Environment Canada Environnement Canada

Canadian Environmental Protection Act, 1999
Federal Environmental Quality Guidelines

Hydrazine

Environment Canada

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Introduction

Federal Environmental Quality Guidelines (FEQGs) provide benchmarks for the quality of the ambient environment. Where the FEQG is met there is low likelihood of adverse effects on the protected use (e.g., aquatic life or the wildlife that may consume them). They are based on the toxicological effects or hazards of specific substances or groups of substances and do not take into account analytical capability or socio-economic factors. 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 under the *Canadian Environmental Protection Act, 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 for the protection of aquatic life from the adverse effects of hydrazine. No FEQGs have been developed for the sediment, soil or biological tissue compartments at this time.

Substance Identity

Hydrazine (N_2H_4) is a clear, fuming, basic, corrosive liquid with an ammonia-like odour. The major source of hydrazine in the environment is attributed to human activities (ATSDR 1997; Choudhary and Hansen 1998; CERI 2007). Government of Canada (2011) considered hydrazine (CAS RN 302-01-2), the form commonly found in the market, and hydrazine hydrate (CAS RN 7803-57-8 and CAS RN 10217-52-4) as being the same substance for the purposes of risk assessment. Government of Canada (2011) has assessed the potential ecological effects of hydrazine (as per section 64 of CEPA 1999), including its persistence and bioaccumulation potential. Based on this assessment, Government of Canada (2011) has concluded that hydrazine is 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 and on human life or health. Hydrazine does not meet the criteria for persistence or bioaccumulation potential as set out in the *Persistence and Bioaccumulation Regulations* (Government of Canada 2000). This factsheet was developed in consideration of the above assessment which was based on data and information identified up to October 2010. The FEQGs for hydrazine are shown in Figures 1 and 2.

Uses

The major use of hydrazine in Canada in 2006 was as an oxygen scavenger/corrosion inhibitor in the boiler water used mainly at power generating plants, accounting for 87% of reported uses (Environment Canada 2009). In Canada and elsewhere, hydrazine may be used in the production of pesticides and other agricultural chemicals, pharmaceuticals, and in the manufacture of chemical blowing agents (Government of Canada 2011). In 2006, 10 000–100 000 kg of hydrazine were used for industrial purposes in Canada (Environment Canada 2009). Most of these imports were as aqueous solutions of hydrazine, the form of the product commonly found in the market (Environment Canada 2009). Historically, hydrazine was primarily used as a rocket propellant. For example, in the United States 73% of hydrazine consumed in 1964 for this purpose had declined to 5% by 1982.

Fate, behaviour and partitioning in the environment

Hydrazine is miscible in water. It has a high vapour pressure (2 100 Pa),a low log K_{ow} (~-2), and a low Henry's Law Constant (~0.06 Pa·m^3/mol). Hydrazine may volatilize from dry soil surfaces based upon its vapour pressure. However, volatilization from moist soil surfaces is probably an unimportant fate process based upon the compound's estimated Henry's Law constant. If released into air, hydrazine will likely be degraded by $OH^{\cdot}$ radicals and ozone, with estimated half-lives of less than 2 days (Harris et al. 1979; Tuazon et al. 1981; Atkinson and Carter 1984). Level III-fugacity modelling conducted with the Equilibrium Criterion model (EQC 2003) indicates that if released to water, hydrazine will remain almost entirely in that compartment (Government of Canada 2011). In water, hydrazine degradation depends on
certain water quality parameters, such as hardness and organic matter content, with degradation ranging from 7 to ~100% after 4 days indifferent types of water and sources (Slonim and Gisclard 1976). It is readily degraded by micro-organisms in water and soil (Ou and Street 1987a,b). Considering the low bioconcentration factor (BCF) for guppy (288 L/kg; Slonim and Gisclard 1976) and low log K_{ow}, hydrazine does not meet the bioaccumulation criterion as set out in the *Persistence and Bioaccumulation Regulations* (Government of Canada 2000).

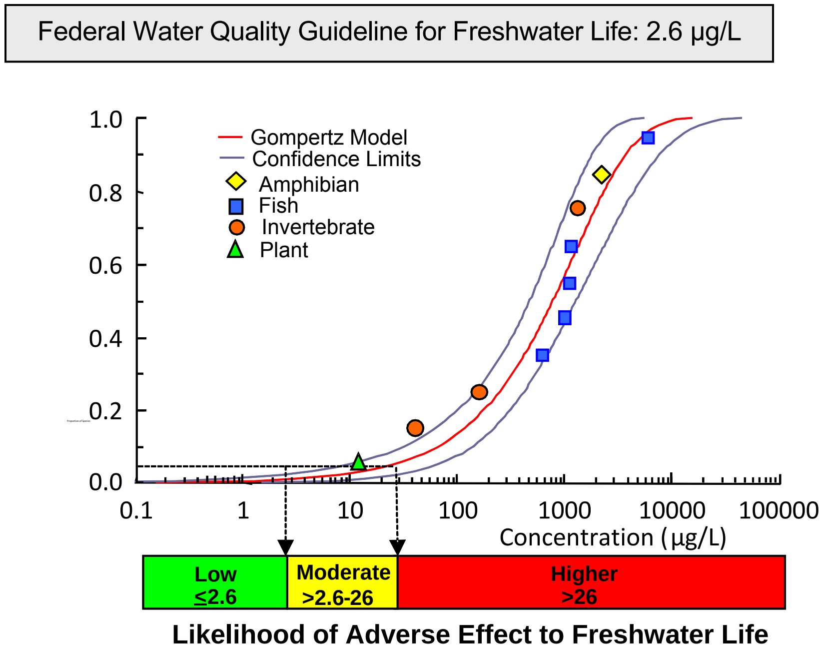

Figure 1. Species sensitivity distribution (SSD) for the acute toxicity of hydrazine on freshwater species. The use of an application factor of 10 to HC_5 (26 µg/L) value gave the FWQG of 2.6 µg/L. Associated effect levels to freshwater aquatic life are also shown.

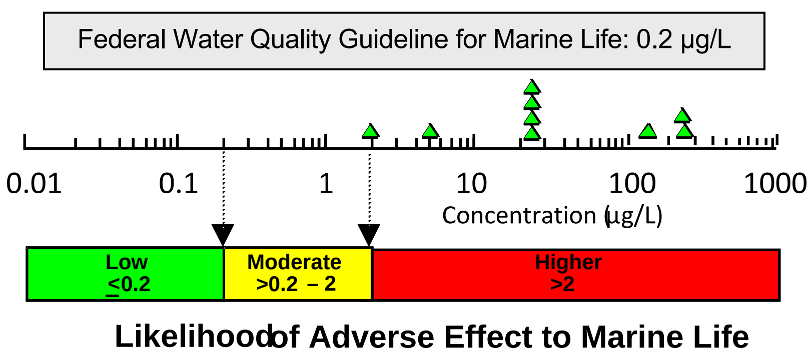

Figure 2. Relative risks of adverse effects of hydrazine to marine aquatic life. The FWQG for marine life is set equal to the Probable No-effect Concentration (PNEC) (Government of Canada 2011).

Ambient concentrations

Limited data exist on concentrations of hydrazine in Canada. Hydrazine concentrations were measured in the main effluents (i.e., cooling water discharge) of nuclear power plants located in Ontario (Environment Canada 2009). These effluent concentrations ranged in yearly average from 0.002 mg/L for the Bruce power plant to 0.01 mg/L for

Pickering A power plant (Government of Canada 2011). Hydrazine has been reported to occur naturally in the algae, *Azotobacter agile*, as a result of nitrogen fixation (ATSDR 1997) and in tobacco plants (Liu et al. 1974; IPCS 1991; Choudhary and Hansen 1998).

Mode of action

The mode of action of hydrazine is not fully understood and several models have been proposed. Hydrazine may bind directly to a free amino group in key cellular molecules; reactive intermediates may inhibit oxygen consumption; and genetoxicity may occur through direct interaction with genetic material (Government of Canada 2011).

Aquatic toxicity

Information regarding hydrazine toxicity on freshwater organisms was gathered from sixteen toxicity papers ranging in date of publication from 1976 to 1986; no toxicity data published after this date was found. Of the sixteen publications, only one reported chronic data (Scherfig et al. 1977). All studies were further evaluated, and only those meeting the CCME (2007) reliability standards are presented in Table 1. The green algae *Pseudokirchneriella subcapitata* was the most sensitive species in the data set with a 72h EC_{50} value of 12 µg/L. All algae data should be considered chronic (CCME 2007). However due to the lack of algal data, and the lack of consensus among regulatory regimes regarding the criteria for defining long/short-term algal testing (ECHA 2008), the value from Scherfig et al. (1977) was considered with other acute data (Government of Canada 2011). Data for fish (96h LC_{50}) range from 610 to 5980 µg/L, the lowest value being for common guppy (*Lebistes rericulatus*) and the highest for fathead minnow (*Pimephales promelas*). Of the three reported values for invertebrates, the amphipod *Hyalella azteca* was the most sensitive having a 48h LC_{50} of 40 µg/L. The least sensitive invertebrate was an isopod (Asillidae) with a 72h LC_{50} of 1300 µg/L. The 96h LC_{50} for larvae of two species of salamander (*Ambystoma maculatum* and *A. opacum*) was 2120 µg/L.

The hydrazine toxicity data available for marine organisms were mainly for the early life stages of phaeophytes (brown seaweed) from the Californian coast (James et al. 1987). However, these data were considered relevant since these species are also found in Pacific waters along the Canadian coast (Government of Canada 2011). These toxicity data are also relevant to species of the Atlantic coast of Canada because many of the genera tested (e.g., *Laminaria*) are part of the indigenous seaweeds found in the Maritimes (South 1981). Lowest hydrazine concentrations leading to significant inhibition of growth (24h LOECs) were calculated for seven algal species; the lowest effect concentration was a 96h LOEC of 2 µg/L.

Table 1. Toxicity endpoints for freshwater aquatic life exposed to hydrazine used in the derivation of the Federal Water Quality Guideline.

Species	Group	Endpoint	Concentration (µg/L)	Reference
Algae *(Pseudokirchneriella subcapitata)*	△	EC_{50} (72h) (growth)	12	Scherfig et al. 1977
Amphipod (*Hyalella azteca*)	⬢	LC_{50} (48h)	40	Fisher et al. 1980a
Daphnid (*Daphnia pulex*)	⬢	EC_{50} (48h) (immobilization)	160	Velte 1984
Common Guppy (*Lebistes reticulatus*)	■	LC_{50} (96h)	610	Slonim 1977
Channel Catfish (*Ictalurus punctatus*)	■	LC_{50} (96h)	1000	Fisher et al. 1980a
Golden Shiner (*Notemigonus crysoleucas*)	■	LC_{50} (96h)	1120	Fisher et al. 1980a
Bluegill (*Lepomis macrochirus*)	■	LC_{50} (96h)	1170*	**
Isopod (Asillidae)	⬢	LC_{50} (72h)	1300	Fisher et al. 1980a
Salamander larvae (*Ambystoma maculatum* and *A. opacum*)	◇	LC_{50} (96h)	2120	Slonim 1986
Fathead Minnow (*Pimephales promelas*)	■	LC_{50} (96h)	5980	Velte 1984

Notes: ◇ = Amphibian; ■ = Fish; ⬢ = Invertebrate; △ = Plant.
* Geometric mean; ** Hunt et al. (1981), Fisher et al. (1978), Fisher et al. (1980b)

Federal Water Quality Guideline Derivation

Freshwater Life

Federal Environmental Quality Guidelines (FEQGs) and the predicted no effect concentrations (PNEC) 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. In the water compartment, experimental toxicity studies for hydrazine were critically reviewed and the acceptable toxicity data (Table 1) for five fish, three invertebrate, one amphibian and one algal species were used for generating an acute 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.

Preferably FEQGs are developed using CCME protocols (CCME 2007). However, in the case of hydrazine, there was a need to develop a PNEC for the ecological screening assessment and a FWQG, although there was insufficient chronic toxicity data and the strict CCME (2007) data requirements could not be met. The PNEC and FWQG (which are identical) were based on the best available data and a combination of the CCME (2007) (SSD method) and the internal guidance for conducting screening risk assessments. 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 Gompertz model provided the best fit for these data and the 5th percentile of the SSD plot is 26 µg/L, with the lower and upper confidence limits of 10 and 67 µg/L, respectively (Figure 1). This 5th percentile of the SSD (i.e., HC_5) was selected as the acute critical toxicity value (CTV) (Government of Canada 2011). In the absence of a chronic SSD, an application factor of 10 was applied to the acute CTV of 26 µg/L. Whereas CCME 2007 would use an application factor of 20 on the lowest data value, the factor of 10 was deemed sufficient since the whole dataset, not simply the lowest value, was considered. The resulting value of 2.6 µg/L is the PNEC which was developed collaboratively with and is identical to the FWQG (Figure 1) which fully protects all aquatic species listed in Table 1.

The PNEC and FWQG represent the concentration below which one would expect either no, or only a low likelihood of adverse effects on freshwater aquatic life. In addition to the FWQG, two additional concentration ranges are provided for use in risk management. At concentrations between the FWQG value and the 5th percentile of the SSD (>2.6 - 26 µg/L), there is a moderate likelihood of adverse effects to aquatic life. Concentrations greater than the 5th percentile (>26 µg/L) of acute SSD 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 range 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 federal water quality guideline.

Marine Water

Separate guidelines for marine and fresh water systems are considered useful and appropriate and were developed since i) aquatic toxicological data are available for both ecosystems, ii) both ecosystems were the focus of the screening risk assessment and iii) hydrazine is known to be released into and has been measured in both marine and fresh water ecosystems. The predicted no effect concentration (PNEC) of 0.2 µg/L (Government of Canada 2011) was adopted as the marine FWQG for hydrazine. The guideline is based on the CTV of 2 µg/L (96-h LOEC) for a brown algal species. An application factor of 10 was used because of the poor data set. With the FWQG for marine water equal to the PNEC, three categories were identified to represent slight, moderate and high relative risks of adverse effects to marine life to aid in the risk management of hydrazine (Figure 2). At concentrations equal to or less than the marine FWQG (≤0.2 µg/L), there is slight relative risk of adverse effects to aquatic life. At concentration greater than the marine FWQG but lower than or equal to the CTV of 2 µg/L, there is moderate relative risk of adverse effects to aquatic life. Concentrations that are greater than 2 µg/L have a high relative risk of causing adverse effects to marine life. Similar to freshwaters, risk managers may find these additional concentration ranges useful in risk management plans. That the FWQG for marine life is lower than the FWQG for freshwater life is a reflection of the limited marine dataset; invertebrates and fish data are lacking. Therefore, 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.

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List of Acronyms

BCF - bioconcentration 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
K_{OW} – octanol: water partition coefficient
LC_{50} – median lethal concentration
LOEC – lowest observable effect concentration
PNEC – predicted no effect concentration
SAR – screening assessment report
SSD – species sensitivity distribution