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Canadian Soil Quality Guidelines for

Chromium: Environmental

**Supporting Document — Final Draft
December 1996**

NOTICE

This final draft document provides the information supporting the derivation of environmental soil quality guidelines for chromium. Development of these soil quality guidelines was initiated through the National Contaminated Sites Remediation Program (NCSRSP) which officially ended in March 1995. Given the need for national soil quality guidelines for contaminated sites management and many other applications, development was pursued under the direction of the CCME Soil Quality Guidelines Task Group after the end of the NCSRSP.

This document is a working document that was released shortly after the publication of "A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines" (CCME 1996). The CCME recognizes that some refinements or changes to the Protocol may become necessary upon application and testing. If required, amendments to the Protocol will be made and the guidelines will be modified accordingly. For this reason guidelines are referred to in this document as CCME Recommended Guidelines. Readers who wish to comment or provide suggestions on the Protocol or on the guidelines presented in this document should send them to the following address:

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This document is a supporting technical document. It is available in English only. A French Abstract is given on page vii.

Ce document technique de soutien n'est disponible qu'en anglais avec un résumé en français présenté à la page vii.

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ABSTRACT

Canadian environmental quality guidelines, developed under the auspices of the Canadian Council of Ministers of the Environment (CCME), are numerical concentrations or narrative statements recommended to support and maintain designated resource uses. CCME Canadian soil quality guidelines can be used as the basis for consistent assessment and remediation of contaminants at sites in Canada.

This report was prepared by the Guidelines Division of the Science Policy and Environmental Quality Branch (Environment Canada), which acts as Technical Secretariat for the CCME Soil Quality Guidelines Task Group. The Guidelines were derived according to the procedures described in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996).

Following the introduction, chapter 2 presents chemical and physical properties of chromium and a review of the sources and emissions in Canada. Chapter 3 discusses chromium's distribution and behavior in the environment while chapter 4 reports the toxicological effects of chromium on microbial processes, plants, and animals. These informations are used in chapter 5 to derive soil quality guidelines for chromium to protect environmental receptors in four types of land uses: agricultural, residential/parkland, commercial, and industrial.

The following soil quality guidelines are recommended by the CCME based on the available scientific data. Since the toxicity of the hexavalent oxidation state of chromium (Cr(VI)) is greater than that of the other environmentally stable oxidation states, a separate series of guidelines was derived for it. Hence, for total chromium, the environmental soil quality guideline (SQG_E) relative to agricultural and residential/parkland land uses is $64 \text{ mg}\cdot\text{kg}^{-1}$ soil, and the SQG_E relative to commercial and industrial land uses is $87 \text{ mg}\cdot\text{kg}^{-1}$ soil. For Cr(VI), the available data were insufficient/inadequate to derive soil quality guidelines according to the CCME 1996 Protocol. Therefore, the Provisional Method, described in CCME (1997) and hereafter was used to derive provisional environmental soil quality guidelines. The provisional environmental soil quality guideline (SQG_E —provisional) relative to Cr(VI) for agricultural and residential/parkland land uses is $0.4 \text{ mg}\cdot\text{kg}^{-1}$ soil whereas for commercial and industrial land uses it is $1 \text{ mg}\cdot\text{kg}^{-1}$ soil. These environmental soil quality guidelines are optimized for soils within the pH range of 4 to 7.8 for total chromium and of 6.1 to 7.5 for Cr(VI) as the toxicological studies on which they are based were conducted within this pH range.

RÉSUMÉ

Les recommandations canadiennes pour la qualité de l'environnement, élaborées sous les auspices du Conseil Canadien des Ministres de l'Environnement (CCME), sont des concentrations ou des énoncés décrivant les limites recommandées dans le but d'assurer le maintien et le développement durable d'utilisations désignées des ressources. Les recommandations canadiennes pour la qualité des sols proposées par le CCME peuvent être utilisées comme base pour l'uniformisation des processus d'évaluation et d'assainissement des terrains contaminés au Canada.

Le présent document a été préparé par la Division des Recommandations de la Direction de la Qualité de l'Environnement et de la Politique Scientifique (Environnement Canada), qui agit comme secrétaire technique pour le Groupe de Travail du CCME sur les Recommandation pour la Qualité des Sols. Les Recommandations ont été élaborées selon les procédures décrites dans le *Protocole d'élaboration de recommandations pour la qualité des sols en fonction de l'environnement et de la santé humaine* (CCME 1996).

Faisant suite à une brève introduction, le chapitre 2 présente les propriétés physiques et chimiques du chrome de même qu'un survol des sources et des émissions au Canada. Le chapitre 3 discute du devenir et du comportement de cette substance dans l'environnement alors que le chapitre 4 rapporte ses effets toxicologique sur les processus microbiens, les plantes et les animaux. Ces informations sont utilisées au chapitre 5 afin d'élaborer des recommandations pour la qualité des sols relatives au chrome en vue de la protection de l'environnement dans le cadre de quatre types d'utilisations de terrains: agricole, résidentiel/parc, commercial et industriel.

Les recommandation pour la qualité des sols suivantes, proposées par le CCME, sont fondées sur les données scientifiques disponibles. Puisque la toxicité du chrome hexavalent (Cr(VI)) est supérieure à celle des autres formes stables dans les conditions environnementale, une série de recommandations a été élaborée séparément pour le Cr(VI) . Ainsi, pour le chrome total, la recommandation pour la qualité des sols en vue de la protection de l'environnement (RQS_E) relative aux terrains à vocation agricole et résidentielle/parc est de $64 \text{ mg}\cdot\text{kg}^{-1}$ de sol et la RQS_E pour les terrains à vocation commerciale et industrielle est de $87 \text{ mg}\cdot\text{kg}^{-1}$ de sol. Pour le Cr(VI) , les données disponibles sont insuffisantes/inadéquates pour permettre l'élaboration de recommandations selon les procédures décrites dans le Protocole du CCME (1996). La Méthode provisoire, décrite dans un document du CCME (1997) et ci-après, a donc été utilisée pour élaborer des recommandations provisoires pour la qualité des sols en vue de la protection de l'environnement. La recommandation provisoire pour la qualité des sols relative au Cr(VI) en vue de la protection de l'environnement (RQS_E —provisoire) est de $0.4 \text{ mg}\cdot\text{kg}^{-1}$ de sol pour les terrains à vocation agricole et résidentielle/parc et elle est de $1 \text{ mg}\cdot\text{kg}^{-1}$ de sol pour les terrains à vocation commerciale et industrielle. Ces recommandations pour la qualité des sols en vue de la protection de l'environnement sont à leur optimum dans des sols avec pH entre 4 et 7.8 pour le chrome total et entre 6.1 et 7.5 pour le Cr(VI) puisque les études toxicologiques utilisées pour leur élaboration ont été effectuées dans ces mêmes conditions de pH.

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1. INTRODUCTION

The Canadian Council of Ministers of the Environment's (CCME) Canadian Environmental Quality Guidelines are numerical limits for contaminants intended to maintain, improve, or protect environmental quality and human health. CCME Canadian Soil Quality Guidelines can be used as the basis for consistent assessment and remediation of contaminants at sites in Canada along with CCME guidelines issued for the protection of water quality, sediment quality and tissue quality. In response to the urgent need to begin remediation of high priority "orphan" contaminated sites, an interim set of criteria was adopted from values currently in use in various jurisdictions across Canada (CCME 1991). Many of the CCME interim soil remediation criteria do not have a complete supporting scientific rationale and are being updated based on current scientific information.

This report reviews the sources and emissions of chromium, its distribution and behaviour in the environment, and its toxicological effects on plants, microbial processes and animals. This information is used to derive guidelines for chromium to protect ecological receptors according to the processes outlined in CCME (1996) for agricultural, residential/parkland, commercial, and industrial land uses.

The values derived herein are environmental soil quality guidelines and are intended as general guidance. Site-specific conditions should be considered in the application of these values. The values may be applied differently in various jurisdictions, therefore, the reader should consult the appropriate jurisdiction for application of these values.

2. BACKGROUND INFORMATION

2.1 Physical and Chemical Properties

Chromium is the 24th element in Group VI A of the Periodic Table and is a member of the first transition series. Chromium is the seventh most abundant element on the earth and ranks fourth among the 29 elements of biological importance (Nriagu and Neibor 1988; WHO 1988). Its relative atomic mass is 51.996, and it has an electronic configuration of $[\text{Ar}] 3d^5 4s^1$ in the ground state (WHO 1988; Langård 1982). There are four naturally occurring isotopes, which include Cr^{50} , Cr^{52} , Cr^{53} , and Cr^{54} . Cr^{52} is by far the most abundant isotope, accounting for approximately 83.8% of the total (Nriagu and Niebor 1988).

Although chromium is a naturally occurring element, elemental chromium does not appear in nature (Shupak 1991). Rather, chromium is found complexed with oxygen, iron or lead, forming oxides such as chromite (FeOCr_2O_3), chromitite (Fe_2O_3 , $2\text{Cr}_2\text{O}_3$) and crocitate (PbCrO_4) (Williams 1988). Chromite (FeOCr_2O_3) ore is the only commercial source of chromium (Shupack 1991). This ore is composed of varying mixtures of iron and chromium oxides. Chromite is a spinel with Cr (III) in octahedral sites and Fe(II) in tetrahedral sites (WHO 1988). It occurs in small concentrations in mineral aluminium oxide (Al_2O_3), magnesium oxide (MgO), calcium oxide (CaO) and silicon oxide (SiO_2). Trace amounts of chromium oxides, ubiquitous in the rock composing the earth's crust,

account for the colouring of many minerals such as rubies and emeralds (Stern 1982; Shupack 1991).

Crystalline chromium is a white-gray, hard, brittle, and lustrous metal that melts at $1903 \pm 10^\circ\text{C}$. This metal dissolves in non-oxidizing mineral acids such as HCl and H_2SO_4 , but does not dissolve in nitric acid (HNO_3) or cold aqua regia. It is believed that chromium is passivated by HNO_3 and aqua regia. Chromium is extremely resistant to ordinary corrosive agents and it is used as a protective corrosion inhibitor (Nriagu and Niebor 1988). The physical and chemical properties of chromium are outlined in Table 1.

Chromium can exist in nine different oxidation or valence states, from (-II) to (VI). Because of their stability in the environment, the trivalent and hexavalent forms are the most common (WHO 1988; Langård 1982; Shupack 1991; US EPA 1984a, b, c). Within the context of this report, only the trivalent and hexavalent forms will be discussed in detail.

Cr (III)

The trivalent form of chromium has an electron configuration of $3d^3 4s^0$ and is generally considered to be the most thermodynamically stable oxidation state under ambient redox conditions. Considerable energy is required in order to convert Cr (III) to a lower or higher oxidation state (Nriagu and Niebor 1988; Shupack 1991). Cr (III) is a positively charged ion that has a strong tendency to form hexacoordinate octahedral complexes with a variety of ligands. The point of attachment of these complexes is the oxygen atom (e.g. water, hydroxyl ions, carboxylic acids, phenols, phosphates), the nitrogen atom (e.g. ammonia, amines, pyridines, purines, pyrimidines, imadazoles) or the sulfur atom (sulfahydryl groups) (Taylor *et al.* 1979; Niebor and Jusys 1988, Saleh *et al.* 1989; Shupack 1991). These stable complexes can prevent the precipitation of Cr (III) at pH values whereby it would otherwise precipitate (US EPA 1990).

Cr (VI)

The hexavalent form of chromium has an electron configuration of $3d^0 4s^0$ and is not thermodynamically stable. Cr (VI) is a strong oxidizing agent, existing only as tetrahedral oxo species such as CrO_3 (chromium oxide), CrO_2Cl_2 (chromyl chloride) and CrO_4 (chromate ion) (Niebor and Jusys 1988). It is produced during the reduction of chromite ore to obtain chromium metal (WHO 1988; Shupack 1991). The principal source of Cr (VI) in the environment is anthropogenic pollution; it rarely occurs naturally due to its affinity to react with organic matter and other reducing substances (Jaworski 1985; Bartlett and James 1988; US EPA 1984c). In solution, Cr (VI) exists as an anion and is thus quite mobile in the environment (Saleh *et al.* 1989).

2.2 Analytical Methods

The CCME has established recommended analytical procedures for the measurement of total Cr and Cr (III) in soil (CCME 1993). This method is referred to as Inductively Coupled Plasma-Atomic Emission Spectroscopy (US EPA Method 6010). The detection limit and precision of this method

is $7 \mu\text{g}\cdot\text{L}^{-1}$ and 18%, respectively. Following corrections for a 1 g soil sample digestion with the extract being diluted to 100 ml, a detection limit of $0.7 \text{ mg}\cdot\text{kg}^{-1}$ would be calculated.

There are four recommended analytical methods for the measurement of total Cr, Cr (III) and Cr (VI) in water, wastewater and soil extracts. These include: Direct Air-Acetylene Flame Method (US EPA Method 3111B) (total Cr, Cr III), Inductively Coupled Plasma (ICP) Method (US EPA Method 3120B) (total Cr, Cr III), Hexavalent Chromium Colorimetric Method (US EPA Method 7196) (Cr VI) and Inductively Coupled Plasma-Atomic Emission Spectroscopy Method (US EPA Method 6010) (Cr III). The detection limits are 20, 7, not available, and $7 \mu\text{g}\cdot\text{L}^{-1}$. For further details refer to the CCME's Guidance Manual on Sampling Analysis and Data Management for Contaminated Sites (1993).

The following is a list of unpublished analytical methods used by various federal, provincial and commercial laboratories in Canada. These methods are used in the measurement of Cr in soil, wastewater and soil extracts. They include: Wastewater Technology Centre (1988), Wastewater Technology Centre (1989a), Wastewater Technology Centre (1989b), Wastewater Technology Centre (1989c), Wastewater Technology Centre (1991), Ministère de l'Environnement du Québec (1990a), Ministère de l'Environnement du Québec (1990b). For further details refer to the appendix of the CCME's Guidance Manual on Sampling Analysis and Data Management for Contaminated Sites (1993).

2.3 Production, Uses and Global Sources

Production

The only commercial source of chromium is chromite ore. Ninety-six percent (96%) of the world's known reserves of chromate are located in southern Africa (Shupack 1991). Deposits of chromite can also be found in Russia, Turkey, Zimbabwe, Albania, the Philippines, Finland and India (Langård 1982).

There are 250 documented chromite deposits in Canada, occurring in Québec, Ontario, British Columbia, Manitoba and Newfoundland. Canadian deposits of chromite are usually low grade, except for some of the deposits located in Newfoundland which are of a medium grade (up to 53% Cr_2O_3 with Cr/Fe ratio of 2.7). It has not been economically feasible to mine these deposits in Canada since 1945 (Phillips 1988). Thus, it is necessary for Canada to import all of its chromite ore and ferrochromium. Canada imported 94 800 tonnes of chromium-bearing materials in 1989, and 74 000 tonnes in 1990 and 1991 (Statistics Canada 1989; 1990; 1991).

Ferrochromium is produced using chromite ore in an electronic arc furnace with carbon or silicon. There are two methods for the commercial production of pure chromium metal. The first is known as the "aluminothermic process" in which a mixture of powdered chromic oxide and granulated aluminum is ignited in a refractory vessel. This exothermic process produces metallic chromium and aluminum oxide. The second and most popular method is referred to as the "silicothermic process".

Chromic oxide, silicon and lime are heated in an electric arc furnace. Silicon dioxide rich slag and molten chromium metal are produced (Shupack 1991; Langård 1982).

Uses

There are three principal industrial applications for chromium. These applications include: metallurgical, refractory, and chemical processes. The major chromium compounds and their uses are presented in Table 2.

The main use of chromium in the metallurgical industry is for the production of ferrochromium alloys such as stainless steel, high-speed steel, alloy cast irons, and nonferrous alloys. The addition of chromium to steel and wrought iron improves its corrosion and wear resistance and enhances its mechanical properties (*e.g.* creep resistance and hardness). The most important industrial application for chromium is the production of stainless steel, which consumes about 75% of all the ferrochromium produced each year (ATSDR 1989; Nriagu 1988; US EPA 1984a; Langård 1982).

The second most important use of chromium is in refractory applications. The high melting point and chemical stability of chromite ore and chrome alloys provides resistance to the corrosivity of acids and bases at high temperatures. Chromium is used in the manufacture of refractory bricks, furnace linings, mortars, castables and in coating materials to close pores and to join bricks in furnaces (ATSDR 1989; Nriagu 1988; US EPA 1984a; Langård 1982).

Another primary use of chromium is in chemical applications such as metal finishing (Cr (VI)), corrosion control, leather tanning (Cr (III)) and finishing, wood treatment (Cr (VI)) and the production of pigments (both Cr (VI) and Cr (III)) (ATSDR 1989; Nriagu 1988; US EPA 1984a; Langård 1982).

There are several other uses for chromium such as the production of fungicides, drilling muds, water treatment, textiles, catalysts, synthetic rubies for lasers, chromium dioxide magnetic tapes, labelling of red blood cells and toner for copying machines. (ATSDR 1989; Nriagu 1988; US EPA 1984a; Langård 1982; Taylor *et al.* 1979).

2.4 Levels in the Canadian Environment

Rock

Chromium is ubiquitous in nature, and is found in ultrabasic and basic rock, particularly feldspar minerals (Nriagu and Niebor 1988). Natural chromium levels in igneous rock varies from $13 \text{ mg}\cdot\text{kg}^{-1}$ (granitic rock) to $1600 \text{ mg}\cdot\text{kg}^{-1}$ (ultramafic/basic and serpentine rock) (Brookes 1987). There are a number of minerals which contain Cr as a major constituent, the most commonly occurring of these minerals is chromite, FeCr_2O_4 (Shiraki 1978). Chromite is found primarily in ultrabasic rocks, such as serpentinites.

Cr (III) closely resembles Fe (III) and Al (III) in its chemical properties and ionic size. Therefore, Cr(III) behaves similarly to these former ions during weathering and is often concentrated by clays. Chromium retention increases with decreasing grain size, and thus is usually found in higher concentration in shales than in sandstones.

Soil

Natural levels of chromium in uncontaminated Canadian soil usually range from 10-100 mg·kg⁻¹ and typically average 43 mg·kg⁻¹ (McKeague and Wolynetz 1980). However, Roberts (1980) has reported chromium concentrations as high as 1000 mg·kg⁻¹ in the serpentine soils of Newfoundland. Regional chromium concentrations in soils across Canada were determined by McKeague and Wolynetz (1980); the mean concentrations ranged from 19 mg·kg⁻¹ (Canadian Shield) to 78 mg·kg⁻¹ (Cordilleran) (Table 3).

Levels of Cr (VI) and total Cr in Ontario rural parkland and urban parkland soils are reported in the Ontario Typical Range (OTR) values for 1991 (OMEE 1993). The OTR₉₈ is a concentration that equals or exceeds 97.5 percent of all samples (i.e. the upper range of the test data). The OTR₉₈ for Cr was 58 mg Cr·kg⁻¹ soil in rural sites and 62 mg Cr·kg⁻¹ soil in urban sites. The OTR₉₈ of Cr (VI) was considerably lower at 0.5 µg Cr·kg⁻¹ soil in both rural and urban sites. In an earlier study examining four different agricultural soil types in Ontario, chromium concentrations were reported to range from 10 mg·kg⁻¹ in sand to 22 mg·kg⁻¹ in clay (Frank *et al.* 1976). In a similar study examining agricultural soils in northwestern Alberta, higher mean concentrations of chromium were found in surface soil with high organic matter content (84 mg·kg⁻¹) than in surface soil with low organic matter content (61 mg·kg⁻¹) (Soon and Abboud 1990).

As a result of industrial and agricultural practices (e.g. application of sewage sludge, fungicides, mineral and organic fertilizers), chromium contamination of soils can occur (Table 4). Chromium concentrations as high as 5000 mg·kg⁻¹ have been surveyed in the vicinity of wood preserving operations in Atlantic Canada (Bamwoya *et al.* 1991). Addition of Cr to soils worldwide has been estimated to range between 480-1300 kt·yr⁻¹ (Nriagu and Pacyna 1988). Significant anthropogenic sources include the application of fly or bottom ashes to land, with an estimated median value of 297.5·10⁶ kg yr⁻¹, and mass wasting of commercial products, with an estimated median value of 457.5·10⁶ kg yr⁻¹.

Water

Natural background levels of chromium in surface water bodies and groundwater aquifers are a direct function of mineral weathering processes, sediment loading rates, and precipitation patterns. Aqueous Cr (VI) exists as water soluble complexed anions. As a strong oxidizing agent, hexavalent Cr can react with dissolved organic molecules to form Cr (III). In surface water bodies, subsequent precipitation removes the trivalent form of chromium from the water column as CrO₃·xH₂O, which ultimately settles to the sediment phase (Taylor *et al.* 1979; Environment Canada 1993). However, in the absence of organic matter or appropriate reducing agents (e.g. Fe²⁺ or H₂S), Cr (VI) can persist indefinitely within the aquatic environment.

In Canada, chromium levels in uncontaminated surface and marine waters are usually less than $1 \mu\text{g}\cdot\text{L}^{-1}$ (Mayer 1988; Rossmann and Barres 1988). However, higher chromium concentrations have been reported in contaminated waters from across Canada. The concentration of total chromium in Ontario rivers exposed to various industrial discharges has been reported to range from $8\text{--}188 \mu\text{g}\cdot\text{L}^{-1}$ (Table 5). Chromium concentrations in the Don River have reached concentrations as high as $188 \mu\text{g}\cdot\text{L}^{-1}$ (MOE 1991). Between 10 and 60% of the total chromium in Canadian waters is present as dissolved Cr (VI).

Ambient total chromium concentrations in the Great Lakes differ by a full order of magnitude (Table 6). Lake Superior is reported to have a mean total Cr concentration of $0.09 \mu\text{g}\cdot\text{L}^{-1}$, whereas the total Cr concentration in Lake Ontario is $0.81 \mu\text{g}\cdot\text{L}^{-1}$ (Rossman and Barres 1988). This difference can probably be attributed to increased industrial activity and urbanization within the lower great lakes region.

Sediments

Elevated concentrations of chromium in sediments have been reported throughout various regions in Canada (Table 7). Portions of the St. Mary's River system and the Welland River are reported to have sediment concentrations of $31\,000 \mu\text{g}\cdot\text{g}^{-1}$ and $5\,120 \mu\text{g}\cdot\text{g}^{-1}$, respectively. Nriagu *et al.* (1983) reported that the chromium concentration in Hamilton Harbour sediment was $564 \mu\text{g}\cdot\text{g}^{-1}$.

Air

There are no naturally occurring gaseous forms of chromium (Cary 1982). The chemical form of chromium in air depends on the source of the emission. Chromium is always in association with airborne particulate matter such as windblown dusts, volcanic debris, seasalt aerosols, dusts from wild fires and vegetative debris (WHO 1988; Nriagu 1990). The most important industrial sources of chromium in the atmosphere originate from ferrochromium production (US EPA 1984b). Other processes such as ore refining, chemical and refractory processing, cement production, automobile catalytic converters and brake linings contribute to the atmospheric concentrations of Cr. Following release into the atmosphere, Cr (VI) reacts with dust particles and is eventually reduced to Cr (III) (US EPA 1990). Both Cr (III) and Cr (VI) are removed from the air by precipitation and atmospheric fallout. Particles smaller than $10 \mu\text{m}$ in diameter may remain airborne for longer periods of time and be transported a considerable distance from the source by wind currents (US EPA 1984a; 1984b; 1990).

Ambient atmospheric Cr concentrations in Canada typically range $<50 \text{ ng}\cdot\text{m}^{-3}$ (Dann 1991). However, there is significant spatial variation in Canadian atmospheric chromium levels (Table 8). The mean atmospheric chromium concentration in non-urban and remote locations is $<1.0 \text{ ng}\cdot\text{m}^{-3}$, whereas in urban areas, it ranges from 5 to $20 \text{ ng}\cdot\text{m}^{-3}$ (Dann 1991). Concentrations of airborne chromium as high as $1250 \text{ ng}\cdot\text{m}^{-3}$ have been measured near point sources of chromium discharge (Environment Canada 1991). Elevated chromium concentrations have also been detected around major industrial centres. The city of Hamilton was reported to have atmospheric concentrations ranging from $26 \text{ ng}\cdot\text{m}^{-3}$ to $680 \text{ ng}\cdot\text{m}^{-3}$ (Environment Canada 1991).

Deposition is the principal mechanism by which chromium is removed from the atmosphere and distributed to terrestrial and aquatic ecosystems. Mean deposition rates for chromium in remote, rural and urban areas are <0.2 , $0.5-3$, and $5-15 \text{ mg}\cdot\text{m}^{-3}$, respectively (Pacyna and Nriagu 1988).

2.5 Existing Criteria and Guidelines

Existing guidelines, criteria or standards for chromium in soil are summarized in Table 9. Concentrations are reported for total chromium, except where indicated.

3. ENVIRONMENTAL FATE AND BEHAVIOUR

An understanding of chromium oxidation and reduction processes is of great importance to ecological risk assessment. In addition to standard modifying parameters (such as pH, organic matter and cation exchange capacity), the oxidation (valence) state of the chromium species determines its mobility, bioavailability, uptake kinetics and toxicity, and hence determines the overall exposure risk. The difference between the observed toxicity of Cr (VI) and Cr (III) species can largely be attributed to differences in bioavailability: Cr (III) is less mobile and cannot penetrate cellular membranes as readily as Cr (VI). Thus the conversion of Cr (VI) to Cr (III) and vice versa are important reactions to consider when assessing the ecological risk associated with chromium contamination.

3.1 Oxidation of Chromium (III) to Chromium (VI)

The degree to which Cr (III) can interact with other soil constituents is limited by the fact that most Cr (III) is present in the form of insoluble chromium oxide precipitates. Thus Cr (III) is relatively stable in most soils (Kabata-Pendias and Pendias 1984), although oxidation of Cr (III) to Cr (VI) can occur under specific environmental conditions. Factors influencing the rate of chromium oxidation include soil pH, Cr (III) concentration, presence of competing metal ions, availability of manganese oxides, presence of chelating agents (i.e. low molecular weight organic compounds), and soil water activity.

Cr (III) oxidation is favoured under acidic conditions (Fendorf et al. 1992; Bartlett and James 1979; Bartlett 1986; Manceau and Charlet 1992). This behaviour is attributable to increased solubility of Cr (III) at lower pH, which enables increased contact with the oxidizing agent (Bartlett 1991). Cr (III) must be in a mobile form to undergo oxidation on the surfaces of manganese oxides (Bartlett 1991). Solubility of Cr (III) is also enhanced by chelation to low molecular weight compounds such as citric or fulvic acids (Bartlett and James 1988).

Relatively few oxidants are known to mediate oxidation of Cr (III) in the soil environment because the redox potential of the Cr (VI)/Cr (III) couple is quite high (Rai *et al.* 1989). Typical oxidizing agents include dissolved oxygen and manganese oxides. The oxidation of Cr (III) by dissolved oxygen is quite slow relative to the rate of oxidation by manganese oxides. Bartlett and James (1979)

demonstrated that manganese oxides present in fresh, moist, nonacid aerobic soil samples serve as the electron link between Cr (III) and oxygen in the atmosphere. Abiotic oxidation of Cr (III) is controlled by the surface characteristics of the manganese oxides and the proximity of Cr (III) to the surface (Bartlett 1991). This reaction may be enhanced in soils exposed to elevated temperatures, such as those that result from brush fires (Cary 1982).

Cr (III) oxidation is not observed in soil samples which have been dried and stored for extended periods of time (Bartlett and James 1979; Bartlett 1991). It is not presently clear whether this is due to physico-chemical alterations within the soil matrix, or due to reduced microbial activity.

3.2 Reduction of Chromium (VI) to Chromium (III)

Factors influencing the reduction of Cr (VI) to Cr (III) in soil include soil pH, the presence of electron donors such as organic matter or ferrous ions, and soil oxygen levels. Many studies have shown that Cr (VI) reduction increases with decreasing soil pH (McGrath et al. 1990; Bartlett and Kimble 1976; Bloomfield and Pruden 1980; Bartlett 1991; Eary and Rai 1991). Soil pH affects the degree of positive and negative charge on the surfaces of soil colloids, thus directly influencing the availability of electron donors (Bartlett and James 1988). Rai et al. (1991) concludes that acidic soil solutions enhance the release of Fe (II) ions from soil minerals, which increases the reduction of Cr (VI). The authors likewise note that the Cr reducing action of organic matter increases with decreasing pH.

Cr (VI) reduction to Cr (III) is significantly retarded in soils that lack appropriate electron donors such as ferrous iron minerals, silicate minerals, reduced sulfur species and soil organic matter (Palmer and Wittbrodt 1991). Bartlett and Kimble (1976) found no evidence for Cr (VI) reduction in soils with very low organic matter (<0.05%) content. Similarly, Ottabong (1989) found that chromium reduction increased linearly with increasing soil humus content. The reduction of Cr (VI) by Fe (II) could be an important fate process in subsoils, where levels of organic matter are typically low (Eary and Rai 1991; Bartlett and James 1988).

Reduction of Cr is enhanced under anaerobic conditions, such as within waterlogged soils (Bloomfield and Pruden 1980; Losi et al. 1994a; Bartlett 1991). Since oxygen is an electron acceptor, it is believed to inhibit Cr (VI) reduction through direct competition for electron donors (Loisi et al. 1994b). Waterlogged soils may also enhance Cr reduction because of increased CO₂ trapping, which tends to lower soil pH (Loisi et al. 1994a). Soil microbial activity may indirectly influence Cr (VI) reduction by decreasing soil oxygen concentrations and increasing CO₂ levels.

3.3 Adsorption

Cr (III) is strongly adsorbed by clay particles, soil organic matter, metal oxyhydroxides and other negatively charged particles. Below pH 4, Cr (III) is strongly adsorbed by both kaolinite and montmorillonite clays. Between pH 4 and 5 the combination of adsorption and precipitation renders

this species immobile in most soils (NRCC 1976; Jaworski 1985). Since clay surfaces become more negatively charged with increasing pH, Cr (III) adsorption by clay minerals increases with increasing soil pH.

Although Cr (VI) is not readily adsorbed to most surfaces, it is adsorbed by clay minerals that possess exposed inorganic hydroxyl groups, including iron and aluminum oxides (Rai *et al* 1989; Zachara *et al.* 1989). Cr (VI) adsorption increases with decreasing pH as a result of protonation of the surface hydroxyl sites. The adsorption process can be described as a surface complexation reaction between Cr (VI) species and a surface hydroxyl site either on iron or aluminum oxides or on the edges of layer silicates (Rai *et al.* 1989; Zachara *et al.* 1989). Thus Cr (VI) adsorption increases in proportion to concentrations of iron and aluminum oxides. Alternatively, the presence of SO_4^{2-} and dissolved inorganic carbon depresses the adsorption of Cr (VI) (Zachara *et al.* 1989). In general, highly weathered (southern) soils dominated by oxide-rich colloids adsorb more Cr (VI) than the less weathered (northern) acid soils (Bartlett and James 1988; Bartlett 1991).

It is important to note that the two processes of chromium adsorption and reduction may occur simultaneously in a soil matrix. Distinguishing which process is responsible for an experimentally observed decline in Cr (VI) soil levels is difficult. This may pose significant implications for site remediation efforts, since adsorbed Cr (VI) can be remobilized by changes in subsurface geochemistry (e.g. pH changes following the application of lime or phosphate-rich fertilizer).

3.4 Leaching

Cr (III) solids, such as Cr (III) oxide (Cr_2O_3) and Cr (III) phosphate complexes, are practically insoluble at $\text{pH} > 4$, and thus do not tend to leach from the soil matrix into the groundwater system (Calder 1988). Rarely exceeding $50 \mu\text{g}\cdot\text{L}^{-1}$, Cr (III) constitutes a very small percentage of the total chromium found in natural and polluted groundwaters.

Cr (VI) solids, except BaCrO_4 , are soluble within the soil environment. Cr (VI) adsorption by clays, soils and natural aquifer materials is low to moderate within the pH range typical of groundwater (e.g. pH 6.8). At a $\text{pH} > 8.5$, Cr (VI) is completely mobile and can readily leach out of the soil and into the groundwater system. Cr (VI) can be stabilized within the soil profile by reduction to relatively immobile Cr (III) or adsorption to mineral solids. However, hexavalent chromium that is not adsorbed or reduced to Cr (III) remains highly mobile within the soil profile.

3.5 Biotransformation and Volatilization

As an element, chromium is not biodegradable and therefore has infinite persistence in the environment (Bartlett 1991; ATSDR 1989). Chromium compounds do not readily volatilize from water or soil.

4. BEHAVIOUR AND EFFECTS IN BIOTA

Cr (III) is considered to be an essential dietary trace element for mammals. It is important in glucose, lipid and protein metabolism (Janus and Krajnc 1989). The daily recommended dose of Cr (III) in human nutrition ranges from 50 to 200 μg per day (Shupack 1991). A few studies have reported stimulatory effects of Cr (III) on plants, although its essentiality has yet to be determined. There is no evidence that Cr is essential to the growth or metabolism of soil microorganisms or invertebrates.

Unlike Cr (III), Cr (VI) is not an essential dietary trace element. This form is more toxic than trivalent chromium, in large part because of its high oxidizing potential and its ability to penetrate cellular membranes. Certain hexavalent chromium compounds are established carcinogens: these include calcium chromate, lead chromate, strontium chromate oxide and cobalt-chromium alloys (US EPA 1984c; WHO 1988).

The LOEC endpoints reported in the toxicity tables represent the lowest-observed-effects concentration at which there was a statistically and biologically significant difference from the controls, as reported by the author(s). If no such statistical tests were reported by the author(s), the percentage of adverse effect, as compared to the controls, resulting from chromium concentrations within the soil have been calculated by the CCME from data presented by the author(s). This percentage of adverse effect is represented by an EC (effects concentration) endpoint within the toxicity tables. Actual EC_{xx} endpoints reported by the author(s), such as EC_{25} or EC_{50} , will be presented as such without any calculation of percentage of adverse effect. Measured concentrations and metal extraction methods are reported in the toxicity tables only if they involve digestion of soil with a strong acid, such as HCl or HNO_3 . Otherwise, the nominal concentrations are reported.

4.1 Soil Microbial Processes

Toxicity studies concerning soil microbial processes selected for use in soil quality guidelines derivation are listed in Table 10. Soil enzyme activities were not included in this table since they may not represent measured effects of chemicals on soil microbial populations. This is because many enzymes produced by plants and microbes can exist and function extracellularly in soil for varying periods of time, depending on soil microenvironmental factors (Tabatabai 1982).

Doelman and Haanstra (1984) investigated the inhibition of soil microbial respiration by chromium in five Dutch soil types: sandy (pH 7.0, 2% clay, 1.6% O.M.), sandy loam (pH 6.0, 9% clay, 5.7% O.M.), silty loam (pH 7.7, 19% clay, 5.7% O.M.), clay (pH 7.5, 60% clay, 3.2% O.M.) and sandy peat (pH 4.4, 5% clay, 12.8% O.M.). Additions of CrCl_3 at concentrations of 0, 55, 150, 400, 1000, 3000, 8000 $\text{mg}\cdot\text{kg}^{-1}$ dw were made and soil respiration was measured over an 18 month period. Soil respiration was significantly reduced ($p < 0.05$) in the sandy peat soil at 150 $\text{mg}\cdot\text{kg}^{-1}$ dw, and in the other four soils at 400 $\text{mg}\cdot\text{kg}^{-1}$ dw. The results of this study were extremely variable. The higher concentrations (1000, 3000, and 8000 $\text{mg}\cdot\text{kg}^{-1}$ dw) were generally inhibitory, although there were instances where significant stimulation of respiration occurred at these higher concentrations. The EC_{50} for each of the five soil types was $> 5000 \text{ mg}\cdot\text{kg}^{-1}$ dw.

Chang and Broadbent (1981) evaluated the influence of Cr (III) on microbial respiration. CO₂ production was measured in Yolo silt loam (2.2% O.M.) amended with alfalfa and sewage sludge, following the addition of chromium (CrCl₃) in solution at concentrations of 0, 50, 100, 200, 300, and 400 mg·kg⁻¹ dw. The 50 mg·kg⁻¹ dw treatment resulted in a 45% decrease in cumulative CO₂ evolution.

In a similar experiment, Chang and Broadbent (1982) evaluated the influence of Cr (III) on N-transformation. Nitrogen immobilization, nitrogen mineralization, and nitrification were measured in Yolo silt loam (2.2% O.M.) following the addition of CrCl₃ in solution at concentrations of 0, 100, 200, and 400 mg·kg⁻¹ dw. The 100 mg·kg⁻¹ dw treatment resulted in a 40% decrease in cumulative CO₂ evolution.

Drucker *et al.* (1979) determined the effects of chromium on soil respiration. CO₂ evolution was measured in a Ritzville surface soil following the addition of K₂CrO₄ at concentrations of 0, 1.0, 10.0 and 100 mg·kg⁻¹ dw. They reported that 1 mg·kg⁻¹ dw of Cr (VI) significantly reduced respiration after 13 days exposure. After 24 days, the NOEC was 10 mg Cr (VI)·kg⁻¹ dw with respiration being significantly reduced at 100 mg Cr (VI)·kg⁻¹ dw.

Liang and Tabatabai (1978) examined the effect of Cr (III) on nitrification of NH₄⁺-N in three different soils: Webster (pH 5.8, 23% clay, 39% silt, 2.6% O.C.) Harps (pH 7.8, 30% clay, 44% silt, 3.7% O.C.) and Okoboji (pH 7.4, 34% clay, 50% silt, 5.4% O.C.). A 10 g sample of soil was treated with 50 μmoles of CrCl₃. Nitrification was inhibited by 96 % in the Webster soil, by 87 % in the Harps soil, and by 59 % in the Okoboji soil after 10 days post-treatment.

Skujinš *et al.* (1986) examined the inhibition rates of soil respiration and nitrification following the addition of Cr (III) as CrCl₃ at levels of 50, 200, 500 and 1000 mg·kg⁻¹ in deciduous forest sandy clay loam (pH 7.0). The EC₅₀ for soil respiration inhibition following a 20 day incubation was >200 μg Cr (III)·kg⁻¹ dw. The authors proposed that microbial populations that are less sensitive to Cr (III) had developed during this test period. Nitrification decreased proportionally with increasing concentration of added CrCl₃.

The toxicity of Cr (III) and Cr (VI) to microbial-mediated soil processes has been compared by Fenke (1977, cited in Williams 1988), who determined Cr (VI) to be a more effective inhibitor of nitrification than Cr (III). Cr (VI) temporarily inhibited nitrification at concentrations of 60 and 120 mg·kg⁻¹ dw, but the rate of nitrification returned to normal after 100 days of incubation. However, the 240 mg·kg⁻¹ dw treatment of Cr (VI) inhibited nitrification beyond 100 days. In contrast, 180 mg·kg⁻¹ dw of Cr (III) slightly enhanced nitrification from day 14 to 100.

Ross *et al.* (1981) also studied the effect of Cr (III) and Cr (VI) on CO₂ evolution in two different soils. Nellis loam and Hinesburg fine sandy loam were treated with 10 and 100 mg·kg⁻¹ dw Cr (VI) (K₂Cr₂O₇) and 100 mg·kg⁻¹ dw Cr (III) (CrCl₃). All three chromium treatments significantly decreased respiration after 3 weeks with no significant difference in inhibition rates between the two soils.

4.2 Terrestrial Plants

Chromium is a natural component of plant tissues, although concentrations vary considerably between different plant species, plant tissues and soil types. Levels in shoots of plants grown on uncontaminated soil usually do not exceed $0.5 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$. Whole plant concentrations $\geq 3 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ indicate possible contamination and/or increased accumulation (Williams 1988; Janus and Krajnc 1989). There are reported cases of plants growing on serpentine soils which accumulate tissue Cr concentrations as high as $100 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$, but plants rarely exceed this value (Brookes 1987).

Although it has been well established that Cr (III) is essential to animal nutrition, the essentiality of chromium to plants has yet to be determined. Detectable concentrations of chromium are found in plants, and there is some evidence that Cr (III) has stimulatory effects on plant growth and yield (Mertz 1969). Nonetheless, chromium has not been demonstrated as an essential element for plant development or growth (WHO 1988).

Uptake and Behaviour

Many studies have demonstrated that chromium uptake from soils or nutrient solution and translocation in plant cells is very low. Thus, concentrations of chromium in the edible portions of the plant remain low, even when growing on Cr contaminated soil (Patterson 1971 cited in Williams 1988; Cunningham *et al.* 1975 a,b,c; Cary *et al.* 1977a, b; Dowdy and Ham 1977; Lahouti and Peterson 1979; Sykes *et al.* 1981; de Haan *et al.* 1985 cited in Janus and Krajnc 1989). In general, roots contain higher chromium concentrations than stems, leaves or fruit (Williams 1988).

Patterson (1971 cited in Williams 1988) studied the uptake and translocation of both Cr (III) and Cr (VI) by barley plants grown in three sandy loam soils (pH 5.6, 6.4, 7.8) with chromium additions of 0, 50 and $200 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$. Cr (III) and Cr (VI) were added as potassium chromium sulfate $\text{KCr}(\text{SO}_4)_2$ and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, respectively. At the highest exposure concentration, chromium levels in the leaves ($2.2\text{--}3.2 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$) were only slightly higher than the controls ($0.5\text{--}0.8 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$). However, Cr concentrations in the root were much higher ($46\text{--}146 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ Cr (III) and $115\text{--}168 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ Cr (VI)) than the controls ($1.9\text{--}2.6 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$).

The uptake and translocation of chromium in plants, using wheat (*Triticum aestivum*), corn (*Zea mays*), potato (*Solanum tuberosum*), pea (*Pisum sativum*), tomato (*Lycopersicon esculentum*), and red kidney bean (*Phaseolus vulgaris*), were examined by Cary *et al.* (1977a) in Johnson's solution containing FeEDTA and using ^{51}Cr as a radioactive label. The plants were exposed for 48 hrs to CrCl_3 , Na_2CrO_4 , Cr oxalate, Cr tartrate, Cr EDTA, Cr methionine and Cr citrate. Very little Cr, except for Cr-EDTA, was translocated from the roots to the tops of any of the species. There was no difference between Cr (III) and Cr (VI) uptake or translocation.

De Haan *et al.* (1985, cited in Janus and Krajnc 1990) studied the uptake and translocation of Cr (III) in oats. Concentrations of up to $800 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ of chromic acetate were added to three loamy clay soils and three sandy soils. All soils were slightly acidic (pH 4.6-5.6). Green crop concentrations $<150 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ were found in the three clay soils and one of the sandy soils (highest organic matter

content). In the two remaining sandy soils, green crop concentrations between 500 and 800 mg·kg⁻¹ dw were found. In the straw portion of the oat plant, lower chromium concentrations (<50 and 25-300 mg·kg⁻¹ dw) were found in plants grown in clay and sandy soils, respectively. In the grain, chromium concentrations were below the detection limit (0.1 mg·kg⁻¹ dw).

Two studies have examined the translocation of foliarly applied chromium. Pickrell and Ellis (1980) applied ⁵¹Cr to the midrib of soybean leaves. The authors determined that only 4% of the chromium was translocated to other parts of the leaf. Parr and Taylor (1980) also observed that Cr (VI) applied to soybean leaves was not translocated from the leaves.

There are conflicting views on the uptake of Cr (III) and Cr (VI) by plants from nutrient solutions. It has been proposed that Cr (VI) is more readily absorbed by the roots of a plant than Cr (III) (Hara and Sonoda 1979). Alternatively, it has been suggested that Cr (III) is absorbed by roots more rapidly than Cr (VI) (Skeffington *et al.* 1976). Alternatively, it has been suggested that Cr (III) and Cr (VI) are equally available to plants grown in Cr spiked nutrient solution (Huffman and Allaway 1973; Cary *et al.* 1977a, McGrath 1982).

In soil, Cr (VI) is much more mobile and bioavailable than Cr (III). Chromium supplied as Cr (VI) appears to be more mobile in plants than Cr (III), since a greater proportion of Cr (VI) has been translocated to plant leaves compared to Cr (III) (Lahouti and Peterson 1979). At neutral or basic soil pH, Cr (III) is insoluble unless it is complexed with low molecular weight organic molecules. Soil precipitates of chromium appear as hydrated oxides of Cr (III) mixed with or occluded in iron oxides. These Cr-oxides do not penetrate biological membranes and are therefore not readily absorbed by plants.

Metabolism

Limited data were available in the literature concerning the metabolism of chromium and its compounds by plants. The speciation of Cr within plant tissues has been poorly characterized (Outridge and Scheuhammer 1993). However, Cr (III) forms a variety of biological complexes such as Cr oxalates, glucose tolerance factor (GTF) and other uncharacterized compounds (Cary *et al.* 1977a; Lahouti and Peterson 1979; Mertz 1969; Smith *et al.* 1989).

Bioaccumulation

Plants grown in soils contaminated by chromium or with elevated background values (i.e. serpentine soils) have significantly higher Cr levels than plants grown in uncontaminated soils. However, terrestrial plants rarely contain higher concentrations of chromium than the soil in which they are grown.

Chromium accumulates in plant roots rather than shoots, with root/shoot concentration ratios ranging from 5 to 250. There is a marked increase of this ratio in soils with relatively high soil chromium concentrations, indicating that there is little Cr translocation from roots to shoots (Williams 1988; Janus and Krajnc 1989).

Huffman and Allaway (1973) found that Cr absorbed by bean and wheat plants grown in culture solutions remained primarily in the roots and was poorly translocated to the leaves. The bean and wheat plants contained about 55% and 81% of the added chromium. However, bean roots contained about 92% and wheat roots 95% of the total plant Cr.

Toxicity

The visual symptoms of Cr toxic injury to plants include: chlorosis, stunted growth, curled and discoloured leaves and poorly developed root systems (NRCC 1976). A summary of plant toxicity studies selected for use in deriving soil quality guidelines for chromium are presented in Table 11.

Acute Toxicity

Results of a study on lettuce (*Lactuca sativa*) seedling emergence following 120 hour exposure to Cr (III) and Cr (VI) was reported by Environment Canada (1995a). The artificial soil used in this experiment consisted of varying proportions of sand (67-69%), silt (9-12%), clay (21-23%) and organic matter (2.4-6.0%), with a pH of 4.0-4.3. The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (III) were estimated at 57, 113, 106 and 146 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 26% inhibition (EC₅₆) (Environment Canada 1995a). The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (VI) were 230, 510, 297 and 397 mg·kg⁻¹, respectively. The Cr (VI) LOEC corresponding to 82% inhibition of lettuce seed germination (EC₈₂) (Environment Canada 1995b).

In a follow up study on *L. sativa*, the effects of Cr (III) and Cr (VI) concentration on seed germination success were quantified following 120 hours exposure in an artificial soil matrix (pH 4.2, OM 6.1%) (Environment Canada 1995b). In addition, an aliquot of test soil amended with CaCO₃ was used to measure the effects of Cr (VI) on lettuce seed germination at neutral soil pH. The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (III) were estimated at 49, 100, 64, and 100 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 53% inhibition of seed germination (EC₅₃) (Environment Canada, 1995b). For Cr (VI), the NOEC, LOEC, EC₂₅ and EC₅₀ values at a soil pH of 4.2 were estimated at 97, 205, 146, and 274 mg·kg⁻¹, respectively. The Cr (VI) LOEC at a soil pH of 4.2 resulted in 33% inhibition of lettuce seed germination (EC₃₃) (Environment Canada, 1995b). In the calcium carbonate amended soil, the NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (VI) were estimated at 12, 24, 18, and 67 mg·kg⁻¹, respectively.

Results of a study on radish (*Raphanus sativa*) seedling emergence following 72 hour exposure to Cr (III) and Cr (VI) was reported by Environment Canada (1995a). The artificial soil used in this experiment consisted of varying proportions of sand (67-69%), silt (9-12%), clay (21-23%) and organic matter (2.4-6.0%), with a pH of 4.0-4.3. The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (III) were estimated at 59, 107, 82 and 127 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 41% inhibition (EC₄₁) (Environment Canada 1995a). The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (VI) were 117, 243, 150 and 207 mg·kg⁻¹, respectively. The Cr (VI) LOEC corresponding to 58% inhibition of radish seed germination (EC₅₈) (Environment Canada 1995b).

In a follow up study on *R. sativa*, the effects of Cr (III) and Cr (VI) concentration on seed

germination success were quantified following 72 hours exposure in an artificial test soil (pH 4.2, OM 6.1%) (Environment Canada 1995b). The NOEC, LOEC, EC₂₅ and EC₅₀ values for Cr (III) were estimated at 24, 49, 59, and 81 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 18% inhibition of seed germination (EC₁₈) (Environment Canada, 1995b). For Cr (VI), the NOEC, LOEC, EC₂₅ and EC₅₀ values were 23, 45, 51, and 116 mg·kg⁻¹, respectively. The Cr (VI) LOEC resulted in 23% inhibition of lettuce seed germination (EC₂₃) (Environment Canada, 1995b).

Chronic Toxicity

Adema and Henzen (1989) examined the toxicity of K₂Cr₂O₇ to three types of plants grown in two soil types according to the OECD Guideline 208. Tomato (*Lycopersicum esculentum*), oats (*Avena sativa*) and lettuce (*Lactuca sativa*) were grown in humic sand (organic matter 3.7%; silt 5.8%; sand 90.5%; pH 5.1) and loam (organic matter 1.4%; silt 17.1%; sand 71.7%; pH 7.5) for two weeks. The EC₅₀ for lettuce, tomato and oats in loam were 1.8, 6.8 and 7.4 mg Cr·kg⁻¹ dry soil, respectively. In the humic sand, the EC₅₀ for lettuce, tomato and oats were >11, 21 and 31 mg Cr·kg⁻¹ dry soil, respectively. The NOEC for lettuce, tomato and oats in loam were 0.35, 3.2 and 3.5 mg Cr·kg⁻¹ dry soil, respectively. In the humic sand, the NOEC for lettuce, tomato and oats were >11, 10 and 11 mg Cr·kg⁻¹ dry soil, respectively.

Günther and Pestemer (1990) studied the effects of potassium dichromate on the growth of oats (*Avena sativa*) and turnips (*Brassica rapa*) cultivated in pots containing a sandy loam soil (pH 6; organic carbon 1.3%; sand 54.3%; silt 35.7%; clay 9.9%). The fresh weight of the oats and turnips were determined after 10 and 14 days, respectively. The EC₅₀ values were 8.25 mg Cr·kg⁻¹ dry soil for turnips and 29 mg Cr·kg⁻¹ dry soil for oats (determined from the histogram provided by the authors). These endpoints were calculated based on the total amount of potassium dichromate in soil. Since not all soil administered chromium was available for plant uptake due to soil matrix factors (e.g. soil adsorption), the authors calculated the availability of this potassium dichromate by comparing the dose-response curves from soil and vermiculite for *Brassica rapa*. Since it was estimated that 60.1% of soil administered potassium dichromate was available to the turnip, the actual EC₅₀ for the turnip was determined to be 4.96 mg Cr·kg⁻¹ dry soil (according to metal availability).

4.3 Terrestrial Invertebrates

Uptake and Behaviour

Heavy metals are generally absorbed across the intestinal wall. Some metals (e.g. Pb) are also absorbed through the skin. Hall (1988) proposed that the mucoid coat surrounding the earthworm *Acini fatuity* can bind and retain heavy metals. This mucus may in fact prevent cuticular exposure to heavy metals (Hall 1988).

Metabolism

Arillo and Melodia (1991) examined several metabolic systems in *Acini fetida*. *In vitro* they

investigated whether mitochondrial, microsomal and cytoplasmic fractions contributed to Cr (VI) reduction. These authors reported that NADPH-dependent chromate reductase activity was present in the earthworm. This metabolic activity is similar to the mammalian microsomal enzyme cytochrome P-450 reductase, which utilizes NADPH as an electron source. The authors suggest that microsomal enzymes are an important contributor to the reduction of Cr (VI) compounds (Arillo and Melodia 1991). Earthworm mitochondria can reduce Cr (VI) compounds by: (1) a succinate-supported reduction that is particularly active in the presence of ADP; (2) a glutamate-supported reduction occurring in the presence of respiratory-chain inhibitors; 3) a nonenzymatic reduction taking place in the absence of respiratory substrates. Cytoplasmic fractions also contribute to the reduction of Cr (VI) compounds. These authors proposed that DT-diaphorase and aldehyde oxidase are involved in the reductive process.

Arillo and Melodia (1991) also examined whether the mucous coating the surface of the earthworm stimulates Cr reduction. These authors reported that simple contact between the earthworm's mucoid coating and Cr (VI) caused a decrease in Cr (VI) concentration *in vivo*, suggesting that *Acini fatuity* skin mucus has the same reductive capacity as fish skin mucus; a phenomenon reported in a previous study (Arillo and Melodia 1990).

Bioaccumulation

Few studies are available concerning the bioaccumulation potential of chromium in soil invertebrates. Research of this nature typically focuses on the simultaneous accumulation of several heavy metals from contaminated soil or sludge. Since combinations of heavy metals can hinder or enhance uptake, mixed metal studies are of limited practical usefulness for assessing the bioaccumulation potential of chromium alone.

Helmke *et al.* (1979) examined earthworms (*Aporrectodea tuberculata*) following sludge application to agricultural soil. The sludge contained 28 different elements including Cr. The authors reported an increased Cr concentration in the earthworm casts, although Cr levels in the earthworms remained constant. The authors proposed that chromium was not biologically available to earthworms in this study.

Beyer and Cromartie (1987) compared the concentration of heavy metals (Pb, Cu, Zn, Cd, Cr, As and Se) in several different species of earthworms with soil concentrations at 20 different sites. The soil concentrations at the uncontaminated sites ranged from 4.9 to 19 mg Cr·kg⁻¹ DW, whereas Cr concentrations at the contaminated ranged from 6.4 to 71 mg·kg⁻¹ DW. Cr concentrations in earthworms were poorly correlated with levels in the soil ($r = -0.20$; $p > 0.05$). The authors explained the poor correlations as a combination of three factors: earthworm preference for specific components of soil; differences between species with respect to their affinity to accumulate metals; the ability of earthworms to regulate both uptake and excretion of some essential metals, particularly Cu, Zn and Se.

Ma (1982) studied the uptake of heavy metals by three species of earthworm (*Allolobophora caliginosa*, *Lumbricus rubellus* and *Dendrobaena rubida*) in six different soils (three loamy soils and

three sandy soils). Chromium behaved similarly in all soils, and did not significantly accumulate in any of the three species of worms. Of the eight metals examined in this study, the Cr concentration factor was the lowest ($\text{Cr} < \text{Mn} < \text{Fe} < \text{Ni} < \text{Pb} < \text{Cu} < \text{Zn} < \text{Cd}$). Ma (1982) concluded that the lack of Cr accumulation reflected its decreased bioavailability to earthworms.

van Gestel *et al.* (1993) examined the bioaccumulation and elimination of chromium (III) nitrate ($\text{Cr}(\text{NO}_3)_3$) in *Acini andrei* in an artificial soil substrate (10% sphagnum peat, 20% kaolin clay, 69% fine sand, $\text{pH } 6.0 \pm 0.5$). Cr concentrations of 0, 10, 32, 100, 320 and 1000 $\text{mg} \cdot \text{kg}^{-1}$ dry soil were added. Actual soil concentrations were determined to be 6.3, 16, 40, 101, 287 and 972 $\text{mg} \cdot \text{kg}^{-1}$. The earthworms were exposed for three weeks and then allowed to recover for another three weeks. To determine Cr bioaccumulation, earthworms were sampled at the end of the three week exposure period. Elimination rates were analyzed at the end of the three week recovery period. At the end of the three week exposure period, analysis of earthworm tissue showed a dose related increase in Cr concentrations. Tissue concentrations (ranging from 0.8 to 18 $\text{mg} \cdot \text{kg}^{-1}$ DW) at the three highest Cr levels were significantly different than those in the control earthworms (mean 0.3 $\text{mg} \cdot \text{kg}^{-1}$ DW). BCF (Bioconcentration Factor) values ranged between 0.031-0.019 (from lowest to highest dose level) for the exposed worms and was 0.048 in the control soil. At the end of the three week recovery period, chromium concentrations returned to normal in all dose groups (0.3-1.1 $\text{mg Cr} \cdot \text{kg}^{-1}$ DW).

In the same study, chromium tissue concentrations had half lives of 51-109 days at the two lowest dose concentrations, while at the three highest doses, chromium had half-lives of 5-7 days (van Gestel *et al.* 1993). Chromium was completely eliminated from the worms after the three week recovery period. The authors suggested that strong binding of chromium to earthworm tissues did not occur; admitting, however, that there was no literature to support this statement.

Toxicity

Invertebrate toxicity studies selected for use in soil quality guidelines derivation are presented in Table 11. There are few toxicity studies examining the effect of chromium on soil invertebrates.

van Gestel *et al.* (1992) studied the effect of chromium (III) nitrate ($\text{Cr}(\text{NO}_3)_3$) on the survival, growth and reproduction of *Acini andrei*. Adult earthworms were exposed for three weeks to chromium in an artificial soil substrate (10% sphagnum peat, 20% kaolin clay, 69% fine sand, $\text{pH } 6.0 \pm 0.5$). Chromium concentrations of 0, 10, 32, 100, 320 and 1000 $\text{mg} \cdot \text{kg}^{-1}$ dry soil were added. There was no mortality observed during the experiment, although earthworm growth and cocoon production were significantly reduced at 1000 $\text{mg} \cdot \text{kg}^{-1}$ ($P < 0.05$). The total number of juveniles produced per worm per week was significantly reduced at $\geq 100 \text{ mg Cr} \cdot \text{kg}^{-1}$ dry soil. After a 3 week recovery period, reproduction and growth rates were almost completely back to normal. The NOEC for growth and cocoon production was 320 $\text{mg} \cdot \text{kg}^{-1}$. An EC_{50} of 155 $\text{mg Cr} \cdot \text{kg}^{-1}$ was calculated for cocoon production but corresponding values were not calculated for growth or fertility.

Results of a study on earthworm (*Eisenia fetida*) mortality following 14 days of exposure to Cr (III) and Cr (VI) was reported by Environment Canada (1995a). The artificial soil used in this experiment consisted of varying proportions of sand (67-69%), silt (9-12%), clay (21-23%) and organic matter (2.4-6.0%), with a pH of 4.0-4.3. The NOEC, LOEC, LC_{25} and LC_{50} values for Cr (III) were

estimated at 320, 680, 420 and 570 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 80% earthworm mortality (Environment Canada 1995a). The NOEC, LOEC, LC₂₅ and LC₅₀ values for Cr (VI) were 900, 1700, 1100 and 1400 mg·kg⁻¹, respectively. The Cr (VI) LOEC corresponding to 72% earthworm mortality (Environment Canada 1995b).

In a follow up study using *E. fetida*, earthworms were exposed for seven days to Cr (III) and Cr (VI) in an artificial soil matrix (pH 4.2, OM 6.1%) (Environment Canada 1995b). The NOEC, LOEC, LC₂₅ and LC₅₀ for Cr (III) were estimated at 235, 466, 543, and 671 mg·kg⁻¹, respectively. The Cr (III) LOEC resulted in 10% earthworm mortality (Environment Canada, 1995b). For Cr (VI), the NOEC, LOEC, LC₂₅ and LC₅₀ were estimated at 748, 1579, 956, and 1195 mg·kg⁻¹, respectively. The Cr (VI) LOEC resulted in 60% earthworm mortality (Environment Canada, 1995b).

4.4 Mammals and Birds

Metabolic Fate and Behaviour

Cr (III) is an essential nutrient for normal metabolism of glucose, cholesterol, and fat. In the form of dinicotinic acid-glutathione complex (GTF), Cr (III) is an essential co-factor for insulin function. GTF may bind insulin to membrane receptors that regulate the transport of glucose into the cell (Mertz 1982). However, it has been recently suggested that GTF and insulin regulate glucose levels by their actions in the liver, rather than in the individual cell. In either case, GTF-insulin prevents hyperglycaemia and hypoglycaemia by maintaining normal glucose homeostasis in the cell (Outridge and Scheuhammer 1993). Major sources of dietary Cr (III) include brewers yeast, meats, mollusks and crustaceans, vegetables, sugars and syrups (NAS 1974; Mertz 1979). The recommended human daily intake of Cr (III) for adults is 50 to 200 µg·day⁻¹ (Mertz 1979). Cr (III) deficiency can result in glucose intolerance, and eventually symptoms indistinguishable from those of diabetes.

Cellular membranes are less permeable to Cr (III) compounds than to Cr (VI) compounds, a difference which may explain the increased availability of Cr (VI) to animals (Langård 1982). Nonetheless, chromium in animal tissues is normally present as Cr (III) because Cr (VI) is reduced in vivo (Wiegand *et al.* 1984). However, the reducing capacity of an animal cell is limited, and at increased chromium exposures, Cr (III) and Cr (VI) may be present simultaneously.

The reduction of Cr (VI) to Cr (III) could occur through various hypothesized enzymatic reactions in mitochondria, microsomes and the cytoplasm of the vertebrate cell. There are also nonenzymatic reactions with ascorbate, thiols, hydrogen peroxide and some compounds present in the saliva, gastric juice and mucus which result in the reduction of hexavalent chromium (Arillo and Melodia 1991).

Ingestion

The major source of exposure to Cr for wild birds and mammals is through food ingestion. Gastrointestinal Cr adsorption is generally low (Taylor and Parr 1978; Halford *et al.* 1983). Cr (VI) compounds are generally absorbed from the GI tract more efficiently (2-10% of dose) than inorganic

Cr (III) compounds (0.5-3%).

Complexation of Cr with various organic molecules can increase the rate of Cr absorption. Inorganic chromates are poorly absorbed compared with the organic Cr forms found in plants. Complexation with oxalate has been shown to increase chromium adsorption. However, complexation with citrate and EDTA has had no effect on adsorption (Outridge and Scheuhammer 1993). It should be noted that chromium-oxalate complexes have been reported in at least two unrelated plant species, *Leptospermum scoparium* (Cr-accumulator) and cauliflower (Lahouti and Peterson 1979) and may occur in most plants (Outridge and Scheuhammer 1993).

Inhalation

Inhalation may be generally less important as a route of uptake than dietary sources. In contrast, however, absorption of inhaled Cr appears to be greater than ingested Cr. Approximately 12% of inhaled Cr (III) and 30% of Cr (VI) are absorbed by the epithelial lining of the lung. In cotton rats inhabiting vegetation downwind from power plant cooling towers, Cr concentrations in the bone, pelt and liver were several times higher than in animals from an uncontaminated site (Taylor and Parr 1978). However, levels in the lungs were identical in both groups. The authors suggested that deposition of Cr on vegetation and hair followed by ingestion during feeding or preening, rather than inhalation, is likely to be the primary route of Cr uptake (Outridge and Scheuhammer 1993).

Excretion

Chromium is eliminated from mammals via urine and feces, with urine accounting for at least 80% of Cr excretion in injection experiments (NAS 1974). In several studies fecal excretion has accounted for between 0.5 and 20% of a given dose of intravenously injected chromium. Most of the chromium present in the urine is in the form of low-molecular weight complexes. Protein bound chromium is excreted to only a small degree (NAS 1974).

Under field conditions, Halford *et al.* (1983) examined the elimination rate of various heavy metals from mallards. Of the 9 radioactive isotopes (^{131}I , ^{140}Ba , ^{58}Co , ^{60}Co , ^{75}Se , ^{134}Cs , ^{51}Cr , ^{137}Cs and ^{65}Zn) used, ^{51}Cr had the slowest rate. The excretion of chromium occurred in two stages, an initial fast phase during which the gut contents were eliminated (half-life of 3 days) and a final slow phase in which assimilated Cr was eliminated. 79% of the initial Cr body burden was associated with the slow phase. Taylor and Parr (1978), who also studied the excretion ^{51}Cr following dietary exposure, found a two phase elimination curve in cotton rats. They examined the excretion of ^{51}Cr following dietary exposure. Unlike Halford *et al.* (1983), 99% of the body burden was accounted for by the initial fast phase, and the slow phase had a half-life of 693 days.

Huffman and Allaway (1973) fed male Sprague-Dawley rats (48 hours old) with a diet treated with radiochromium from plant and inorganic Cr sources. After 48 hr, less than 0.5% of the Cr from either source remained in the rats. Over 95% of the initial activity was present in the 24 hr fecal sample. The organ and tissue samples contained less than 0.2% of the initial dose.

Concentrations in Wildlife and Livestock

Chromium concentrations in wild mammals from uncontaminated environments range from 0.1-10 $\mu\text{g}\cdot\text{g}^{-1}$ DW. In contrast, chromium levels in animals from contaminated environments, such as mine spoil dumps, soil amended with sewage sludge or within proximity to Cr emissions from smelters, range from 0.3-20 $\mu\text{g}\cdot\text{g}^{-1}$ DW. The chromium concentrations in birds from uncontaminated environments range from 0.1-15 $\mu\text{g}\cdot\text{g}^{-1}$ DW compared to 1 to 700 $\mu\text{g}\cdot\text{g}^{-1}$ DW in polluted areas (Outridge and Scheuhammer 1993).

Higher chromium concentrations have been found in bone tissue than in soft tissues (Taylor and Parr 1978; Fitzgerald *et al.* 1985a,b). Other organs or tissues of wildlife have also demonstrated increased levels of chromium, including the brain in prefledgling tree swallows and the feathers of mallard ducks (Kraus 1989; Halford *et al.* 1983). Measuring chromium levels in a single organ or a few organs such as liver or/and kidney may not necessarily reflect the extent of contamination. Outridge and Scheuhammer (1993) recommend whole-body analyses as a more appropriate method for the biomonitoring of small mammals and birds. Table 14 summarizes chromium concentrations detected in field populations of mammalian species assayed from contaminated sites.

Bioaccumulation and Tissue Distribution

Following oral exposure to Cr (III), the liver is the principal site of chromium accumulation. In contrast, Cr (VI) is more widely distributed within the kidneys, spleen, liver, lungs and bone (Outridge and Scheuhammer 1993). Significantly elevated Cr (VI) concentrations were noted in the liver, kidneys, spleen and muscles of domestic cattle fed 9.6 $\text{mg}\cdot\text{kg}^{-1}$ BW per day for 12 months. The same dose of Cr (III) did not result in Cr accumulation (Kreuzer *et al.* 1985).

Long term chromium exposure results in significant Cr accumulation in bone tissue. Fitzgerald *et al.* (1985a) found that bone concentrations (0.61-0.93 $\mu\text{g}\cdot\text{g}^{-1}$ DW) were higher than levels in kidneys, liver, or heart muscle (0.2-0.4 $\mu\text{g}\cdot\text{g}^{-1}$ DW) in cattle exposed for 8 yrs to a pasture amended with Cr-contaminated sewage sludge. Calves born to the exposed cows had significantly higher Cr concentrations in their kidneys, liver, heart and diaphragm after 30 days of nursing than the calves of the control herd. At day 60, the Cr concentrations in the soft tissues of the test calves were similar to those in the control herd, while the concentrations in the bone were an order of magnitude greater (0.75 v. 0.075 $\mu\text{g}\cdot\text{g}^{-1}$ DW) (Fitzgerald *et al.* 1985b). Taylor and Parr (1978) also found that Cr concentrated in the bone.

Anthony and Kozlowski (1982) compared concentrations of heavy metals, including Cr, in the liver and kidney of small mammals from forested and reed canarygrass areas irrigated with effluent to those from non-irrigated areas. White-footed mice (*Peromyscus leucopus*) were collected from the forested sites and meadow voles (*Microtus pennsylvanicus*) were collected from the field sites. Cr concentrations in the liver and kidney were significantly higher in meadow voles from the control field site than those from the canarygrass field site. In contrast, Cr concentrations in the liver and kidney of the white-footed mice did not significantly differ between the control forested site and the irrigated forested site. Bioaccumulation of chromium in these two small mammal species was not observed.

Toxicity

Few studies have examined the toxicological effects of chromium on wildlife, bird species or livestock in controlled experiments, and none of these studies have involved animal exposure from the soil environment. Table 13 presents a summary of estimated NOAEL's for chromium in livestock, wildlife and domestic animals.

Acute Toxicity

No controlled lab or field studies involving acute lethality endpoints for wildlife species are available, although a limited number of toxicological assessments have been conducted following accidental poisonings of livestock.

An accidental poisoning in cattle resulted from exposure to chromate compounds (Cr (VI)) associated with oil field activities. A herd of 20 mature cows and their 8-month old calves were grazing on pasture contaminated with sodium chromate, resulting in the death of one cow and two calves. Toxic symptoms included lack of coordination, weight loss, and bloody mucus in the feces. Liver tissue from one of the dead calves contained $14.8 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$ compared to $1.8 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$ in the control herd (Reagor and MacDonald 1980). In separate cases, two of 80 heifers died after consuming concentrated zinc chromate and 10 cows and one calf died after ingesting ammonium chromate (Kerr and Edwards 1981). The kidney and blood Cr concentrations in each poisoning incident were 15.8 and $1.1 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$, respectively, whereas they were 3.0 and $0.02 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$ in the control herds.

A single dose of $30\text{--}40 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$ for calves and $700 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ FW}$ for mature cattle has been reported as the acute lethal dose (Janus and Krajnc 1989). Outridge and Scheuhammer (1993) reported that $500 \text{ mg} \cdot \text{kg}^{-1} \text{ FW}$ of dietary chromium may be acutely lethal for most ruminant animals. Levels of $30 \text{ } \mu\text{g Cr} \cdot \text{kg}^{-1} \text{ FW}$ in the liver and $4 \text{ mg Cr} \cdot \text{L}^{-1}$ in whole blood are indicative of acute chromate poisoning (Clark and Clark 1975). Liver and kidney concentrations $>15 \text{ } \mu\text{g Cr} \cdot \text{kg}^{-1} \text{ FW}$ or blood concentrations $>1.0 \text{ mg} \cdot \text{L}^{-1}$ are further indicative of Cr intoxication (Clark and Clark 1975).

Chronic Toxicity

Few chronic Cr toxicity studies involving wildlife or livestock are available. Three studies examining wild bird species (black ducks and common terns) and two studies involving domestic bird species (chickens and turkey hens) were found (Haseltine *et al.* 1985; Heinz and Haseltine 1981; Custer *et al.* 1986; Rosomer *et al.* 1961; Frobish 1980).

Haseltine *et al.* (1985, as cited in Eisler 1986 and Custer *et al.* 1986) fed adult american black ducks (*Anas rubripes*) with diets containing $10 \text{ mg} \cdot \text{kg}^{-1}$ or $50 \text{ mg} \cdot \text{kg}^{-1}$ Cr (III) as $\text{CrK}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ for 5 months. In this study, survival, reproduction and blood chemistry in the treated ducks remained normal. However, the 10 week old ducklings from the treated group, which were fed the same Cr diets, showed altered growth patterns and reduced survival. Also, Haseltine *et al.* (in pers. comm. to Custer *et al.* 1986) observed a doubling in duckling blood uric acid levels, and decreased growth

rates at $10 \text{ mg}\cdot\text{kg}^{-1}$ DW of dietary chromium.

In a similar study, pairs of adult black ducks (*Anas rubripes*) were fed 0, 20, or $100 \text{ mg}\cdot\text{kg}^{-1}$ Cr (III). Ducklings from these pairs were also fed the same Cr diets for 7 days. The authors observed no significant effect on the fright response of the ducklings (Heinz and Haseltine 1981).

Custer *et al.* (1986) compared clutch size, reproductive success, and growth of young for the common tern (*Sterna hirunda*), at a heavy metal contaminated site and at a control site. The authors observed no effects of Cr on these biological parameters. However, uric acid levels were found to be elevated in the blood of terns from the contaminated site. This effect was attributed to altered kidney function as a response to Cr toxicity (Custer *et al.* 1986).

Male domestic chickens were fed with diets containing up to $100 \text{ mg}\cdot\text{kg}^{-1}$ of Cr (VI) as Na_2CrO_4 for 32 days. There were no adverse effects on chicken survival, growth or food utilization efficiency (Romoser *et al.* 1961).

In another study, 180 large white turkey hens (30 weeks of age) were fed one of four different diets (Frobish 1980). Each diet was administered in combination with a 0 or $10 \text{ mg}\cdot\text{kg}^{-1}$ supplemental as chromium chloride (CrCl_3) over a 20 week period. Each bird was artificially inseminated and eggs were collected daily. Additions of chromium to the diet significantly reduced egg production, but did not effect fertility or hatchability (Frobish 1980).

4.5 Biominification in the Terrestrial Food Chain

Chromium does not biomagnify in terrestrial or aquatic food chains. In fact, chromium concentrations decrease with each successive ascending level in the food chain. This has been referred to as "biominification" and has been observed in various terrestrial habitats (Jenkins 1980; Outridge and Scheuhammer 1993). For instance, cotton rats feeding on fescue grass contaminated by cooling tower drift (Taylor and Parr 1978) and cattle grazing on Cr contaminated pasture (Fitzgerald *et al.* 1985a) have exhibited biominification. In many cases, Cr concentrations in the organs of exposed animals is similar to (but not higher than) Cr concentrations in their diet (Outridge and Scheuhammer 1993).

There is a little evidence suggesting that Cr contained in vegetation is transferred and bioconcentrated in wildlife consumers. Plants typically become stunted before accumulating amounts of Cr that would be toxic to animal consumers (NRCC 1976). Certain endemic plant species growing on serpentine soils may contain total Cr concentrations between 1000 and $50,000 \text{ mg}\cdot\text{kg}^{-1}$ DW. These concentrations could be potentially toxic to wildlife consumers. However, no studies have reported wildlife poisoning relating to these elevated Cr levels (Brookes 1987). In most cases, Cr concentrations reported in wildlife species were lower than the soil or vegetation concentrations (Beyer and Miller 1990; Campa *et al.* 1986; Woodyard *et al.* 1986, Anthony and Kozlowski 1982).

5. DERIVATION OF ENVIRONMENTAL SOIL QUALITY GUIDELINES

5.1 Introduction

Canadian soil quality guidelines are designed to protect four different land uses: agricultural, residential/parkland, commercial, and industrial. The Canadian soil quality guidelines for chromium are based on the procedures described in CCME (1996).

All data selected for use in the following derivations have been screened for ecological relevance and are presented in Tables 10, 11 and 12. Studies were excluded from use because of one or more of the following reasons:

- soil pH was not recorded;
- soil pH was below 4 (as this is considered outside the normal pH range for most soils in Canada);
- no indication of soil texture was provided;
- inappropriate statistical analysis was used;
- test was not conducted using soil or artificial soil;
- test soil was amended with sewage sludge or a mixture of toxicants;
- test did not use controls;

LOEC and EC data used in the following derivations were considered to be biologically significant in addition to statistically significant according to the study from which the data were taken.

According to section 7.5.2.2 of the soil quality guidelines derivation protocol (CCME 1996), the geometric mean should be used when multiple data are available for the same endpoint with the same species. For the Cr (total) data, the geometric mean has been applied to the NOEC, LOEC, LC₂₅ and LC₅₀ values for the earthworm *E. fetida*, and the NOEC, LOEC, EC₂₅ and EC₅₀ values for lettuce (*L. sativa*) and radish (*R. sativa*) (Environment Canada 1995a; 1995b). Both the CrO₂ (Cr VI) and CrCl₃ (Cr III) data from these studies were incorporated into the final geometric average because they were considered to provide equivalent toxicological measurements under the reducing soil conditions reported by the authors (see section 5.2.1). No statistical averaging was applied to the data used for the Cr (VI) derivation (Table 12).

5.2 Soil Quality Guidelines for Agricultural and Residential/Parkland Land Uses

5.2.1 Soil Quality Guideline for Soil Contact (SQG_{sc})

The derivation of a soil quality guideline for soil contact (SQG_{sc}) is based on toxicological data for vascular plants and soil invertebrates. The toxicological data for plants and invertebrates selected according to CCME (1996) are presented in Table 11 (Cr (total)) and Table 12 (Cr (VI)). Due to the unique chemistry of chromium and the strong effect of valence state on toxicity, guidelines were

developed for both Cr (total) and Cr (VI). In situations where chromium speciation and/or soil chemistry data is available for a contaminated site, professional judgement should be used to assess the applicability of the respective guidelines.

5.2.1.1 Derivation of SQG_{sc} for Cr (total)

Total chromium is a gross parameter which is commonly measured by performing an elemental scan for chromium metal. Since this measurement encompasses all chromium species and does not differentiate between Cr (III) and Cr (VI), Cr (total) is not a sensitive indicator of toxicological risk. Two sites with an equivalent Cr (total) soil concentration could vary widely in associated toxicological risk depending upon the valence state of the Cr specie(s). In most real-world situations, however, a mixture of chromium species will be present within the soil matrix of Cr contaminated sites. Under reducing conditions, Cr (III) is the principal form of chromium present in soil. Therefore, as long as soil conditions favour the predominance of Cr (III), Cr (total) concentrations can be used as a bulk parameter for predicting overall toxicological risk.

Studies selected for use in deriving the Cr (total) guideline comprise experiments in which a single chromium species (either Cr (III) or Cr (VI)) was added to the test soil, but for which test conditions likely favoured the predominance of the Cr (III) species (e.g. low pH, high organic matter). The resulting Cr (total) guidelines are intended to be protective of soils for which Cr (VI) is a small component of the total mixture of chromium species. In situations where Cr (VI) exists in the mg·kg⁻¹ concentration range, it is recommended that both the Cr (total) and Cr (VI) guidelines be utilized in accordance with professional judgement.

Calculation of Threshold Effects Concentration (TEC):

For total chromium, there were sufficient toxicological data to use the preferred weight of evidence method for guideline derivation. The threshold effects concentration (TEC) was calculated as follows:

$$\text{TEC} = \text{NPER} / \text{UF}$$

where,

- TEC = threshold effects concentration (mg·kg⁻¹ soil)
- NPER = no potential effects range (25th percentile of data distribution) (mg·kg⁻¹ soil)
- UF = uncertainty factor (if needed); no uncertainty factor was applied.

Out of a total of 22 no observable effects and observable effects data points, the 25th percentile corresponds to the 6th datum point. The concentration associated with this datum point corresponds to the average radish germination EC₂₅ (78 mg Cr·kg⁻¹) value established by Environment Canada (1995a and b).

Thus,
TEC = 78 mg Cr·kg⁻¹

Nutrient and Energy Cycling Check

The nutrient and energy cycling check was calculated using the selected microbial processes data presented in Table 10. Nitrification and nitrogen fixation data are considered to be primary data, whereas nitrogen mineralization, denitrification, and carbon cycling data are considered secondary data. Insufficient primary data were available for the calculation, so the primary and secondary data were combined. The nutrient and energy cycling check is carried out using a modified median effects concentration method whereby the lowest experimental concentration that resulted in a response $\geq EC_{50}$ is divided by an application factor.

The nutrient and energy cycling check (NECC) for total chromium is calculated as follows:

$$NECC = \text{lowest } EC_{50} / AF$$

where,

NECC = nutrient and energy cycling check ($\text{mg} \cdot \text{kg}^{-1}$ soil)

EC_{50} = concentration for which the response is greater or equal to the median effective concentration ($\text{mg} \cdot \text{kg}^{-1}$ soil)

AF = application factor (5 if EC_{50} data, 10 if LC_{50} data)

Thus,

$$\begin{aligned} NECC &= 260/5 \\ &= 52 \text{ mg} \cdot \text{kg}^{-1} \text{ soil} \end{aligned}$$

Calculation of SQG_{sc} for Cr (total) for Agricultural and Residential/Parkland Land Uses:

Since the NECC ($52 \text{ mg} \cdot \text{kg}^{-1}$ soil) is lower than the TEC ($78 \text{ mg} \cdot \text{kg}^{-1}$ soil), the geometric mean of these values is calculated in order to derive the SQG_{sc} for agricultural and residential/parkland uses.

Thus,

$$\begin{aligned} SQG_{sc} &= (52 \cdot 78)^{0.5} \\ &= 63.7 \approx 64 \text{ mg Cr} \cdot \text{kg}^{-1} \text{ soil} \end{aligned}$$

5.2.1.2 Derivation of SQG_{sc} for Cr (VI)

Data which fulfilled the selection criteria established for use in deriving the Cr (VI) guidelines are presented in Table 12. Studies were only selected for use in Cr (VI) guideline derivation if the chromium species added to the test soil was initially in a hexavalent form. In addition, one or both of the following criteria had to be met in order to limit the probability of Cr (VI) reduction to Cr (III):

- soil pH ≥ 6 , or
- soil organic matter $\leq 1\%$

These selection criteria are based upon current scientific understanding of the chemistry and subsurface behaviour of chromium species. The importance of pH and soil organic matter in regulating Cr (VI) reduction in soil has been widely recognized in the literature (McGrath et al. 1990; Bartlett and Kimble 1976; Bloomfield and Pruden 1980). Ideally, study authors would have conducted additional soil chemistry tests to determine the composition of other potential reducing agents (such as Fe (II)) and monitored Cr (VI) soil concentrations throughout the study.

Calculation of Threshold Effects Concentration (TEC):

There were an insufficient number of toxicological datapoints to use the preferred weight of evidence method or the LOEC method for guideline derivation. The Cr (VI) derivation was carried out using a modified median effects concentration method whereby :

$$\text{TEC} = \text{lowest EC}_{50} / \text{AF}$$

where,

TEC = threshold effects concentration ($\text{mg} \cdot \text{kg}^{-1}$ soil)
 EC_{50} = median effective concentration ($\text{mg} \cdot \text{kg}^{-1}$ soil)
 AF = application factor (5 if EC_{50} data, 10 if LC_{50} data)

Out of a total of five EC_{50} data points, the lowest value corresponded to the study by Adema and Henzen (1989) on the effects of Cr (VI) concentration on lettuce yield ($1.8 \text{ mg Cr} \cdot \text{kg}^{-1}$ soil).

Thus, for Cr (VI)

$$\begin{aligned} \text{TEC} &= 1.8/5 \\ &= 0.36 \approx 0.4 \text{ mg} \cdot \text{kg}^{-1} \text{ soil} \end{aligned}$$

Whereas this calculation normally requires that both plant and invertebrate data be used in the derivation process, only plant data was available. Therefore, the TEC for Cr (VI) is provisional as it may not be protective of invertebrate species (see Provisional method, CCME 1997).

Nutrient and Energy Cycling Check

Due to insufficient toxicological data, a nutrient and energy cycling check was not performed for Cr (VI).

Calculation of SQG_{SC} for Cr (VI) for Agricultural and Residential/Parkland Land Uses:

Due to the absence of an NECC value, the TEC—provisional is adopted directly as the SQG_{SC} —provisional for Cr (VI). Therefore, the SQG_{SC} —provisional is $0.4 \text{ mg Cr (VI)} \cdot \text{kg}^{-1}$ soil.

5.2.2 Soil Quality Guidelines for Soil and Food Ingestion (SQG_I)

The soil quality guideline for ingestion applies only to agricultural land use.

Calculation of the SQG_I is based on the lowest-observed-adverse-effects level (LOAEL) taken from the selected mammalian and avian toxicological data. Unfortunately, very little information exists concerning toxicological effects of chromium on higher organisms. Therefore, no soil quality guideline for soil and food ingestion could be derived.

5.3 Soil Quality Guidelines for Commercial and Industrial Land Uses

5.3.1 Soil Quality Guidelines for Soil Contact (SQG_{SC})

The derivation of the SQG_{SC} is also based on toxicological data for vascular plants and soil invertebrates presented in Table 11. However, for commercial and industrial land uses, only the effects data are used and uncertainty factors are not applied.

5.3.1.1 Derivation of SQG_{SC} for Cr (total)

Calculation of Effects Concentration Low (ECL):

There were sufficient toxicological data to use the preferred weight of evidence method for guideline derivation.

The effects concentration low (ECL) is calculated as

$$\text{ECL} = \text{ERL}$$

where,

ECL = effects concentration low (mg·kg⁻¹soil)

ERL = effects range low (25th percentile of effects data distribution) (mg·kg⁻¹ soil)

Out of a total of 14 data points, the 25th percentile corresponds to the 4th datum point. The concentration associated with this datum point corresponds to the average radish germination LOEC (geometric mean = 87 mg Cr·kg⁻¹) established by Environment Canada (1995a and b).

Thus, for total Cr

$$\text{ECL} = 87 \text{ mg Cr} \cdot \text{kg}^{-1}$$

Nutrient and Energy Cycling Check

The nutrient and energy cycling check is calculated using the selected microbial data presented in Table 10. Nitrification and nitrogen fixation studies are considered to be primary data, whereas nitrogen mineralization, denitrification, and carbon cycling studies are considered secondary data. According to this derivation method, LOEC data as reported by the author are used directly, while effective concentration (EC) data producing >15% and <50% effects in primary data (i.e., EC₁₅ to EC₅₀) and >15% and <35% effects in secondary data (i.e., EC₁₅ to EC₃₅) are interpreted as LOEC values. Insufficient primary and secondary data were available for completing this calculation. Therefore, the nutrient and energy cycling check could not be completed for commercial and industrial land use

Calculation of SQG_{SC} for Cr (total) for Commercial and Industrial Land Uses

The ECL is adopted as the SQG_{SC} for commercial and industrial land uses. Therefore, the SQG_{SC} for this land use designation is 87 mg Cr·kg⁻¹.

5.3.1.2 Derivation of SQG_{SC} for Cr (VI)

Calculation of Effects Concentration Low (ECL):

There were an insufficient number of toxicological datapoints to use the preferred weight of evidence method or the supplementary LOEC method for guideline derivation. Since the median effects concentration method is not recommended for deriving soil quality guidelines for commercial/industrial land use categories, the Cr (VI) derivation was carried out using a modified lowest observable effects method :

$$ECL = (LOEC_1 \cdot LOEC_2 \cdot \dots \cdot LOEC_n)^{1/n}$$

where,

ECL = effects concentration low (mg·kg⁻¹ soil)

LOEC = lowest observed effects concentration (mg·kg⁻¹ soil)

n = the number of available LOECs

The datapoints used for this derivation consisted of one LOEC value for lettuce seed germination (Environment Canada 1995b), and four EC₅₀ values obtained for yield reductions in lettuce, oats, tomato and turnip species (see Table 12). Although uncertainty factors are not usually used for deriving soil quality guidelines for commercial and industrial land uses, an uncertainty factor of 5 was applied to this calculation to reflect the substitution EC₅₀ data for LOEC values.

Thus, the ECL for Cr (VI)

$$= (24 \cdot 1.8 \cdot 7.4 \cdot 6.8 \cdot 8.25)^{1/5} / 5$$

$$= 1 \text{ mg} \cdot \text{kg}^{-1} \text{ soil}$$

Whereas this calculation normally requires that both plant and invertebrate data be used in the derivation process, only plant data was available. Therefore, the ECL for Cr (VI) is provisional as it may not be protective of invertebrate species (see Provisional method, CCME 1997).

Nutrient and Energy Cycling Check

Due to insufficient toxicological data, a nutrient and energy cycling check was not performed for Cr (VI).

Calculation of SQG_{SC} for Cr (VI) for Commercial and Industrial Land Uses:

Due to the absence of an NECC value, the ECL—provisional is adopted directly as the SQG_{SC}—provisional for Cr (VI). Therefore, the SQG_{SC}—provisional is 1 mg Cr (VI)·kg⁻¹ soil.

5.4 Derivation of the Final Environmental Soil Quality Guidelines (SQG_E)

The following environmental soil quality guidelines are optimized for soils within the pH ranges of 4.0–7.8 (total Cr) and 6.1–7.5 (Cr (VI)). The toxicological studies upon which these guidelines are based were conducted within this pH range. A summary of all the derived soil quality guidelines is presented in Table 15.

Agricultural Land Use

Cr (total):

The lower value derived from the two procedures (SQG_{SC} and SQG_I) is selected as the final environmental soil quality guideline for agricultural land. Since no SQG_I could be calculated from the existing database, the SQG_{SC} (total chromium) of 64 mg·kg⁻¹ soil is adopted as the final SQG_E for total chromium.

Cr (VI):

The SQG_{SC}—provisional (hexavalent chromium) of 0.4 mg·kg⁻¹ soil is adopted as the agricultural SQG_E—provisional for hexavalent chromium.

Residential/Parkland Land Use

Cr (total):

The SQG_{SC} (total chromium) of 64 mg·kg⁻¹ soil is the final SQG_E for total chromium.

Cr (VI):

The SQG_{SC}—provisional (Cr VI) of 0.4 mg·kg⁻¹ soil is the SQG_E—provisional for hexavalent chromium.

*Commercial and Industrial Land Use***Cr (total):**

The SQG_{SC} (total chromium) of 87 mg·kg⁻¹ soil is the final SQG_E for total chromium.

The SQG_{SC}—provisional (Cr VI) of 1 mg·kg⁻¹ soil is the SQG_E—provisional for hexavalent chromium.

6. DATA GAPS

There are sufficient data to derive Soil Quality Guidelines for Soil Contact (SQG_{SC}) for total and hexavalent chromium. However, additional data are required to derive Soil Quality Guidelines for Soil and Food Ingestion (SQG_I) and to perform the microbial check for hexavalent chromium. Additional data are also required to improve current understanding of the fate and effects of chromium in the Canadian environment. In particular, there is a need for a more thorough examination of the effect of chromium on wildlife species and domestic animals. Most of the studies to date are descriptive in nature, and do not appropriately quantify the toxicity of chromium in controlled laboratory or field studies.

Although there are several studies examining chromium phytotoxicity, there is a paucity of data which are considered acceptable according to the soil guideline derivation protocol. Many of the existing studies examined the effects of sewage or tannery sludge on plants. Few of the studies have used a soil medium or generated an appropriate dose-response curve.

Within the existing literature, there is also a shortage of scientific bioaccumulation and toxicity studies involving soil dwelling organisms. Further research is required in order to adequately assess the effects of chromium on soil invertebrates. The influence of soil characteristics on chromium toxicity should also be explored in greater detail. In particular, the role of organic matter, soil moisture, pH, clay content, manganese oxides, and iron oxides as modifiers of chromium valency warrants further study. Finally, there is a need to standardize procedures for testing the ecotoxicity of chromium. It is important that variation in chromium valency and the effects of soil characteristics be addressed.

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TABLES

Table 1: Chemical and physical properties of chromium.

Property	Value
Atomic weight	51.996
Isotopes, % abundance	
50	4.3
52	83.8
53	9.6
54	2.4
Crystal structure	Body-centred cube
Density at 20°C, g·cm ⁻³	7.2
Melting point, °C	1875
Boiling point, °C	2680
Vapour pressure 130 Pa, °C	1610
Half-life of ⁵¹ Cr isotope, days	27.8

* US EPA (1984a cited from Radian Corporation 1984).

Table 2: Chromium compounds and their applications.

Industrial Use	Chromium Compound
Corrosion Inhibitor	Cr (VI)
	Barium potassium chromate
	Lithium chromate
	Lithium dichromate
	Magnesium chromate
	Strontium chromate
	Zinc chromate
	Zinc sodium chromate
Metal Finishing and Plating	Cr (VI)
	Cadmium dichromate
	Calcium dichromate
	Strontium chromate
	Cr (III)
	Chromic chloride
	Chromic fluoborate
	Chromic fluoride
Refractories	Cr (VI)
	Magnesium chromate
	Magnesium dichromate
	Cr (III)
Catalysts	Magnesium chromite
	Cr (VI)
	Cadmium chromate
	Chromic chromate
	Copper chromate
	Magnesium dichromate
	Nickel chromate
	Silver chromate
	Tetramino copper chromate
	Cr (III)
	Chromic acetylacetonate
	Chromic fluoride
	Chromic nitrate
	Cobalt chromite
	Copper chromite
Paints and Pigments	Zinc chromite
	Cr (VI)
	Barium potassium chromate
	Cadmium chromate
	Copper sodium chromate
	Strontium chromate
	Zinc sodium chromate
	Cr (III)
	Chromic phosphate
	Cobalt chromite
Leather Tanning	Cr (III)
	Chromic chloride

Industrial Use	Chromium Compound
Wood Preservatives	Cr (VI)
	Chrome copper arsenate
	Chrome zinc chloride
	Copper dichromate
Textiles, Mordants and Dyes	Cr (VI)
	Chromic chromate
	Cr (III)
	Chromic acetate
	Chromic chloride
	Chromic fluoride
	Chromic lactate
	Chromic naphthenate
	Chromic nitrate
	Chromic potassium oxalate

* Cited from Nriagu (1988) and US EPA 1990

Table 3: Total chromium soil concentrations in various regions of Canada.

Sampling Site	Range of Cr Concentrations (mg kg ⁻¹)	Mean Cr Concentration (mg kg ⁻¹)
Cordilleran	41-106	78
St. Lawrence Lowlands	10-141	51
Interior Plains	5-76	38
Appalachians	2-100	30
Canadian Shield	7-41	19

* Cited from McKeague and Wolynetz (1980).

* These regions have been classified according to the Canadian Soil Survey Committee.

Table 4: Total chromium concentrations in soil sampled from Canadian industrial sites.

Industrial Site	Mean Total Cr Concentration Adjacent to Site (mg · kg⁻¹)	Control Total Cr Concentration (mg · kg⁻¹)
2 Scrap Yards ^a	> 100	38
Smelter ^b	40-120	—
Wood Preservers Plant ^c	243	10
Wood Treatment Plant ^d	718	30

^a Surface soil at sites located in Winnipeg as cited from Manitoba Environment and Workplace (1989)

^b Soil around a smelter site located in Belledune, New Brunswick as cited from MacMillan (1982).

^c Surface soil at site located at the Prendiville Wood Preservers Ltd. Property in Neepawa, Manitoba, as cited from Manitoba Environment and Workplace Safety and Health (1989).

^d Surface soil at site located around the Roblin Forest Wood Treatment Plant in Roblin, Manitoba, as cited from Manitoba Environment and Workplace Safety and Health (1989).

Table 5: Total chromium concentrations in contaminated rivers and creeks in Ontario.

Site Sampled	Mean Total Cr Concentration ($\mu\text{g}\cdot\text{L}^{-1}$)
Don River	11-188
Humber River	8
Oshawa Creek	8
Brougham Creek	11
Jock River	24
Kaministiquia River	10-38
Mission River	18
McKellar River	8-14

* Cited from MOE 1991

Table 6: Total and dissolved chromium concentrations in the Great Lakes.

Site Sampled	Mean Dissolved Cr Concentration ($\mu\text{g}\cdot\text{L}^{-1}$)	Mean Total Cr Concentration ($\mu\text{g}\cdot\text{L}^{-1}$)
Superior	0.08	0.09
Huron		0.13
Erie	0.27	0.39
Michigan	0.68	0.68
Ontario	0.71	0.81

* Cited from Rossman and Barres (1988)

Table 7: Total chromium concentrations in contaminated sediments from various Canadian lakes, rivers and harbours.

Site Sampled	Mean Total Cr Concentration (mg kg ⁻¹)	Location of Site	Reference
Lake Simcoe	174.6	Ontario	Johnson and Nicholls 1988
St Mary's River (Tannery Bay)	31000	Ontario	St. Mary's River RAP Report 1992
Welland Canal		Ontario	Dickman <i>et al.</i> 1990
Upstream	10		
Downstream	> 5120		
Hamilton Harbour	564	Ontario	Nriagu <i>et al.</i> 1983
Saguenay Fjord	55.7	Québec	Pelletier and Canuel 1988
Belledune Harbour	41.6	New Brunswick	Samant <i>et al.</i> 1990
Dalhousie Harbour	24.6	New Brunswick	Samant <i>et al.</i> 1990
Fraser River Drainage Basin	217	British Colombia	Shreier <i>et al.</i> 1987

Table 8: Atmospheric concentration of total chromium from different regions of Canada.

Site Sampled	Range of Total Cr Concentration (ng m ⁻³)
Canadian Arctic ^a	0.15-0.32
Jasper National Park ^a	<0.7
Twin Gorges, NWT ^a	<0.6
Southern Ontario (1986-1987) ^b	3-20
Western Ontario (1986-1987) ^b	5-6
Central Ontario (1986-1987) ^b	3-10
Northern Ontario (1986-1987) ^b	4-11

^a Cited from Barrie and Hoff (1985)

^b Cited from Environment Canada (1991)

Table 9: Existing soil quality criteria or guidelines for chromium.

Jurisdiction	Criteria / Guideline	Conc. (mg·kg⁻¹)	Reference
Canada (national)	Interim Assessment Criteria Cr (VI) Cr (total) Interim Remediation Criteria Agriculture Cr (VI) Cr (total) Residential/parkland Cr (VI) Cr (total) Commercial/industrial Cr (VI) Cr (total)	2.5 20 8 750 8 250 — 800	CCME 1991
British Columbia	A Cr (total) B Cr (total) C Cr (total)	20 250 800	BC MOE 1989
Alberta	Tier 1 Cr (total) Cr (VI)	100 5	Alberta Environment 1990
Ontario	Residential/parkland Medium and Fine Textures Cr (VI) Cr (total) Coarse Texture Cr (VI) Cr (total) Commercial/industrial Medium and Fine Textures Cr (VI) Cr (total) Coarse Texture Cr (VI) Cr (total)	10 1000 8 750 10 1000 8 750	MOEE 1989
Québec	A Cr (total) B Cr (total) C Cr (total)	75 250 800	MENVIQ 1988
The Netherlands	A Cr (total) B Cr (total) C Cr (total)	— 250 800	Moen 1988

Jurisdiction	Criteria / Guideline	Conc. (mg·kg ⁻¹)	Reference
The Netherlands	Ecotoxicological C-Values Cr (III) Cr (VI) Reliability Score Cr (III) Cr (VI) Integrated C-Values Cr (III) Cr (VI)	230 --- 7 --- 230 ---	van den Berg and Roels 1991
The Netherlands	Target Values for Risk Assessment Cr (values for standard soil: 10% O.M. and 25% clay)	100	Environmental Quality Standards for Soil and Water 1991
AN New Jersey	Interim Soil Action Level Cr (total)	100	NJ DEP 1990
United Kingdom	Threshold Trigger Values All uses Cr (VI) Domestic gardens, allotments Cr (total) Parks, playing fields, open space Cr (total)	25 600 1000	UK DOE 1990

Table 10. Selected toxicity studies on microbial processes for total chromium

Microbial process (length of exposure)	Endpoint*	Concentration (mg Cr · kg ⁻¹)	Form of Cr	Soil pH	Test substrate	Extraction method	Reference
Nitrification (3 weeks)	EC ₆₂	1 000	Chromic Sulphate	7.1	Sandy loam; clay 17%, silt 24%, sand 53%; OC 2.0 %	Nominal	Premi and Cornfield 1969
	EC ₁₀₀	10 000	Chromic Sulphate	7.1			
Nitrification (10 d)	EC ₉₆	260	CrCl ₃	5.8	Silt 39%, clay 23%, sand 38%; OC 2.6%	Nominal	Liang and Tabatabai 1978
	EC ₃₉	260	CrCl ₃	7.4	Silt 50%, clay 34%, sand 16%; OC 5.5%		
	EC ₄₇	260	CrCl ₃	7.8	Silt 44%, clay 30%, sand 26%; OC 3.7%		
Nitrogen mineralization (20 d)	EC ₂₀	260	CrCl ₃	5.8	Silt 39%, clay 23%; sand 38%; OC 2.6%	Nominal	Liang and Tabatabai 1977
	EC ₁₅	260	CrCl ₃	6.6	Silt 54%, clay 45%; sand 1%; OC 3%		
	EC ₂₄	260	CrCl ₃	7.4	Silt 50%, clay 34%; sand 16%; OC 5.5%		
	EC ₁₃	260	CrCl ₃	7.8	Silt 44%, clay 30%; sand 24%; OC 3.7%		
Respiration - CO ₂ evolution (3 months)	EC ₉₉	200	CrCl ₃	7.0	Deciduous forest sandy clay loam	Nominal	Skujins et al. 1979
Respiration - CO ₂ evolution (3 weeks)	EC ₃₆ EC ₄₀	10 100	K ₂ Cr ₂ O ₇	6.4	Nellis loam (Typic Eutrochrept)	Nominal	Ross et al. 1981
	EC ₄₆	100	CrCl ₃	6.4	Nellis loam (Typic Eutrochrept)		
	EC ₂₃ EC ₃₃	10 100	K ₂ Cr ₂ O ₇	5.4	Hinesburg fine sandy loam (Entic Haplorthod)		
	EC ₄₀	100	CrCl ₃	5.4	Hinesburg fine sandy loam (Entic Haplorthod)		

*The EC endpoints represent the percentage of adverse effect, compared to controls, as calculated by the CCME from the data presented by the author(s).

Table 11. Selected invertebrate and plant toxicity studies for total chromium

Organism	Effect Parameter (length of exposure)	Endpoint*	Concentration mg Crkg ⁻¹ (SD)	Form of Cr	Soil pH	Test substrate	Extraction method	Reference
Invertebrates								
Earthworm (<i>Eisenia andrei</i>)	Growth (3 weeks)	NOEC EC ₆₆	287 972	Chromium (III) nitrate Cr(NO ₃) ₃ · 9H ₂ O	6.0± .5	Artificial soil, 10% sphagnum peat, 20% kaolin clay, 69% fine sand	Nominal	van Gestel et al. 1992
	Cocoon Production (3 weeks)	NOEC EC ₄₀	287 972					
Earthworm (<i>Eisenia fetida</i>)	Mortality (14 day)	NOEC LOEC (72%) EC ₂₅ EC ₃₀	900 (500) 1733 (764) 1133 (321) 1400 (346)	CrO ₂	4.2- 4.3	Artificial soil, OM 2.4-4.1%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (a)
		NOEC LOEC (80%) EC ₂₅ EC ₃₀	323 (87) 677 (178) 423 (93) 573 (93)	CrCl ₃	4.0- 4.3	Artificial soil, OM 3.7-6%		
Earthworm (<i>Eisenia fetida</i>)	Mortality (14 day)	NOEC LOEC (60%) EC ₂₅ EC ₃₀	748 1579 956 1195	CrO ₂	4.2	Artificial Soil, OM 6.1%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (b)
		NOEC LOEC (10%) EC ₂₅ EC ₃₀	235 466 543 671	CrCl ₃	4.2	Artificial Soil, OM 6.1%		
Plants								
Com (<i>Zea mays</i>)	Forage yield (7 weeks)	NOEC LOEC	80 320	Cr ₂ (SO ₄) ₃	5.5	Hartsells fine sandy loam	Nominal	Morteveldt and Giordano 1975

Organism	Effect Parameter (length of exposure)	Endpoint*	Concentration mg Cr kg ⁻¹ (SD)	Form of Cr	Soil pH	Test substrate	Extraction method	Reference
Lettuce (<i>Lactuca sativa</i>)	Seed germination (120 hours)	NOEC LOEC (82%) EC ₂₅ EC ₅₀	230 (44) 510 (17) 297 (41) 397 (12)	CrO ₂	4.0- 4.3	Artificial Soil, OM 3.7-6%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (a)
		NOEC LOEC (26%) EC ₂₅ EC ₅₀	57 (8) 113 (17) 106 (8) 146 (16)	CrCl ₃	4.0- 4.3	Artificial Soil, OM 3.7-6%		
Lettuce (<i>Lactuca sativa</i>)	Seed germination (120 hours)	NOEC LOEC (33%) EC ₂₅ EC ₅₀	97 205 146 274	CrO ₂	4.2	Artificial Soil, OM 6.1%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (b)
		NOEC LOEC (53%) EC ₂₅ EC ₅₀	49 100 64 100	CrCl ₃	4.2	Artificial Soil, OM 6.1%		
Oats (<i>Avena sativa</i>)	Yield (2 weeks)	NOEC EC ₅₀	11 31	K ₂ Cr ₂ O ₇	5.1	Humic sand (3.7% OM)	Nominal	Adema and Henzen 1989
Radish (<i>Raphanus sativa</i>)	Seed germination (72 hours)	NOEC LOEC (58%) EC ₂₅ EC ₅₀	117 (49) 243 (108) 150 (17) 207 (42)	CrO ₂	4.0- 4.3	Artificial Soil, OM 3.7-6%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (a)
		NOEC LOEC (41%) EC ₂₅ EC ₅₀	59 (9) 107 (15) 82 (6) 127 (14)	CrCl ₃	4.0- 4.3	Artificial Soil, OM 3.2-6%		
Radish (<i>Raphanus sativa</i>)	Seed germination (72 hours)	NOEC LOEC (23%) EC ₂₅ EC ₅₀	23 45 51 116	CrO ₂	4.2	Artificial Soil, OM 6.1%	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (b)
		NOEC LOEC (18%) EC ₂₅ EC ₅₀	24 49 59 81	CrCl ₃	4.2	Artificial Soil, OM 6.1%		

Organism	Effect Parameter (length of exposure)	Endpoint*	Concentration mg Cr kg ⁻¹ (SD)	Form of Cr	Soil pH	Test substrate	Extraction method	Reference
Ryegrass (<i>Lolium hybridum</i>)	Dry matter yield (35 days)	EC ₆₈ (tops) EC ₄₅ (roots)	500† 500†	Cr (III) Oxide	5.2	Soil I, 36.1 % clay	Nominal	Otabbong 1989
		EC ₆₈ (tops) EC ₄₅ (roots)	500† 500†	Cr (III) Oxide	6.9	Soil IV, 54.3% clay		
Tomato (<i>Lycopersicum esculentum</i>)	Yield (2 weeks)	NOEC EC ₃₀	10 21	K ₂ Cr ₂ O ₇	5.1	Humic sand (3.7% OM)	Nominal	Adema and Henzen 1989

*The EC endpoints represent the percentage of adverse effect, compared to controls, as calculated by the CCME from the data presented by the author(s).

†Single concentration study.

Table 12. Selected plant toxicity studies for chromium (VI)

Organism	Effect Parameter (length of exposure)	Endpoint*	Concentration mg Cr kg ⁻¹ (SD)	Form of Cr	Soil pH	Test substrate	Extraction method	Reference
Plants								
Lettuce (<i>Lactuca sativa</i>)	Seed germination (120 hours)	NOEC LOEC (39%) EC ₂₅ EC ₅₀	12 24 18 67	CrO ₂	7.0	Artificial Soil, OM 6.1%, pH adjusted to neutral with 2% CaCO ₃	Digestion with HNO ₃ , H ₂ O ₂ , and HCl; measured colorimetrically	Environment Canada 1995 (b)
Lettuce (<i>Lactuca sativa</i>)	Yield (2 weeks)	NOEC EC ₅₀	0.35 1.8	K ₂ Cr ₂ O ₇	7.5	Loam (1.4% OM)	Nominal	Adema and Henzen 1989
Oats (<i>Avena sativa</i>)	Yield (2 weeks)	NOEC EC ₅₀	3.5 7.4	K ₂ Cr ₂ O ₇	7.5	Loam (1.4% OM)	Nominal	Adema and Henzen 1989
Tomato (<i>Lycopersicum esculentum</i>)	Yield (2 weeks)	NOEC EC ₅₀	3.2 6.8	K ₂ Cr ₂ O ₇	7.5	Loam (1.4% OM)	Nominal	Adema and Henzen 1989
Turnip (<i>Brassica rapa</i>)	Yield (10 days)	EC ₅₀	8.25	K ₂ Cr ₂ O ₇	6.1	Sandy loam (1.3% OM)	Nominal	Günther and Pestemer 1990

*The EC endpoints represent the percentage of adverse effect, compared to controls, as calculated by the CCME from the data presented by the author(s).

Table 13: Estimated NOELs for chromium in livestock, wildlife and domestic animals.

Species	Chromium Compound	Target Tissue	NOAEL	Parameter Tested	Reference
Dog, Cat, Rabbit	Cr (VI)	NR	5.5 mg·kg ⁻¹ BW ·d ⁻¹ of exposed animals	histopathological changes	Lehman 1914 (cited in NRCC 1976)
Chicken	(Na ₂ CrO ₄)	NR	100 mg·kg ⁻¹ FW in diet items	growth rate mortality	Romoser <i>et al.</i> 1961
Dog	Cr (VI)	Liver 23-33 µg·g ⁻¹ FW Kidney 3.7-4.8 µg·g ⁻¹ FW	11 mg·L ⁻¹ in drinking water	growth rate food and water intake blood chemistry urine chemistry histopathological changes	Anwar <i>et al.</i> 1961
<i>Anas rubripes</i> (Black duck)	Cr (III)	NR	200 mg·kg ⁻¹ FW in diet items	Fright stimulus	Heinz and Haseltine 1981
Cow	Cr (III)	Kidney 0.5-2.0 µg·g ⁻¹ FW	9,6 mg·kg ⁻¹ BW ·d ⁻¹ of exposed animals	histopathological changes in kidney	Kreuzer <i>et al.</i> 1985
<i>Sterna hirundo</i> (Common tern)	chromium	liver < 18 µg·g ⁻¹ DW	< 8 mg·kg ⁻¹ DW	growth rate reproductive success clutch size	Custer <i>et al.</i> 1986

Refer to Outridge and Scheuhammer 1993

BW= body weight

Table 14: Chromium concentrations in field populations of mammalian species.

Species	Study Location	Source of Cr Contamination	Tissue	Cr Concentration in Assayed Organism: Contaminated Site	Cr Concentration in Assayed Organism: Uncontaminated Sites (control)	Reference
<i>Microtus agrestis</i> (field vole)	England	Sewage sludge	Liver Kidney Brain Femur Remaining carcass	0.3 mg·kg ⁻¹ DW 0.5 mg·kg ⁻¹ DW 0.3 mg·kg ⁻¹ DW < 0.8 mg·kg ⁻¹ DW 5 mg·kg ⁻¹ DW	0.5 µg·g ⁻¹ DW 1.1 µg·g ⁻¹ DW 1 µg·g ⁻¹ DW < 0.6 µg·g ⁻¹ DW 4 µg·g ⁻¹ DW	Beardsley <i>et al.</i> 1978
<i>Sigmodon hispidus</i> (cotton rat)	Tennessee, U.S.	Cooling towers-chromate released into the atmosphere	Bone Pelt Hair Muscle Heart Liver Kidney Spleen Lung	0.46 µg·g ⁻¹ DW 1.06 µg·g ⁻¹ DW 4.40 µg·g ⁻¹ DW 0.29 µg·g ⁻¹ DW 0.12 µg·g ⁻¹ DW 0.16 µg·g ⁻¹ DW 0.12 µg·g ⁻¹ DW 0.71 µg·g ⁻¹ DW 0.29 µg·g ⁻¹ DW	0.16 µg·g ⁻¹ DW 0.09 µg·g ⁻¹ DW 0.40 µg·g ⁻¹ DW 0.23 µg·g ⁻¹ DW 0.11 µg·g ⁻¹ DW 0.05 µg·g ⁻¹ DW 0.09 µg·g ⁻¹ DW 0.49 µg·g ⁻¹ DW 0.29 µg·g ⁻¹ DW	Taylor and Parr 1978
<i>Microtus pennsylvanicus</i> (meadow vole)	Reed canary grass field Pennsylvania, U.S.	Secondary treated municipal sewage effluent	Liver Kidney	1.3 µg·g ⁻¹ FW 5.2 µg·g ⁻¹ FW	3.2 µg·g ⁻¹ FW 14.5 µg·g ⁻¹ FW	Anthony and Kozlowski 1982
<i>Peromyscus Leucopus</i> (white-footed mouse)	Forest Pennsylvania, U.S.	Secondary treated municipal sewage effluent	Liver Kidney	2.2 µg·g ⁻¹ FW 8.0 µg·g ⁻¹ FW	2.2 µg·g ⁻¹ FW 8.0 µg·g ⁻¹ FW	Anthony and Kozlowski 1982
<i>Odocoileus virginianus</i> (white tailed deer)	Sludge disposal site Michigan, U.S.	Sludge	Muscle Heart Kidney Liver	1.3 µg·g ⁻¹ DW 0.4 µg·g ⁻¹ DW 0.9 µg·g ⁻¹ DW 1.6 µg·g ⁻¹ DW	NR	Campa <i>et al.</i> 1986
<i>Peromyscus Leucopus</i> (white-footed mouse)	Sludge disposal site Michigan, U.S.	Sludge	Kidney**	8.6 µg·g ⁻¹ DW	0.7 µg·g ⁻¹ DW	Woodyard <i>et al.</i> 1986
<i>Blarina brevicauda</i> (short-tailed shrew)	Northeastern U.S.	Cr-contaminated dredge spoil	Whole body	21 µg·g ⁻¹ DW	NR	Beyer <i>et al.</i> 1990
<i>Microtus pennsylvanicus</i> (meadow vole)	Northeastern U.S.	Cr-contaminated dredge spoil	Whole body	6.9 µg·g ⁻¹ DW	NR	Beyer <i>et al.</i> 1990

Species	Study Location	Source of Cr Contamination	Tissue	Cr Concentration in Assayed Organism: Contaminated Site	Cr Concentration in Assayed Organism: Uncontaminated Sites (control)	Reference
<i>Mus musculus</i> (house mouse)	Northeastern U.S.	Cr-contaminated dredge spoil	Whole body	11 $\mu\text{g}\cdot\text{g}^{-1}$ DW	NR	Beyer <i>et al.</i> 1990
<i>Peromyscus Leucopus</i> (white-footed mouse)	Northeastern U.S.	Cr-contaminated dredge spoil	Whole body	7.1 $\mu\text{g}\cdot\text{g}^{-1}$ DW	NR	Beyer <i>et al.</i> 1990

Refer to Outridge and Scheuhammer 1993

DW= dry weight

FW= fresh weight

NR= not reported

Table 15. Summary of environmental soil quality guidelines for chromium

Soil Quality Guideline	Land use		
	Agricultural (mg Cr·kg ⁻¹)	Residential/parkland (mg Cr·kg ⁻¹)	Commercial/industrial (mg Cr·kg ⁻¹)
TEC or ECL* Cr (total) Cr (VI) (provisional)	78 0.4	78 0.4	87 1
Nutrient and energy cycling check: Cr (total) Cr (VI)	52 Insufficient data	52 Insufficient data	Insufficient data Insufficient data
SQG _{sc} Cr (total) Cr (VI) (provisional)	64 0.4	64 0.4	87 1
SQG _i	Insufficient data	NA	NA
SQG _e Cr (total) Cr (VI) (provisional)	64 0.4	64 0.4	87 1
CCME interim criteria§ Cr (total) Cr (VI)	750 8	250 8	800 —

*As per the CCME 1996 protocol, the TEC for agricultural and residential/parkland land uses corresponds to the 25th percentile of the effects and no effects data distribution when using the weight of evidence method, while the ECL for commercial/industrial land use corresponds to the 25th percentile of the effects data distribution. The other percentiles are presented for comparison purposes only.

NA = not applicable.

§CCME 1991.

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