

Canadian Environmental Protection Act, 1999 Federal Environmental Quality Guidelines Hexabromocyclododecane (HBCD)

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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 effect 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-beexceeded" 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 FEOGs 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 FEQGs for water, sediment and mammalian wildlife diet to protect aquatic life and mammalian consumers of aquatic life from adverse effects of hexabromocyclododecane (HBCD) (Table 1). This HBCD factsheet was based largely on the screening assessment report published under Canada's Chemical Management Plan. It is based on data and information identified up to July 2010 (GC 2011).

Table 1. Federal Environmental Quality Guidelines for Hexabromocyclododecane HBCD.

Water (µg/L)	Sediment* (mg/kg dw)	Mammalian Wildlife Diet** (mg/kg food ww)	
0.56	1.6	40	

^{*}Normalized to 1% organic carbon

Substance Identity

HBCD ($C_{12}H_{18}Br_6$) is an anthropogenic cyclo aliphatic bromide that is produced by the bromination of cyclododecatriene (Mack 2004). HBCD is a white to off-white powder at room temperature of molecular weight 641.7 g/mol (CCOHS 1999). The commercial mixture of HBCD consists of three stereoisomers alpha (α ; CAS No. 134237-50-6), beta (β ; CAS No. 134237-51-7) and gamma (γ ; CAS No. 134237-52-8) in the proportion of 8-9%, 6% and 80-85%, respectively (ACCBFRIP 2005). The Screening Assessment Report (SAR), GC (2011) concluded that HBCD is entering or may enter 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. HBCD meets the criteria for persistence and bioaccumulation potential as set out in the *Persistence and Bioaccumulation Regulations* (GC 2000). As a result, HBCD was added to the List of Toxic Substances on Schedule 1 of CEPA on November 12, 2011.

Uses

HBCD is not manufactured in Canada. However, between 100 000 to 1000 000 kg of the substance were imported in 2000 (GC 2011). The substance is added to various plastic and polystyrene products as flame retardants for manufacturing thermal insulation material and products. HBCD is used primarily as a flame retardant in expanded and extruded polystyrene foams to manufacture thermal insulation materials for use in the residential and industrial sectors (GC 2011). Common end products have included furniture, seating

^{**}The mammalian wildlife diet guideline is intended to protect mammals that consume aquatic biota. It is the concentration of a TBBPA in aquatic biota, expressed on whole body, wet weight basis that could be eaten by terrestrial or semi-aquatic wildlife.

dw = dry weight; ww = wet weight

upholstery in vehicles, draperies and wall coverings (FRCA 1998). The substance may also be added to high-impact polystyrene used in electrical and electronic equipment, such as audio video equipment (BSEF 2003). HBCD is an "additive" flame retardant that is physically combined with, rather than chemically reacted with, the host polymer material. Therefore there is a potential for HBCD to migrate out of the polymer matrix into the environment during the use and disposal of products containing the substance (US NRC 2000).

Fate, Behaviour and Partitioning in the Environment

Given the low vapour pressure of HBCD (6.27×10^{-5} Pa at 21° C), Henry's Law constant (0.14 to 68.8 Pa m³/mol), and solubility (3.4×10^{-3} mg/L at 25° C) but high partition coefficients (log $K_{ow} = 5.62$ to 5.81; log $K_{oc} = 5.10$), HBCD released to the environment is not expected to partition into air and/or remain in water, however, it moves to sediment or soil compartments (GC 2011). Modelling data suggest that when released into water, 17% and 83% of HBCD partition to water and sediment, respectively (EQC 2003).

HBCD is persistent in the environment and because of the lack of hydrolyzable functional groups, hydrolysis is not a significant degradation pathway (Harris 1990; ACC 2002). Over a 28-day period, only 1% of HBCD was biodegraded under laboratory environment (MITI 1992). Similarly, the aquatic and soil half-lives were reported to range from 182 days to 5 years (ACC 2002). The rate of degradation of HBCD in sediment cores ranged from years to decades (Remberger et al. 2004; Minh et al. 2007; Kohler et al. 2008; Tanabe 2008). In contrast, rapid biodegradation of HBCD through step-wise debromination has been observed in a sewage treatment plant sludge digester, with a half-life of ~0.6 days (Gerecke et al. 2006).

HBCD is bioaccumulative. A bioconcentration factor (BCF) of 18100 is reported for fathead minnow and BCFs for rainbow trout ranged between 4650 and 12866 (Veith et al. 1979). Tomy et al. (2004) observed a strong correlation between HBCD biota tissue concentration and trophic level in Lake Ontario pelagic food web, with the lipid normalized biomagnification factors (BMFs) of greater than 1 for most feeding relationships. BMFs of 9.2, 4.3 and 7.2 were found for α -, β - and γ -HBCD, respectively, between rainbow trout and the diet (Law et al. 2006a,b). Typically in fish bodies, α -HBCD predominates (65-70%) followed by β -HBCD (14-20%) and γ -HBCD (9-15%) in relative abundance. Inter-conversion of these stereoisomers within some fishes has also been documented (CMABFRIP 2001).

Ambient Concentrations

The environmental presence of HBCD is ubiquitous. Total HBCD ranging from <0.075 to 3.7 ng/g dry weight (dw) was detected in Detroit River sediments on the Canadian side (Marvin et al. 2004). Law et al. (2006a) reported 0.011 ng/L of α -HBCD in surface water of the southern basin of Lake Winnipeg in 2004. In the Great Lakes Basin, up to 35 ng/L of HBCD was found in snow (Backus et al. 2005). The total mean HBCD levels in fish from Lake Winnipeg in 2000-2002, expressed as lipid weight (lw), ranged from 3 ng/g in whitefish, 8 ng/g in white sucker, 12 ng/g in walleye and 65 ng/g in burbot (Law et al. 2006a). In Lake Ontario, mean total level of 40 and 92 ng/g lw was found in walleye and whitefish, respectively (Tomy et al. 2004), and 4.5 ng/g wet weight (ww) in trout (Davis et al. 2006). In the Canadian Arctic, 2.1 ng/g lw of total HBCD was detected in ivory gull on Seymour Island in 2004 (Braune et al. 2007) and in an Arctic marine food web total HBCD concentrations ranged from 0.6 pg/g lw in cod to 3.9 ng/g lw in narwhal in the Eastern Arctic (Tomy et al. 2008).

Mode of Action

The mode of action for HBCD is not fully understood. As a neutral organic substance HBCD is expected to exhibit effects through nonpolar narcosis (GC 2011). Sublethal exposures of HBCD may affect the thyroid and liver systems of fish (Ronisz et al. 2004; Palace et al. 2008, 2010) and mammals (Legler 2008). Embryo toxicity studies have shown HBCD effects on oxidative stress and cell apoptosis in fish (Deng et al. 2009) and hepatic gene expression in bird embryos (Crump et al. 2010).

Federal Environmental Quality Guidelines Derivation

Federal Water Quality Guideline

Federal Water Quality Guidelines (FWQGs) are preferably developed using CCME (2007) protocols. In the case of HBCD, there was a need to develop a predicted no effect concentration (PNEC) for the ecological screening assessment and the FWQG, although there was insufficient acceptable chronic toxicity data to meet the minimum data requirements for CCME Type A or Type B guidelines ¹. The FWQG and the PNEC both define levels at which no harm is expected to the environment. The FWQG developed herein identifies benchmarks for aquatic ecosystems that are intended to protect all forms of aquatic life for indefinite exposure periods. The FWQG applies to both freshwater and marine waters unless it can be demonstrated that the toxicity differs significantly between these two environments (e.g., due to ionization).

Chronic aquatic toxicity data identified in the SAR (GC 2011) and considered acceptable for developing FWQG are presented in Table 2. Aqueous HBCD can significantly reduce the growth of the zooplankton *Daphnia magna* within 21 days at a concentration of 5.6 µg/L (CMABFRIP 1998) and decrease the population density, biomass, and growth rates of alga (*Skeletonema costatum* and *Thalassiosira pseudomona*) by 50% within 72 hours at 9.3 to 370 µg/L (Walsh et al. 1987).

Table 2. Chronic aquatic toxicity for HBCD (Source: GC 2011).

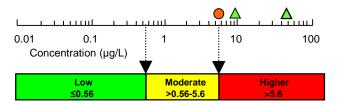
Species	Group	Endpoint	Concentration (µg/L)	Reference
Water Flea (Daphnia magna)	•	21-d LOEC (growth)	5.6	CMABFRIP (1998)
Marine Algae Skeletonema costatum	_	3-d EC50 (growth)	9.3	Walsh et al. (1987)
Marine Algae (Thalassiosira pseudonana)		3-d EC50 (growth)	50	Walsh et al. (1987)

Legend: \bigcirc = Invertebrate; \triangle = Plant

Legena. — invertebrate, — - 1 iant

The PNEC from the SAR and the FWQG are based on the same critical toxicity value (CTV) of 5.6 μ g/L for *Daphnia magna* and an application factor (AF) of 10 to account for inter- and intra-species variations and laboratory-to-field extrapolation. 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 greater than the FWQG of 0.56 μ g/L to the CTV of 5.6 μ g/L, there is a moderate likelihood of adverse effects to aquatic life. Concentrations that are greater than 5.6 μ g/L have a higher likelihood of causing adverse effects to aquatic life. 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 high 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 federal water quality guideline.

¹ 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).



Likelihood of Adverse Effects to Aquatic Life

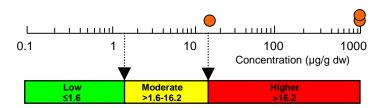
Figure 1. Relative likelihood of adverse effects of HBCD to aquatic life. The FWQG $(0.56 \,\mu\text{g/L})$ and CTV $(5.6 \,\mu\text{g/L})$ are marked by arrows.

Federal Sediment Quality Guideline

The Federal Sediment Quality Guideline (FSeQG) is intended to protect sediment dwelling animals as well as pelagic animals which bioaccumulate HBCD from sediments (Table 1). The FSeQG applies to indefinite exposure periods to freshwater and marine sediments, and specifies the concentration of total HBCD found in bulk sediment (dry weight) not expected to result in adverse effects. It may not be appropriate to evaluate the impacts of HBCD in sediments to plants.

Sediment toxicity tests for HBCD for freshwater oligochaete, *Lubriculus variegates*, gave the 28-d NOEC and LOEC values of 32.5 and 29.3 mg/kg dw, respectively (Oetken et al 2001). ACCBFRIP (2003a,b) tested this species as well as amphipod, *Hyalella azteca* and chironomid, *Chironomus riparius*, and found no dose-response effects up to concentrations of 1000 mg/kg dw of sediment.

As in the SAR (GC 2011), the 28-d LOEC of 29.25 mg/g dw (1.8% organic carbon) for freshwater worm *Lumbriculus variegatus* (Oetken et al. 2001) was selected as the CTV to derive the FSeQG. The CTV was adjusted to 1% organic carbon in sediment (16 mg/kg dw) and an AF of 10 was applied. The resulting value of 1.6 mg/kg dw is the FSeQG. In addition to the FSeQG value, three concentration ranges were identified to represent low, moderate and higher relative risks of adverse effects to aquatic life to aid in the risk management of HBCD (Figure 2). At concentrations equal to or less than the FSeQG (1.6 mg/kg dw), there is low likelihood of adverse effects to aquatic life. At concentrations greater than the FSeQG and the CTV of 16 mg/kg dw, there is a moderate likelihood of adverse effects to aquatic life. At concentrations that are greater than 16 mg/kg dw have a higher likelihood of causing adverse effects to aquatic life. Similar to water, risk managers may find these additional concentration ranges useful in risk management planning. Also, 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 federal sediment quality guideline.



Likelihood of Adverse Effects to Aquatic Life

Figure 2. Relative likelihood of adverse effects of HBCD to benthic organisms in aquatic sediments. The FSeQG (1.6 mg/kg dw at 1% OC) and CTV (16.2 mg/kg dw at 1% OC) are marked by arrows.

Federal Wildlife Dietary Guideline

The Federal Wildlife Dietary Guideline (FWiDG) is intended to protect non-human mammalian consumers of aquatic biota. This is a benchmark concentration of a substance in aquatic biota (whole body, wetweight) that is consumed by terrestrial and semi-aquatic wildlife. The FWiDG for mammals may not be appropriate to extrapolate the impacts of HBCD to other terrestrial consumers (e.g., birds or reptiles).

The FWiDG is based on the PNEC for terrestrial organisms for HBCD as developed by the GC (2011). The PNEC was based on a two-generation reproductive toxicity LOAEL in rats of 101.6 mg/kg bw/day (Ema et al. 2008). Interspecies scaling was applied to extrapolate the LOAEL as a tolerable daily intake (TDI) in rats to a concentration of food in mink, *Mustela vison*, a wildlife species. Assuming that all exposure to the substance is via food and that the substance is completely bioavailable for uptake by the organism, the calculation used the typical adult body weight (bw; 0.6 kg) and daily food ingestion rate (DFI; 0.143 kg ww/d) of a female mink to estimate a CTV in mink based on exposure through food (CCME 1998). That is, CTV_{food} = (CTV_{TDI in rats} x bw_{mink}) / FI_{mink} = (101 mg/kg bw per day x 0.6 kg bw) ÷ 0.143 kg ww/d = 423 mg HBCD kg ww food). An allometric scaling factor of 0.94 (Sample and Arenal 1999) was then applied to the CTV value in order to account for observed higher sensitivities in larger animals (i.e., mink) when compared with smaller ones (i.e., rat). The final CTV, incorporating both interspecies and allometric scaling, is therefore 398 mg/kg food ww. An AF of 10 was applied to account for extrapolation from lab to field conditions and the final FWiDG (and PNEC) was determined to be 40 mg/kg food ww.

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List of Acronyms and Abbreviations

- AF application factor
- BCF bioconcentration factor
- BFR brominated flame retardant
- BMF biomagnification factor
- CAS Chemical Abstracts Service
- CMP- Chemicals Management Plan
- CTV critical toxicity value
- dw dry weight
- FEOG Federal Environment Quality Guideline
- FFTG -Federal Fish Tissue Guideline
- FI: bw food intake-to-body weight ratio
- FSeQG Federal Sediment Quality Guideline
- FWQG Federal Water Quality Guideline
- FWiDG Federal Wildlife Diet Guideline
- HBCD hexabromocyclododecane
- K_{oc} organic carbon-water partitioning coefficient
- K_{ow} octanol-water partitioning coefficient
- LOEC lowest observed effect concentration
- LOAEL lowest observed adverse effect level
- lw lipid weight
- NOEC no observed effect concentration
- PNEC probable no effect concentration
- SAR Screening Assessment Report
- TDI tolerable daily intake
- ww wet weight