osborne	Apk	1.93	0.21	2.83	4.12	4.64	1.59	0.28
	Ahk1	2.14	0.33	1.26	4.14	4.96	2.73	0.42
	Ahk2	2.05	0.16	2.40	2.88	4.41	1.64	0.20
	Ckg1	2.26	0.16	1.63	5.68	5.73	0.76	0.17
	Ckg2	2.18	0.16	0.55	5.95	6.17	1.21	0.12

* The amount of water soluble Cr in the extracts was below detection limits.

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complexed in some other fraction then it precipitated, because it would be only very slightly soluble in these soils (James and Bartlett 1983b). Further, since the soils studied have pH greater than six and contain essentially Cr(III) which precipitates in soils above pH 4 (Bartlett and Kimble 1976a), the majority of the total soil Cr would exist as compounds which are not water soluble. This explanation is corroborated by the results of Cary et al. (1977b), who showed that even after one day of either Cr(III) or Cr(VI) addition to soil, very little (less than 3%) of the added Cr was water soluble or extractable with a weak (0.01 mol L^{-1}) $Ca(NO_3)_2$ solution.

Ammonium chloride (1 mol L^{-1} NH_4Cl) was used as an extractant to determine the amount of Cr in the exchangeable form (Grove and Ellis 1980a; Otabbong 1989a). The concentration of Cr extracted by 1 mol L^{-1} NH_4Cl ranged from 0 in all of the horizons in the Waitville soil to 0.33 μg Cr g^{-1} in the Ahk1 horizon in the Osborne soil. There was no significant variation in the amounts of Cr extracted by 1 mol L^{-1} NH_4Cl among the horizons within any of the soils (Table 3.4). The greatest amounts of Cr were extracted from the Almasippi and Osborne soils (Table 3.4), suggesting a poor correlation with the texture of these soils (Table 3.5), since the Almasippi soil is a coarse-textured soil, and the Waitville soil is a medium-textured soil. It should be noted that the concentration of exchangeable Cr present in soils represents a very small portion of the total Cr, and the results obtained for this extractant correspond to those of other researchers (Grove and Ellis 1980a; Otabbong 1989a). Ammonium acetate has also been used as an extractant to determine exchangeable Cr in serpentine soils:

Table 3.5. Correlation matrix relating soil properties, total Cr, Fe and Mn and extractable Cr.

	pH	total Cr	total Fe	total Mn	organic matter	%CaCO₃	%sand	%silt	%clay	CBD	DTPA	NH₄Cl	HCl	HNO₃	Na₄P₂O₇	KH₂PO₄
										------Extractable Cr------						
pH	x															
total Cr	ns	x														
total Fe	ns	0.84010 **	x													
total Mn	-0.56752 **	0.46714 **	0.67295 **	x												
organic matter	ns	ns	ns	ns	x											
%CaCO₃	0.48404 **	ns	ns	ns	ns	x										
%sand	ns	-0.63159 **	-0.80173 **	-0.49655 **	-0.34271 *	ns	x									
%silt	ns	0.45948 **	0.63094 **	0.37378 *	ns	ns	-0.91909 **	x								
%clay	ns	0.67479 **	0.83209 **	0.51762 **	0.35665 *	ns	-0.98179 **	0.83669 **	x							
CBD	-0.61374 **	0.54877 **	0.72355 **	0.80140 **	ns	ns	-0.35005 *	ns	0.42671 **	x						
DTPA	0.59849 **	0.37674 *	0.36084 *	ns	0.33954 *	ns	-0.62321 **	0.59357 **	0.58862 **	ns	x					
NH₄Cl	0.49961 **	ns	ns	-0.61551 **	ns	ns	ns	ns	ns	-0.58696 **	0.50113 **	x				
HCl	ns	ns	ns	ns	ns	-0.39644 *	ns	ns	ns	-0.34678 *	ns	ns	x			
HNO₃	0.36263 *	ns	0.43100 **	0.37946 *	ns	0.74883 **	-0.51792 **	0.65426 **	0.42143 **	ns	ns	ns	-0.52533 **	x		
Na₄P₂O₇	ns	0.44309 **	0.49083 **	ns	0.57142 **	-0.47923 **	-0.61754 **	0.38276 *	0.68833 **	ns	0.42207 **	ns	ns	ns	x	
KH₂PO₄	ns	ns	ns	ns	0.40057 *	ns	ns	ns	ns	ns	ns	ns	0.40483 *	ns	0.45032 **	x

*   the correlation coefficient was significant at the P=0.05 level.
** the correlation coefficient was significant at the P=0.01 level.
ns the correlation coefficient was not significant at the P=0.05 level.

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despite the fact that these soils contain substantial amounts of total Cr, it was determined that very little of the total Cr was in the exchangeable form (Shewry and Peterson 1976). The amount of Cr extracted by 1 mol L^{-1} NH_4Cl was, in fact, not correlated with the total Cr content of the soils (Table 3.5), indicating that if the total Cr content of a soil was increased, the amount of exchangeable Cr would probably not. A significant positive correlation coefficient was obtained between the amount of Cr extracted by NH_4Cl and the initial soil pH. This was interesting and showed that the amount of Cr extracted from soil by NH_4Cl will increase with pH.

One of the best known extracting agents for Cr(VI) is potassium dihydrogen phosphate (KH_2PO_4) and it has been used as a means of measuring soil Cr that is readily available to plants (Bartlett and Kimble 1976b; Reisenauer 1982; Otabbong 1989a). Bartlett and Kimble (1976b) reported that orthophosphate and Cr(VI) will compete for the same adsorption sites in soils, and that the presence of orthophosphate will prevent the adsorption of Cr(VI). Therefore, if adsorbed Cr(VI) is extracted by KH_2PO_4, it could potentially be available for plant uptake.

The results in Table 3.4 show that less than 0.5 μg Cr g^{-1} soil was obtained by extracting these soils with 0.01 mol L^{-1} KH_2PO_4. A very close agreement was obtained between the results of Cr extracted by 0.01 mol L^{-1} when analyzed by atomic absorption spectrometry for total Cr and the colorimetric determination of Cr(VI) using the colour reagent s-diphenyl carbazide, suggesting that the majority of the Cr extracted by KH_2PO_4 was Cr(VI). It should be noted that the extraction with 0.01 mol L^{-1} KH_2PO_4 as outlined by Reisenauer (1982) utilized fresh field moist

samples. The results reported herein (Table 3.4) may therefore be underestimates since air dried soil samples were used. It is known that drying of soil samples will increase the solubility and oxidizability of organic matter (Bartlett and James 1980) and thus, this may in turn decrease the amount of $Cr(VI)$ in the soil because reduction of $Cr(VI)$ to $Cr(III)$ by organic matter may have occurred. Despite the fact that organic matter donates electrons for the reduction of $Cr(VI)$ and thus, should decrease the amount of $Cr(VI)$ in soils, the amount of Cr extracted by 0.01 mol L^{-1} KH_2PO_4 was positively correlated with the organic matter content of the soils (Table 3.5). Further, since no Cr was obtained upon extraction with water, and most of the Cr extracted by 0.01 mol L-1 KH_2PO_4 was $Cr(VI)$, the $Cr(VI)$ present in these soils is adsorbed onto soil components which also adsorb phosphate anions, and hence, is potentially available to plants (Bartlett and Kimble 1976b).

The concentrations of Cr extracted by DTPA ranged from 0.75 in the Ae horizon of the Waitville Series soil to 2.26 μg Cr g^{-1} soil in the Ckg1 horizon of the Osborne Series soil, and slightly, but not significantly, increased with depth in the profile (Table 3.4). The amount of Cr extracted by DTPA was positively correlated with the initial soil pH, total Cr and Fe contents, as well as the organic matter, silt and clay contents of the soil (Table 3.5). Therefore, as expected from these correlation coefficients, the Red River and Osborne Series soils contain larger amounts of DTPA extractable Cr because they contain greater amounts of total Cr and Fe, and clay. DTPA is commonly used to measure available divalent micronutrients in soils (Lindsay and Norvell 1978); it has also been used to measure other extractable

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divalent heavy metals such as Pb, Ni, and Cd (Whitby et al. 1978). Researchers do not commonly use DTPA to extract Cr because it has been noted that DTPA and other chelating agents are not very useful in extracting Cr because of the slow rates of ligand exchange of Cr(III) complexes (Reisenauer 1982).

DTPA consistently extracted more Cr from the soils compared to deionized water, 1 mol L^{-1} NH_4Cl and 0.01 mol L^{-1} KH_2PO_4. Thus, it is possible that there was more Cr in these soils that was available to plants than determined by the later three extractants. In the literature, however, no one has termed DTPA as a measure for plant available Cr. Thus the significance of the DTPA extractable Cr is not known but it does indicate that organic ligand added to a soil may increase the availability of Cr (Bartlett and Kimble 1976a).

Cr extracted by 0.1 mol L^{-1} HCl ranged from 0 in the Bt, BC and C horizons of the Waitville Series soil to 2.83 μg Cr g^{-1} soil in the Apk horizon of the Osborne Series soil (Table 3.4). Results obtained for two agricultural soils in Nova Scotia (a fine textured North Shore and a coarse textured Annapolis Valley) have given a range between 0.102 to 2.90 μg g^{-1} for Cr extracted by 0.1 mol L^{-1} HCl which is similar to those reported in Table 3.4 (MacLean and Langille 1980). Further, the Cr content of the Nova Scotia, along with the results in Table 3.4, did not vary with depth, pH, clay or organic matter content (Table 3.5) (MacLean and Langille 1980). The amounts of Cr extracted were, however, negatively correlated with the calcium carbonate content of the soils, indicating that as the amount of calcium carbonate in the soil increases, less Cr would be extracted by 0.1 mol L^{-1} HCl. This result

is due to the fact that the added acid was consumed upon reaction with the carbonates to form water and carbon dioxide, which extract very little Cr from these soils.

Nitric-acid-extractable Cr ranged from 1.65 in the Ae horizon of the Waitville Series soil to 7.26 μg Cr g^{-1} soil in the Ck horizon of the same soil (Table 3.4). The amounts of Cr extracted were, on average, approximately 30% of the total Cr, and displayed a significant increase with depth, except in the Almasippi Series soil where the Cr content decreased with depth. A range from 3.1 to 9.0 μg Cr g^{-1} soil for the nitric-acid-extractable Cr in soils has been reported for 16 major soil series in Minnesota (Pierce et al. 1982) which is similar to the results in Table 3.4. This fraction has been termed as "biodiagenetically" available (Jenne 1974; Pierce et al. 1982) and has been noted that the amount of Cr obtained by extracting the soil with HNO_3 increases as the total Cr content in soils increases, indicating that available Cr does increase with increasing total Cr content. The results in Table 3.4, except in the Waitville Series soil, also show that the HNO_3 extractable Cr increases with total Cr content in the soil, but there was no significant correlation between total Cr and HNO_3 extractable Cr. The amount of Cr extracted by HNO_3 was however, positively correlated with many soil properties including the initial soil pH, the clay, silt and calcium carbonate content, as well as the total contents of Fe and Mn. It is interesting to note that the amount of Cr extracted by HNO_3 was positively correlated with the calcium carbonate content of the soil, while the amount of Cr extracted by HCl was negatively correlated. As well, the former extractant was much more efficient in solubilizing Cr

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than the later. This is most likely due to the fact that the HNO_3 added was more concentrated than HCl and was able to overcome the neutralizing effect of the carbonates, and thus solubilize more Cr.

Sodium pyrophosphate ($Na_4P_2O_7$) has been reported to be quite efficient in extracting organically bound Cr(III) (Bartlett and Kimble 1976a). It has also been shown that most of the Cr(III) extracted by $Na_4P_2O_7$ is complexed by fulvic acids (Schnitzer et al. 1958). The amounts of Cr extracted by $Na_4P_2O_7$ ranged between 0.09 in the Ck2 horizon of the Almasippi Series soil and 2.81 μg Cr g^{-1} soil in the Ahk1 horizon of the Osborne Series soil (Table 3.4). The concentrations of Cr obtained were the greatest in the surface horizons and significantly decreased with depth, except in the Osborne Series soil (Table 3.4). These results are essentially due to the decrease in the amount of organic matter with depth in the soil profiles and hence the amount of Cr extracted by $Na_4P_2O_7$ is positively correlated with the organic matter content of the soils (Table 3.5). As well, the amount of Cr extracted by $Na_4P_2O_7$ was positively correlated with the total content of Cr, signifying that if the total amount of Cr in the soil increased the amount of organically bound Cr may increase.

Bartlett and Kimble (1976a) reported that 0.12 mol L^{-1} $Na_4P_2O_7$ was able to extract between 0 and 6.5 μmol g-1 soil of the 10 μmol Cr(III) g^{-1} soil added to a soil. It was also observed that added P and $CaCO_3$ reduced the amounts extracted. They explained the decrease in the amount of organically bound Cr(III) due to the conversion of added Cr(III) into inorganic hydroxides and phosphates. Thus it is possible that the uniform distribution of Cr extracted by $Na_4P_2O_7$ within the

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Osborne Series soil, despite the high content of organic matter in the A horizons, may in part be due to the high carbonate levels in this soil which may have reduced the amount of Cr that would be available to become organically bound.

Other extractants have been used to measure the amount of organically bound Cr. Pierce et al. (1982) reported a range from traces in the parent material, to a maximum of 2.4 μg Cr g^{-1} soil in the A horizons for organically bound Cr in 16 major soil series from Minnesota, using 0.1 mol L^{-1} K$_4$P$_2$O$_7$·3H$_2$O as the extractant. The amount of Cr, thus extracted decreased with depth. Grove and Ellis (1980a), using 0.1 mol L^{-1} CuSO$_4$ as a means of measuring organically bound Cr, found this fraction to be negligible compared to the amounts of Cr extracted by CBD. However, they questioned the effectiveness of CuSO$_4$ as an extractant for organic bound Cr because divalent ions are not efficient in their ability to displace trivalent ions from the organic complex.

Citrate-bicarbonate-dithionite (CBD) has been employed as an extractant to remove free iron oxides from soils (Mehra and Jackson 1960). The concentration of Cr extracted by CBD ranged from a low of 3.85 in the AC horizon of the Almasippi Series soil to a high of 10.32 μg Cr g^{-1} soil in the Bt horizon of the Waitville Series soil. The contents of Cr extracted by CBD did not vary significantly within the profiles, except in the Bt horizon of the Waitville Series soil, where an accumulation of Cr has occurred (Table 3.4). CBD extracted the most Cr compared to all the other extractants utilized, thus Cr is concentrated in this fraction (that is, specific for oxides). There are

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several reasons why Cr may be concentrated here including the fact that the oxides are highly reactive due to their large surface areas and high surface charges.

The amounts of Cr extracted by CBD were negatively correlated with the initial soil pH (Table 3.5). This means that as the pH increases less Cr will be extracted by CBD. There were positive correlation coefficients obtained between Cr extracted with CBD and the total contents of Cr, Fe, and Mn, as well as the clay content of the soil. These results give evidence that if the total Cr content of a soil increased the amount of Cr associated with the oxides would also increase.

3.3.4 Chromium Oxidation Potential of the Soils

The chromium oxidation quick test described by Bartlett and James (1979) was developed in response to the concern about the oxidative behaviour of Cr(III) in soils: the test measures directly the soil's ability to oxidize Cr(III) to Cr(VI). Prior to their work with fresh moist field samples, no studies demonstrated that Cr(III) could be oxidized in soils to Cr(VI), since drying of soil samples was subsequently found to decrease this ability. The key to the oxidation is the presence of oxidized Mn compounds, which serve as electron acceptors in the reaction; these compounds get reduced upon drying of soil samples, thus decreasing the potential to oxidize.

The ability in each soil to oxidize added Cr(III) to Cr(VI) is reported in Table 3.6. This tendency was the greatest in the surface horizons and decreased with depth in the profiles. The amounts of Cr(III) oxidized and measured in solution were in the range between 0.11

Table 3.6. Amounts of Cr(III) oxidized to Cr(VI) during the Cr oxidation quick test (Bartlett and James 1979).

Soil Series	Horizon	Cr(III) oxidized ($\mu g\ g^{-1}$)
Almasippi	Ah	10.12
	AC	3.15
	Ck1	1.32
	Ck2	2.82
Red River	Ap	9.64
	Ck1	0.81
	Ck2	1.42
Waitville	Ae	0.87
	Bt	1.63
	BC	8.71
	Ck	5.31
Osborne	Apk	5.47
	Ahk1	0.54
	Ahk2	0.41
	Ckg1	0.20
	Ckg2	0.11

in the Ckg2 horizon of the Osborne Series soil and 10.12 μg Cr g^{-1} soil in the Ah horizon of the Almasippi Series soil (Table 3.6). These results serve to emphasize that the potential for toxicity of Cr(VI) from a Cr(III) source is not too great in Manitoba's soils when compared to an average value for the oxidation of Cr(III) of 10.4 $\mu g\ g^{-1}$ soil reported by Bartlett and James (1979) for 150 soils analyzed in the field moist condition. It should be noted, however, that the results of

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Bartlett and James (1979) were for Cr(VI) both in the soil solution and adsorbed, while those in Table 3.6 are only for the soil solution, thus it is possible that more Cr(VI) was formed than reported in Table 3.6.

It has been shown that when Cr(III) becomes oxidized in soils, there is an accompanying increase in the amounts of Mn that can be extracted from soils (Bartlett and James 1979). With this evidence in mind, Bartlett and James (1979) reported that oxidized Mn compounds present in soils (such as Mn_3O_4, $MnOOH$, Mn_2O_3 and MnO_2) played a key role in the oxidation of Cr(III) as electron acceptors in the reaction. They, however, did not exclude the fact that there may be other highly oxidized species in soils that could serve as electron acceptors when Cr(III) oxidizes. As well, certain microorganisms could also be important (Bartlett and James 1979).

IV. THE EFFECT OF SOIL MINERALS ON THE ADSORPTION, EXTRACTABILITY AND SPECIATION OF APPLIED CHROMIUM

4.1 Introduction

Chromium, when added to soils, can undergo several reactions with soil minerals that can significantly affect its mobility and availability to plants. Three of these reactions are the adsorption and desorption of Cr, plus the oxidation of Cr(III) to Cr(VI). The first two reactions occur at the solid-solution interface, whereas redox reactions can be surface catalyzed or occur purely in solution.

Adsorption reactions in soils can be important in removing Cr(III) or Cr(VI) from the soil solution, thus reducing the mobility and toxicity of Cr. The adsorption of Cr, as with other transition elements, is affected by its oxidation state (Griffin et al. 1977), and by common soil factors, including pH and Eh (Bartlett and Kimble 1976a), competing ions (Bartlett and Kimble 1976b; Griffin et al. 1977), and the soil mineralogy, particularly the types of clay minerals and the amount and degree of crystallinity of free oxides of iron, manganese, and aluminum (Griffin et al. 1977; Stollenwerk and Grove 1985; Goh et al. 1986 1988; Zachara et al. 1989).

Experiments have shown that the soil immobilizes large amounts of added Cr, since Cr has to be added to the soils in quantities several times greater than in nutrient solution, to produce the same effects on plant growth and nutrition (Turner and Rust 1971; Breeze 1973; McGrath 1982; Sheppard et al. 1984). Therefore, if the soils ability to

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immobilize Cr is great, then there should be little effect of Cr on plant growth and nutrition.

Once Cr has been adsorbed, it can be displaced by certain ions into solution, where it can remain and be available to plants, or undergo further reactions. Recent studies on the release of Cu and Zn adsorbed on oxide surfaces (Goh et al. 1988) show a steady release over time with Ca in solution and the reaction rate was dependent on the degree or crystallinity and surface charge density of the oxides. Trivalent Cr, existing as a cation, can undergo cation exchange with other cations in the soil solution (Griffin et al. 1977). Hexavalent Cr, existing as an anion, can be desorbed by certain oxyanions, such as phosphate (Bartlett and Kimble 1976b). In both instances, adsorbed Cr can be replaced by important plant nutrients, such as Ca, Mg and P.

Oxidation of Cr(III) to Cr(VI) can occur under redox potentials normally found in well-aerated soils (Bartlett and Kimble 1976a). Bartlett and James (1979) reported that the key to the oxidation was the presence of oxidized Mn compounds, which serve as electron acceptors in the reaction. Thus there is a potential for Cr(VI) toxicity from Cr(III) additions, in soils that contain sufficient oxidized Mn compounds.

Three precepts provide the rationale for this study: (1) if Cr is adsorbed either as Cr(III) or Cr(VI), it may not be available and hence not toxic; (2) if some Cr(III) is oxidized to Cr(VI) during the adsorption, then there is a potential of Cr(VI) toxicity; and (3) if Cr(VI) is displaced from soil minerals by other anions, it can be available to plants and is therefore potentially toxic. The purpose of

this study was to determine the effects of various common soil minerals on the adsorption, extraction and speciation of Cr, in order to assess its availability to plants.

4.2 Materials and Methods

The oxides used in this experiment were haematite (αFe_2O_3, 400 mesh) and birnessite (δMnO_2, 60 mesh)). The haematite used was reagent grade iron oxide purchased from FISHER Scientific and its mineralogy confirmed by x-ray diffraction analyses using Ni-filtered Cu Kα radiation. Birnessite was prepared by adding concentrated HCl to a boiling solution of $KMnO_4$ (McKenzie 1971). The sample was washed with deionized distilled water, dried at 308 K and then lightly ground. The x-ray diffraction pattern obtained for birnessite consisted of one strong sharp peak at 0.727 nm and three other prominent lines near 0.360, 0.244 and 0.141 nm. The clay minerals (<2 μm) used were montmorillonite (Upton, Wyoming) and vermiculite (Transvaal).

Four chromium solutions were prepared: two 10^{-3} mol L^{-1} solutions of $CrCl_3 \cdot 6H_2O$ and two 10^{-2} mol L^{-1} K_2CrO_4 solutions. The pH of the solutions were adjusted to 4 or 5, using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH.

One gram samples of the clay minerals and 250 mg samples of the oxides, along with 20 mL of Cr solution were placed in 50 mL centrifuge tubes. The resulting Cr to mineral ratios were therefore, either of 0.02 mmol Cr(III) g^{-1} clay mineral, 0.08 mmol Cr(III) g^{-1} oxide, 0.2 mmol Cr(VI) g^{-1} clay mineral, or 0.8 mmol Cr(VI) g^{-1} oxide. The experiment, was conducted in duplicate, and included controls with no oxides or clay

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minerals. The tubes and their contents were shaken for two hours and then allowed to stand for 20 hours at room temperature (298 ± 1 K). The suspensions were then centrifuged for 30 minutes at 12 000 g. The supernatants collected were analyzed for total Cr by atomic absorption spectroscopy. The amounts of Cr adsorbed were calculated from the difference in the initial concentration of Cr added and the concentrations of Cr remaining in solution after the reaction period.

The residues remaining were washed five times, using 20 mL of deionized water each time, to remove excess free Cr. The residues now containing only adsorbed Cr were extracted twice with 20 mL of 0.1 mol L^{-1} KH_2PO_4 and the supernatants were combined. This extractant was used essentially to remove adsorbed Cr(VI) (Bartlett and Kimble 1976b). The residues were then extracted with 20 mL of a 0.5 mol L^{-1} $CaCl_2$ solution followed by 10 mL of the same solution in an attempt to displace adsorbed Cr(III). The supernatants were analyzed for total Cr by atomic absorption spectroscopy and for Cr(VI) by measuring the absorbance of the samples at 540 nm on the spectrophotometer using the s-diphenyl carbazide reagent (Reisenauer 1982).

To investigate the possibility that Cr(III) may become fixed in the interlayers of vermiculite x-ray analyses and measurements of cation exchange capacity were conducted. Orientated clay samples for x-ray analysis were prepared on glass slides, using the paste method of Theisen and Harward (1962). Four slides were prepared and included a slide of Transvaal vermiculite with no pretreatment as the x-ray diffraction standard.

Saturation of vermiculite with Cr(III) was achieved in the

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following manner. One gram of vermiculite was suspended in 20 mL of 0.1 mol L^{-1} $CrCl_3 \cdot 6H_2O$ for four days. The suspension was centrifuged and the supernatant was discarded. The residue remaining was washed five times with 20 mL of 80% ethanol and 5 mL of 50% acetone to remove excess Cl^- anions and to promote flocculation of the vermiculite. A portion of the Cr(III) saturated vermiculite was then resuspended and washed thrice in 20 mL of 1 mol L^{-1} KCl to induce possible collapse of the layers. The sample was also washed with 80% ethanol and 50% acetone. A separate one gram sample of vermiculite was saturated with potassium, using three washings of 20 mL of 1 mol L^{-1} KCl and removing the Cl^{-1} as described above.

X-ray diffraction patterns were obtained with a Philipps XRD instrument using Ni filtered Cu Kα radiation generated at 40 kv, and 20 ma, over a range of 2 to 30° 2θ. The slits used were 1°, 1° and 0.2 mm for the divergence, scatter, and receiving slits, respectively. After x-ray diffraction patterns of the orientated specimens were obtained, the slides were placed in a muffle furnace and heated for four hours, at 383, 573, and 723 K and additional x-ray diffraction analyses were conducted.

The cation exchange capacity of Transvaal vermiculite (<2 μ fraction) was determined on a Na saturated sample and on a Cr saturated sample (described above) by first saturating with Ca and using Mg to replace the Ca as described by Alexiades and Jackson (1965).

4.3   Results and Discussion

Table 4.1 displays the amounts of Cr(III) or Cr(VI) adsorbed by the soil minerals, as well as the percentage of the initial amounts of Cr added that were adsorbed. The soil minerals differed in their capacities to adsorb Cr and much more Cr(III) was adsorbed compared to Cr(VI) in the pH range of this study. These differences in the amounts of Cr adsorbed are likely the result of different bonding mechanisms, specific surface areas and reactive surfaces on the soil minerals. The oxides, haematite and birnessite, were equilibrated with four times the amount of Cr than the clay minerals because it was suspected, from their surface properties and from results of James and Bartlett (1983) for $Fe(OH)_3$ and Griffin et al. (1977) for clay minerals, that the oxides would adsorb more Cr than clay minerals. As well, more Cr(VI), added as the bichromate anion ($HCrO_4^-$), was equilibrated with the soil minerals than Cr(III) to increase its probability of coming into contact with the soil minerals since Cr(VI) is the more mobile form of Cr in soils. The inference from the adsorption data between Cr(III) and Cr(VI) is that anion exclusion is probably the reason that Cr(VI) is more mobile in soils and available to plants, and hence is of the greater environmental concern.

Haematite adsorbed 1328 μg Cr(III) g^{-1} at pH 4 and 1336 μg Cr(III) g^{-1} at pH 5 (Table 4.1). These were the greatest amounts of Cr(III) that were adsorbed by the soil minerals studied. However, in terms of the initial amounts of Cr(III) added, montmorillonite and vermiculite were more efficient in removing Cr(III) from solution, and may have adsorbed more Cr(III) than haematite if given more Cr(III) initially.

Table 4.1. Effect of soil mineral, pH, and oxidation state
Cr on the amounts of Cr(III) and Cr(VI) adsorbed.

Minerals and Cr solution	initial pH	final pH	Total Cr adsorbed ($\mu g\ g^{-1}$)	% Added Cr adsorbed[*]
Haematite and Cr(III)	4	3.8	1328	32
"	5	4.6	1336	32
Haematite and Cr(VI)	4	4.6	905	2
"	5	5.1	1084	3
Birnessite and Cr(III)	4	5.5	920	22
"	5	6.0	768	18
Birnessite and Cr(VI)	4	5.5	670	2
"	5	5.6	560	1
Vermiculite and Cr(III)	4	4.7	1040	100
"	5	7.1	1040	100
Vermiculite and Cr(VI)	4	5.5	79	1
"	5	6.4	52	<1
Montmorillonite and Cr(III)	4	5.8	1040	100
"	5	6.1	1040	100
Montmorillonite and Cr(VI)	4	4.8	400	4
"	5	5.6	0	0
Cr(III) Solution	4	3.6		
	5	4.7		
Cr(VI) Solution	4	4.0		
	5	4.9		

[*] The clay minerals were equilibrated with 10400 μg Cr(VI) g^{-1} and 1040 μg Cr(III) g^{-1} . The oxides were equilibrated with 41600 μg Cr(VI) g^{-1} and 4160 μg Cr(III) g^{-1}.

Birnessite was the least efficient soil mineral at removing Cr(III) from solution since it adsorbed only 20% of the Cr(III) that it was equilibrated with (Table 4.1).

The adsorption of Cr(III) by birnessite decreased from 920 to 768 μg Cr(III) g^{-1} as the pH increased from 4 to 5 (Table 4.1). In comparison, pH had little effect on the adsorption of Cr(III) by haematite and the effect could not be discerned for the clay minerals (Table 4.1). The results obtained for birnessite are in contrast to those reported by Griffin et al. (1977), where the adsorption of Cr(III) by montmorillonite and kaolinite increased as the pH increased. They suspected however, that precipitation became an important mechanism in the removal of Cr(III) when the pH of the suspensions exceeded pH 5. Since the majority of Cr(III) in soils is cationic, the principle method of Cr(III) adsorption has been accepted as cation exchange on soil and clay minerals (Griffin et al. 1977) but no method has been given for oxides. Nevertheless, the adsorption of a cation, such as Cr(III), onto a negatively charged substance should increase as the pH increases because of the increasing negative charge on that substance.

Haematite adsorbed a much greater amount of Cr(VI) than the other soil minerals studied (Table 4.1). However, in contrast to the other soil minerals, the adsorption of Cr(VI) by haematite increased from 905 to 1084 μg Cr(VI) g^{-1} haematite as the pH increased (Table 4.1). This result for haematite conflicts with reports given by several researchers where the adsorption of Cr(VI), an anion, decreased as the pH was increased (Griffin et al. 1977; James and Bartlett 1983c; Stollenwerk and Grove 1985; Zachara et al. 1989). Decreases is amounts adsorbed

with increases in pH are characteristic of anion adsorption, and the result of a lower positive net surface charge resulting from decreasing hydrogen ion activity (Cary et al. 1977b; Griffin et al. 1977; James and Bartlett 1983c). In other words, the pH-dependent negative charge on the soil minerals increases with pH, thus the adsorption of Cr(VI), an anion, should decrease because of repulsion. It has been suggested that the adsorption of Cr(VI) by certain soils appears to be the specific type (Bartlett and Kimble 1976b; Stollenwerk and Grove 1985). Specific anion adsorption occurs when anions coordinate directly with the metal ion of a mineral surface by ligand exchange (Hingston et al. 1967) as shown below. [It should be noted that in the pH range of this study the majority of the Cr(VI) anions would exist as bichromate ($HCrO_4^-$) given that the pKa of H_2CrO_4 is -0.61 and that of $HCrO_4^-$ is 5.9 (Cotton and Wilkinson 1972).]

at pH 5

(PZC = 7) (Borggaard 1983)

[Eq. 1]
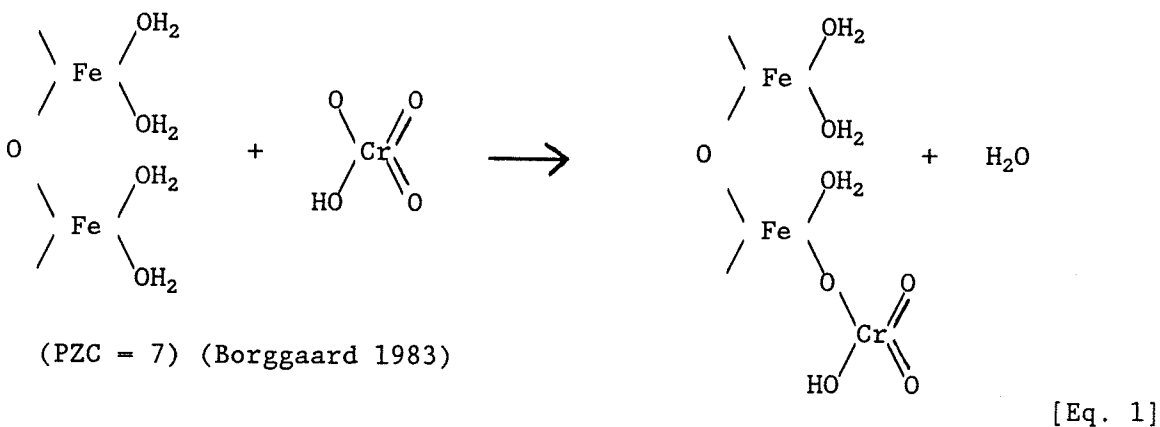
This mechanism of adsorption of the bichromate anion onto haematite would not be accompanied by a change in pH. In fact, no pH

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change was detected (Table 4.1). It would be expected that the bichromate in the mononuclear complex, as shown in Equation 1, would not be easily extracted by simple anions such as Cl^-, NO_3^-, or $SO_4^=$. However, mononuclear complexes may be exchanged with other complex anionic ligands such as phosphate. The data in Table 4.2 does show that most of the Cr(VI) adsorbed on haematite was extracted by 0.1 mol L^{-1} KH_2PO_4.

The adsorption of bichromate on birnessite was deemed to have occurred by specific adsorption via formation of binuclear surface complexes as shown in Equation 2.

at pH 5
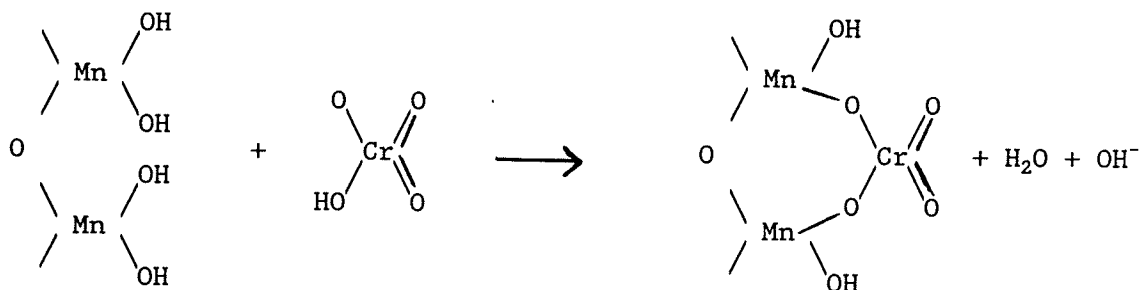
(PZC = 1.5) (McKenzie 1989)

[Eq. 2]

This mechanism of adsorption is accompanied by an increase in pH (Table 4.1). Furthermore, data in Table 4.2 show that bichromate adsorbed on birnessite was less extractable by 0.1 mol L^{-1} KH_2PO_4 than bichromate adsorbed on haematite. There are two possible reasons that can be provided for the formation of strong binuclear complexes on birnessite surface compared to the formation of mononuclear complexes on haematite. In the first place, the electronegativity difference between

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the O and Mn atoms is greater (3.44-1.55) than between O and Fe atoms (3.44-1.83) (Cotton and Wilkinson 1972). Thus, the bonding is stronger. Secondly, the ionic size of Fe^{+3} (0.064 nm) is larger than Mn^{+4} (0.060 nm) (Weast and Astle 1978). This creates a steric hinderance to the bichromate to form a binuclear bridge between two Fe^{+3} ions.

A distinct difference was found in the strength with which all the soil minerals held the two species of Cr as was determined upon extracting adsorbed Cr with of 0.1 mol L^{-1} KH_2PO_4 (Table 4.2) and 0.5 mol L^{-1} $CaCl_2$ (Table 4.3). In general, the results showed that adsorbed Cr(VI) was more easily extracted by KH_2PO_4 or $CaCl_2$ from the soil minerals than adsorbed Cr(III). These results further emphasized that Cr(VI) is more mobile and plant available than Cr(III). Furthermore, in comparing the extracting powers between 0.1 mol L^{-1} KH_2PO_4 and 0.5 mol L^{-1} $CaCl_2$, the former extractant was more efficient for both Cr(III) and Cr(VI) systems (cf. Tables 4.2 and 4.3).

Vermiculite and haematite held adsorbed Cr(III) very strongly and no Cr(III) could be extracted from their surfaces with either KH_2PO_4 or $CaCl_2$ (Tables 4.2 and 4.3), indicating that adsorbed Cr(III) was not exchangeable with K^+ or Ca^{2+} and most likely not available to plants. Similarly, Cr(III) could not be extracted from birnessite (Tables 4.2 and 4.3). However, Cr(VI) was extracted from birnessite regardless of the initial oxidation state of the Cr that was added (Tables 4.2 and 4.3). Therefore, some of the Cr(III) added and adsorbed by this mineral was oxidized to Cr(VI). Birnessite was the only soil mineral in this study that was capable of oxidizing Cr(III): ie. in the pH range of this study, for every gram of birnessite approximately 30 μg Cr(VI)

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Table 4.2. Amounts of adsorbed chromium extracted by 0.1 M KH_2PO_4

Minerals and Cr solution	pH	Total Cr extracted ($\mu g\ g^{-1}$)	Cr(VI) extracted ($\mu g\ g^{-1}$)	% adsorbed Cr extracted
Haematite and Cr(III)	4	0	0	0
"	5	0	0	0
Haematite and Cr(VI)	4	889	880	98
"	5	796	748	73
Birnessite and Cr(III)	4	33	23	4
"	5	28	30	4
Birnessite and Cr(VI)	4	180	184	27
"	5	40	45	7
Vermiculite and Cr(III)	4	0	0	0
"	5	0	0	0
Vermiculite and Cr(VI)	4	20	22	25
"	5	8	8	15
Montmorillonite and Cr(III)	4	59	0	6
"	5	32	0	3
Montmorillonite and Cr(VI)	4	20	18	5
"	5	0	0	0

Table 4.3. Amounts of adsorbed chromium extracted by 0.5 M $CaCl_2$

Minerals and Cr solution	pH	Total Cr extracted ($\mu g\ g^{-1}$)	Cr(VI) extracted ($\mu g\ g^{-1}$)	% adsorbed Cr extracted
Haematite and Cr(III)	4	0	0	0
"	5	0	0	0
Haematite and Cr(VI)	4	10	8	1
"	5	107	87	10
Birnessite and Cr(III)	4	0	0	0
"	5	0	0	0
Birnessite and Cr(VI)	4	13	17	2
"	5	80	97	14
Vermiculite and Cr(III)	4	0	0	0
"	5	0	0	0
Vermiculite and Cr(VI)	4	0	0	0
"	5	0	0	0
Montmorillonite and Cr(III)	4	47	0	5
"	5	34	0	3
Montmorillonite and Cr(VI)	4	23	20	6
"	5	0	0	0

could be formed and brought into solution by KH_2PO_4 (Table 4.2).

The possibility of oxidation of Cr(III) by birnessite and haematite was investigated thermodynamically. The thermodynamics of two such possible reactions, one is the oxidation of Cr(III) by birnessite (MnO_2) and the other is the oxidation of Cr(III) by haematite (Fe_2O_3) are given in Appendix C. Through the use of the equilibrium constants calculated from the standard free energies of formation (Garrels and Christ 1965) for each reaction, the possible extent of Cr(III) oxidation and the formation of Mn(II) or Fe(II) at pH 5 were determined.

The oxidation of Cr(III) to Cr(VI) through the reduction of Mn(IV) to Mn(II) is thermodynamically possible and at equilibrium quantitative reduction of Mn(IV) would occur. In contrast, the oxidation of Cr(III) to Cr(VI) through the reduction of Fe(III) to Fe(II) is very unlikely. The quantity of Fe(II) that would be formed at equilibrium would be insignificant. These results serve to emphasize that the oxidation of Cr(III) by MnO_2 is possible, under specified pH, and if the reactants, both Cr(III) and MnO_2, are not limiting, the concentration of Cr(VI) formed could be toxic to plants.

It has been suggested that the adsorption of Cr(III) on to oxidized Mn compounds is possibly the first step in the oxidation of Cr(III) (Bartlett and James 1979). Manganese oxides typically accumulate on the surfaces of clays and Fe oxides and have large surface areas and tend to have high negative charges which enable them to have high absorptive capacities (Bartlett and James 1979). Soils in which Mn oxides may be present (for example, acid-sulphate soils) in significant amounts may, therefore, show a high propensity to convert Cr(III) to

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Cr(VI), and at the same time enhance the level of Cr toxicity. If this adsorbed Cr(VI) is displaced from the oxide by complex anions, such as phosphate it can be available to plants.

A small percentage of the Cr(III) adsorbed on montmorillonite was extracted by both KH_2PO_4 and $CaCl_2$, indicating that some of the Cr(III) adsorbed by montmorillonite was exchangeable with K^+ and Ca^{2+}(Tables 4.2 and 4.3). This result is in contrast to vermiculite, and indicates that different adsorption mechanisms were involved in the immobilization of Cr(III) by the two clay minerals. The results in Tables 4.2 and 4.3 also display that the strength, and possibly the amount of Cr(III) adsorbed by montmorillonite, increases with pH since less Cr(III) was extracted at pH 5 than 4.

The strength with which these soil minerals held Cr(VI) was much lower than that for Cr(III) (Tables 4.2 and 4.3). Haematite, which adsorbed the most Cr(VI) (Table 4.1), released most of the adsorbed Cr(VI) upon extraction with KH_2PO_4 (Table 4.2) and whatever remained was extracted by $CaCl_2$ (Table 4.3). This means that Cr(VI) anions may be held onto haematite by both specific (as shown in Eq. 1.) and nonspecific adsorption mechanisms because the Cr(VI) anions were exchangeable with both phosphate anions which are adsorbed specifically and chloride anions which are adsorbed nonspecifically (James and Bartlett 1983c; Stollenwerk and Grove 1985). The adsorption of Cr(VI) to birnessite was stronger than to haematite, since less than 30% of the adsorbed Cr(VI) on birnessite was exchangeable with KH_2PO_4 and $CaCl_2$. Much more Cr(VI) was extracted from birnessite and haematite by KH_2PO_4 than $CaCl_2$, indicating that phosphate anions were more efficient in

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extracting Cr(VI) compared to the chloride anions (cf. Tables 4.2 and 4.3). Also the release of Cr(VI) from the two oxides decreased with pH, indicating that as the pH increased the surfaces became increasingly negative in charge, and may have prevented the phosphate anions to come close enough to exchange with the Cr(VI) anions. These results provide further evidence for the reactions with the bichromate anion with haematite and birnessite given in Equations 1 and 2.

Adsorbed Cr(VI) could be extracted from vermiculite by KH_2PO_4 only, indicating a specific adsorption mechanism, and as with the oxides more Cr(VI) was removed at pH 4 than pH 5 (Table 4.2). Similar amounts of Cr(VI) were extracted by KH_2PO_4 and $CaCl_2$ from montmorillonite at pH 4 (Tables 4.2 and 4.3). Therefore, as with Cr(III), there are different adsorption mechanisms involved in the adsorption of Cr by the clay minerals. It should be noted that montmorillonite does not hold adsorbed Cr(VI) as strongly as vermiculite, and at pH 5 montmorillonite was unable to adsorb Cr(VI) (Table 4.1).

It is possible that vermiculite may have immobilized all of the Cr(III) it was equilibrated with, simply by cation exchange or adsorption because the amount of Cr(III) added to the vermiculite (0.02 mmol g^{-1} vermiculite) was much less than the measured cation exchange capacity of the vermiculite of 118 cmol ($\frac{1}{2}$ Ca^{2+}) kg^{-1}. However, cation exchange or adsorption does not explain why the Cr(III) was not exchangeable with K^+ or Ca^{2+}. Thus it is possible that the Cr(III) may have undergone reactions other than adsorption. One such reaction is precipitation. Precipitation could also account for the removal of Cr(III) because the pH of the suspensions after the 22 hour reaction

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period was increased to values which would precipitate the concentrations of Cr(III) studied (Table 4.1). It is also possible that Cr(III) may have become fixed in the interlayers of vermiculite in a manner that has been reported for Al, because the chemistry of Cr(III) and Al in soils are very similar (Bartlett and Kimble 1976a). When Al becomes fixed in the interlayers it is not exchangeable with other cations. Also, the fixed Al will produce stable d-spacings in the mineral and will decrease its cation exchange capacity considerably (Sawhney 1968). Therefore, to verify if Cr(III) did undergo interlayer fixation by vermiculite x-ray analyses and measurements of cation exchange capacity were conducted.

The x-ray diffraction patterns of Transvaal vermiculite with the various saturating cations at room temperature is given in Figure 4.1. Sodium saturated vermiculite had a cation exchange capacity (CEC) of 118 cmol ($\frac{1}{2}Ca^{2+}$) kg^{-1} and exhibited a sharp peak at 1.1262 nm d-spacing and a 1.4255 nm shoulder (Fig. 4.1.A). Since the CEC of vermiculite is dependent on the K (mica) content, that is, the higher the K content the lower the CEC, and the Na saturated sample had a CEC somewhat less than the range of 135 to 189 cmol ($\frac{1}{2}Ca^{2+}$) kg^{-1} given for pure vermiculites, it is possible that the vermiculite used in this and the adsorption experiment was a mixed layer mica-vermiculite (Harward et al. 1969; Moore and Reynolds 1989). After saturating the vermiculite with potassium (K), a 1.0281 nm peak was observed rather than a 1.4255 nm peak (Fig. 4.1.B).

Chromium saturation resulted in the formation of a 1.4255 and 1.2450 nm peak (Fig. 4.1.C). Since Cr is a much larger cation than Na

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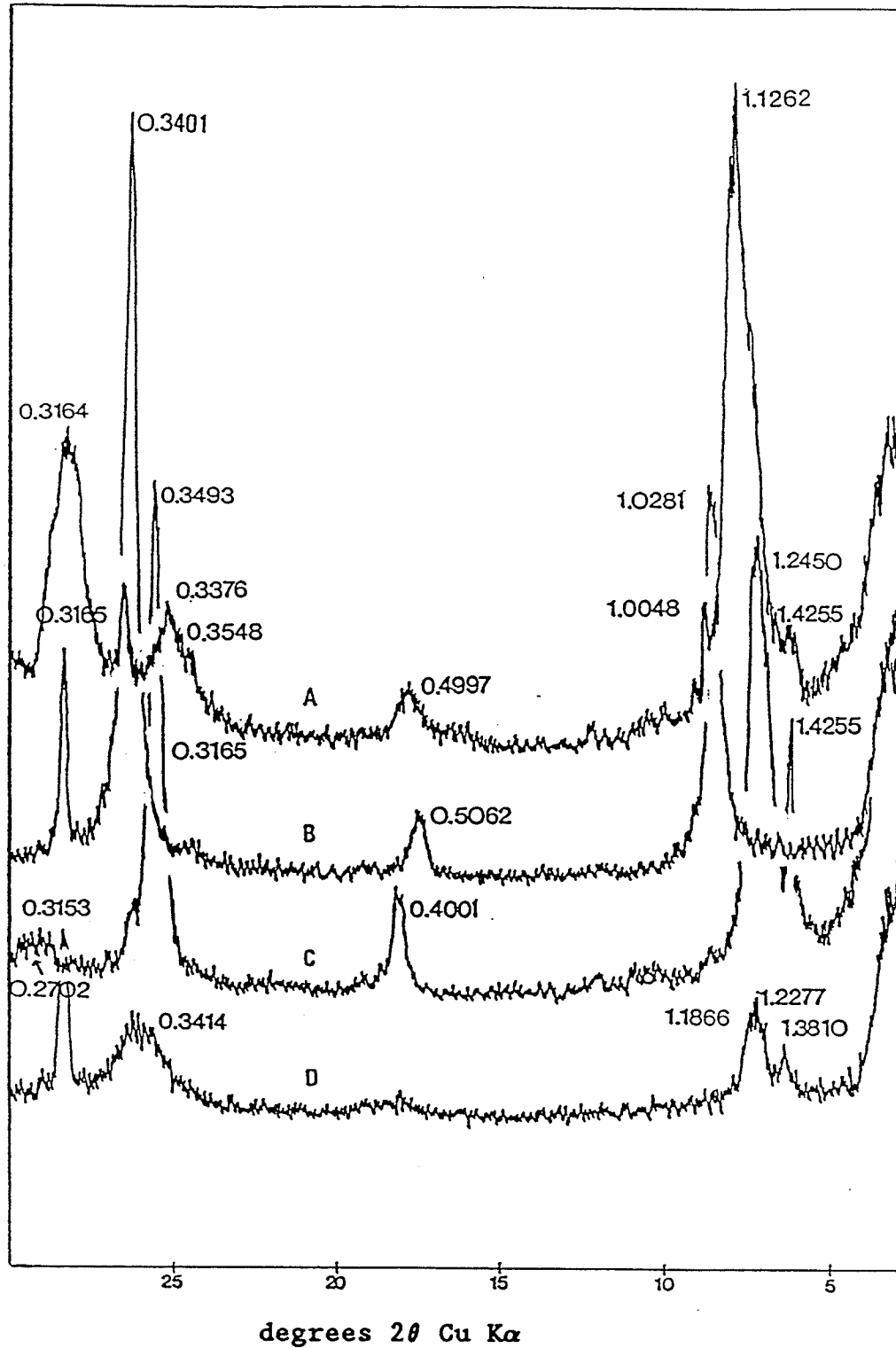
Figure 4.1. X-ray diffractograms of vermiculite saturated with various cations at room temperature: (A) sodium, (B) potassium, (C) chromium, and (D) chromium followed by potassium.

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or K, the basal spacings are expected to be larger. The CEC of the Cr saturated vermiculite was 19 cmol ($\frac{1}{2}Ca^{2+}$) kg^{-1}, which was approximately six times lower than that of the Na saturated vermiculite. Shen and Rich (1962) found that when Al reduced the CEC of montmorillonite, it was caused by actual coverage and neutralization of the exchange sites rather than blocking of pathways to these sites by Al(OH)$_3$. It is possible that Cr may be forming non-exchangeable groups in the interlayers of vermiculite similar to Al. Even though the atomic radii of the Cr(III) and Al are not extremely close in size, namely 0.065 and 0.047 nm (Weast and Astle 1978), there are many examples of parallels in their chemistry. Both ions tend to coordinate oxygen atoms in octahedral configuration, both become anions as the pH is raised above neutrality, as well Cr(III) ions can form complexes in six coordination with water and hydroxy groups analogous to the formation of Al polymers (Hsu and Bates 1964; Bartlett and Kimble 1976a; Goh and Huang 1984 1986).

Figure 4.1.D provides further evidence to suggest that Cr is fixed in the interlayers of vermiculite. Three peaks, 1.3810, 1.2277, and 1.1866 nm, are formed when vermiculite is first saturated with Cr then K. Thus Cr saturation prior to K saturation prevented the complete collapse to 1.0281 which occurred when the vermiculite was treated with K only (Fig. 4.1.B) since a partial collapse of the interlayer occurred when the vermiculite was first saturated with Cr then K .

There are two well-known treatments which could collapse the Na-vermiculite to 1.0 nm: one is to replace the Na with K, and the other is to heat the Na-saturated sample at 573 K for an hour (Moore and

Reynolds 1989). Figure 4.2 displays the effect of heating on the Cr saturated vermiculite samples (A to D) and the samples first treated with Cr then K (E and F). It is evident that Cr saturation prevented the complete collapse of vermiculite at 573 K (Fig. 4.2.C). Moore and Reynolds (1989) have suggested that the reason some vermiculites do not completely collapse is that there are some hydroxy-cation complexes present that are not developed into complete sheets in the interlayer space. Complete collapse to 1.0048 nm did not occur until the sample was heated to 723 K (Fig. 4.2.D). This means that the water or hydroxyl ions associated with the interlayer Cr are not completely removed, at 573 K and thus, the interlayer of hydroxy-Cr is stable. Sawhney (1968) reported that the stable 1.4 nm spacing obtained when Al becomes fixed by vermiculite is due to hydroxy-Al polymers in the interlayers of vermiculite. The vermiculite samples treated with Cr, followed by K, also displayed peaks which would not completely collapse (Fig. 4.2.E) until heated to 723 K (Fig. 4.2.F).

The results of XRD analyses and CEC measurements give some evidence to suggest that Cr may be fixed in the interlayers of vermiculite in a similar manner to that which has been reported to occur by Al. This means that if Cr(III) does become fixed it will be held tightly by the vermiculite and unavailable to plants. It may also alter some properties of vermiculite including the CEC, the K^+ and NH_4^+ fixation capacity, swelling and shrinkage, the acidity of the clay plus the thermal properties (Shen and Rich 1962; Goh and Huang 1985).
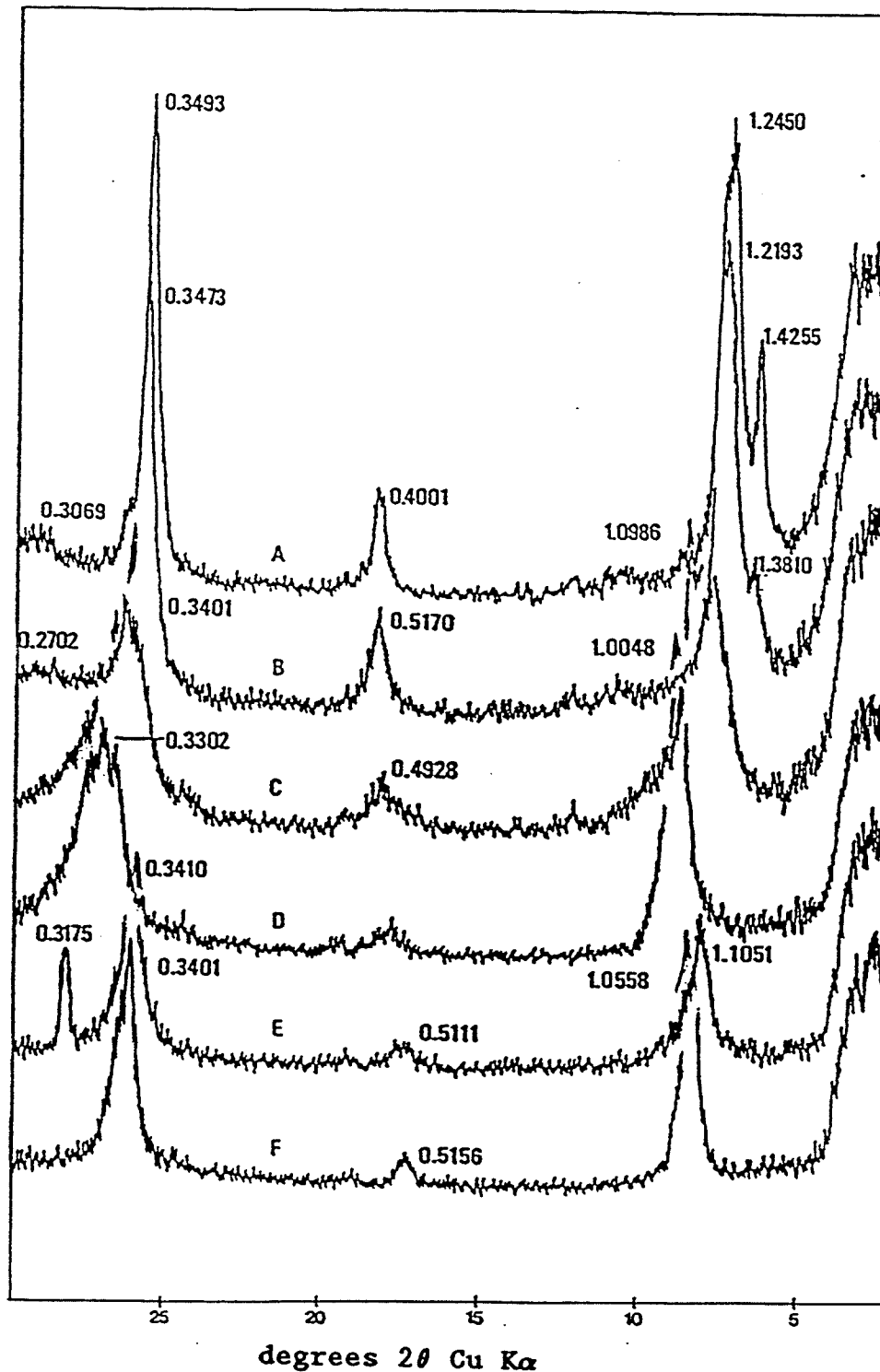
Figure 4.2. X-ray diffractograms of vermiculite saturated with chromium as a function of temperature: (A) 298 K, (B) 383 K, (C) 573 K, and (D) 723 K and with chromium followed by potassium saturation at (E) 573 K and (F) 723 K.

V. EFFECT OF CHROMIUM IN COMBINATION WITH MANGANESE DIOXIDE
AND FERTILIZER PHOSPHORUS ON THE YIELD AND QUALITY OF BARLEY PLANTS

5.1 Introduction

Solution culture experiments have shown that Cr(III) and Cr(VI) will be equally toxic to plants in the solution concentration range of one to five μg Cr g^{-1} (Turner and Rust 1971; Wallace et al. 1976; McGrath 1982; Barcelo et al. 1985). Experiments using soil as a growth medium have indicated that the toxic thresholds for both Cr(III) and Cr(VI) will be much higher and depend on many soil factors, including the cation exchange capacity, the pH, the organic matter content and mineralogy of a soil (Soane and Saunder 1959; Breeze 1973; Cary et al. 1977a; Bartlett and James 1979; McGrath 1982). It is well known that Cr(VI) is the more active and mobile oxidation state of Cr in soils, and thus the addition or existence of Cr(VI) in soils presents the greatest potential for Cr toxicity to develop in plants.

In the previous study, it was shown that soil minerals have a high capacity to adsorb both Cr(III) and Cr(VI), thereby reducing the mobility and plant availability of Cr. It was, however, also established that the presence of manganese dioxide and phosphorus could increase the potential for Cr toxicity, by either creating Cr(VI) upon adsorption of Cr(III) onto manganese dioxide (MnO_2) or by displacing adsorbed Cr(VI) with KH_2PO_4. Therefore, under the defined conditions of high soil MnO_2 concentration and heavy application of fertilizer phosphorus (P), low levels of added Cr(III) or Cr(VI) may be toxic to plants. Thus, growth chamber studies were conducted, to first establish

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the effect of Cr(III) and Cr(VI) on plant yield and quality; and then to further investigate the influence of MnO_2 and P fertilizer on Cr toxicity.

5.2 Materials and Methods

5.2.1 Soil

The soil chosen for use in the growth chamber was the top 0-15 cm of the Ah horizon of the Almasippi Series soil analyzed in the soil survey in Chapter 3. This soil was selected because it has many properties which make it a good representative agricultural soil found in the Red River Valley of southern Manitoba.

The soil was collected in May, 1988 for the first two experiments and in August, 1988 for the third experiment. In each case, the soil was immediately air-dried and passed through a 2 mm sieve and thoroughly mixed before potting.

The air-dry soil moisture content and field capacity moisture content were determined. The field capacity of the soil was determined by the following procedure. The soil was added to a plastic cylinder which had one end covered to keep the soil in. Water was then added to the soil until the wetting front had moved about one third of the way down the cylinder. The top of the cylinder was then covered with parafilm and the cylinder and soil were incubated for 48 hours. After incubation, a soil sample was take from the centre of the wetted soil. The soil sample was then weighed and oven dried at 105 °C for 24 hours and the percent moisture at field capacity was calculated.

Some of the physical and chemical characteristics of the soil

selected in this experiment are outlined in table 5.1.

Table 5.1   Selected physical and chemical properties of the soil used
in the growth chamber.

Soil Series	Almasippi
Soil Subgroup	Gleyed Rego Black - Carbonated Phase
Texture	VFSL
pH (0.01 M $CaCl_2$)	7.8
Inorganic Carbonate	12.5%
Organic Matter	5%
Total Chromium	17 $\mu g\ g^{-1}$
Total Manganese	405 $\mu g\ g^{-1}$
Field Capacity Moisture	25% by weight

5.2.2 Experimental Design and Procedures

To determine the effect of Cr in combination with MnO_2 and
fertilizer P (11-51-0) on the yield and quality of barley three
experiments in factorial design were conducted. The first experiment
was carried out to study the effects of Cr(III) and Cr(VI), as well as
the addition of MnO_2, on the yield and plant uptake of Cr, Mn and P.
Four kg (oven dry equivalent) of soil was weighed into plastic pots and

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thoroughly mixed with a basal dressing of NPK and Cr and Mn treatments. The N and K were dissolved in deionized distilled water and added to the soil at rates of 100 μg N g^{-1} as NH_4NO_3 and 40 μg K g^{-1} as KCl respectively. P was added at a rate equal to 50 μg P g^{-1} soil using finely ground monoammonium phosphate. The Cr treatments consisted of Cr(III) and Cr(VI) applied as $CrCl_3 \cdot 6H_2O$ and K_2CrO_4 respectively, at rates of 0, 5 and 50 μg Cr g^{-1} soil. The various sources and rates of Cr were applied in solution form. Two rates of MnO_2 were added to the Cr treatments, 0 and 490 μg MnO_2 g^{-1} soil. The MnO_2 was lightly ground to pass a 60 mesh sieve. In each case, the dry forms of P and Mn were thoroughly mixed into the soil prior to the addition and mixing of the solution treatments. Each treatment was replicated three times.

Twelve germinated barley seeds (Hordeum vulgare var. Bonanza) were placed approximately 1.5 cm deep into the soil in each pot. The soil was maintained at 75% of field capacity for two weeks and then brought up to field capacity daily until harvest. The amount of water added to bring the soil up to field capacity was determined gravimetrically.

At the change in the moisture regime, the plants were thinned to eight plants per pot, and after another week of growth plants were further thinned to six plants per pot. Four weeks after planting, an additional dressing of nutrients, consisting of 100 μg N g^{-1} and 40 μg K g^{-1} was applied. The plants were grown under 16 hours of artificial light and 8 hours of darkness. Temperatures were maintained at 24 °C and 17 °C during the day and night periods, respectively. The relative humidity was kept at 40% during the day and 70% at night. The light intensity close to the plant canopy ranged from 500 to 550 μE m^{-2} s^{-2}.

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The plants were grown to maturity which occurred between 65 and 90 days after planting, depending upon the treatments. The above ground portions of the six plants from each pot were harvested by cutting the plant shoots approximately 2 cm above the soil surface using a sharp knife. Any adhering soil particles were removed by a distilled water rinse. The plant material was then air dried in paper bags, the heads were separated from the straw, and then threshed by hand. The grain and straw weights were obtained and both were finely ground, using a Wiley mill and analyzed for nutrient composition.

The concentrations of Cr, Mn and P in the grain and straw were determined using the method of Isaac and Kerber (1971). One gram of finely ground plant material was predigested in 5 mL HNO_3 and 2.5 mL 70% $HClO_4$ for one-half hour. The samples were further digested on a digestion block at 228 °C until the contents in the digestion tubes turned clear. The samples were then cooled and contents washed into 25 mL volumetric flasks and made up to volume. Cr and Mn concentrations in the digest were then determined using an atomic absorption spectrophotometer. P concentration was determined using the molybdate-ascorbic acid method of Murphy and Riley (1962).

In the first experiment it was suspected that the added P may have increased the availability and toxicity of Cr(VI), as well as being a source of Cr. Thus a second experiment was conducted, concurrently with the first experiment in the same growth chamber, to test the hypothesis that the use of high rates of P may increase Cr toxicity. Cr(III) and Cr(VI) were added at one rate, 50 μg Cr g^{-1} soil, using $CrCl_3 \cdot 6H_2O$ and K_2CrO_4, respectively. MnO_2 was also added, as in the first experiment,

at rates of 0 and 490 μg MnO_2 g^{-1} soil. The P treatments consisted of three rates, 0, 50 and 100 μg P g^{-1} soil. The source of P was finely ground monoammonium phosphate. (The P fertilizer used contained 121 μg Cr g^{-1} fertilizer. Thus, the addition of 50 and 100 μg P g-1 soil resulted in the addition of 0.03 and 0.05 μg Cr g^{-1} soil, respectively, from the fertilizer.) The basal dressing of nutrients consisted only of N and K supplied at the same rates as in experiment one. The soil was prepared as described before. Application of the basal nutrients and treatments, seeding, maintenance of plants, harvesting and digestion procedures were the same as those described for the first experiment.

A third experiment was conducted using a much higher rate of MnO_2 to determine if plant toxicity of Cr was dependent on the concentration of MnO_2 in the soil. In this experiment 2000 g (oven dry equivalent) of soil was used and the basal NPK dressing consisted of a nutrient solution prepared from reagent grade NH_4NO_3, $NH_4H_2PO_4$, and KCl which when applied to the soil resulted in rates of 100 μg N g^{-1} soil, 75 μg P g^{-1} soil and 40 μg K g^{-1} soil. The Cr treatments consisted of Cr(III) and CrVI) applied as $CrCl_3 \cdot 6H_2O$ and K_2CrO_4, respectively, at rates of 0, 25, 50 and 75 μg Cr g^{-1} soil. MnO_2 was added to the Cr treatments at rates of 0 and 1900 μg MnO_2 g^{-1} soil. The procedures used in the preparation of the soil, application of basal nutrients and treatments, maintenance of the plants, harvesting and digestion of the plant samples were as described for experiment one. In addition, the roots were also harvested. The soil was washed completely from the roots with tap water, followed by a thorough rinsing with distilled water. The roots were then placed in their original pots which had also been thoroughly

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cleaned with tap water and distilled water. The pots were filled with distilled water to approximately two-thirds full. The root-water suspension was then gently shaken for one-half hour and then the water was removed from the roots with the aid of a plastic screen. This procedure was carried out three times to ensure that any adhering soil particles were removed from the roots. Following the washing, the roots were air dried in the pots, and then placed in paper bags and dried in an oven at 65 °C for three days. The weight of the oven dried roots was measured. The roots were ground in a Wiley mill and then analyzed for Mn and Cr as previously described for the grain and straw for experiments one and two.

5.3 Results and Discussion

Yields of grain and straw, obtained in the first growth chamber experiment, are presented in Table 5.2. An explanation of the LSD values reported in this table will be given to simplify the discussion which follows. Using grain yield, for example, the $LSD_{(Cr(III))} = 3.0$ can be used to test for significant differences among the yield means for the three rates of Cr(III) added, 27.8, 24.0 and 27.1 g pot^{-1}. Similarly, the $LSD_{(Cr(VI))} = 3.1$ can be used to test for significant differences among the yield means of the three rates of Cr(VI) added, 27.8, 26.5 and 6.2 g pot^{-1}, The $LSD_{(source)} = 1.6$, compares the yield means calculated for the two sources of Cr, that is 26.3 g pot^{-1} for Cr(III) and 20.2 g pot^{-1} for Cr(VI). The $LSD_{(rate(source))} = 2.8$ enables one to define at which rate of Cr the two sources significantly differ by comparing the means of each rate of Cr between the two sources.

Table 5.2. Effect of chromium source and rate, and manganese dioxide on grain and straw yields. *

Chromium source and rate

Yield (g pot^{-1})	MnO$_2$ rate (µg g^{-1})	Cr(III) (µg g^{-1})				Cr(VI) (µg g^{-1})			
		0	5	50	Mean	0	5	50	Mean
Grain	0	27.0	25.1	26.0	26.0	27.0	24.5	5.6	19.1
	490	28.6	23.0	28.3	26.6	28.6	28.5	6.8	21.3
	Mean	27.8	24.0	27.1	26.3	27.8	26.5	6.4	20.2
Straw	0	22.2	21.9	24.0	22.7	22.2	21.4	7.2	16.9
	490	26.1	25.5	26.8	26.1	26.1	26.9	9.1	20.7
	Mean	24.2	23.7	25.4	24.4	24.2	24.2	8.1	18.8

Grain, Cr(III): LSD$_{(Cr(III))}$ = 3.0

Grain, Cr(VI): LSD$_{(source)}$ = 1.6   LSD$_{(rate[source])}$ = 2.8   LSD$_{(Cr(VI))}$ = 3.1

Straw, Cr(III): LSD$_{(Mn)}$ = 1.8

Straw, Cr(VI): LSD$_{(Mn)}$ = 2.5   LSD$_{(source)}$ = 1.9   LSD$_{(rate[source])}$ = 3.3   LSD$_{(Cr(VI))}$ = 3.1

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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Therefore, for example, for the 50 μg g^{-1} rate of Cr, the mean for Cr(III) = 27.1 g pot^{-1} is compared with that of Cr(VI) = 6.2 g pot^{-1}. Finally, the LSD$_{(Mn)}$ which is not shown for both sources of Cr under grain yield, (because the effect of MnO$_2$ was not significant) is shown when straw yields are considered. Thus, for Cr(III) straw yield, the LSD$_{(Mn)}$ = 1.8 compares the means 22.7 and 26.1 g pot^{-1} , and for Cr(VI) straw yield, the LSD$_{(Mn)}$ = 2.5 compares the means 16.9 and 20.7 g pot^{-1}.

Yield of both grain and straw was similar with Cr(III) and Cr(VI) added at 5 μg Cr g^{-1} soil but was less with Cr(VI) at 50 μg g^{-1}. Cr(III) had little effect on grain and straw yields while Cr(VI) was toxic and significantly reduced grain yields from 27.8 to 6.4 g pot^{-1} and straw yields from 24.2 to 8.1 g pot^{-1} when added at 50 μg Cr(VI) g^{-1} soil. It is of interest to note that the addition of 5 μg Cr(III) g^{-1} soil resulted in a significant decrease in grain yield, while 50 μg Cr(III) g^{-1} soil had no effect. Since the yield of straw was not significantly affected by the addition of Cr(III), the result for grain yield may have been in error. Nevertheless, the effect of Cr(III) was much less drastic than that of Cr(VI), which at the 50 μg g^{-1} rate reduced yields more than 50 percent, suggesting that Cr(III) may have been fixed by the soil in forms which were less available than Cr(VI) to plants. Therefore, in soil culture, as many other studies have reported, Cr(VI) is the more active and toxic oxidation state of Cr (Hewitt 1953; Mortvedt and Giordano 1975; McGrath 1982). It should be noted, that although the toxicity of Cr(VI) was manifested only at the 50 μg g^{-1} level, the addition of either 5 or 50 μg Cr(VI) g^{-1} soil resulted in delayed maturity of the barley plants, indicating that the soil

immobilization process for Cr(VI) was different than for Cr(III).

The addition of 490 μg MnO_2 g^{-1} soil significantly increased the straw yields for both sources of Cr (Table 5.2). The mean straw yields for the Cr(III) treated plants increased from 22.7 to 26.1 g pot^{-1} and for the Cr(VI) treated plants the straw yields increased from 7.2 to 9.1 g pot^{-1} when MnO_2 was added. A similar trend was exhibited by the grain yields but the effect was not significant. It is therefore, most probable that the addition of Mn, an essential micronutrient, improved the nutrition of the plant, and hence its subsequent growth. Further, if MnO_2 did react with Cr(III) in the soil, the resultant Cr(VI) formed was either negligible or was immobilized by other reactions in the soil, since the yields measured for the Cr(III) treated plants did not decline upon MnO_2 addition.

Although Cr(III) had little effect on yields, its addition to the soil, resulted in the uptake of Cr (Table 5.3). Thus some of the added Cr(III) was in the plant available form in the soil, but its quantity was insufficient to produce toxicity. Similarly, the addition of Cr(VI) increased the concentration of Cr in the plants. At the 50 μg Cr g^{-1} soil rate, the concentrations of Cr were greater in the plants grown in the soil treated with 50 μg Cr(VI) g^{-1} than in the plants grown in the Cr(III) treated soil at the same rate of Cr. Further, at 50 μg Cr(VI) g^{-1} soil, there was an accompanying reduction in yields (Table 5.2). The addition of 490 μg MnO_2 g^{-1} soil to the Cr(III) treated soil increased the concentration of Cr in the grain and decreased the concentration of Cr in the straw. MnO_2 had no effect on the Cr concentration in the grain of the Cr(VI) treated plants, but reduced the

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Table 5.3. Effect of chromium and manganese dioxide on the concentration of chromium in the grain and straw.*

Chromium Concentration	MnO$_2$ rate (μg g^{-1})	Cr(III) (μg g^{-1})				Cr(VI) (μg g^{-1})			
		0	5	50	Mean	0	5	50	Mean
Grain (μg g^{-1})	0	0.00	0.44	0.44	0.29	0.00	0.35	0.68	0.34
	490	0.00	0.79	0.35	0.38	0.00	0.35	0.68	0.34
	Mean	0.00	0.62	0.40	0.34 LSD(Cr(III)) = 0.20	0.00	0.35	0.68	0.34 LSD(Cr(VI)) = 0.34
									LSD(rate[source]) = 0.24
Straw (μg g^{-1})	0	0.00	0.44	0.44	0.29	0.00	0.70	4.70	0.80
	490	0.00	0.17	0.26	0.14	0.00	0.53	3.50	1.34
	Mean	0.00	0.31	0.35	0.22 LSD((CrIII)) = 0.14	0.00	0.62	4.10	1.57 LSD(Cr(VI)) = 0.64
				LSD(Mn) = 0.11				LSD(source) = 0.31	
								LSD(rate[source]) = 0.53	

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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Table 5.4. Effect of chromium and manganese dioxide on the concentration of manganese in the grain and straw.*

Manganese Concentration	MnO$_2$ rate (µg g^{-1})	Chromium source and rate							
		Cr(III) (µg g^{-1})				Cr(VI) (µg g^{-1})			
		0	5	50	Mean	0	5	50	Mean
Grain (µg g^{-1})	0	11.5	9.0	10.5	10.3	11.5	8.5	9.2	9.7
	490	11.5	9.5	10.5	10.5	11.5	8.8	10.7	10.3
	Mean	11.5	9.3	10.5	10.4	11.5	8.7	9.9	10.0
		LSD$_{(Cr(III))}$ = 1.0				LSD$_{(Cr(VI))}$ = 1.0			
Straw (µg g^{-1})	0	21.8	18.8	23.7	21.4	21.8	21.2	26.7	23.2
	490	21.2	19.2	29.0	23.1	21.2	23.0	45.3	29.8
	Mean	21.5	19.0	26.4	22.3	21.5	22.1	36.0	26.5
		LSD$_{(Cr(III))}$ = 4.6				LSD$_{(Cr(VI))}$ = 10.8			

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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Table 5.5. Effect of chromium and manganese dioxide on the concentration of phosphorus in the grain and straw.*

		Chromium source and rate							
Phosphorus Concentration	MnO_2 rate (μg g^{-1})	Cr(III) (μg g^{-1})				Cr(VI) (μg g^{-1})			
		0	5	50	Mean	0	5	50	Mean
Grain (μg g^{-1})	0	3118	3493	2563	3058	3118	2830	2777	2908
	490	3107	2971	2430	2836	3107	2896	2467	2823
	Mean	3113	3232	2497	2947	3113	2863	2622	2866
									$LSD_{(Cr(VI))} = 275$
Straw (μg g^{-1})	0	324	283	277	295	324	231	710	422
	490	277	285	196	253	277	274	633	395
	Mean	301	284	237	274	301	253	672	409
									$LSD_{(Cr(VI))} = 183$

$LSD_{(source)} = 71$
$LSD_{(rate[source])} = 123$

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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Cr concentration in the straw in the Cr(VI) treated plants.

The concentration of Mn in the grain decreased as the rates of Cr(III) and Cr(VI) increased (Table 5.4). In contrast, the Mn concentration in the straw increased as the rates of added Cr(III) and Cr(VI) increased. The addition of MnO_2 to both the Cr(III) and Cr(VI) treated soil increased the concentration of Mn in the grain and straw.

The concentrations of phosphorus in the grain decreased as the rates of added Cr(III) and Cr(VI) increased (Table 5.5). The P concentration also decreased in the straw of the plants grown in the Cr(III) soil. The concentration of P in the straw of the Cr(VI) treated plants increased at the 50 μg Cr(VI) g^{-1} soil rate, most likely because the plants were much smaller. The addition of MnO_2 to both the Cr(III) and Cr(VI) treated soil decreased the concentration of P in the grain and straw.

The first growth chamber experiment established the fact the Cr(VI) was toxic to plants grown in soil treated with 50 μg g^{-1} Cr(VI). In this experiment, however, the addition of 50 μg P g^{-1} soil to each treatment may have increased the availability of Cr(VI) by competing for the same adsorption sites on the soil. Thus a second experiment was conducted to test the hypothesis that the use of P may increase Cr toxicity.

Table 5.6 displays the grain and straw yields obtained in the second experiment. P significantly increased the grain and straw yields for both Cr(III) and Cr(VI), and hence, the addition of P did not increase the toxicity of Cr(VI). The results for grain and straw confirmed the observations of the first experiment, which showed that

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Table 5.6. Effect of chromium source (supplied at 50 μg Cr g^{-1} soil), phosphorus rate, and manganese dioxide on grain and straw yields.*

Yield (g pot^{-1})	MnO$_2$ rate (μg g^{-1})	Chromium source and phosphorus rate (μg g^{-1})							
		P rate (μg g^{-1}) [Cr(III)]				P rate (μg g^{-1}) [Cr(VI)]			
		0	50	100	Mean	0	50	100	Mean
Grain	0	9.3	26.0	31.6	22.3	0.5	5.6	21.1	9.1
	490	8.0	28.3	31.7	22.7	0.0	6.8	14.7	7.2
	Mean	8.7	27.1	31.7	22.5	0.3	6.2	17.9	8.1
		LSD$_{(P)}$ = 3.0				LSD$_{(P)}$ = 3.7			
						LSD(source) = 2.2			
						LSD(phosphorus[source]) = 3.2			
Straw	0	15.4	24.0	25.3	21.5	1.6	7.2	17.0	8.6
	490	14.7	26.8	24.7	22.1	0.7	9.1	17.0	9.0
	Mean	15.0	25.4	25.0	21.8	1.2	8.1	17.0	8.8
		LSD$_{(P)}$ = 3.0				LSD$_{(P)}$ = 3.3			
						LSD(source) = 1.7			
						LSD(phosphorus[source]) = 2.5			

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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yields with Cr(III) were always greater than with Cr(VI).

The concentrations of Cr in the grain of the Cr(III) treated plants decreased as the rate of P added increased. Thus, the yield increased as a result of P addition, and diluted the concentration of Cr(III) in the grain (Table 5.7). In contrast, the concentrations of Cr in the grain of Cr(VI) plants increased as the rate of P added increased. Therefore, P increased the availability of Cr(VI) in the soil. The addition of MnO_2 to the Cr(III) treated soil decreased the concentrations of Cr in the grain, but had no effect on the Cr conceptions in the grain of the Cr(VI) treated plants.

The Mn concentration of grain from the Cr(III) treated plants also decreased as the rate of P added increased, most likely the result of biological dilution (Table 5.7). In contrast, P increased the Mn concentration in the grain of the Cr(VI) treated plants. The addition of MnO_2 slightly increased the Mn concentrations in grain from both the Cr(III) and Cr(VI) treated plants.

The concentrations of P in grain increased as the rate of P added to both the Cr(III) and Cr(VI) treated soil increased (Table 5.7).

The Cr concentrations in the straw of the Cr(VI) treated plants was much greater than that of the Cr(III) treated plants (Table 5.8). The concentrations of Cr in straw decreased as the rate of P added to both the Cr(III) and Cr(VI) treated soil increased, most likely because of the increase in straw yields as a result of P (Table 5.8). The Mn concentration in the straw of the Cr(III) treated plants decreased as the rate of P added increased. The addition of MnO_2 increased the Mn concentration in the straw of the Cr(III) treated plants. The

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Table 5.7. Effect of chromium, phosphorus, and manganese dioxide on the grain concentrations of chromium, manganese, and phosphorus in grain.*

Grain Concentration	MnO₂ rate (µg g⁻¹)	Chromium source and phosphorus rate (µg g⁻¹)							
		[Cr(III)] P rate (µg g⁻¹)				[Cr(VI)] P rate (µg g⁻¹)			
		0	50	100	Mean	0	50	100	Mean
Chromium (µg g⁻¹)	0	0.53	0.44	0.26	0.41	(0.68)	0.68	0.88	0.60
	490	0.35	0.35	0.17	0.29	-	0.68	0.68	0.45
	Mean	0.44	0.40	0.22	0.35	0.12	0.68	0.78	0.53
						LSD(source) = 0.17			
						LSD(phosphorus[source]) = 0.29			
				LSD(P) = 0.9					LSD(P) = 0.40
Manganese (µg g⁻¹)	0	12.7	10.5	8.8	10.7	(13.0)	9.2	18.7	10.7
	490	12.5	10.5	9.7	10.9	-	10.7	15.7	8.8
	Mean	12.6	10.5	9.3	10.8	2.2	10.0	17.2	9.8
						LSD(phosphorus[source]) = 3.7			
				LSD(P) = 276					LSD(P) = 5.3
Phosphorus (µg g⁻¹)	0	1905	2563	2896	2455	(2247)	2777	2287	1938
	490	1871	2430	3000	2434	-	2467	2299	1589
	Mean	1888	2497	2948	2445	375	2622	2293	1763
						LSD(source) = 286			
						LSD(phosphorus[source]) = 495			
									LSD(P) = 758

* An LSD value is shown only if the effect was significant at the P=0.05 level.
Values given in parentheses represent the concentration of the element in the one surviving replicate that produced grain.

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Table 5.8. Effect of chromium, phosphorus, and manganese dioxide on the concentrations of chromium, manganese, and phosphorus in straw.*

Straw Concentration	MnO₂ rate (µg g⁻¹)	P rate (µg g⁻¹) [Cr(III)]				P rate (µg g⁻¹) [Cr(VI)]			
		0	50	100	Mean	0	50	100	Mean
Chromium (µg g⁻¹)	0	0.70	0.44	0.18	0.44	9.68	4.70	3.90	6.09
	490	0.26	0.26	0.26	0.26	(8.50)	3.50	3.70	3.34
	Mean	0.48	0.35	0.22	0.35	6.26	4.10	3.80	4.72
							LSD(source) = 1.62		
Manganese (µg g⁻¹)	0	43.8	23.7	27.0	31.5	(34.0)	30.5	26.5	28.5
	490	52.8	29.0	29.7	37.2	22.7	45.3	32.8	33.6
	Mean	48.3	26.4	28.4	34.4	25.6	37.9	29.7	31.1
				LSD(P) = 13.1		LSD(phosphorus[source]) = 12.0			
Phosphorus (µg g⁻¹)	0	272	277	302	284	(1483)	710	280	639
	490	538	196	294	343	988	633	438	686
	Mean	405	237	298	314	958	672	359	663
				LSD(P) = 121		LSD(source) = 181			

* An LSD value is shown only if the effect was significant at the P=0.05 level.
Values in parentheses represent the concentration of the element in the two surviving replicates.

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concentrations of Mn in the straw of the Cr(VI) treated plants decreased when MnO_2 was not added. However, when MnO_2 was added, the concentrations of Mn in the straw increased as the rate of P added to the Cr(VI) treated soil increased. The P concentration in the straw of the Cr(III) treated plants decreased as the rate of P added increased when 490 μg MnO_2 g^{-1} was added to the soil. Added P had no effect on the P concentration in the straw of the Cr(III) treated plants when MnO_2 was not added. The P concentration in the straw of the Cr(VI) treated plants decreased as the rate of P added increased.

A third growth chamber experiment was conducted to further investigate the effect of MnO_2 on Cr toxicity. In this experiment a much higher rate of MnO_2 was added to the soil than in the first two experiments, in an attempt to produce Cr(VI) toxicity from added Cr(III) oxidation.

The yields obtained in the third growth chamber experiment are presented in Table 5.9. In general, the addition of Cr(III) up to 75 μg Cr(III) g^{-1} soil increased yields; however, this effect on yield was significant for grain yield when Cr(III) was added at a rate of 50 μg Cr(III) g^{-1} and for root yield when Cr(III) was added at both 50 and 75 μg Cr(III) g^{-1} soil. Nevertheless, these data show that the addition of Cr(III) up to 75 μg Cr(III) g^{-1} soil was not toxic to plants. It is possible that the yield increase was due to the addition of Cl$^-$ along with the Cr(III). The results also exhibit the fact that high levels of MnO_2 had no significant effect on Cr(III) treatment, indicating that if Cr(VI) was formed, as in experiment one, the levels were too low to produce toxicity.

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Table 5.9. Effect of chromium source and rate, and manganese dioxide on grain, straw and root dry matter yields.*

Yield (g pot⁻¹)	MnO₂ rate (μg g⁻¹)	Chromium source and rate (μg g⁻¹)									
		Cr(III)					Cr(VI)				
		0	25	50	75	Mean	0	25	50	75	Mean
Grain	0	14.1	15.8	17.1	15.0	15.5	14.1	9.7	2.4	0.7	6.7
	1900	12.9	15.2	17.7	16.8	15.7	12.9	7.9	1.4	0.0	5.6
	Mean	13.5	15.5	17.4	15.9	15.6	13.5	8.8	1.9	0.3	6.1
Straw	0	13.2	14.0	14.3	13.4	13.7	13.2	14.3	13.0	4.0	11.1
	1900	12.7	13.3	14.4	13.3	13.4	12.7	14.2	3.8	0.0	7.7
	Mean	13.0	13.7	14.4	13.4	13.6	13.0	14.3	8.4	2.0	9.4
Root	0	3.0	3.5	3.5	3.6	3.4	3.0	6.7	3.9	1.3	3.7
	1900	2.9	2.8	3.8	3.5	3.3	2.9	5.7	1.2	0.0	2.5
	Mean	3.0	3.1	3.7	3.6	3.4	3.0	6.2	2.5	0.7	3.1

Grain:
$LSD_{(Cr(III))} = 2.1$ $LSD_{(source)} = 1.0$ $LSD_{(rate[source])} = 1.9$ $LSD_{(Cr(VI))} = 1.8$

Straw:
$LSD_{(source)} = 1.8$ $LSD_{(rate[source])} = 3.5$ $LSD_{(Cr(VI))} = 4.1$ $LSD_{(Mn)} = 2.9$

Root:
$LSD_{(Cr(III))} = 0.5$ $LSD_{(rate[source])} = 1.2$ $LSD_{(Cr(VI))} = 1.4$ $LSD_{(Mn)} = 1.0$

* An LSD value is shown only if the effect was significant at the P=0.05 level.

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The yields obtained from the Cr(III) treated plants were much greater than from plants treated with the higher rates of Cr(VI) (Table 5.9). Grain yield was the most susceptible to decline upon Cr(VI) addition to the soil: that is, grain yields were significantly reduced by the addition of 25 μg Cr(VI) g^{-1} soil. In comparison, straw yields significantly decreased when Cr(VI) was applied at 50 μg Cr(VI) g^{-1} soil and root yields declined significantly when Cr(VI) was added at 75 μg Cr(VI) g^{-1} soil. The improved root growth displayed at the rate of 25 μg Cr(VI) g^{-1} soil may in part be due to the fact that these plants were harvested much later, and thus once they overcame the initial toxicity of Cr(VI), root growth was improved. The addition of 1900 μg MnO$_2$ g^{-1} soil increased the toxicity of Cr(VI) and hence the yields of grain, straw and roots decreased when the higher rate of MnO$_2$ was added to the Cr(VI) treated soil. In the first growth chamber experiment the addition of 490 μg MnO$_2$ g^{-1} soil increased grain and straw yields when added with Cr(VI). It is possible that the higher rates of MnO$_2$ increased the toxicity of Cr(VI) due to the oxidation of Cr(III). A portion of Cr(VI) added to soil can be reduced by soil organic matter, forming Cr(III) (Bartlett and Kimble 1976b; Bloomfield and Pruden 1980; James and Bartlett 1983c). The very high rate of MnO$_2$ may have prevented the soil organic matter mediated reduction of Cr(VI) to Cr(III) or oxidized Cr(III) to Cr(VI) even if Cr(III) was formed upon reaction with organic matter. Either reaction would increase Cr toxicity.

The concentration of Cr in the grain, straw and roots increased as the rate of Cr added to the soil increased (Table 5.10). However,

Table 5.10. Effect of chromium and manganese dioxide on the chromium concentrations in grain, straw, and roots.*

Chromium Concentration	MnO₂ rate (µg g⁻¹)	Cr(III)					Cr(VI)				
		0	25	50	75	Mean	0	25	50	75	Mean
Grain (µg g⁻¹)	0	0.00	0.56	0.56	0.83	0.49	0.00	0.83	4.63	(2.78)	1.60
	1900	0.00	0.47	0.65	0.83	0.49	0.00	0.92	(6.10)	-	0.74
	Mean	0.00	0.52	0.61	0.83	0.49	0.00	0.88	3.33	0.47	1.17
		LSD$_{(Cr(III))}$ = 0.10					LSD$_{(Cr(VI))}$ = 1.85				
Straw (µg g⁻¹)	0	0.00	0.65	1.39	1.48	0.88	0.00	6.20	7.41	(1.94)	3.57
	1900	0.00	1.39	1.48	1.85	1.18	0.00	6.11	(5.56)	-	1.99
	Mean	0.00	1.02	1.44	1.67	1.03	0.00	6.16	4.63	0.33	2.78
		LSD$_{(Mn)}$ = 0.22 LSD$_{(Cr(III))}$ = 0.31					LSD$_{(Mn)}$ = 1.23 LSD$_{(Cr(VI))}$ = 1.73				
		LSD$_{(source)}$ = 0.88									
		LSD$_{(rate[source])}$ = 1.75									
Root (µg g⁻¹)	0	3.24	31.03	40.09	66.67	35.26	3.24	260.19	470.37	(536.71)	228.18
	1900	4.63	40.74	43.52	58.33	36.81	4.63	319.00	(538.21)	-	125.74
	Mean	3.94	35.89	41.81	62.50	36.04	3.94	289.60	324.85	89.45	176.96
		LSD$_{(Cr(III))}$ = 8.53					LSD$_{(Cr(VI))}$ = 200.79				
		LSD$_{(source)}$ = 73.70									
		LSD$_{(rate[source])}$ = 147.31									

* An LSD value is shown only if the effect was significant at the P=0.05 level.
Values given in parentheses represent the concentrations of chromium in the one surviving replicate.

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above 50 μg Cr(VI) g^{-1} soil the concentrations of Cr in the grain and straw of the surviving plants decreased because of the toxic effects of Cr(VI) on plant growth. These data show the decreasing gradient in the amounts of Cr from roots to grain as a result of the limited translocation of Cr from roots to shoots (Turner and Rust 1971; Huffman and Allaway 1973b; Myttenaere and Mousny 1974; Cary et al 1977a). The addition of 1900 μg MnO$_2$ g^{-1} to the Cr(III) treated soil, increased the concentrations of Cr(III) in the straw and roots, and hence increased the availability of Cr(III) in the soil. The addition of 1900 μg MnO$_2$ g^{-1} to the Cr(VI) treated soil, increased the availability of Cr(VI) and there was a slight increase in the Cr concentration in the grain and roots.

The Mn concentration in the grain, straw and roots of the Cr(III) treated plants increased as the rate of Cr(III) added increased (Table 5.11). The Mn concentrations in the grain and roots of the Cr(VI) treated plants increased as the rate of Cr(VI) added to the soil increased. The concentration of Mn in the straw of the Cr(VI) treated plants was increased by the addition of 25 μg Cr(VI) g^{-1} soil and then decreased by the addition of 50 and 75 μg Cr(VI) g^{-1} soil.

The addition of 1900 μg MnO$_2$ g^{-1} to the Cr(III) treated soil increased the concentrations of Mn in the grain, straw and roots (Table 5.11). The concentration of Mn in the grain and roots of the Cr(VI) treated plants also increased when 1900 μg MnO$_2$ g^{-1} was added to the soil. There was, however, a slight decrease in the Mn concentration in the straw when MnO$_2$ was added and this may be the result of the increased toxicity of Cr(VI) when MnO$_2$ was added.

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Table 5.11. Effect of chromium and manganese dioxide on the manganese concentrations in grain, straw, and roots.[*]

Manganese Concentration (µg g⁻¹)	MnO₂ rate (µg g⁻¹)	Cr(III)					Cr(VI)				
		0	25	50	75	Mean	0	25	50	75	Mean
Grain (µg g⁻¹)	0	6.5	7.9	9.0	9.2	8.2	6.5	9.4	8.3	(14.5)	7.3
	1900	7.9	8.2	9.4	9.8	8.8	7.2	9.0	(9.5)	-	5.0
	Mean	7.2	8.1	9.2	9.5	8.5	7.2	9.2	5.8	2.4	6.2
		$LSD_{(Cr(III))} = 1.3$					$LSD_{(source)} = 1.8$				
							$LSD_{(rate[source])} = 3.8$				
Straw (µg g⁻¹)	0	14.3	14.9	20.1	20.9	17.6	14.3	22.7	10.9	(7.5)	12.6
	1900	17.3	17.1	19.9	38.4	23.2	17.3	21.8	(10.0)	-	10.6
	Mean	15.8	16.0	20.0	29.7	20.4	15.8	22.3	7.1	1.3	11.6
		$LSD_{(Cr(III))} = 10.17$					$LSD_{(source)} = 4.2$				$LSD_{(Cr(VI))} = 5.3$
							$LSD_{(rate[source])} = 8.5$				
Root (µg g⁻¹)	0	77.5	88.3	81.7	90.8	84.6	77.5	104.0	174.2	(187.5)	104.6
	1900	140.3	140.0	145.0	189.2	153.6	140.3	493.7	(673.0)	-	214.6
	Mean	108.9	114.2	113.4	140.0	119.1	108.9	298.9	199.3	31.3	159.6
		$LSD_{(Mn)} = 43.1$					$LSD_{(rate[source])} = 158.68$				

Chromium source and rate (µg g⁻¹)

[*] An LSD value is shown only if the effect was significant at the P=0.05 level.
Values in parentheses represent the manganese concentrations in the surviving replicate.

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SUMMARY AND CONCLUSIONS

In response to the concern that the Cr concentrations in
agricultural soils may be increasing, four pedons representing four of
Manitoba's mineral agricultural were surveyed to establish baseline
levels of chromium in terms of the total content and extractable forms,
as well as to correlate these contents with various soil properties. In
order to determine the possibility of potential toxicity of Cr(VI) from
the addition of Cr(III), the ability of these soils to oxidize added
Cr(III) to Cr(VI) was also examined. The soils collected represented a
range in soil physical and chemical properties and consisted of an
Orthic Gray Luvisol, a Humic Rego Gleysol, and two Gleyed Rego Blacks.

The total Cr concentration in the soils varied from 13 (for a
coarse-textured soil) to 27 μg Cr g^{-1} soil (for a fine-textured soil),
and was uniformly distributed within the profiles except in the
Luvisolic soil where an accumulation of Cr had occurred in the Bt
horizon. Since there was no significant accumulation of Cr in the A
horizons of the soils and the total Cr content was in the lower portion
of the ranges reported in the literature, the soils appeared to be
uncontaminated. The differences in the total Cr content among soils
were believed to be due to differences in the mineralogy and texture of
the parent materials because total Cr was significantly correlated with
the total contents of Fe and Mn, and the amount of sand, silt and clay.

Extracting the soils with eight different solutions led to the
general conclusion that most of the total Cr present in the soils was
Cr(III) and most of this Cr was present in forms that were relatively

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unavailable to plants. The presence of Cr(VI) was detected in all soils following extraction with KH_2PO_4 but the amounts were so small that toxicity would not be a problem. There was no water soluble Cr in any of the soils and very little Cr was exchangeable with NH_4Cl, which indicated that naturally occurring Cr(III) was present in forms which were relatively immobile and unavailable to plants. It was believed, however, that more Cr may be available to plants than predicted by deionized water, NH_4Cl and KH_2PO_4 because DTPA extracted more Cr from the soils compared to these three extractants which were deemed to remove Cr which was potentially available to plants.

Organically bound Cr, extracted by 0.1 mol L^{-1} NaP_2O_7, was present in the greatest amounts in the surface A horizons and decreased with depth due to the decrease in the content of organic matter. The amount of organically bound Cr extracted was positively correlated with the total content of Cr, as well as with the organic matter content, which indicated that if the total amount of Cr in a soil was increased there may be an increase in the amount of organically bound Cr. The efficiency of extracting the soils with acids, 0.1 mol L^{-1} HCl and 2 mol L^{-1} HNO_3, was dependent on the concentration of the acid since the soils studied were quite calcareous in nature. Thus, more Cr was solubilized by HNO_3 than HCl. The majority of Cr in these soils was associated with the free iron oxides as extracted with citrate-bicarbonate-dithionite (CBD). The amount of Cr associated with the free iron oxides was positively correlated with the total contents of Cr, Fe and Mn, as well as the clay contents of the soils. Chromium was most likely concentrated in the oxide fraction of the soils because oxides are

highly reactive due to their large surface areas and high surface charges.

Each soil was capable of oxidizing added Cr(III) to Cr(VI) and this ability was greatest in the surface horizons and decreased with depth. The amount of Cr(VI) formed and measured in solution was in the range between 0.11 and 10.12 μg g^{-1} soil and was somewhat lower than the values found in the literature for average aerated soils which included both free and adsorbed Cr(VI). It was thus suggested that more Cr(VI) may have been formed than was reported because some of it may have become adsorbed on to certain soil components. Nonetheless, the results obtained indicated that the potential for Cr(VI) toxicity to occur from Cr(III) additions would be very low.

Based on the findings of the survey a laboratory study was undertaken to investigate the interactions of added Cr(III) and Cr(VI) with common soil minerals. Thus, two oxides, haematite and birnessite, and two clay minerals, montmorillonite and vermiculite, were equilibrated with solutions of either $CrCl_3 \cdot 5H_2O$ and K_2CrO_4 at pH values of 4 or 5. The soil minerals differed in their capacities to adsorb Cr(III) and Cr(VI) and adsorbed much more Cr(III) than Cr(VI). These differences in the amounts adsorbed were attributed to different bonding mechanisms, specific surface areas, and reactive surfaces on the soil minerals. The adsorption of Cr(III) by haematite was not affected by pH. However, the adsorption of Cr(III) by birnessite decreased as the pH increased. The decrease in the amount of Cr(III) adsorbed by birnessite as the pH increased was in contrast to findings in the literature and was suspected to have been in error. The effect of pH on

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the adsorption of Cr(III) by the clay minerals could not be discerned because all of the Cr(III) added was adsorbed at both pH four and five. In general, the adsorption of Cr(VI) decreased as the pH increased which is characteristic of anion adsorption and this was attributed to the increased negative charge on the soil minerals as the pH increased.

The strength with which the soil minerals held adsorbed Cr(III) and Cr(VI) was assessed by extracting the adsorbed Cr on the minerals with solutions of 0.01 mol L^{-1} KH_2PO_4 and 0.05 mol L^{-1} $CaCl_2$. Cr(III) was held very strongly to haematite, vermiculite and birnessite as it could not be extracted from the surfaces, which indicated that Cr(III) adsorbed by these soil minerals would most likely not be or only be slightly available to plants. Adsorbed Cr(III) was released from montmorillonite by both extracting solutions. Thus, it was suggested that because montmorillonite released some of the adsorbed Cr(III) and vermiculite did not, differences in their structure could account for the difference in immobilization of Cr(III) by the two clay minerals. Although Cr(III) could not be released from birnessite, Cr(VI) was extracted when Cr(III) was added initially, and it was concluded that some of the Cr(III) adsorbed by birnessite was oxidized to Cr(VI). Adsorbed Cr(VI) was not held as strong as Cr(III) to the soil minerals which meant that Cr(VI) would be much more mobile and plant available than adsorbed Cr(III). Although KH_2PO_4 was more efficient than $CaCl_2$ at extracting adsorbed Cr(VI), it was suggested that adsorbed Cr(VI) may be held by both nonspecific and specific adsorption mechanisms since both extracting solutions removed adsorbed Cr(VI). It was concluded from this study that the soil minerals possess a good capacity to reduce the

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mobility and potential toxicity of Cr(III) with the possible exception of birnessite. Further, since the minerals did not immobilize added Cr(VI) to the same extent as Cr(III) it was suggested that chemical reduction of Cr(VI) to Cr(III) is the best means to decrease the potential toxicity of Cr(VI) in soils.

Since Cr(III) was bonded differently by the clay minerals and no Cr(III) could be removed from vermiculite a study was conducted to determine the possibility that the Cr(III) may become fixed in the interlayers of vermiculite. The results showed a remarkable similarity between the interactions of Cr(III) and highly charged 2:1 aluminosilicates and that of aluminum and 2:1 clays. Evidence was also obtained to show that Cr(III) was fixed in the interlamellar sheets of vermiculite.

The results of the previous studies led to the initiation of a series of growth chamber experiments to determine the effects of Cr(III) and Cr(VI), in combination with manganese dioxide and fertilizer phosphorus on the yield and quality of barley plants.

In each experiment, although the addition of Cr(III) resulted in the uptake of Cr, it did not produce significant toxic effects on yield and nutrient concentrations, and may have, in fact, been of some benefit to yields at higher rates. It was thus concluded that when Cr(III) was added to the soil very little of it would remain in solution and be taken up by plants because it would be quickly immobilized by the soil. By comparison, Cr(VI) additions resulted in decreased yields, delayed maturity, reduced nutrient concentrations and caused death at rates of 50 μg Cr(VI) g^{-1} soil or greater, since it was not as easily immobilized

by the soil as was Cr(III).

It was suspected that the addition of 50 μg P g^{-1} soil as finely ground 11-51-0 fertilizer may have increased the toxicity of the Cr(VI) treatments in one of two ways: that is, by either adding more Cr since the fertilizer was known to contain Cr (121 μg Cr g^{-1} fertilizer) as an impurity or by interfering with the adsorption of Cr(VI). Thus, a second experiment was conducted to test the hypothesis that P may increase the toxicity of Cr. The Cr found as an impurity in the fertilizer did not promote Cr toxicity because very small amounts of Cr were added. The P improved the growth significantly in the Cr(III) treatments and although it may have increased the mobility and plant concentrations of Cr(VI), it reduced the toxicity for the Cr(VI) treatments, by enhancing plant growth.

In the first two experiments low rates of manganese dioxide, 490 μg MnO$_2$ g^{-1} soil, despite its role as an oxidizing agent, did not produce symptoms of Cr(VI) toxicity when combined with Cr(III) treatments. In fact, although the effect was not always significant, the addition of 490 μg MnO$_2$ g^{-1} soil improved grain and straw yields for both Cr(III) and Cr(VI) and this was attributed to better nutrition. Thus a third experiment was conducted using a higher rate of manganese dioxide in an attempt to produce Cr(VI) toxicity from a Cr(III) source. The addition of 1900 μg MnO$_2$ g^{-1} soil had little effect on plant yield and quality, when the initial source of Cr was Cr(III). However, if the initial source of Cr was Cr(VI), the addition of 1900 μg MnO$_2$ g^{-1} soil increased the toxicity of Cr(VI).

The studies reported in this manuscript showed that for the four

representative agricultural soils surveyed, there is no danger of Cr toxicity as they presently exist. Trivalent Cr additions (mainly from fertilizer sources) would not present a potential problem for three reasons: (1) the added Cr(III) would be quickly immobilized due to precipitation, adsorption and possibly interlayer fixation reactions; (2) although the soils are capable of oxidizing Cr(III) the resultant Cr(VI) levels are quite low since the soils do not contain sufficient amounts of oxidized Mn compounds to bring about toxic levels of Cr(VI); (3) the resultant Cr(VI) formed may not be available to plants due to fixation reactions and also to the conversion back to Cr(III). There still exists a potential problem from Cr(VI) additions, however, since the existence of Cr(VI) in soils seems to be the key to toxicity. Thus, wastes containing Cr(VI) should be chemically reduced prior to disposal to ensure that the potential for Cr toxicity in these soils will remain as nil.

APPENDIX A

DESCRIPTION OF SOILS

The four pedons sampled for analysis in chapter three were described and named by Michele Cheslock and Tee Boon Goh in the field. Bob Eilers provided pedological confirmation in the laboratory. These soils were selected to provide a range in texture, organic matter content, pH (soil reaction), drainage and parent material found in Manitoba's mineral agricultural soils.

Preliminary potential sites were determined by referencing various soil reports. In the Morden-Winkler area a clay soil which developed under poor drainage was selected (Smith et al. 1973). In the Riding Mountain area a Luvisolic soil was surveyed from the Rossburn and Virden report (Ehrlich et al. 1956). Two imperfectly drained Gleyed Rego Black soils, one which developed from a clay parent material and the other from a sandy parent material were collected from the area described in the soil survey report of the rural municipalities of Grey, Dufferin, Roland, Thompson and part of Stanley (Michalyna et al. 1988).

SOIL ONE

Soil Series	Almasippi Series
Subgroup	Gleyed Rego Black (Carbonated Phase)
Location	SW25-8-6w
Date	May 3, 1988
Topography	Flat to gently undulating
Drainage	Imperfectly drained
Vegetation	Consists of <u>Agropyron</u> <u>repens</u> (L.) Beauv.
Parent Material	Moderately calcareous, uniform, sandy lacustrine sediments to 80cm.

Ah 0-26 cm Brownish black (7.5YR 2/2 m) fine sandy loam; weak granular; moderate effervescence; abrupt irregular boundary between 24 and 30 cm to:

AC 26-37 cm Dark grayish yellow (2.5Y 4/2 m) fine sand; structureless (single-grained); strong effervescence; common (2-20%), fine (<5 mm diameter), distinct reddish brown mottles; lineations of iron and lime were are also evident; clear, smooth boundary to:

Ck1 37-52 cm Olive brown (2.5Y 4/6 m) fine sand; structureless (single-grained); strong effervescence; common, fine, distinct mottles; gradual, smooth boundary to:

Ck2 >52 cm Yellowish brown (2.5Y 5/6 m) sand; structureless (single-grained); strong effervescence; common, medium, distinct mottles.

SOIL TWO

Soil Series	Red River Series
Subgroup	Gleyed Rego Black
Location	SE24-5-4w
Date	May 3, 1988
Topography	Level to very gently undulating
Drainage	Imperfectly drained
Vegetation	Under cultivation: crop is Pisum sativum L.
Parent Material	Moderately calcareous, fine to very fine clayey lacustrine deposits

Ap   0-25 cm   Black (10YR 3/1 d, 10YR 2/1 m) heavy clay; fine, medium subangular blocky; non-carbonated; clear, irregular boundary to:

Ck1   25-72 cm   Brownish black (2.5Y 3/2 m) clay; coarse granular to subangular blocky; strong effervescence; clear, smooth boundary to:

Ck2   >72 cm   Dark grayish yellow (2.5Y 4/2 m) clay; medium subangular blocky; strong effervescence; faint iron stains are evident.

SOIL THREE

Soil Series	Waitville Series
Subgroup	Orthic Gray Luvisol
Location	NW16-20-22w
Date	May 5, 1988
Topography	Hummocky to rolling
Drainage	Well drained
Vegetation	Populus tremuloides (Michx.), intermixed with Cornus alba L., Betula papyrifera Marsh., etc.
Parent Material	Boulder Till

LFH 10-0 cm Consists of light to dark brown roots, leaves and branches in various stages of decomposition. There are roots and a fine mat of root hairs as well.

Ah 0-2 cm Fine granular; irregular, distinct boundary to:

Ae 2-12 cm Brown (7.5YR 4/3 m) loam to silt loam; well developed fine platy; non-carbonated; abrupt, distinct boundary to:

Bt 12-25 cm Dark brown (7.5YR 3/4 m) clay; medium subangular blocky; non-carbonated; ped surfaces have very prominent clay skins; abrupt, distinct boundary to:

BC 25-39 cm Yellowish brown (10YR 4/3 m) sandy clay loam; granular; moderate effervescence; abundant pebbles with a stone line evident on top of BC; iron stains are prominent (7.5YR 4/6); distinct boundary to:

Ck >39 cm Olive brown (2.5Y 4/3 m) silty clay loam; granular; strong effervescence with lime streaks; less pebbles than BC horizon; iron stains and concretions.

SOIL FOUR

Soil Series	Osborne Series
Subgroup	Rego Humic Gleysol (Carbonated Phase)
Location	NE24-2-3w
Date	May 27, 1988
Topography	Depressional
Drainage	Poorly drained (improved)
Vegetation	Under cultivation: _Zea_ _mays_ L.
Parent Material	Moderately calcareous, fine textured lacustrine clay

Apk   0-18 cm   Black (10YR 2/1 d, 10YR 1.7-2/1 m) clay; friable, fine granular; weak to moderate effervescence; clear, smooth boundary to:

Ahk1   18-30 cm   Black (10YR 1.7/1 m) clay; strong, fine subangular blocky; weak to moderate effervescence; few shell fragments; clear, smooth boundary to:

Ahk2   30-42 cm   Black (10YR 1.7/1 m) clay; friable, fine subangular blocky; weak to moderate effervescence; evidence of some very narrow tonguing; clear, irregular boundary to:

Ckg1   42-70 cm   Olive black (5Y 3/1-2 m) heavy clay; massive, breaking to weak subangular blocky; moderate effervescence; many, fine, prominent mottles; gypsum crystals; clear, smooth boundary to:

Ckg2   70-105 cm   Dark grayish yellow (2.5Y 4/2 m) heavy clay; massive; moderate effervescence (more dolomite than in Ckg1); abundant iron staining; few, medium, distinct mottles; small occlusions of calcium carbonate.

APPENDIX B

Table B.1 Extractable iron in the four pedons studied in Chapter III.

Soil Series	Horizon	Water	1M NH$_4$Cl	0.01M KH$_2$PO$_4$	DTPA	0.1M HCl	2M HNO$_3$	0.1M Na$_4$P$_2$O$_7$	CBD
					(μg Fe g^{-1} soil)				
Almasippi	Ap	0.97	0.51	0.09	31.6	120.8	1081.1	64.8	1592.2
	AC	2.29	0.91	0.00	6.0	130.4	790.7	22.7	2681.2
	Ck1	2.01	1.00	0.08	3.2	219.4	458.8	13.5	2892.1
	Ck2	1.73	1.58	0.04	4.3	79.5	582.6	10.4	5153.1
Red River	Ap	5.82	0.00	0.13	91.3	124.6	2576.3	282.3	4690.0
	Ck1	1.20	0.16	0.00	19.1	289.9	3488.4	100.1	5276.0
	Ck2	0.34	0.05	0.45	18.3	220.1	4167.4	78.3	6727.1
Waitville	Ae	39.44	0.00	2.19	95.6	147.8	915.5	209.3	6190.2
	Bt	142.48	0.00	1.21	93.0	134.9	1635.7	720.9	16511.6
	BC	12.03	0.00	0.85	17.9	152.0	2122.1	201.7	9089.7
	Ck	5.06	0.00	0.04	16.1	145.1	2486.8	64.5	6094.6
Osborne	Apk	1.45	0.17	0.69	9.1	248.2	1982.0	225.4	1919.4
	Ahk1	0.44	0.00	0.00	10.3	78.9	1730.1	321.8	2235.8
	Ahk2	0.45	0.00	0.45	10.2	95.7	1198.2	189.8	1742.3
	Ckg1	0.49	0.00	0.00	13.9	152.9	3073.7	120.0	5432.4
	Ckg2	0.44	0.00	0.45	13.5	148.6	3977.3	157.9	7087.5

Table B.2. Extractable manganese in the four pedons studied in chapter III.

Soil Series	Horizon	Water	1M NH$_4$Cl	0.01M KH$_2$PO$_4$	DTPA	0.1M HCl	2M HNO$_3$	0.1M Na$_4$P$_2$O$_7$	CBD
					(μ g Mn g^{-1} soil)				
Almasippi	Ah	0.05	1.53	0.38	18.78	183.4	378.1	7.95	196.8
	AC	0.03	0.71	0.25	4.57	93.6	139.2	2.74	175.0
	Ck1	0.00	0.62	0.17	1.83	134.8	68.3	0.97	91.9
	Ck2	0.00	0.63	0.17	1.69	379.2	100.8	0.79	133.1
Red River	Ap	0.05	0.84	0.35	19.54	74.0	360.2	19.48	492.9
	Ck1	0.00	0.37	0.22	6.24	150.2	296.4	0.92	387.9
	Ck2	0.00	0.32	0.26	7.39	110.8	315.5	0.65	406.2
Waitville	Ae	0.56	11.87	2.91	25.88	101.3	177.0	24.79	614.0
	Bt	0.42	5.25	0.65	29.42	68.5	212.5	17.57	716.8
	BC	0.10	0.20	0.30	9.35	85.8	326.6	5.88	433.4
	Ck	0.08	0.10	0.21	14.77	85.2	291.9	1.60	458.4
Osborne	Apk	0.03	0.60	0.32	3.85	152.8	285.0	9.69	163.6
	Ahk1	0.06	0.61	0.32	1.70	172.6	141.9	5.10	81.2
	Ahk2	0.05	0.85	0.62	1.52	189.2	85.4	3.37	84.8
	Ckg1	0.03	0.76	0.54	1.70	287.2	262.7	4.66	324.5
	Ckg2	0.00	0.60	0.27	2.07	148.6	148.6	2.20	422.4

APPENDIX C

Oxidation of Cr(III) by MnO$_2$

The following is one possible oxidation-reduction reaction that may occur when MnO$_2$ is equilibrated with a solution of Cr(III).

Half reactions:
$$2Cr^{3+} + 8H_2O = 2HCrO_4^- + 14H^+ + 6e^-$$

$$3MnO_2 + 12H^+ + 6e^- = 3Mn^{++} + 6H_2O$$

Overall reaction:
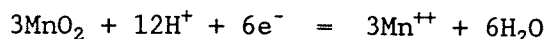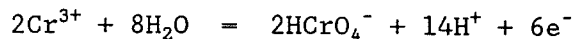
$$2Cr^{3+} + 3MnO_2 + 2H_2O = 2HCrO_4^- + 2H^+ + 3Mn^{++}$$

$\Delta G° = 34.64$ kJ $\qquad K_1 = \dfrac{(HCrO_4^-)^2 \ (H^+)^2 \ (Mn^{++})^3}{(Cr^{3+})^2}$

The $\Delta G°$ of the reaction is related to the equilibrium constant of that reaction by the relationship:

$$\Delta G° = -RT \ln K_1$$

Therefore $K_1 = 10^{-\Delta G°/2.303RT} = 10^{-6.07} = 8.51 \times 10^{-7}$

The activity of Mn^{++} at equilibrium can be calculated, using initial conditions and approximations. The initial concentration of Cr^{3+} was $C_o = 10^{-3}$ mol L^{-1} and the pH was 5. Therefore, values for the reactants and products can be assigned as follows:

$\quad$ (Mn^{++}) = x $\qquad\qquad$ (HCrO$_4^-$) = 2/3x
$\quad$ (Cr^{3+}) = C$_o$-2/3x $\qquad$ (H$^+$) = 10^{-5} mol L^{-1}

Thus,
$$K_1 = \frac{(2/3x)^2(10^{-5})^2(x)^3}{(C_o-2/3x)^2} = 8.51 \times 10^{-7}$$

By graphical approximation, the value for x was obtained:

$$x = 1.5 \times 10^{-3} \text{ mol Mn}^{++} \text{ L}^{-1} = 84 \ \mu g \text{ Mn}^{++} \text{ g}^{-1}$$

Once equilibrium is reached, the activity of Mn^{++} would be 84 μg Mn^{++} g^{-1} which is a measurable quantity. As well, the amount of HCrO$_4^-$ formed could be measured.
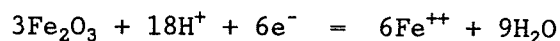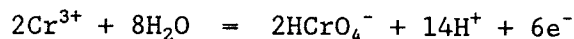
Since the kinetics were not taken measured in the experiment in Chapter 4, the time to reach equilibrium is not known. Thus, the value for x after a reaction time of 22 hours is in between 0 and 1.5×10^{-3} mol L^{-1}.

The thermodynamics reported above indicate that almost all of the 10^{-3} mol L^{-1} Cr(III) equilibrated with the MnO$_2$ was oxidized to Cr(VI), and thus, MnO$_2$ may be a limiting factor in this reaction in soils.

Oxidation of Cr(III) by Fe_2O_3

The following is one possible oxidation-reduction reaction that may occur when Fe_2O_3 is equilibrated with a solution of Cr(III).

Half reactions:

$$2Cr^{3+} + 8H_2O = 2HCrO_4^- + 14H^+ + 6e^-$$

$$3Fe_2O_3 + 18H^+ + 6e^- = 6Fe^{++} + 9H_2O$$

Overall reaction:

$$2Cr^{3+} + 3Fe_2O_3 + 4H^+ = 2HCrO_4^- + 6Fe^{++} + H_2O$$

$$\Delta G^\circ = 359.87 \text{ kJ} \qquad K_2 = \frac{(HCrO_4^-)^2 \ (Fe^{++})^6}{(Cr^{3+})^2 \ (H^+)^4}$$

At equilibrium, the value for $K_2 = 10^{-\Delta G^\circ/2.303RT} = 10^{-63.03} = 9.33 \times 10^{-64}$

The initial concentration of Cr^{3+} was $C_o = 10^{-3}$ mol L^{-1} and the pH at which the reaction occurred was 5. Thus, the following values can be given to the reactants and products as follows:

$$(Fe^{++}) = x \qquad\qquad (H^+) = 10^{-5} \text{ mol } L^{-1}$$
$$(HCrO_4^-) = 1/3x \qquad\qquad (Cr^{3+}) = C_o - 1/3x$$

Therefore,

$$K_2 = \frac{(1/3x)^2(x)^6}{(C_o - 1/3x)^2 \ (10^{-5})^4} = 9.33 \times 10^{-64}$$

Solving for x:

$$x = 9.8 \times 10^{-12} \text{ mol } L^{-1} = 5.5 \times 10^{-7} \ \mu\text{g } Fe^{++} \ g^{-1}$$

Therefore, at equilibrium, the activity of Fe^{++} would be 5.5×10^{-7} μg Fe^{++} g^{-1} which is a concentration that is below the detection limits for this element. Also, the amount of $HCrO_4^-$ formed would be insignificant. Since the time to reach equilibrium was not measured, it is not known if it was obtained. Therefore, if equilibrium was not achieved then the quantity of Fe^{++} formed would be between 0 and 9.8×10^{-12} mol L^{-1} and hence, considered as zero.

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