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***Canadian Environmental Protection Act, 1999***  
**Federal Environmental Quality Guidelines**

***Vanadium***

**Environment and Climate Change Canada**

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### Introduction

Federal Environmental Quality Guidelines (FEQGs) provide benchmarks for the quality of the ambient environment. They are based solely on the toxicological effects or hazard of specific substances or groups of substances. FEQGs serve three functions: first they can be an aid to prevent pollution by providing targets for acceptable environmental quality; second they can assist in evaluating the significance of concentrations of chemical substances currently found in the environment (monitoring of water, sediment and biological tissue); and third, they can serve as performance measures of the success of risk management activities. The use of FEQGs is voluntary unless prescribed in permits or other regulatory tools. Thus FEQGs, which apply to the ambient environment are not effluent limits or “never-to-be-exceeded” values but may be used to derive effluent limits. The development of FEQGs is the responsibility of the Federal Minister of Environment and Climate Change under the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999). The intent is to develop FEQGs as an adjunct to risk assessment/risk management of priority chemicals identified in the Chemicals Management Plan (CMP) or other federal initiatives. This factsheet describes the Federal Water Quality Guidelines (FWQGs) for the protection of aquatic life from adverse effects of vanadium (Table 1). This vanadium factsheet was based largely on the Screening Assessment Report (SAR) for vanadium oxide published under Canada’s Chemicals Management Plan. However, the FEQG derived here (see Table 1) is for the vanadium ion/moiety and can be applied to vanadium from all sources or forms. It is based on data and information identified up to June 2010 (GC 2010). No FEQGs have been developed for the biological tissue compartments and sediment at this time.

Table 1. Federal Water Quality Guidelines for Vanadium.

Aquatic Life	Guideline Value (µg/L)*
Freshwater	120
Marine	5
*Total vanadium	

### Substance Identity

Vanadium is not found in metallic form in nature, but occurs as vanadates of other metals (e.g., copper, zinc, lead, uranium, iron, manganese). Vanadium exists in oxidation states of 1<sup>-</sup> to 5<sup>+</sup> and vanadium oxide (CAS Number 1314-62-1) is a common name for vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), the most common commercial form. South Africa contains the world’s largest deposit and produces nearly half of the global demand for high purity (≥ 99.5%) vanadium oxide (Perron 2001; IARC 2006). In Canada, Lac Doré, Québec has the world’s second largest deposit of titaniferous magnetite containing the mid-average grade (0.55%) of V<sub>2</sub>O<sub>5</sub>; however, it is not mined in Canada (Apella Resources 2009).

The Government of Canada (GC 2010) has assessed the potential ecological effects of vanadium oxide or more specifically, vanadium pentoxide, including its persistence and bioaccumulative potential. Based on this assessment, GC (2010) has concluded that vanadium oxide is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends. It is concluded that vanadium oxide may be entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health. Vanadium oxide meets the criteria for persistence but not the criteria for bioaccumulation potential as set out in the *Persistence and Bioaccumulation Regulations* (GC 2000).

### Uses

In 2004, worldwide production of vanadium oxide was approximately 86 200 tonnes (Woolery 2005). The main uses of vanadium oxide are as a formulation component in the production of metal alloys (mainly ferrovanadium) and as a catalyst in the production of sulphuric acid (Perron 2001). Other uses include as a catalyst in the production of maleic anhydride for the manufacture of polyester and alkyd resins (Haber 2009), an electrolyte in vanadium redox batteries (Magyar 2003), and as a pigment in the production of ceramics and glass (Motolese et al. 1993; Moskalyk and Alfantazi 2003; Vanitec 2009). In Canada, between 1 and 10 000 tonnes of vanadium oxide was used in 2006 (EC 2009). The majority of the vanadium oxide (92%) was used in the production of ferrovanadium alloys for the manufacture of hardened steel. Vanadium oxide was also widely used as a catalyst to manufacture sulphuric acid, for catalytic cracking applications, and for the selective catalytic reduction of NO<sub>x</sub> and sulphur emissions from power plants (EC 2009). Minor uses of vanadium oxide in Canada include its use as an oxidizing agent and for corrosion protection.

Vanadium pentoxide is not currently mined in Canada, and its release into the Canadian environment is mainly atmospheric emissions from various industrial activities, in particular as an incidental release as a by-product of the combustion of fossil fuels such as oil and coal (GC 2010). The Athabasca oil sands contain higher concentrations of vanadium than most oils and therefore there is also a potential for vanadium to leach from the coke into the environment (Jeansen-Fontaine et al. 2014). According to the most recent data from the National Pollutant Release Inventory (2012), releases of 48 tonnes of vanadium and its compounds to air, 1.2 tonne to water and 36 tonnes to land were reported from 106 Canadian facilities. The highest releases were from petroleum refineries and power generation plants, mostly as by-products such as fly ash, soot and bottom ash from the combustion of fossil fuels and coal.

### Fate, Behaviour and Partitioning in the Environment

Vanadium can be found in various states in ambient air, surface water, sediments and soils. Being a non-gaseous element with a negligible vapour pressure, vanadium is emitted to air principally in the oxide form, as a component of fine particulate matter (GC 2010). In water, its concentrations are influenced by several factors, such as chemical weathering of silicate rocks (Shiller and Mao 2000), adsorption/desorption between dissolved and particulate phases (Harita et al. 2005), redox reactions (Wang and Wilhelmy 2009), aqueous concentrations of ferric oxyhydroxides and manganese oxides (Harita et al. 2005), levels of H<sub>2</sub>S (Wanty and Goldhaber 1992) and organic matter (Szalay and Szilágyi 1967). Vanadium is expected to be more mobile under oxidizing than under reducing conditions (Garrett 2005), likely in part reflecting the difference in mobilities of the oxidized anionic and reduced cationic forms. Oxidized forms are generally less mobile under acidic conditions than under neutral to alkaline conditions (Reimann and deCaritat 1998).

Dissolved cationic V(IV) (see list of acronyms and abbreviations) species VO<sup>2+</sup> (vanadyl) and VO(OH)<sup>+</sup> are in low concentrations in oxic waters, (Harita et al. 2005), but could form at the water/sediment interface where reducing and anoxic conditions are more likely to be encountered. Since these cations are more readily adsorbed onto particles or complexed with organic matter, they are more likely to be deposited into sediments (Wang and Wilhelmy 2009). Available log partition coefficients for suspended sediment-water range from 3.15 to 5.47, and the sediment-water log partition coefficient is 2.28 (GC 2010). The behaviour of vanadium in soils is also linked to chemical and physical properties of both the soil and the vanadium-containing compound entering this compartment. The log soil-water partition coefficients obtained for Canadian soils range from 2.58 to 5.08 (GC 2010).

In experiments carried out in rivers affected by metal mining in Quebec, vanadium was accumulated by the transplanted organisms (*Hyalella azteca*) in a dose-dependent manner (Couillard et al. 2008). The results supported the idea that total dissolved vanadium is bioavailable and is a good predictor of bioaccumulated vanadium for organisms that take up most of this metal from the water column (Borgmann et al. 2007). Overall, the bioaccumulation potential of vanadium in natural ecosystems is considered low based on (i) moderate to low BCFs and BAFs (5 to 333); (ii) BSAF-sediment and a BSAF-soil are well below 1; and (iii) the absence of biomagnification of vanadium in natural food webs in field studies (GC 2010).

### Ambient Concentrations

Similar to other metals, monitoring data for vanadium are only reported as total vanadium and thus it is not possible to identify the form of vanadium measured or whether it originated from the pentoxide compound. Vanadium has been measured in Canadian river and lake water (0.001 to 16.1 µg/L) in sediments (5 to 730 mg/kg) and in soils (4 to 358 mg/kg), and the site-specific concentrations are presented in GC (2010).

### Mode of Action

Vanadium is considered an essential trace element (Markert 1994, Nielsen 1991) and has been identified in enzyme systems in bacteria, algae and marine invertebrates (IPCS 2001). Vanadium anion (vanadate) is bioavailable, entering living cells via anion-exchange systems dedicated to phosphate in a phenomenon called ionic mimicry (GC 2010). Vanadate or vanadyl ions are known to be potent inhibitors of certain phosphatases such as ATPase, phosphotransferase, nuclease and kinase. Inhibition of Na-K-ATPase activity has been shown in gills of fish and crab (Bell and Sargent 1979; Holleland and Towle 1990).

### Aquatic Toxicity

Chronic aquatic toxicity data identified in the SAR (GC 2010) and considered acceptable for developing freshwater Federal Water Quality Guideline (FWQG) are presented in Table 2. All data from reliable studies conducted with soluble vanadium compounds were considered in deriving the FWQGs, even though different vanadium species may exist in solution following the dissolution of these compounds. It is well documented that the toxicity of metals depends on the pH and ionic strength of the external media (DiToro et al. 2001). As a result, toxicity data may be normalized for the effects of pH, ionic strength and dissolved organic carbon depending on assessment needs. However, given the available data, this was not done for vanadium as no equation could be derived to account for these toxicity modifying factors. Also, there is evidence that toxicity modifying factors may be less important for the vanadate anions (expected to be the dominant species in oxic waters) than for some cationic metals, given results of the speciation modeling and field studies of speciation of dissolved forms of vanadium (GC 2010).

Table 2. Chronic toxicity endpoints for freshwater aquatic life used in the derivation of the Federal Water Quality Guideline for vanadium.

Species	Group	Endpoint	Concentration (µg V/L)*	Reference
American Flagfish ( <i>Jordanella floridae</i> )	■	34-d MATC (growth)	140	Holdway and Sprague (1979)
Algae ( <i>Chlorella pyrenoidosa</i> )	▲	7-d MATC (growth)	320	Lee et al. (1979)
Algae ( <i>Scenedesmus obliquus</i> )	▲	7-d MATC (growth)	320	Lee et al. (1979)
Fathead minnow ( <i>Pimephales promelas</i> )	■	28-d LOEC (growth)	480	Kimball (1978)
Brook trout ( <i>Salvelinus fontinalis</i> )	■	30-d EC <sub>10</sub> (survival)	610**	Ernst and Garside (1987)
Water Flea ( <i>Daphnia magna</i> )	●	21-d EC <sub>10</sub> (reproduction)	1000	Van Leeuwen et al. (1987)
Algae ( <i>Navicula pelliculosa</i> )	▲	7-d NOEC (growth)	1000	Lee et al. (1979)
Algae ( <i>Scenedesmus quadricauda</i> )	▲	12-d EC <sub>50</sub> (growth)	2230	Fragašová et al. (1999)

**Legend:** ■ = Fish; ● = Invertebrate; ▲ = Plant

\*total vanadium

\*\*calculated from data provided in the original paper

The acceptable endpoints for developing freshwater FWQG range from no- or low-level to medium-level chronic effects with values ranging from 140 to 2230 µg V/L. The sensitivity to vanadium overlapped among taxa. The most sensitive species was American flagfish (*Jordanella floridae*) and the least sensitive species was green algae (*Scenedesmus quadricauda*).

The acute and chronic toxicity data for marine organisms ranged from 50 to 6500 µg V/L and from 250 to 8000 µg V/L, respectively (GC 2010). The lowest acute endpoint (50 µg V/L) was a 48-h LOEC for development in oyster larvae (*Crassostrea gigas*), while the lowest chronic endpoint (250 µg V/L) was a 8-day LOEC for mortality in brine shrimp (*Artemia salina*).

### **Federal Water Quality Guideline Derivation**

Federal Water Quality Guidelines (FWQGs) are preferably developed using CCME (2007) protocols. In the case of vanadium, there was a need to develop a predicted no effect concentration (PNEC) for the ecological screening assessment and the FWQG, although there was insufficient chronic toxicity data to meet the minimum data requirements for a CCME Type A or Type B guideline<sup>1</sup> when the SAR was developed. The FWQG and the PNEC used in the ecological screening assessment both define levels at which no harm is expected to the environment. The FWQGs developed here identify benchmarks for aquatic ecosystems that are intended to protect all forms of aquatic life for indefinite exposure periods.

#### **Freshwater**

In the freshwater compartment, experimental chronic toxicity studies were critically reviewed and the acceptable toxicity data (Table 2) for three fish, one invertebrate and four algal species were used for generating a species sensitivity distribution (SSD) curve (Figure 1). Each species for which appropriate toxicity data were available was ranked according to sensitivity, and its position on the SSD was determined. Several cumulative distribution functions were fit to the data using regression methods and the best model was selected based on consideration of goodness-of-fit. The logistic model provided the best fit of the models tested and the 5<sup>th</sup> percentile of the SSD plot was 120 µg/L, with lower and upper confidence limits of 85 and 170 µg/L, respectively.

The 5<sup>th</sup> percentile calculated from the SSD (120 µg/L) is selected as the PNEC and the FWQG for chronic toxicity to freshwater organisms. The guideline represents the concentration below which one would expect either no, or only a low likelihood of adverse effects on aquatic life. In addition to this guideline, two other concentration ranges are provided for use in risk management (Figure 1). At concentrations between >5<sup>th</sup> and 50<sup>th</sup> percentile of the SSD (>120-550 µg/L), there is a moderate likelihood of adverse effects to aquatic life. Concentrations greater than the 50<sup>th</sup> percentile (>550 µg/L) have a higher likelihood of causing adverse effects. Risk managers may find these additional concentration ranges useful in defining short-term or interim risk management objectives for a phased risk management plan. The moderate to higher concentration ranges may also be used in setting less protective interim targets for waters that are already highly degraded or where there are socio-economic considerations that preclude the ability to meet the FWQG.

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<sup>1</sup> CCME (2007) provides two approaches for developing water quality guidelines, depending on the availability and quality of the available data. The preferred approach is to use the statistical distribution of all acceptable data to develop Type A guidelines. The second approach is based on extrapolation from the lowest acceptable toxicity endpoint to develop Type B guidelines. For further detail on the minimum data requirements for CCME guidelines see CCME (2007).

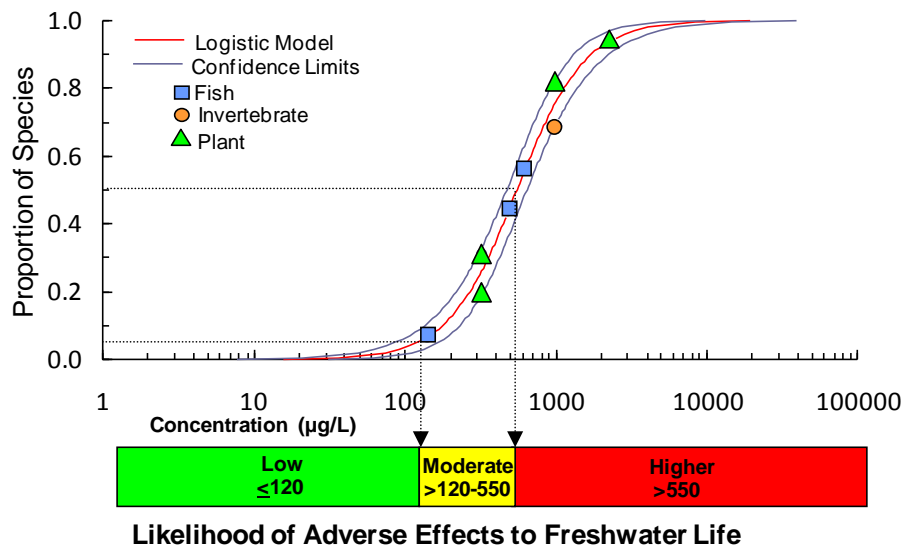


Figure 1. Species sensitivity distribution (SSD) for the chronic toxicity of vanadium and relative likelihood of adverse effects for freshwater aquatic life. Chronic toxicity endpoints are plotted for fish (■), invertebrates (●) and plant (▲).

**Marine Water**

The critical review of chronic toxicity data identified the lowest acute endpoint of 50 µg/L (48-h LOEC for development) in oyster larvae and the lowest chronic endpoint of 250 µg/L (8-d LOEC for mortality) for brine shrimp (GC 2010). Although chronic exposure to vanadium is expected in the environment, the lowest acute value of 50 µg/L for the oyster larvae was selected as a critical toxicity value (CTV) and an application factor of 10 was applied to obtain the PNEC and FWQG for marine aquatic life of 5 µg/L (Figure 2). The FWQG for marine life is lower than for freshwater life given the limited marine toxicity dataset. There is higher uncertainty in the toxic threshold and thus a conservative approach was used. Should additional marine data become available, the FWQG for marine life may be revised.

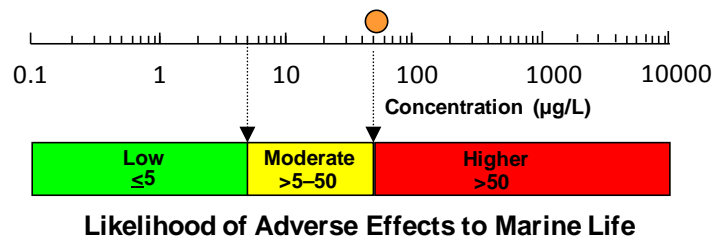


Figure 2. Relative likelihood of adverse effects of vanadium to marine aquatic life. The FWQG (5 µg/L) and CTV (50 µg/L) are marked by arrows.

Three concentration ranges were also identified to represent low, moderate and higher likelihoods of adverse effects to marine aquatic life to aid in the risk management of vanadium (Figure 2). At concentrations of vanadium equal to or less than the marine FWQG (≤5 µg/L), there is low likelihood of adverse effects to aquatic life. At concentrations greater than the marine FWQG and the CTV of 50 µg/L, there is a moderate likelihood of adverse effects to aquatic life. Concentrations of vanadium that are greater than 50 µg/L have a higher likelihood of causing adverse effects to marine aquatic life. Similar to freshwater, risk managers may find these additional concentration ranges useful in risk management

planning.

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### List of Acronyms and Abbreviations

- BAF - bioaccumulation factor
- BCF - bioconcentration factor
- BSAF - biota-sediment accumulation factor
- CCME - Canadian Council of Ministers of Environment
- CMP - Chemicals Management Plan
- CTV - critical toxicity value
- EC - effect concentration
- FEQG - Federal Environmental Quality Guideline
- FWQG - Federal Water Quality Guideline
- LOEC - lowest observable effect concentration
- MATC - maximum acceptable toxicant concentration and is equal to the geometric mean of the NOEL and LOEL for a test species
- NOEC - no observable effect concentration
- PNEC - predicted no-effect concentration
- SSD - species sensitivity distribution
- V(IV) - vanadium in valence state 4
- V(V) - vanadium in valence state 5