



# Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health

## VANADIUM 1997

This fact sheet provides soil quality guidelines for vanadium (V) in Canada for the protection of environmental health (Table 1). A supporting scientific document is also available (Environment Canada 1996).

### Background Information

Vanadium (CAS 7440-62-2) is a transition metal with an atomic number of 23 and an atomic weight of 50.94. It is a silvery-white ductile metal with two naturally occurring isotopes. Like other elements in the transition group, 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 nonmetal and can form both cationic and anionic salts, but the exact nature of many of its ions in aqueous solution is still unknown.

Vanadium (+2) and vanadium (+3) salts are strong reducing agents and are readily oxidized in air (API 1985). Vanadium (+4) and vanadium (+5) are usually found bonded to oxygen as a negatively charged polymeric oxyanion that tends to complex with polarizable ligands such as phosphorus and sulphur (WHO 1988). Vanadium (+5) is reduced to vanadium (+4) by relatively mild reducing agents. Nearly all complexes of vanadium (+4) are anionic and a few are nonelectrolytes. 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.

**Table 1. Soil quality guidelines for vanadium (mg·kg<sup>-1</sup>).**

	Land use			
	Agricultural	Residential/ parkland	Commercial	Industrial
<b>Guideline</b>	<b>130<sup>a</sup></b>	<b>130<sup>a</sup></b>	<b>130<sup>b</sup></b>	<b>130<sup>b</sup></b>
SQG <sub>HH</sub>	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>
Limiting pathway for SQG <sub>HH</sub>	ND	ND	ND	ND
Provisional SQG <sub>HH</sub>	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>
Limiting pathway for provisional SQG <sub>HH</sub>	ND	ND	ND	ND
SQG <sub>E</sub>	130	130	130	130
Limiting pathway for SQG <sub>E</sub>	Soil contact	Soil contact	Soil contact	Soil contact
Provisional SQG <sub>E</sub>	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>
Limiting pathway for provisional SQG <sub>E</sub>	ND	ND	ND	ND
Interim soil quality criterion (CCME 1991)	200	200	No value	No value

**Notes:** NC = not calculated; ND = not determined; SQG<sub>E</sub> = soil quality guideline for environmental health; SQG<sub>HH</sub> = soil quality guideline for human health.

<sup>a</sup>Data are sufficient and adequate to calculate an SQG<sub>E</sub>. It is less than the existing interim soil quality criterion (CCME 1991) for this land use. Therefore, the soil quality guideline supersedes the interim soil quality criterion for this land use.

<sup>b</sup>Data are sufficient and adequate to calculate only an SQG<sub>E</sub>. An interim soil quality criterion (CCME 1991) was not established for this land use, therefore, the SQG<sub>E</sub> becomes the soil quality guideline

<sup>c</sup>There is no SQG<sub>HH</sub> for this land use at this time.

<sup>d</sup>There is no provisional SQG<sub>HH</sub> for this land use at this time.

<sup>e</sup>Because data are sufficient and adequate to calculate an SQG<sub>E</sub> for this land use, a provisional SQG<sub>E</sub> is not calculated.

The guidelines in this fact sheet are for general guidance only. Site-specific conditions should be considered in the application of these values. The values may be applied differently in various jurisdictions. The reader should consult the appropriate jurisdiction before application of the values.

Vanadium has important industrial uses, mainly in ferrous metallurgy, where 75–85% 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 40–80% vanadium) or vanadium carbide (Zenz 1980). Vanadium is also a major alloying element in high-strength titanium alloys. Alloys of vanadium with nonferrous metals (e.g., aluminum, titanium, and copper) 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 sulphuric 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 (Energy, Mines and Resources Canada 1990). The remaining 5% is primarily used in the chemical industry as catalysts in the production of polymeric plastics, sulphuric and nitric acids, as a mordant in dyes and printing fabric inks, and in vanadium–gallium tape for use in superconductors (van Zinderen Bakker and Jaworski 1980).

Power and heat-producing plants using fossil fuels (petroleum, coal, and 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 (USEPA 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).

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 Yukon. Most of the approximately 20 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 (van Zinderen Bakker and Jaworski 1980).

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).

According to the Soil Metal Database of the Alberta Soil Protection Branch, natural mean concentrations in Canadian soils range from 38 to 42 mg·kg<sup>-1</sup>, with concentrations tending to increase with depth (G. Dinwoodie 1995, Alberta Soil Protection Branch, Edmonton, pers. com.). Minimum values are 10 mg·kg<sup>-1</sup> and maximum are 90 mg·kg<sup>-1</sup>.

Soil samples collected throughout Ontario from undisturbed old urban and rural parklands not impacted by local point sources of pollution were analyzed to determine average background vanadium concentrations. The 98th percentiles of the sample population analyzed were 71 mg·kg<sup>-1</sup> for old urban parkland and 77 mg·kg<sup>-1</sup> for rural parkland (OMEE 1993).

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

### Environmental Fate and Behaviour in 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.

Vanadium (+5) 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 (van Zinderen Bakker and Jaworski 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 ( $\text{VO}_2^+$ ) may be an important form of vanadium in many soils and may result from reduction of the metavanadate anion ( $\text{VO}_3^-$ ). 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 (e.g., orthovanadate anion,  $\text{VO}_4^{3-}$ ; metavanadate anion,  $\text{VO}_3^-$ ) are known to be mobile in soils and relatively more toxic to soil microbiota.

## **Behaviour and Effects in Biota**

### *Microbial Processes*

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). 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.

Liang and Tabatabai (1978) determined that  $255 \text{ mg V}\cdot\text{kg}^{-1}$  soil produced a 62% reduction in nitrification at a pH of 5.8. At pH 7.8,  $255 \text{ mg V}\cdot\text{kg}^{-1}$  soil resulted in a 12% reduction in nitrification.

Wilke (1989) also studied the effects of vanadium on nitrification and nitrogen mineralization. No inhibition of nitrification was observed at 100 and  $400 \text{ mg V}\cdot\text{kg}^{-1}$ . In fact, nitrification actually increased by 9 and 20%, respectively. Nitrogen mineralization was reduced by 7% at a concentration of  $400 \text{ mg}\cdot\text{kg}^{-1}$ .

The effects of vanadyl sulphate on soil respiration were examined by Lighthart et al. (1983) in a 45-d microcosm study involving four different soils. Respiration, measured in terms of  $\text{CO}_2$  release, was actually increased by 5 and 10% for two soils at the lowest vanadyl sulphate concentration of  $2.55 \text{ mg V}\cdot\text{kg}^{-1}$ . Reductions in respiration ranged between 7 and 40% for all four soils at the three other vanadyl sulphate concentrations (25.5, 255, and  $2550 \text{ mg V}\cdot\text{kg}^{-1}$ ).

### *Terrestrial Plants*

Vanadium has been recognized as an essential element for certain species of green algae (Arnon and Wessel 1953), but claims supporting its essentiality in higher plants are inconclusive (Welch and Huffman 1973; Morrell et al. 1986; Kabata-Pendias and Pendias 1992).

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).

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 ( $14.5 \text{ mg V}\cdot\text{kg}^{-1}$ ) 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 BCF of 0.1 for vanadium (Cannon 1963; van Zinderen Bakker and Jaworski 1980; WHO 1988).

Kaplan et al. (1990) conducted laboratory and greenhouse studies to evaluate the effects of vanadium on seed germination and radicle growth of cabbage (*Brassica oleracea*). The presence of vanadium had no negative effect on cabbage seed germination up to a treatment concentration of  $75 \text{ mg}\cdot\text{L}^{-1}$ . However, for radicle growth, a concentration of  $1 \text{ mg}\cdot\text{L}^{-1}$  was found to increase radicle length by 51.7%, while a concentration of  $3 \text{ mg}\cdot\text{L}^{-1}$  significantly reduced radicle elongation by 53%.

In the greenhouse portion of their study, Kaplan et al. (1990) found that vanadium tissue concentrations and toxicity to cabbage (*Brassica oleracea*) varied with soil type. In a sandy soil significant reduction of 24% in biomass occurred after 98 d at  $80 \text{ mg}\cdot\text{kg}^{-1}$ . In the case of loamy-sand soil, no significant decrease was found at  $100 \text{ mg V}\cdot\text{kg}^{-1}$ . Kaplan et al. (1990) attributed the higher toxicity in the sandy soil to an appreciably greater accumulation of vanadium by plants. 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.

The effects of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) on the seedling emergence of radishes (*Raphanus sativa*) and lettuce (*Lactuca sativa*) grown in an artificial soil were studied by Environment Canada (1995). The 3-d NOEC, LOEC,  $\text{EC}_{25}$ , and  $\text{EC}_{50}$  values for radish seedling emergence were

200, 410, 330, and 580 mg V·kg<sup>-1</sup> soil, respectively. The 5-d NOEC, LOEC, EC<sub>25</sub>, and EC<sub>50</sub> values for lettuce seedling emergence were 55, 127, 134, and 251 mg V·kg<sup>-1</sup>, respectively. The LOEC values corresponded to decreases in seedling emergence of 33% for radishes and 29% for lettuce.

### *Terrestrial Invertebrates*

Very little information exists on the metabolic processes of vanadium within terrestrial invertebrates.

Soil invertebrate toxicity data for vanadium, like toxicity data for soil microbes, is nearly nonexistent. In the only soil invertebrate toxicity study available for vanadium, Environment Canada reported the effects of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) on the earthworm *Eisenia foetida* in an artificial soil. The NOEC, LC<sub>25</sub>, LC<sub>50</sub>, and LOEC values were reported at concentrations of 210, 290, 370, and 410 mg V·kg<sup>-1</sup>, respectively (Environment Canada 1995).

### *Livestock and Wildlife*

Animals are susceptible to vanadium deficiency and overexposure. Berg (1963) demonstrated a 21% reduction in body weight in chickens fed 15 mg V·kg<sup>-1</sup> in feed. Puls (1988) reported that vanadium deficiency was not known to occur under practical farm conditions in cattle, but that 10–20 mg V·kg<sup>-1</sup> bw per day in the diet is toxic.

## **Guideline Derivation**

Canadian soil quality guidelines are derived for different land uses following the process outlined in CCME (1996a) using different receptors and exposure scenarios for each land use (Table 1). Detailed derivations for vanadium soil quality guidelines are provided in Environment Canada (1996).

### *Soil Quality Guidelines for Environmental Health*

Environmental soil quality guidelines (SQG<sub>ES</sub>) are based on soil contact data from toxicity studies on plants and invertebrates. In the case of agricultural land use, soil and food ingestion toxicity data for mammalian and avian species are included. To provide a broader scope of protection, a nutrient and energy cycling check is calculated. For industrial land use, an off-site migration check is also calculated.

For all land uses, the preliminary soil contact value (also called threshold effects concentration [TEC] or effects concentration low [ECL], depending on the land use) is

compared to the nutrient and energy cycling check. If the nutrient and energy cycling check is lower, the geometric mean of the preliminary soil contact value and nutrient energy cycling check is calculated as the soil quality guideline for soil contact. If the nutrient and energy cycling check is greater than the preliminary soil contact value, the preliminary soil contact value becomes the soil quality guideline for soil contact.

For agricultural land use, the lower of the soil quality guideline for soil contact and the soil and food ingestion guideline is recommended as the SQG<sub>E</sub>.

For residential/parkland and commercial land uses, the soil quality guideline for soil contact is recommended as the SQG<sub>E</sub>.

For industrial land use, the lower of the soil quality guideline for soil contact and the off-site migration check is recommended as the SQG<sub>E</sub>.

For all land uses, the SQG<sub>E</sub> for vanadium is based on the soil contact guidelines.

### *Soil Quality Guidelines for Human Health*

There are no human health guidelines or check values available at this time (Table 2).

## **Soil Quality Guidelines for Vanadium**

The soil quality guidelines for vanadium are the lower of the SQG<sub>ES</sub> and the interim soil quality criteria (CCME 1991).

For all land uses, the SQG<sub>E</sub> is less than the existing interim soil quality criterion. Therefore the soil quality guidelines supersede the interim soil quality criteria for all land uses.

CCME (1996b) provides guidance on potential modifications to the final recommended soil quality guideline when setting site-specific objectives.

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Table 2. Soil quality guidelines and check values for vanadium ( $\text{mg}\cdot\text{kg}^{-1}$ ).

Guideline	Land use			
	Agricultural	Residential/ parkland	Commercial	Industrial
	130 <sup>a</sup>	130 <sup>a</sup>	130 <sup>b</sup>	130 <sup>b</sup>
Human health guidelines/check values <sup>b</sup>				
SQG <sub>HH</sub>	NC	NC	NC	NC
Soil ingestion guideline	NC	NC	NC	NC
Inhalation of indoor air check	NC	NC	NC	NC
Off-site migration check	—	—	—	NC
Groundwater check (drinking water)	NC	NC	NC	NC
Produce, meat, and milk check	NC	NC	—	—
Provisional SQG <sub>HH</sub>	NC	NC	NC	NC
Limiting pathway for provisional SQG <sub>HH</sub>	ND	ND	ND	ND
Environmental health guidelines/check values				
SQG <sub>E</sub>	130 <sup>d</sup>	130 <sup>d</sup>	130 <sup>d</sup>	130 <sup>d</sup>
Soil contact guideline	130	130	130	130
Soil and food ingestion guideline	NC <sup>e</sup>	—	—	—
Nutrient and energy cycling check	255	255	255	255
Off-site migration check	—	—	—	830
Groundwater check (aquatic life)	NC <sup>f</sup>	NC <sup>f</sup>	NC <sup>f</sup>	NC <sup>f</sup>
Provisional SQG <sub>E</sub>	NC <sup>g</sup>	NC <sup>g</sup>	NC <sup>g</sup>	NC <sup>g</sup>
Limiting pathway for provisional SQG <sub>E</sub>	ND	ND	ND	ND
Interim soil quality criterion (CCME 1991)	200	200	No value	No value

**Notes:** NC = not calculated; ND = not determined; SQG<sub>E</sub> = soil quality guideline for environmental health; SQG<sub>HH</sub> = soil quality guideline for human health. The dash indicates guideline/check value that is not part of the exposure scenario for this land use and therefore is not calculated.

<sup>a</sup>Data are sufficient and adequate to calculate an SQG<sub>E</sub>. It is less than the existing interim soil quality criterion for this land use. Therefore the soil quality guideline supersedes the interim soil quality criterion for this land use.

<sup>b</sup>Data are sufficient and adequate to calculate only an SQG<sub>E</sub>. An interim soil quality criterion (CCME 1991) was not established for this land use, therefore, the SQG<sub>E</sub> becomes the soil quality guideline.

<sup>c</sup>There are no values for the human health at this time.

<sup>d</sup>Based on the soil contact guideline.

<sup>e</sup>There are insufficient/inadequate data to calculate this guideline for this land use.

<sup>f</sup>The environmental groundwater check (aquatic life) applies to organic compounds and is not calculated for vanadium. Concerns about vanadium should be addressed on a site-specific basis.

<sup>g</sup>Because data are sufficient and adequate to calculate an SQG<sub>E</sub> for this land use, a provisional SQG<sub>E</sub> is not calculated.

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This fact sheet was originally published in the working document entitled “Recommended Canadian Soil Quality Guidelines” (Canadian Council of Ministers of the Environment, March 1997, Winnipeg). A revised and edited version is presented here.

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Canadian Council of Ministers of the Environment. 1999. Canadian soil quality guidelines for the protection of environmental and human health: Vanadium (1997). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

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