



Phenols and phenolic substances are aromatic hydroxy compounds classified as monohydric (e.g., phenol, cresols [methylphenols], xylenols [dimethylphenols]), dihydric (e.g., catechols [*o*-dihydroxybenzenes], resorcinols [*m*-dihydroxybenzenes]) or polyhydric (with three or more hydroxy groups), depending on the number of hydroxyl groups attached to the aromatic benzene ring (McNeely et al. 1979). The chemical formula for phenol (parent structure) is C_6H_5OH , and its CAS number is 108-95-2. Mono- and dihydric phenols have not been produced in Canada since 1992, although imports for 1995 and 1996 totaled 0.76 and 1.03×10^5 t, respectively, with 98% in the form of pure phenol (Environment Canada 1997). Phenols are a major by-product of the pulp and paper, mineral (nonmetallic), chemical, steel and metal, and petroleum industries (Environment Canada 1997). Phenols are used as disinfectants, biocides, preservatives, dyes, pesticides, and medical and industrial organic chemicals (CIS 1984). In Canada, approximately 84% of phenols are used in the production of phenolic resins (Environment Canada 1997).

Phenols may occur naturally in aquatic environments from the decomposition of aquatic vegetation (Dobbins et al. 1987). The major anthropogenic sources are industrial effluents and domestic sewage. In 1996, 414 t of phenol were released into the Canadian environment, with 58.5 t being discharged into water, 76% of which was from the pulp, paper, and wood industry (Environment Canada 1997). Phenolic wastes may contain cyanide, aldehydes, ketones, alcohols, organic acids, and gases (e.g., as ammonia and carbon dioxide) (Alabaster and Lloyd 1982).

Phenolic resins, which are used as a binding material in insulation materials, chipboard, paints, and casting sand foundries, are the major source of phenol emissions (WHO 1994). These materials contain 2 to >50% phenol, and the emissions are approximately proportional to the concentration of free phenol present as a monomer (Bollig and Decker 1980). Phenols are also released through automobile exhaust, fireplaces, cigarette smoke, and gases from incinerators (Groenen 1978; Verschueren 1983; Den Boeft et al. 1984; Health Canada 1994). While these do not release directly into water, transfer to water systems

may occur, as $1.3\text{--}15 \mu\text{g}\cdot\text{L}^{-1}$ has been found in precipitation (Levsen et al. 1991).

The concentration of total phenol is monitored more often than monohydric or dihydric phenol (NAQUADAT 1985). Most natural sources release only trace amounts of phenolic substances to water. Phenol concentrations in surface waters are generally $<2 \mu\text{g}\cdot\text{L}^{-1}$ (Environment Canada 1998a). Phenols levels ranging from $<0.1 \mu\text{g}\cdot\text{kg}^{-1}$ (detection limit) to $200 \text{mg}\cdot\text{kg}^{-1}$ in sediment samples have also been reported (Paul and Laliberté 1987; Laliberté 1990).

Monohydric phenols such as phenol, *o*-, *m*- and *p*-cresol and xylenols (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5- xyleneol) and dihydric phenols such as the derivatives of catechol, resorcinol, and quinol (hydroquinone) all have relatively low vapour pressures ($0.0053\text{--}0.67 \text{kPa}$) and high water solubilities ($24\text{--}840 \text{g}\cdot\text{L}^{-1}$) (USEPA 1979; Verschueren 1983; Merck Index 1983).

Most of the information concerning the aquatic fate of mono- and dihydric phenols refers to the compound phenol. Using a Level III fugacity model, it was shown that when phenol is released to water, >99% partitions to water (Mackay and AEL 1996). Photooxidation, oxidation, and microbial degradation are expected to be the major fate processes of phenols in the aquatic environment. Phenol is not expected to dissociate in the environment at $\text{pH} < 9$ based on its high pK_a (10.02), (Herington and Kynaston 1957). Howard (1989) suggests that phenol may exist in a partially dissociated state in water. Coordination with dissolved or suspended di- and trivalent metal cations can markedly increase ionization, leading to enhanced solubility (USEPA 1979).

Table 1. Water quality guidelines for mono- and dihydric phenols for the protection of aquatic life (Environment Canada 1998a).

Aquatic life	Guideline value ($\mu\text{g}\cdot\text{L}^{-1}$)
Freshwater	4.0
Marine	NRG*

*No recommended guideline.

Sorption appears to be a relatively minor process. Phenol, like other monohydric phenols, has a low log K_{ow} of 1.46 and is not expected to sorb to organic-rich sediments (USEPA 1980; MacKay and AEL 1996). Phenol is reported to readily desorb from clay surfaces and is ineffective as a flocculant for clays and soils (Chang and Anderson 1968; Saltzman and Yariv 1975).

In the presence of coordination or charge-transfer complexes, phenol may photolyze with the possible production of hydroquinone (quinol) (Perelshtein and Kaplan 1968; Kinney and Ivanuski 1969). *o*-Cresol may be degraded by visible light in the presence of a photosensitizer (Moussavi 1979). In addition, quinol may be photolyzed by ultraviolet light (Visser et al. 1977). The oxidative half-life of phenol decreased from 26 d at pH 7 to 12 d at pH 9. *o*-Cresol was very resistant, with a half-life of 462 d at pH 9. Catechol has an oxidation half-life of 17–19 d over the pH range of pH 7–9, whereas the oxidation half-life of quinol is <1 h at pH 9 but 5 d at pH 7. Resorcinol has a half-life for autooxidation of 67 d at pH 9 (Moussavi 1979).

As these compounds are relatively water soluble and have low vapour pressures, volatilization is not expected to be significant. If any phenol is volatilized it would probably be rapidly photooxidized in the atmosphere (USEPA 1979). The half-life of phenol due to volatilization is 3.2 months (USEPA 1990). The mean half-life of phenols in water is 55 h.

A major biotic process for the removal of phenol from the water column is microbial degradation. Laboratory studies have demonstrated phenol to be the sole carbon source for a number of isolated and adapted microorganisms (USEPA 1979). In natural waters, phenol (initial concentration of 0.1 mg·L⁻¹) was removed at a rate of 0.03 mg·L⁻¹ per hour in an in vitro investigation of the degrading capacity of bacteria in river water. By comparison, <1 mg·L⁻¹ per hour of phenol was removed by sterilized samples (Visser et al. 1977). Aquatic organisms other than bacteria are capable of degrading phenol. Goldfish (*Carassius auratus*), for example, converted phenol to phenol sulphate and rapidly eliminated it (Kobayashi et al. 1976). Phenol is also rapidly eliminated, with a half-life of approximately 1 d for dimethylphenol as a result of depuration by bluegills (*Lepomis macrochirus*) (Barrows et al. 1980). Other mono- and dihydric phenols are readily degraded by activated sludge and by soil microflora with a half-life of <1–6 d (Alexander and Lustigman 1966; Bunch and Chamber 1967; Bridié 1969). Complete biodegradation of

phenol has been reported to occur within 70 h (Ananyeva et al. 1992).

Bioaccumulation is not expected to be significant because of the low log K_{ow} s (0.5–2.5) of phenols (Verschuere 1983; Merck Index 1983; Mackay and AEL 1996). Howard (1989) concluded that phenol is not expected to significantly bioconcentrate in aquatic organisms.

Water Quality Guideline Derivation

The Canadian water quality guideline for monohydric and dihydric phenols for the protection of freshwater life was developed based on the CCME protocol (CCME 1991). For more information, see Environment Canada 1998a and 1998b.

Freshwater Life

The toxicity of phenolic compounds varies widely with the organism tested, dissolved oxygen content, and water temperature (Alabaster and Lloyd 1982). The LC₅₀ values for fathead minnows (*Pimephales promelas*) exposed to phenol range from 8.3 mg·L⁻¹ (48 h) (Phipps et al. 1981) to 68 mg·L⁻¹ (96 h) (DeGraeve et al. 1980). For 2,4-dimethylphenol, the 96-h LC₅₀ was 16.8 mg·L⁻¹ (Phipps et al. 1981). For rainbow trout (*Oncorhynchus mykiss*) the 48-h LC₅₀ values range from 5.2 to 16.6 mg·L⁻¹ (Sastry and Devi 1987; Tisler and Zagorc-Koncan 1995).

The chronic toxicity of phenol to rainbow trout (*O. mykiss*) includes 27-d LC₅₀s of 0.07 and 0.12 mg·L⁻¹ (Birge et al. 1979; Millemann et al. 1984). For the embryo-larval stage of the leopard frog (*Rana pipiens*), the 9- and 5-d LC₅₀s were 0.04 and 0.05 mg·L⁻¹, respectively (Birge et al. 1980).

Water-soluble fractions of a coal-liquid dispersion in which 95% of the organic carbon was present as phenols significantly reduced growth of larval *P. promelas* at 0.25 mg·L⁻¹ phenolic compounds (as determined by dye photometry) and spawning at 0.62 mg·L⁻¹ (Dauble et al. 1983). Thus, the toxicity of phenolic wastes containing other compounds appears to be greater than the toxicity of pure phenol (Holcombe et al. 1982).

Fish toxicity studies comparing the various mono- and dihydric phenols report differential toxicity (Devi and Sastry 1987). The descending order of toxicity is phenol, *p*-cresol, *o*-cresol, *m*-cresol, and catechol.

Acute toxicities for *Daphnia magna* include a 96-h LC₅₀ of 2.12 mg·L⁻¹ 2,4-dimethylphenol (USEPA 1978) and a 96-h LC₅₀ of 4 mg·L⁻¹ phenol (Ewell et al. 1986). Other 48-h values for phenol include a LOEL (reproduction) of 0.19 mg·L⁻¹ for the rotifer *Brachinous calyciflorus* (Snell and Moffat 1992) and an LC₅₀ of 3.1 mg·L⁻¹ for *Ceriodaphnia dubia* (Oris et al. 1991).

The 96-h EC₅₀s for the alga *Selenastrum capricornutum* are between 46.5 and 84.5 mg·L⁻¹ (Thellen et al. 1989; Hickey et al. 1991). Toxicity to *Lemnaceae* in 7-d growth tests ranged from 7.5 to 312 mg·L⁻¹ (Cowgill et al. 1991; Barber et al. 1995).

Wastewaters containing mono- and dihydric phenols have different proportions of phenolic compounds. The toxicity of phenols is assumed to be additive because they have a similar mode of action (Devi and Sastry 1987). Phenol appears to be the most toxic among the mono- and dihydric phenolic compounds and, therefore, was used as the basis for the guideline derivation. The water quality guideline for mono- and dihydric phenols for the protection of freshwater life is 4.0 µg·L⁻¹. It was derived by multiplying the 9-d LC₅₀ for *R. pipiens* of 40 µg·L⁻¹ (Birge et al. 1980) by a safety factor of 0.1 (CCME 1991).

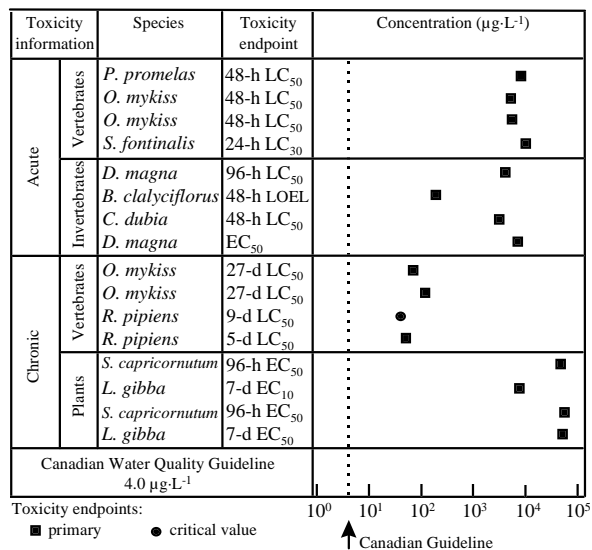


Figure 1. Select freshwater toxicity data for mono- and dihydric phenols.

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