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Canadian Soil Quality Guidelines for

Vanadium: Environmental

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NOTICE

This final draft document provides the information supporting the derivation of environmental soil quality guidelines for vanadium. Development of these soil quality guidelines was initiated through the National Contaminated Sites Remediation Program (NCSRP) 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 NCRSP.

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.

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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 vanadium and a review of the sources and emissions in Canada. Chapter 3 discusses vanadium's distribution and behavior in the environment while chapter 4 reports the toxicological effects of vanadium on microbial processes, plants, and animals. These informations are used in chapter 5 to derive soil quality guidelines for vanadium 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. For vanadium, the environmental soil quality guideline (SQG_E) relative to all land uses (agricultural, residential/parkland, commercial and industrial) is 130 $mg \cdot kg^{-1}$ soil. This environmental soil quality guideline is optimized for soils within the pH range of 4.3 to 8.2 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 vanadium 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 vanadium 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. Pour le vanadium, la recommandation pour la qualité des sols en vue de la protection de l'environnement (RQS_E) relative à tout les types d'utilisations de terrains (agricole, résidentiel/parc, commercial et industriel) est de 130 $mg \cdot kg^{-1}$ de sol. Cette recommandations pour la qualité des sols en vue de la protection de l'environnement est à son optimum dans des sols avec pH entre 4.3 et 8.2 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 for Contaminated Sites 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 the 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 vanadium, 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 vanadium 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 the values.

2. BACKGROUND INFORMATION

2.1 Natural Occurrence

Vanadium occurs commonly but not uniformly in the earth's crust, ranking 22nd among the elements in the earth's crust (WHO 1988). The average concentration of vanadium in the earth's crust is approximately 150 $mg \cdot kg^{-1}$, which is of the same order as nickel, copper, zinc, and lead, although vanadium is more dispersed than these metals (Jones et al. 1990). Small amounts are found in iron ores, particularly titaniferous magnetites, petroleum crudes, asphaltites and phosphate rock, with few deposits containing over 1% vanadium. Among the 65 different minerals which contain vanadium, patronite, carnotite, roscoelite, descloizite, cupro-descloizite, and vanadinite are important sources (CRC Handbook of Chemistry and Physics 1994).

2.2 Physical and Chemical Properties

Vanadium is a member of the subgroup VA metals of the periodic table with an atomic number of 23 and a molecular weight of 50.94. It is a silvery-white ductile metal with two naturally-occurring isotopes and, like other elements in the transition group VA, vanadium forms numerous and

frequently complicated compounds because of its many valence states, which may range from +2 to +5, with +5 being the principle oxidation state (Lagerkvist et al. 1986). Vanadium can act as a metal or non-metal and can form both cationic and anionic salts, but the exact nature of many of its ions in aqueous solution in still unknown. Besides occurring in over 65 mineral species, it also tends to be associated with organic matter (API 1985).

Vanadium II (+2 valence) and vanadium III (+3 valence) salts are strong reducing agents and are readily oxidized in air (API, 1985). Vanadium IV (+4 valence) and vanadium V (+5 valence) are usually found bonded to oxygen as a negatively charged polymeric oxyanion that tends to complex with polarizable ligands such as phosphorus and sulfur (WHO 1988). Vanadium V is reduced to vanadium IV by relatively mild reducing agents. The +4 oxidation state is the most stable oxidation state for vanadium. Nearly all complexes of vanadium IV are anionic and a few are non-electrolytes. Vanadium in this oxidation state forms a large number of five or six coordinate complexes, such as vanadyl acetylacetonate and vanadyl porphyrins which are found in crude petroleum. Vanadium's ability to be either an electronegative or an electropositive metal results in a great variety of chemical compounds. In fact, vanadium is second only to carbon in the number of chemical compounds it is able to form (WHO 1988). Pure vanadium is very resistant to corrosion in simple aerated saline solutions. It is amphoteric and basic at the lower oxidation states and acidic in the higher ones. The properties of vanadium and its principle compounds are listed in Table 1.

2.3 Analytical Methods

Analytical methods recommended for vanadium by the CCME include Method SM 3111D, Method SM 3120B, and U.S. EPA Method 6010 - Revision 0 (CCME 1993).

Method SM 3111D is entitled "Direct Nitrous Oxide-Acetylene Flame Method for the Determination of Metals" and is applicable in the determination of ten elements in water and wastewater samples. The detection limit for vanadium is 0.2 $mg \cdot L^{-1}$ with a range of 2 to 100 $mg \cdot L^{-1}$ (CCME 1993).

Method SM 3120B is entitled "Inductively Coupled Plasma (ICP) Method for the Determination of Metals" and is applicable in the determination of metals in water and wastewater samples. The detection limit for vanadium is 8 $\mu g \cdot L^{-1}$ with a range of 13 to 4698 $\mu g \cdot L^{-1}$. The accuracy of the method is 0.9615 to 2.0 $\mu g \cdot L^{-1}$ and the precision is 0.0618·(mean concentration) +/- 1.7 $\mu g \cdot L^{-1}$ (CCME 1993).

U.S. EPA Method 6010 - Revision 0 is entitled "Inductively Coupled Plasma-Atomic Emission Spectroscopy" and is applicable in the determination of trace elements, including metals, in groundwater, soils, sludges, sediments, and other solid wastes. All matrices require digestion prior to analysis. The method of standard addition (MSA) must be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required. The detection limit for vanadium is 8 $\mu g \cdot L^{-1}$ with a spiked concentration 70 $\mu g \cdot L^{-1}$, a mean reported value of 69, and a precision (relative standard deviation) of 2.9% (CCME 1993).

2.4 Production, Uses, and Global Sources

Production and Uses

Vanadium has important industrial uses, mainly in ferrous metallurgy, where 75 to 85% of all vanadium produced is used as an alloy additive in making special steels. Pure vanadium is very seldom used as it reacts easily with oxygen, nitrogen, and carbon at a relatively low temperature of 300°C (WHO 1988). Vanadium is combined with chromium, nickel, manganese, boron, tungsten, and other elements to produce various high-resistance carbon steels. Vanadium may be a component of structural steels used in building, transport, engineering, and boiler-making and in tool steels. It is added to steel in the form of either ferrovanadium (an iron-vanadium alloy containing 40 to 80% vanadium) or vanadium carbide (Zenz 1980). Vanadium is also a major alloying element in high-strength titanium alloys. Alloys of vanadium with non-ferrous metals (e.g., aluminum, titanium, copper, etc.) are widely used in the atomic industry, aircraft construction, and space technology (WHO 1988).

In the chemical industry, vanadium oxides and vanadates have important uses as catalysts in: the synthesis of sulfuric acid and plastics, the oxidation of organic compounds, petroleum cracking, exhaust gas purification, and ethanol oxidation. The pentoxide and various other salts of vanadium are used in producing lacquers and paints, and as developers, sensitizers, and colouring agents in photography and cinematography. The quantities of vanadium used in the chemical industry are often small and some recycling of vanadium used as catalysts takes place (WHO 1988).

In Canada, vanadium's main industrial use is in the production of high-strength, low-alloy steel and tool and die steels, which account for approximately 85% of its total consumption. Another 10% is used in the manufacture of titanium-aluminum alloys for the aerospace industry (EMR 1990). The remaining 5% is primarily used in the chemical industry as catalysts in the production of polymeric plastics, sulfuric and nitric acids, as a mordant in dyes and printing fabric inks, and in vanadium-gallium tape for use in superconductors (NRCC 1980).

Sources and Releases

Power and heat producing plants using fossil fuels (petroleum, coal, oil) cause the most widespread discharge of vanadium into the environment. Vanadium is present in flue gas and fly ash. Burning of coal wastes or dumps of coal dust in mining areas are other important sources of atmospheric discharge (U.S. EPA 1987). Other important air emission sources are the re-smelting of scrap steel, the transformation of titaniferous and vanadic magnetite iron ores into steel, the roasting of vanadium slags, the vanadium pentoxide smelting furnaces, and the electric furnaces in which ferrovanadium is smelted (WHO 1988).

In 1972, the combustion of fuel oil alone accounted for over 94% of all the vanadium emitted to the atmosphere in Canada (Fisheries and Environment Canada 1976). Fairly high emission rates have been reported for all the provinces east of Ontario, with Quebec accounting for 64% of the Canadian total. This is probably a reflection of the Venezuelan fuel oil imported and utilized in Eastern Canada.

Zoller et al. (1973) estimated that emissions of vanadium to air by man through petroleum combustion are about equal on a global scale to the amount of vanadium in the atmosphere arising from natural sources. This would imply that man has doubled the atmospheric vanadium flux. Natural sources of vanadium are continental dust, marine aerosols, and volcanic emissions (NRCC 1980).

2.5 Levels in the Environment

Air

Natural sources of vanadium, such as continental dust and marine aerosols, cause only low natural background levels of vanadium in air. In remote areas, such as the South Pole, atmospheric concentrations range from 0.001 to 0.002 $ng \cdot m^{-3}$ and in the eastern Pacific Ocean, from 0.02 to 0.8 $ng \cdot m^{-3}$ (Zoller et al. 1973). Ambient concentrations in remote areas are fairly low while increased concentrations are often seen in urban atmospheres chiefly as a result of combustion of residual fuel oil which may contain several hundred parts per million of vanadium (API 1985). Vanadium concentrations recorded in rural areas of the United Kingdom, Canada, and the United States range from 0.25 to 75 $ng \cdot m^{-3}$ with annual averages frequently below 1 $ng \cdot m^{-3}$ (Rahn and Winchester 1971). Annual urban averages range from 20 to 100 $ng \cdot m^{-3}$, though exceptionally higher averages exceeding 200 to 300 $ng \cdot m^{-3}$ have been recorded in large cities (U.S. EPA 1977).

Water

No exact figures for vanadium in Canadian waters are available. In the United States, concentrations of vanadium in freshwater depend largely on geographical location and range from 0.2 to more than 100 $\mu g \cdot L^{-1}$ (Kopp and Kroner 1968). Typical values in drinking water in the U.K. are approximately 1 $\mu g \cdot L^{-1}$ while the average concentration in seawater worldwide is 0.1 to 2 $\mu g \cdot L^{-1}$ (Bengtsson and Tyler 1976).

Soil

Vanadium concentrations in soils range from 5 to 140 $mg \cdot kg^{-1}$ worldwide and may reach very high levels in soils polluted by fly-ash (up to 400 $mg \cdot kg^{-1}$) (Bengtsson and Tyler 1976). According to the Soil Metal Database of the Alberta Soil Protection Branch, natural mean concentrations in Canadian soils range from 38 to 42 $mg \cdot kg^{-1}$, with concentrations tending to increase with depth (Dinwoodie 1995, Alberta Soil Protection Branch, Edmonton, pers. com.). Minimum values are 10 $mg \cdot kg^{-1}$ and maximum are 90 $mg \cdot kg^{-1}$.

The vanadium contents of soils are related to those of the parent rocks from which they are formed with the highest concentrations being found in shales and clays. Vanadium is evenly distributed in the soil horizons, but there is sometimes a higher level in the A horizon, possibly caused by plant biocycling (WHO 1988). Vanadium is concentrated mainly in mafic rocks and in shales, within the common range of 100 to 250 ppm (Kabata-Pendias and Pendias 1992).

According to the Geological Survey of Canada, deposits of vanadium and vanadiferous occurrences can be found in all provinces and territories. The most significant known deposits are in Quebec, Alberta, British Columbia, and the Yukon Territory. The geological age of the vanadium bearing strata ranges from 2700 million years up to the present (NRCC 1980). Most of the approximately twenty primary vanadium-bearing minerals have been found in Canada while only a few of the secondary minerals occur. The primary minerals are generally associated with igneous rocks, carbonate complexes, titaniferous magnetite complexes and chromite, uranium, iron, and manganese deposits (NRCC 1980)

2.6 Existing Criteria and Guidelines

Relatively few jurisdictions have established soil guidelines for vanadium. Existing guidelines, criteria, and standards for vanadium in soil from provincial, national, and international agencies are summarized in Table 2 and typically range from 100 to 200 $mg \cdot kg^{-1}$.

3. ENVIRONMENTAL FATE AND BEHAVIOUR

3.1 Soil

Vanadium is found in rocks and soils in a relatively insoluble trivalent form. It does not form its own minerals nor does it exist as free metal, but rather, it is present as vanadates of copper, zinc, lead, uranium, ferric iron, manganese, calcium, and potassium (API 1985). In addition, vanadium tends to replace other metals such as iron, titanium, and aluminum in crystal structures (Cannon 1963). Weathering decomposes parent rock and increases vanadium availability in soils. The soil layers with greater humic acid content (A horizon) usually contain more vanadium than other soil layers (API 1985).

Vanadium is involved in various geochemical processes occurring in the earth's crust. There is extremely wide dispersion of vanadium during the formation of volcanic rocks. Sporadic accumulation also occurs with the formation of vanadium minerals as a result of postmagmatic processes (WHO 1988). During weathering, the mobility of vanadium is dependent on the host minerals. Vanadium will eventually come to rest in the residual rock-forming minerals or will be adsorbed or incorporated into mineral structures of clays or ferrous oxides (Kabata-Pendias and Pendias 1992). A high degree of association of vanadium with the manganese and the potassium content of soil has also been reported (Norrish 1975). Vanadium also tends to associate with organic matter and therefore elevated concentrations of vanadium in organic shales and bioliths are common. The geochemical characteristics of vanadium are strongly dependent on its oxidation state (+2, +3, +4, and +5) and on the acidity of the media. Vanadium is known to form various complexes of cationic and anionic oxides and hydroxy oxides, therefore, vanadium displays various behaviours (Kabata-Pendias and Pendias 1992).

Vanadium in the +5 oxidation state is more soluble and is therefore more mobile than vanadium +4;

vanadium +3 is the least mobile form. In bituminous coal deposits, vanadium +4 is oxidized to vanadium +5 which is soluble in water and therefore is able to enter biological systems (NRCC 1980). According to Brooks (1972), vanadium is highly mobile in neutral or alkaline soils relative to other metals. Norrish (1975) reported that mobile ferrous oxides hold a substantial fraction of the vanadium in soil and could supply vanadium to plants. Berrow et al. (1978) suggested that in certain horizons of podzols, the role of clay minerals as well as organic acids in attenuation of vanadium is more significant than the vanadium fraction adsorbed by ferrous oxides. According to these authors, the vanadyl cation (VO_2^+) may be an important form of vanadium in many soils and may result from reduction of the metavanadate anion (VO_3^-). Goodman and Cheshire (1975) and Bloomfield (1981) stated that much of the soil vanadium, mainly the vanadyl cation, is mobilized as complexes with humic acids while anionic forms of vanadium (eg. orthovanadate anion, VO_4^{3-}; metavanadate anion, VO_3^-) are known to be mobile in soils and relatively more toxic to soil microbiota.

3.2 Air

Vanadium in the atmosphere is mainly the result of industrial processes (U.S. EPA 1987). This metal is often associated with small particles which usually do not settle quickly, and thus vanadium is subject to long distance transport by atmospheric dispersion, the extent of which depends on wind speed, direction, and meteorological conditions. Vanadium-containing particles are removed from the atmosphere by sedimentation, impaction onto obstacles, or rainout and washout. Sedimentation or settling out plays a greater role in the removal of larger (greater than 10 μm diameter) particles (U.S EPA 1977). Washout and rainout was also shown to be more effective for particles less than 7 μm in diameter (NRCC 1980). However, most vanadium is associated with particulate matter in the 0.1 to 2 μm diameter range. As a result, washout and rainout would not be very efficient in the removal of atmospheric vanadium. These smaller particles are therefore subject to greater transport and diffusion in the environment.

Since the principal sources of atmospheric vanadium are emissions from the combustion of vanadium-rich fuel oils and particulate emissions from the catalytic processing of petroleum refineries, vanadium oxides combine into particulate fly ash during combustion. Lower oxides of vanadium will ultimately oxidize to V_2O_5, especially at the high temperatures encountered in combustion stacks. Vanadium pentoxide may also exist in equilibrium with sulfur and its compounds resulting from stack reactions with SO_2 (U.S. EPA 1987).

Tullar and Suffet (1975) modelled the fate of vanadium in the lower Delaware valley air shed. Using an average falling distance of 500 m, and a specific gravity of 2 units for fly ash and fine particulates, a residence time of 21 days was calculated for vanadium particles in the 1000 m^2 air shed located roughly between Philadelphia and Delaware City.

3.3 Water

Vanadium generally enters water via atmospheric deposition or polluted waterways (WHO 1988).

The migratory characteristics of vanadium within water are poor and the bulk of vanadium will precipitate onto the seabed and become bound to silts. Monitoring data usually show a 100-fold or higher concentration of vanadium in sediment than in aqueous solution (U.S. EPA 1987). Ocean sediments are considered to be the long-term sink in the global circulation pattern of vanadium (API 1985). Bowen (1966) estimated that only 0.001 percent of vanadium in the ocean is retained as soluble forms in seawater. The dissolved vanadium is present usually as $H_2VO_4^-$ or HVO_4^{2-} ions (Duce and Hoffman 1976; Bowen 1979). Vanadium does not react chemically with seawater and is continuously precipitated from water by ferric hydroxides and organic matter (WHO 1988). Vanadium may also reenter the atmosphere via sea salt aerosol particles generated at ocean surfaces (U.S. EPA 1987). Duce and Hoffman (1976) estimated that 10 to 15% of anthropogenically derived vanadium particles are deposited in the ocean and will tend to dissolve and thus increase the vanadium concentration of sea water.

Movement of vanadium through aquatic and marine systems is highly dependent upon the species of vanadium, the presence of complexing ligands, pH of water and sediments, and salinity (API 1985). The major processes regulating vanadium behaviour in these media are speciation and sorption. The effects of photolysis, volatilization, and biotransformation have not been as extensively studied.

Certain marine organisms and plants play an important role in the biogenic migration of vanadium. Although bioaccumulation of vanadium is generally rare, marine ascidians (eg. tunicates or sea-squirts) may have blood vanadium concentrations of up to 10 000 times that of the ambient sea water (U.S. EPA 1977). Some marine algae also accumulate vanadium and upon their death, promote accumulation of vanadium in silt and sediments (WHO 1988).

4. BEHAVIOUR AND EFFECTS IN BIOTA

The LOEC endpoints reported in the toxicity tables (Tables 3, 4, 5, and 6) represent the lowest observed effects concentration at which there was a statistically 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 vanadium concentrations within the soil will be 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}, are presented as such without any calculation of a 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

Metabolic Fate and Behaviour

Microbial oxidation or reduction of elements with variable valence, metals in particular, is of great

importance in understanding bio-geochemical cycles of elements in nature (Lyalikova and Yurkova 1992). The role of microorganisms in the cycling of elements such as nitrogen, sulfur, and iron has been studied extensively, whereas the participation of microorganisms in the vanadium cycle has not. Thus, little information exists on microbial processes involving vanadium.

There is evidence that vanadium is a specific catalyst of nitrogen fixation and may partially substitute for molybdenum (Mo) in this function (Kabata-Pendias and Pendias 1992). Other authors have reported that vanadium is chemically similar to molybdenum and have also suggested that the former substitutes the latter in the fixation process (API 1985). Yopp et al. (1974) reported that nitrogen fixation by bacteria in the root nodules of several legumes was stimulated by low concentrations of vanadium in soil.

Lyalikova and Yurkova (1992) have demonstrated that certain strains of *Pseudomonas* bacteria are capable of reducing sodium metavanadate ($NaVO_3$) to tetra- and trivalent states anaerobically within growth cultures. Optimum temperatures and pH for these processes are respectively between 28 and 30°C, between 7 and 8.

Toxicity

Toxicity studies on soil microbial processes which were selected for use in soil quality guidelines derivation are listed in Table 3. Soil enzyme activities were not included in this table since they may not represent measured effects of chemicals on soil microbial populations. This is due to the fact that many enzymes produced by plants and microbes can exist and function extracellularly in soil for varying periods of time, depending on soil micro-environmental factors (Tabatabai 1982).

Liang and Tabatabai (1978) studied the inhibitive effects of vanadium on nitrification in a 10-day incubation experiment using three different soil compositions and pH levels: soil #1 had a clay-silt-sand composition of 39-23-38% and a pH of 5.8; soil #2 had a corresponding composition of 44-30-26% and a pH of 7.8; and soil #3 had a composition of 50-34-16% with a pH of 7.4. Single-concentration applications of 5000 $\mu mole \cdot kg^{-1}$, or 255 mg $V \cdot kg^{1}$, in the form of vanadyl sulfate ($VOSO_4$) were applied to all three soils. Reductions in nitrification were reported to be 62, 12, and 38%, respectively, for soil #1, 2, and 3.

In an earlier study, Liang and Tabatabai (1977) also examined inhibition of nitrogen mineralisation by vanadium. Four soils with different compositions were used: soil #1 had a clay-silt-sand composition of 39-23-38% and a pH of 5.8; soil #2 had a composition of 54-45-1% with a pH of 6.6; soil #3 had a composition of 34-50-16% and a pH of 7.4; and soil #4 had a composition of 44-30-26% with a pH of 7.8. Single-concentration applications of 5000 $\mu mole \cdot kg^{-1}$, or 255 mg $V \cdot kg^{-1}$, in the form of vanadyl sulfate ($VOSO_4$) were applied to all four soils followed by an incubation period of 20 days. Reductions in nitrogen mineralisation were reported to be 8, 14, 14, and 11%, respectively, for soil #1, 2, 3, and 4.

Wilke (1989) studied the effects of vanadium applied as sodium metavanadate ($NaVO_3$) on nitrification and nitrogen mineralization in a 28-day experiment. No inhibition of nitrification was

observed at 100 and 400 mg $V \cdot kg^{-1}$. In fact, nitrification actually increased by 9 and 20%, respectively. Nitrogen mineralization was only reduced by 7% at a single concentration of 400 $mg \cdot kg^{-1}$.

The effects of vanadyl sulfate on soil respiration were examined by Lighthart et al. (1983) in a 45-day microcosm study involving four different soils. Respiration, measured in terms of CO_2 release, was actually increased by 5 and 10% for two soils at the lowest vanadyl sulfate concentration of 2.55 mg $V \cdot kg^{-1}$. Reductions in respiration ranged between 7 to 40% for all four soils at the three other vanadyl sulfate concentrations (25.5, 255, and 2550 mg $V \cdot kg^{-1}$).

4.2 Terrestrial Plants

Metabolic Fate and Behaviour

Among the transition elements having atomic numbers of 22 to 30, manganese, iron, copper, and zinc are generally considered essential for the growth of higher plants. Vanadium has been recognized as an essential element for certain species of green algae (Arnon and Wessel 1953) but there exists inconclusive evidence to support claims for its essentiality in higher plants (Welch and Huffman 1973; Morrell et al. 1986; Kabata-Pendias and Pendias 1992). Any requirement for vanadium in the metabolism of higher plants must be of a minute order of magnitude (Morrell et al. 1986). No evidence of vanadium deficiency in higher plants has been observed however, and Welch and Cary (1975) claimed that if vanadium is essential for plants, adequate levels in their tissues are less than 2 ppb dry weight.

Soluble soil vanadium appears to be easily taken up by roots, and a few plant species show a great ability to accumulate this metal, especially certain bryophytes and fungi (Kabata-Pendias and Pendias 1992). The sporophore of the basidiomycete fungus *Amanita muscaria* is well known to contain elevated levels of vanadium. Lepp et al. (1987) reported that sporophores of *A. muscaria* collected in unpolluted woodland contained vanadium up to 345 $mg \cdot kg^{-1}$ dry weight, even though the total vanadium in the soil was relatively low at 6.7 $mg \cdot kg^{-1}$ dry weight.

Results from controlled laboratory and field experiments indicate a strong tendency for vanadium to accumulate in roots of most vascular plants (Jones et al. 1990), with very little being translocated to leaves and shoots (Nowakowski 1993). Welch (1973) studied the uptake of vanadium by barley roots from labelled vanadium solution and concluded that this contaminant is passively absorbed by roots. The uptake was highly dependent upon vanadium concentration and pH, as higher vanadium concentrations within roots were observed with increasing acidity and increasing concentrations of vanadium in test soil (Welch 1973). Vanadium concentrations in leaves appear to be somewhat independent of soil concentrations (U.S. EPA 1977).

In general, higher plants do not bioaccumulate vanadium to any significant degree. Welch and Cary (1975) reported accumulation of vanadium in cereals and vegetables grown in nutrient solutions but concluded that bioaccumulation rates were low considering the high concentration of vanadium in

solution. Similarly, Cary et al. (1983) reported that the vanadium content of several vegetables grown on coal bottom ash-amended soil (14.5 mg V·kg^{-1}) was less than or equal to the vanadium content of controls. On average, the concentration of vanadium in plants is one-tenth the concentration of vanadium in soil, thus plants in general have a soil bioconcentration factor (BCF) of 0.1 for vanadium (Cannon 1963; NRCC 1980; WHO 1988).

Vanadium taken up by roots is usually in the form of vanadyl (VO^{2+}; 4+ oxidation state) or vanadate (VO_3^-; 5+ oxidation state) (NRCC 1980). Laboratory experiments using higher plants suggest that there are differences in the way vanadyl and vanadate are absorbed and translocated (Morrell et al. 1983), with vanadyl generally being more rapidly absorbed (Hopkins et al. 1977). There is also evidence to indicate that vanadium is biotransformed from vanadate to vanadyl during uptake by plants. The reduction of vanadium in plants is of great significance since vanadate is recognized as a potent inhibitor of several enzymes which are largely unaffected by the reduced form, vanadyl (Morrell et al. 1986). Thus, vanadium in plant tissues exists predominantly in the reduced tetravalent form of vanadyl.

Toxicity

Plant toxicity studies selected for use in soil quality guidelines derivation are presented in Table 4 while additional plant studies which were consulted but not used in guidelines derivation are presented in Table 5.

Few soil toxicity studies involving vanadium exist for plants, although a large number of hydroponic studies involving culture solutions exist. Numerous studies indicate that, while increasingly higher concentrations produce various toxic effects, low concentrations of vanadium seem to benefit certain species in the form of increased growth relative to unexposed controls.
Kaplan et al. (1990a) conducted laboratory and greenhouse studies to evaluate the effects of vanadium on seed germination and radicle growth of cabbage (*Brassica oleracea*). In the laboratory portion of their experiment, Kaplan et al. (1990) germinated cabbage seeds on filter paper treated with $VOSO_4$. The presence of vanadium had no negative effect on cabbage seed germination up to a treatment concentration of 75 mg·L^{-1}. However, for radicle growth, a concentration of 1 mg·L^{-1} was found to increase radicle length by 51.7% while a concentration of 3 mg·L^{-1} significantly reduced radicle elongation by 53%.

In the greenhouse portion of their study, Kaplan et al. (1990a) found that vanadium tissue concentrations and toxicity to cabbage (*Brassica oleracea*) varied with soil type. In Blanton sandy soil (pH 5.35; OM 1.1%), a significant reduction of 24% in biomass occurred after 98 days at 80 mg·kg^{-1}. In the case of Orangeburg loamy-sand soil (pH 5.1; OM 1.9%), no significant decrease was found even after 133 days at the highest treatment level (100 mg V·kg^{-1}). Vanadium concentration within cabbage tissue increased steadily for plants grown in both types of soil. Collards grown on Blanton soil had increasing wet tissue concentrations ranging from 1.37 to 11.8 mg V·kg^{-1} over a treatment range of 0 to 100 mg V·kg^{-1} dry soil. Cabbage grown on Orangeburg soil had tissue concentrations ranging from 1.59 to 7.34 mg V·kg^{-1} over the same treatment range. Kaplan et al. (1990) attributed the higher toxicity in the sandy Blanton soil to an appreciably greater accumulation

of vanadium by plants, even though the exposure period in this soil was 35 days less than that of the Orangeburg soil. Differences in the physical and chemical properties of these two soils are likely responsible for the varying amounts of vanadium accumulated in the plants at a given treatment level.

Carlson et al. (1991) reported results similar to those of Kaplan et al. (1990a) for various crop plants in a hydroponic study involving vanadyl sulfate ($VOSO_4$). Millet (*Panicum miliaceum*) radicle lengths increased steadily up to 170%, relative to controls, between treatment concentrations of 0 to 20 mg $V \cdot L^{-1}$. Lettuce (*Lactuca sativa*) and radish (*Raphanus sativa*) also displayed faster radicle growth than controls between 0 and 2 mg $V \cdot L^{-1}$ (up to an increase of 130%) and between 0 and 5 mg $V \cdot L^{-1}$ (up to an increase of 110%), respectively. All test plants exhibited some degree of reduced radicle growth at higher concentrations of vanadium and certain plants did not exhibit increased growth at low concentrations. A significant reduction of 49% and 42% in radicle elongation was observed at 2.5 mg $V \cdot L^{-1}$ for turnip (*Brassica rapa*) and cabbage (*Brassica oleracea*), respectively.

The effects of vanadium pentoxide (V_2O_5) on the seedling emergence of radish (*Raphanus sativa*) and lettuce (*Lactuca sativa*) grown in an artificial soil (68% sand, 10% silt, and 22% clay) were studied by Environment Canada (1995). The 3-day NOEC, LOEC, EC_{25}, and EC_{50} values for radish seedling emergence were 200, 410, 330, and 580 mg $V \cdot kg^{-1}$ soil, respectively. The 5-day NOEC, LOEC, EC_{25}, and EC_{50} values for lettuce seedling emergence were 55, 127, 134, and 251 mg $V \cdot kg^{-1}$, respectively. The LOEC values corresponded to decreases in seedling emergence of 33% for radish and 29% for lettuce.

Environment Canada (1995) also examined the effects of vanadium pentoxide (V_2O_5) on the root elongation of radish (*Raphanus sativa*) and lettuce (*Lactuca sativa*) in a culture solution. The 3-day NOEC, LOEC, EC_{25}, and EC_{50} values for radish root elongation were 12, 38, 15, and 13, mg $V \cdot L^{-1}$, respectively, while the 5-day NOEC, LOEC, EC_{25}, and EC_{50} values for lettuce root elongation were estimated at 3, 8, 4, and 4 mg $V \cdot L^{-1}$, respectively. The LOECs corresponded to decreases in root elongation of 27% for radish and 29% for lettuce.

In a 134-day hydroponic study involving vanadium chloride (VCl_3), Hara et al. (1976) reported decreases of 9, 34, and 86% in dry plant yield of cabbage (*Brassica oleracea*) at 0.4, 4, and 20 mg $V \cdot L^{-1}$, respectively. In addition, decreases of 20 and 60% in inner leaf yield were reported at 0.4 and 4 mg $V \cdot L^{-1}$, respectively. In a similar hydroponic study on bush beans (*Phaseolus vulgaris*), Wallace et al. (1977) reported decreases of 10 and 52% for dry leaf yield and decreases of 41% and 68% for dry root yield at 1.17 and 11.7 mg $V \cdot L^{-1}$, respectively, over a 14 day period.

4.3 Terrestrial Invertebrates

Metabolic Fate and Behaviour

Very little information exists on the metabolic processes of vanadium within terrestrial invertebrates. It has been shown that many marine species within the genus *Ascidia* have the unique property of accumulating vanadium from seawater into their blood cells (Anderson et al. 1991). Vanadium levels

within blood plasma of certain ascidians may be as high as 0.01 to 0.06 mM. However, no evidence of such accumulation has been observed in any terrestrial invertebrate.

Toxicity

The single invertebrate toxicity study selected for use in soil quality guidelines derivation is presented in Table 4. Interest has developed in the use of soil invertebrates, especially earthworms, as indicators of environmental contamination (Neuhauser et al. 1985). Unfortunately, soil invertebrate toxicity data for vanadium, as is the case for soil microbes, is nearly non-existent. In the only soil invertebrate toxicity study available for vanadium, Environment Canada (1995) reported the effects of vanadium pentoxide (V_2O_5) on the earthworm *Eisenia fetida* in an artificial soil (68% sand, 10% silt, and 22% clay). The earthworms were kept inside 400 mL vessels containing 200 g of artificial soil and maintained at 24°C in continuous light for 14 days. The NOEC, LC_{25}, LC_{50}, and LOEC values were reported at concentrations of 210, 290, 370, and 410 mg $V \cdot kg^{-1}$, respectively.

4.4 Terrestrial Mammals and Birds

Metabolic Fate and Behaviour

Absorption

The most likely environmental exposure of mammals to vanadium is by inhalation of the oxide forms following combustion of fossil fuels. Oberg et al. (1978) studied the translocation and clearance of intratracheally administered radioactive vanadium oxytrichloride ($^{48}VOCl_3$) in the rat. More than half of the administered vanadium was removed from the lungs after the first day and only 3% of the burden remained after 63 days. Similar results were reported by Conklin et al. (1982) who reported that intratracheally administered radioactive vanadium pentoxide ($^{48}V_2O_5$) was rapidly cleared from the lung into blood, liver, and bone.

In general, ingested vanadium compounds are poorly absorbed (Lagerkvist et al. 1986). Uptake of radioactive vanadium pentoxide given orally to rats was only 2.6% of the administered dose (Conklin et al. 1982).

Slight dermal absorption and skin irritation were reported in a study in which sodium metavanadate ($NaVO_3$) was applied to the skin of rabbits (Stockinger et al. 1967). However, U.S. EPA (1977) reported that the skin appears to be a minor route of vanadium uptake for mammals. Furthermore, in an *in vitro* study using a vanadium radiotracer, no penetration of human skin samples was reported (Roshchin et al. 1980).

Distribution

Absorbed vanadium is transported in the serum mainly bound to transferrin (Harris et al. 1984). Extracellular vanadium will be in the vanadate (5+) form and intracellular vanadium will most likely

be in the vanadyl (4+) form (Nechay 1984).

Roschin et al. (1980) examined the distribution of radioactive vanadium in albino rats. Four routes of administration were used: intratracheal, subcutaneous, intraperitoneal, and intragastric. For all four routes, vanadium was present in blood in large quantities during the first day while only trace amounts were measured in blood after 2 days. When administered intratracheally, subcutaneously, and intraperitoneally, vanadium was found after 30 minutes in all internal organs whereas after intragastric administration, it was measured in large quantities in the gastrointestinal tract and in very small amounts in other organs. Within 2 days, vanadium had accumulated in the bone, kidney, liver, and lung tissues after intratracheal administration of vanadium pentoxide (Conklin et al., 1982). Vanadium levels in the brain are generally found to be considerably lower than in other organs, suggesting a blood-brain barrier for vanadium (Oberg et al. 1978; Conklin et al. 1982). Results from other mammalian studies confirm that, for nearly all routes of exposure, highest concentrations of vanadium are usually found within the kidney, liver, lung, bone, and spleen (Lagerkvist et al. 1986).

Excretion

Absorbed vanadium is excreted chiefly in the urine. Vanadium found within feces usually represents the portion which was ingested but not absorbed. Conklin et al. (1982) reported that 40% of intratracheally instilled radioactive vanadium pentoxide had been excreted, primarily in urine, after 3 days. In that study, rats and rabbits given intravenous and intraperitoneal injections of sodium metavanadate ($NaVO_3$) demonstrated a 5 to 1 ratio of urinary excretion versus fecal excretion. Excretion via urine represented 61% of the total dose whereas excretion via feces represented 10% to 12% (Talvitie and Wagner 1954).

Metabolic Effects

Vanadium, in its +5 oxidation state vanadate (VO_3^-), is well-known as a one of the most potent inhibitors of the $Na^+ + K^+$ ATPase enzyme system in mammals and birds (Jandhyala and Hom 1983; Nechay 1984). Many other enzyme systems are also inhibited or modified by vanadate, including Ca^{2+} - ATPase, adenylate kinase, ribonuclease, phosphofructokinase, and glucose-6-phosphatase (Jandhyala and Hom 1983; Nechay 1984; Lagerkvist et al. 1986).

There are obscure species differences in the renal, cardiac, and ocular actions of vanadate. Administration of vanadate may cause diuresis or antidiuresis, may have a positive or a negative inotropic effect on the heart, and may have variable differences in reducing intraocular pressure. The understanding of vanadium effects is incomplete due to multiple mechanisms which may be involved (Nechay 1984).

Nutritional Importance

Vanadium is distributed extensively in nature and is present in almost all living organisms (Jandhyala and Hom 1983). Naturally occurring vanadium is among the lowest of trace elements in mammals (Nechay 1984). Vanadium is considered an essential trace element for chicks and rats and its

deficiency may result in growth reduction, impairment of reproduction, and disturbances in lipid metabolism (Jandhyala and Hom 1983). Hopkins and Mohr (1974) observed reduced feather growth and weight gain in chicks along with impaired reproduction, due to decreased fertility, and increased perinatal mortality in rats, which were both fed a low vanadium diet (10 $\mu g \cdot kg^{-1}bw$) over four generations. A positive growth response in rats was observed by Schwarz and Milne (1971) when vanadium salts, were added at levels of between 50 and 500 $\mu g\ V \cdot kg^{-1}bw$ to a semi-purified diet for 26 to 28 days.

The mechanism of vanadium deficiency is not understood. No naturally occurring vanadium-deficiency disease has been described and no natural mammalian or avian metalloprotein which contains vanadium is known (Nechay 1984). Other than chickens and rats, vanadium essentiality has not been proven for other mammalian and avian species.

Toxicity

Mammalian and avian oral toxicity studies for vanadium which were selected for possible use in soil quality guidelines derivation are presented in Table 6. The available oral toxicity data for vanadium is almost exclusively based upon laboratory studies conducted on rats, mice, and chickens. In general, vanadium at low concentrations is tolerated well by rats and mice. The toxicity of vanadium tends to be low when administered orally, moderate when inhaled, and high when injected (WHO 1988).

Llobet and Domingo (1984) administered sodium metavanadate ($NaVO_3$) and vanadyl sulfate ($VOSO_4$) orally to Sprague-Dawley rats and Swiss mice. The LD_{50} values for rats were 98 and 448 $mg\ V \cdot kg^{-1}bw$ for sodium metavanadate and vanadyl sulfate, respectively, while the corresponding LD_{50} values for mice were 74.6 and 467.2 $mg \cdot kg^{-1}bw$, respectively. Rats and mice are generally equally sensitive to sodium metavanadate but mice seem to be more resistant to vanadyl sulfate than rats.

Paternain et al. (1990) examined the effects of vanadyl sulfate ($VOSO_4$), on pregnant Swiss mice. Maternal and fetal body weights were significantly reduced by 18 and 13% after 18 days of treatment at an average daily dose of 6.25 $mg\ V \cdot kg^{-1}bw$. The number of total implants, dead fetuses, late resorptions, sex ratio, and post-implantation losses were not significantly different between vanadium-treated mice and controls.

In a chronic study, Zychlinski et al. (1991) examined the effects of vanadium pentoxide (V_2O_5) on adult Wistar rats. A dose of 0.56 $mg\ V \cdot kg^{-1}bw$ was given once a month for 12 months to the test animals through intratracheal injection. A significant decrease in body weight was observed at 11 months while a significant increase in lung weight and a significant decrease in blood serum glucose level occurred at 12 months. These observations suggest that during the chronic exposure to vanadium pentoxide via the respiratory tract, the lung is the main target organ for its toxicity. It is possible that the pro-oxidant properties of vanadium, and especially its ability to initiate lipid peroxidation, are responsible for the inflammatory and early fibrotic changes in the lung, which led to the weight increase seen for this organ (Zychlinski et al. 1991).

Mravcova et al. (1993) investigated the immunotoxic effects of long term exposure to vanadium on rats and mice. Adult Wistar rats and mice were given vanadium pentoxide (V_2O_5) in deionized water at concentrations of 100 mg $V \cdot L^{-1}$ for rats and 6 mg $V \cdot L^{-1}$ for mice by gavage 5 days a week for 6 weeks. Significant enlargement in the size of spleens in both rats and mice was observed. As well, the number of peripheral blood leucocytes was significantly increased. A depression of phagocytosis was found in both animals but mice exhibited higher T and B cell activation than rats.

Nelson et al. (1962) and Romoser et al. (1961) studied the effects of vanadium on the body weight of young chicks. After 4 weeks, Nelson et al. reported that the addition of ammonium metavanadate (NH_4VO_3) to feed at a concentration of 47 mg $V \cdot kg^{-1}$ significantly reduced chick body weight by 10%, while Romoser et al. reported the similar results at a feed concentration of 47 mg $V \cdot kg^{-1}$ using calcium vanadyl [$Ca_3(VO_4)_2$]. All feed and water were consumed *ad libitum*. In a similar study, Berg (1963) reported reductions of 14, 21, and 28% in chick body weight after 4 weeks of treatment at concentrations of 10, 15, and 20 mg $V \cdot kg^{-1}$ food using ammonium metavanadate.

In a chronic study, Kubena and Phillips (1982) examined the effects of calcium orthovanadate ($CaVO_4$) on Leghorn hens. Hens were fed *ad libitum* diets containing calcium orthovanadate concentrations of 0, 12.5, 25, 50, or 100 mg $V \cdot kg^{-1}$ feed, for 5 months. Hens in groups fed 12.5, 25, or 50 mg $V \cdot kg^{-1}$ gained body weight throughout the experiment and did not differ from the controls. However, the average body weight of hens fed 100 mg $V \cdot kg^{-1}$ began to decline during the first month and declined rapidly during the second and third months. Mortality in the 100 mg $V \cdot kg^{-1}$ group was 11, 39, and 56% at the end of the third, fourth, and fifth months, respectively. A decline in overall egg production was observed in the group fed 50 and 100 mg $V \cdot kg^{-1}$.

In general, vanadium may be classified as a weak teratogen. However, the overall lack of dose-response relationships and the overall low incidence of anomalies from past studies indicate that further research is required to confirm the teratogenicity of vanadium (API 1985). No animal studies have been reported on the carcinogenic properties of vanadium or its compounds.

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 vanadium are based on the procedures described in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME, 1996).

All data selected for use in the following derivations have been screened for ecological relevance and are presented in Tables 3, 4, and 6. Plant toxicological studies that have been consulted but not used in guideline derivation are presented in Table 5. Studies were excluded from use because of one or more of the following reasons:

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

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 the SQG_{SC} is based on toxicological data for vascular plants and soil invertebrates. The toxicological data for plant and invertebrates selected according to CCME (1996) are presented in Table 4. 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:

$$TEC = NPER / UF$$

where,

TEC = threshold effects concentration ($mg \cdot kg^{-1}$ soil)
NPER = no potential effects range (25th percentile of effects and no effects data distribution) ($mg \cdot kg^{-1}$ soil)
UF = uncertainty factor (if needed); no uncertainty factor was applied.

Out of a total of 14 data points, the 25th percentile corresponds to the 4th datum point of 127 $mg \cdot kg^{-1}$ soil from the Kaplan et al. (1990) study on biomass of cabbage (*Brassica oleracea*).

Thus, TEC = 127 ≅ 130 $mg \cdot kg^{-1}$ soil

Nutrient and Energy Cycling Check

The nutrient and energy cycling check was calculated using the selected microbial processes data presented in Table 3. Nitrification and nitrogen fixation data are considered to be primary data, whereas nitrogen mineralisation, denitrification, and carbon cycling data are considered secondary data. LOEC data, as reported by the author are used directly while effective concentration (EC) data producing >15 and <40% effects in primary data (i.e., EC_{15} to EC_{40}) and >15 and <25% effects in secondary data (i.e., EC_{15} to EC_{25}) are interpreted as LOEC values. Insufficient primary data were

available for the calculation, so the primary and secondary data were combined and the check was carried out using a modified LOEC method whereby the geometric mean of available LOECs is calculated as the nutrient and energy cycling check.

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

$$NECC = (LOEC_1 \cdot LOEC_2 \cdot LOEC_3 \cdot \ldots \cdot LOEC_n)^{1/n}$$

where,
NECC = effects concentration low ($mg \cdot kg^{-1}$ soil)
LOEC = lowest observed effects concentration ($mg \cdot kg^{-1}$ soil)
n = number of available LOECs

Thus, NECC = $(255 \cdot 2.55 \cdot 255 \cdot 255 \cdot 2550 \cdot 2550)^{1/6}$
= 255 $mg \cdot kg^{-1}$ soil

Since the TEC (130 $mg \cdot kg^{-1}$ soil) is lower than the NECC (255 $mg \cdot kg^{-1}$ soil), the TEC is considered to be protective of microbial nutrient and energy cycling processes and is adopted directly as the SQG_{SC} for agricultural and residential/parkland land uses.

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

The soil quality guideline for soil and food 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 mammalian and avian toxicological data listed in Table 6. The minimum data requirements for deriving a soil quality guideline for ingestion are as follows:

- A minimum of three studies must be considered.
- At least two of these studies must be oral mammalian studies and one must be an oral avian study.

- A maximum of one laboratory rodent study may be used to fulfil the data requirements for mammalian species if needed.

No acceptable oral mammalian studies other than rodent studies were available. Thus, the minimum data requirements were not met and therefore no soil quality guidelines for soil and food ingestion will be set.

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 4. However, for commercial and industrial land uses only the effects data are used and uncertainty factors are not applied. There were sufficient toxicological data to use the preferred weight of evidence method for guideline derivation.

The effects concentration low (ECL) is calculated as:

$$ECL = ERL$$

where,
ECL = effects concentration low ($mg \cdot kg^{-1}$soil)
ERL = effects range low (25th percentile of effects data distribution) ($mg \cdot kg^{-1}$ soil)

Out of a total of 10 data points, the 25th percentile corresponds to the 3rd datum point of 134 $mg \cdot kg^{-1}$ soil from the Environment Canada (1995) study on seedling emergence by lettuce (*Lactuca sativa*).

Thus, ECL = 134 ≅ 130 $mg \cdot kg^{-1}$ soil

Nutrient and Energy Cycling Check

The nutrient and energy cycling check was calculated using the selected microbial processes data presented in Table 3. Nitrification and nitrogen fixation data are considered to be primary data, whereas nitrogen mineralisation, denitrification and carbon cycling data are considered secondary data. 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., EC_{15} to EC_{50}) and >15 and < 35% effects in secondary data (i.e., EC_{15} to EC_{35}) are interpreted as LOEC values. Insufficient primary data were available for the calculation, so the primary and secondary data were combined and the check was carried out using a modified LOEC method whereby the geometric mean of available LOECs is calculated as the nutrient and energy cycling check.

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

$$NECC = (LOEC_1 \cdot LOEC_2 \cdot LOEC_3 \cdot \ldots \cdot LOEC_n)^{1/n}$$

where,
NECC = effects concentration low ($mg \cdot kg^{-1}$ soil)
LOEC = lowest observed effects concentration ($mg \cdot kg^{-1}$ soil)
n = number of available LOECs

Thus, NECC $= (255 \cdot 2.55 \cdot 255 \cdot 255 \cdot 2550 \cdot 2550)^{1/6}$
$= 255 \text{ mg} \cdot \text{kg}^{-1}$ soil

Since the ECL (130 $\text{mg} \cdot \text{kg}^{-1}$ soil) is lower than the NECC (255 $\text{mg} \cdot \text{kg}^{-1}$ soil), the ECL is considered to be protective of microbial nutrient and energy cycling processes and is adopted directly as the SQG_{SC} for commercial and industrial land uses.

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 range of 4.3-8.2. 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 7.

Agricultural Land Use

The lower value 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 was derived, the SQG_{SC} will be used. Therefore, the final SQG_E is 130 $\text{mg} \cdot \text{kg}^{-1}$ soil.

Residential/Parkland Land Use

The SQG_{SC} of 130 $\text{mg} \cdot \text{kg}^{-1}$ soil is the final SQG_E for residential/parkland land use.

Commercial and Industrial Land Use

The SQG_{SC} of 130 $\text{mg} \cdot \text{kg}^{-1}$ soil is the final SQG_E for commercial and industrial land use.

6. DATA GAPS

Sufficient data exist on the toxicity of vanadium to soil ecosystem receptors to derive a soil quality guidelines for the three major uses of land, including Agricultural, Residential/Parkland, and Commercial and Industrial land uses. Additional data are required however, to refine our understanding of the fate and effects of vanadium in the environment. There is also a considerable lack of data on the effects of vanadium on terrestrial invertebrates and mammalian wildlife. Further research on these two animal groups would aid in the derivation of new soil quality guidelines for vanadium in the future.

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TABLES

Table 1. Physical and Chemical Properties of Vanadium and Its Common Salts

Chemical Form	Chemical Formula	CAS No.	Molecular Weight ($g \cdot mol^{-1}$)	Density (water = 1)	Melting Point (°C)	Boiling Point (°C)	Solubility ($g \cdot 100\ mL^{-1}$ cold water)
Vanadium	V	7440-62-2	50.9	5.96	1890	3380	insoluble
Vanadium pentoxide	V_2O_5	1314-34-7	181.9	3.36	690	1750	insoluble
Vanadium oxydichloride	$VOCl_2$	10213-09-9	137.9	2.88	NA	NA	decomposes
Vanadyl sulfate	$VOSO_4$	12439-96-2	163.0	NA	NA	NA	very soluble
Sodium metavanadate	$NaVO_3$	13718-26-8	121.9	NA	630	NA	very soluble
Sodium orthovanadate	Na_3VO_4	13721-39-6	183.9	NA	858	NA	soluble
Sodium pyrovanadate	$Na_4V_2O_7$	13517-26-5	305.9	NA	643	NA	soluble
Ammonium metavanadate	NH_4VO_3	7803-55-6	117.0	2.33	200	NA	insoluble

NA = not available
Source: CRC Handbook of Chemistry and Physics 1994.

Table 2. Existing Soil Criteria and Guidelines for Vanadium in Various Jurisdictions

Jurisdiction	Category	Criterion/ Guideline	Reference
Ontario	Surface soil and groundwater clean-up criteria in a potable groundwater situation		OMOE 1994
	Agricultural	200 $mg \cdot kg^{-1}$	
	Residential/Parkland	200 $mg \cdot kg^{-1}$	
	Industrial/Commercial	200 $mg \cdot kg^{-1}$	
	Groundwater (all land uses)	200 $\mu g \cdot L^{-1}$	
	Surface soil and groundwater clean-up criteria in a non-potable groundwater situation		
	Residential/Parkland	200 $mg \cdot kg^{-1}$	
	Industrial/Commercial	200 $mg \cdot kg^{-1}$	
	Groundwater (all land uses)	200 $\mu g \cdot L^{-1}$	
	Sub-surface soil clean-up criteria in a potable groundwater situation		
	Residential/Parkland	200 $mg \cdot kg^{-1}$	
	Industrial/Commercial	no value	
	Sub-surface soil clean-up criteria in a non-potable groundwater situation		
	Residential/Parkland	200 $mg \cdot kg^{-1}$	
	Industrial/Commercial	no value	
Alberta	Tier 1 Criteria for Soil Assessment and Remediation	100 $mg \cdot kg^{-1}$	Alberta Environmental Protection 1994
New Jersey	Interim soil-action level (for identification of contamination)	100 $mg \cdot kg^{-1}$	NJDEP 1991
Canada	Interim Remediation Criteria		CCME 1991
	Agricultural	200 $mg \cdot kg^{-1}$	
	Residential/Parkland	200 $mg \cdot kg^{-1}$	
	Commercial/Industrial	not available	

Table 3. Toxicity studies on Microbial Processes Selected for Use in Deriving Soil Quality Guidelines for Lead

Microbial Process (Length of Exposure)	Effect	Endpoint*	Concentration (mg V·kg^{-1})	Form of Vanadium	Soil pH	Test Substrate	Extraction Method	Reference
Nitrification (10 days)	62% reduction	EC†	255	$VOSO_4$	5.8	Silt 23%, clay 39%, sand 38%; OC 2.6%	Nominal	Liang and Tabatabai 1978
	38% reduction	EC†	255	$VOSO_4$	7.4	Silt 34%, clay 50%, sand 16%; OC 5.5%		
	12% reduction	EC†	255	$VOSO_4$	7.8	Silt 30%, clay 44%, sand 26%; OC 3.7%		
Nitrogen mineralisation (20 days)	8% reduction	EC†	255	$VOSO_4$	5.8	Silt 23%, clay 39%, sand 38%; OC 2.6%	Nominal	Liang and Tabatabai 1977
	14% reduction	EC†	255	$VOSO_4$	6.6	Silt 45%, clay 54%, sand 1%; OC 3%		
	14% reduction	EC†	255	$VOSO_4$	7.4	Silt 50%, clay 34%, sand 16%; OC 5.5%		
	11% reduction	EC†	255	$VOSO_4$	7.8	Silt 30%, clay 44%, sand 26%; OC 3.7%		
Nitrogen mineralisation (4 weeks)	7% reduction	EC†	400	$NaVO_3$	6.0	Sandy cambisol; clay 9%, silt 12%, sand 79%; OC 1.2%	Nominal	Wilke 1989
Respiration - CO_2 release (45 days)	5% increase No effect 40% reduction 40% reduction	EC -- EC EC	2.55 25.5 255 2550	$VOSO_4$	8.2	Sand 33%, silt 61%, clay 11%; OM 4.7%	Nominal	Lighthart et al. 1983
Respiration - CO_2 release (45 days)	18% reduction 10% reduction 25% reduction 38% reduction	EC EC EC EC	2.55 25.5 255 2550	$VOSO_4$	7.2	Sand 21%, silt 57%, clay 21%, OM 1.7%	Nominal	Lighthart et al. 1983
Respiration - CO_2 release (45 days)	8% reduction 7% reduction 20% reduction 19% reduction	EC EC EC EC	2.55 25.5 255 2550	$VOSO_4$	6.7	Sand 10%, silt 63%, clay 27%, OM 3.1%	Nominal	Lighthart et al. 1983
Respiration - CO_2 release (45 days)	10% increase 2% increase 4% reduction 20% reduction	EC EC EC EC	2.55 25.5 255 2550	$VOSO_4$	7.0	Sand 19%, silt 30%, clay 51%, OM 5.5%	Nominal	Lighthart et al. 1983

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

Table 4. Invertebrate and Plant Toxicity Studies Selected for Use in Deriving Soil Quality Guidelines for Vanadium.

Organism	Effect (Exposure period)	Endpoint*	Concentration (mg V·kg^{-1})	Form of Vanadium	Soil pH	Test Substrate	Extraction Method	Reference
Invertebrates								
Earthworm (*Eisenia fetida*)	Mortality (14 days)	NOEC LC_{25} LC_{50} LOEC (66% mortality)	210 290 370 410	V_2O_5	4.3	Artificial soil; sand 68%, silt 10%, clay 22%; OM 5.6%	HNO_3, H_2O_2, HCl w/ AAS	Environment Canada 1995
Plants								
Cabbage (*Brassica oleracea*)	Aboveground biomass (98 days)	NOEC LOEC (24% reduction)	60 80	$VOSO_4$	5.35	Sandy soil; sand 92%, silt 3%, clay 5%; OM 1.1%	Nominal	Kaplan et al. 1990a
Lettuce (*Lactuca sativa*)	Seedling emergence (5 days)	NOEC EC_{25} EC_{50} LOEC (29% reduction)	55 134 251 127	V_2O_5	4.3	Artificial soil; sand 68%, silt 10%, clay 22%; OM 5.6%	HNO_3, H_2O_2, HCl w/ AAS	Environment Canada 1995
Radish (*Raphanus sativa*)	Seedling emergence (3 days)	NOEC EC_{25} EC_{50} LOEC (33% reduction)	200 330 580 410	V_2O_5	4.3	Artificial soil; sand 68%, silt 10%, clay 22%; OM 5.6%	HNO_3, H_2O_2, HCl w/ AAS	Environment Canada 1995

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

Table 5. Additional Plant Toxicity Studies.

Organism	Effect (Exposure period)	Endpoint*	Concentration (mg V·L^{-1})	Form of Vanadium	pH	Test Substrate	Analytical Method	Reference
Radish (*Raphanus sativa*)	Root elongation (3 days)	NOEC EC_{25} EC_{50} LOEC (27% reduction)	12 15 13 38	V_2O_5	NR†	Culture solution	ICP	Environment Canada 1995
Lettuce (*Lactuca sativa*)	Root elongation (5 days)	NOEC EC_{25} EC_{50} LOEC (29% reduction)	3 4 4 8	V_2O_5	NR	Culture solution	ICP	Environment Canada 1995
Bush beans (*Phaseolus vulgaris*)	Dry leaf yield (14 days)	EC (8% increase) EC (10% decrease) EC (52% decrease)	0.117 1.17 11.7	NH_4VO_3	NR	Culture solution	Nominal	Wallace et al. 1977
	Dry stem yield (14 days)	No effect EC (4% increase) EC (27% decrease)	0.117 1.17 11.7					
	Dry root yield (14 days)	EC (9% increase) EC (41% decrease) EC (68% decrease)	0.117 1.17 11.7					
Soybean (*Glycine max*)	Biomass (33 days)	NOEC LOEC (38% reduction)	3 6	$VOSO_4$	5.5	Culture solution composed of half-strength Hoagland's solution	Nominal	Kaplan et al. 1990b
Cabbage (*Brassica oleracea*)	Radicle elongation (7 days)	NOEC LOEC (53% reduction)	2 3	$VOSO_4$	NR	Filter paper treated with 4 mL of 5 mmol $Ca(NO_3)_2$	Nominal	Kaplan et al. 1990a
Cabbage (*Brassica oleracea*)	Radicle elongation (3 days)	NOEC LOEC (42% reduction)	1 2.5	$VOSO_4$	NR	Filter paper treated with 0.01 M calcium nitrate as a background solution	Nominal	Carlson et al. 1991

Organism	Effect (Exposure period)	Endpoint*	Concentration (mg V·L^{-1})	Form of Vanadium	pH	Test Substrate	Analytical Method	Reference
Turnip (*Brassica rapa*)	Radicle elongation (3 days)	NOEC LOEC (49% reduction)	1 2.5	$VOSO_4$	NR	Filter paper treated with 0.01 M calcium nitrate as a background solution	Nominal	Carlson et al. 1991
Lettuce (*Lactuca sativa*)	Radicle elongation (3 days)	NOEC LOEC (27% reduction)	1 2.5	$VOSO_4$	NR	Filter paper treated with 0.01 M calcium nitrate as a background solution	Nominal	Carlson et al. 1991
Cabbage (*Brassica oleracea*)	Dry whole plant yield (134 days)	EC (9% decrease) EC (34% decrease) EC (86% decrease)	0.4 4 20	VCl_3	5	Culture solution	Nominal	Hara et al. 1976
	Dry inner leaf yield (134 days)	EC (20% decrease) EC (60% decrease)	0.4 4					
Corn (*Zea mays*)	Plant height (67 days)	EC (6% increase) EC (6% increase) EC (2% decrease) EC (22% decrease)	0.05 mg V·kg^{-1} 0.25 mg V·kg^{-1} 1.25 mg V·kg^{-1} 6.25 mg V·kg^{-1}	V	NR	Sand culture	Nominal	Singh, 1971
	Grain yield (67 days)	EC (13% increase) EC 13% increase) EC (9% decrease) EC (38% decrease)	0.05 mg V·kg^{-1} 0.25 mg V·kg^{-1} 1.25 mg V·kg^{-1} 6.25 mg·kg^{-1}					

*The EC endpoints represent the percentage adverse effect, compared to controls, as calculated by the CCME from the data presented by the author(s).
†NR = Not reported.

Table 6. Mammalian and Avian Oral Toxicity Studies Selected for Use in Deriving Soil Quality Guidelines for Vanadium.

Organism	Effect (Exposure period)	Endpoint*	Feed Concentration (mg V·kg^{-1})	Average Feed Intake (kg·day^{-1})	Average Body Weight (kg)	Average Daily Dose (mg V·kg^{-1}bw·day^{-1})	Form of Vanadium	Reference
Sprague-Dawley rats	Mortality§ (14 days)	LD_{50} LD_{50}	NR† NR	NR NR	0.25 0.03	98 448	$NaVO_3$ $VOSO_4$	Llobet and Domingo 1984
Swiss mouse	Mortality§ (14 days)	LD_{50} LD_{50}	NR "	NR "	0.25 0.03	74.6 467.2	$NaVO_3$ $VOSO_4$	Llobet and Domingo 1984
Swiss mouse	Maternal body weight (18 days)	LOEC (18% reduction)	NR	NR	0.03	6.25	$VOSO_4$	Paternain et al. 1990
Swiss mouse	Fetal body weight (18 days)	LOEC (13% reduction)	NR	NR	0.03	6.25	$VOSO_4$	Paternain et al. 1990
Chicken	Body weight (4 weeks)	EC (14% reduction) EC (21% reduction) EC (28% reduction)	10 15 20	0.023‡ 0.023‡ 0.023‡	0.601 0.601 0.601	0.38‡ 0.57‡ 0.77‡	NH_4VO_3	Berg 1963
Chicken	Body weight (4 weeks)	NOEC LOEC (10% reduction)	20 30	0.018‡ 0.018‡	0.47 0.47	0.77‡ 1.15‡	$Ca_3(VO_4)_2$	Romoser et al. 1961
Chicken	Body weight (4 weeks)	NOEC LOEC (10% reduction)	35 47	0.018‡ 0.018‡	0.47 0.47	1.34‡ 1.8‡	NH_4VO_3	Nelson et al. 1962

*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).
†NR = Not reported.
‡Calculated from standard equations for daily feed and water intake by livestock and wildlife (Warrington 1995, British Columbia Ministry of the Environment, Lands and Parks, pers. com.).
§Single-concentration study.

Table 7. Soil Quality Guidelines for Vanadium.

Guideline	Land Use		
	Agricultural ($mg\ V \cdot kg^{-1}$)	**Residential/ Parkland ($mg\ V \cdot kg^{-1}$)**	**Commercial/ Industrial ($mg\ V \cdot kg^{-1}$)**
TEC or ECL*			
20th percentile	80	80	NA†
25th percentile	130	130	130
30th percentile	130	130	130
35th percentile	NA	NA	251
Nutrient and Energy Cycling Check	255	255	255
SQC_{sc}	130	130	130
SQC_{I}	Insufficient data.	NA	NA
SQC_{E}	130	130	130
Ontario background levels‡	91	91	No value.
CCME Interim Criteria§	200	200	No value.

*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 and Industrial land use also corresponds to the 25th percentile of the effects data distribution. The other percentiles are presented for comparison purposes only.
†NA = not applicable
‡OMOE 1994
§CCME 1991

CANADIAN SOIL QUALITY GUIDELINES FOR VANADIUM: ENVIRONMENTAL

CANADIAN SOIL QUALITY
GUIDELINES FOR VANADIUM:
ENVIRONMENTAL