



**D**ioxane-1,4 (CAS Registry Number 123-91-1) is a colourless liquid at standard temperature and pressure (Verschuere, 1983; WHO, 2005; Budavari et al., 1989). Its chemical formula is  $C_8H_{10}O_2$  with a molecular weight of  $88.1 \text{ g mol}^{-1}$  (Budavari et al., 1989).

*Uses and Sources:* 1,4-dioxane has been, and continues to be, widely used in a variety of commercial and industrial solvent applications including: the manufacturing and chemical processing of adhesives, cleaning and detergent agents, cosmetics, deodorants, fumigants, emulsions, polishing compounds, fats, lacquers, resins, oils, pulping of wood, varnishes, waxes, paints, dyes, plastics, rubber, cellulose acetate, pesticides, and a polymerization catalyst (NTP, 1978; EU, 2002; HSDB, 2003; ATSDR, 2004; WHO, 2005). Some other uses of 1,4-dioxane include the manufacture of membrane filters for measuring optical activity, a degreasing agent, a wetting and dispersion agent in the textile industry, and laboratory uses such as a fluid for scintillation counting, spectroscopy and photochemistry, a reagent or element in chromatography, and a dehydrating agent in the preparation of tissue sections for histology (NTP, 1978; EU, 2002; CalEPA OEHA, 2003; HSDB, 2003; ATSDR, 2004). In the past, 1,4-dioxane was heavily used as a stabilizer in chlorinated solvents, particularly 1,1,1-trichloroethane. Before 1995, roughly 90% of 1,4-dioxane production was for this use (ATSDR, 2004). It was typically added to chlorinated solvent mixtures at a concentration of around 3.5%. As the use of 1,1,1-trichloroethane has been reduced since 1995, under the Montreal Protocol (due to its ozone depletion potential), current use of 1,4-dioxane as a stabilizer of 1,1,1-trichloroethane is not believed to be significant (EU, 2002; HSDB, 2003).

The European Union (2002) notes that the main source categories for 1,4-dioxane are i) production; ii) use in processing; iii) end-use products; and, iv) unintentional formation. With respect to the unintentional formation, it is generally known that 1,4-dioxane can be formed as a by-product in several ethoxylation reactions (EU, 2002), particularly those used in the production of surfactants for detergent formulations (e.g., alkyl ether sulphates, non-ionic surfactants). A variety of other products that are formed by ethoxylation reactions have

the potential to contain 1,4-dioxane as a by-product (e.g., alkyl-, alkylphenol- and fatty amine ethoxylates, polyethylene glycols and their esters, and sorbitan ester ethoxylates (Aus, 1997). Uses of these chemical products include in foods, cosmetics, agricultural/veterinary products, therapeutic products, household products and various industrial applications (EU, 2002). Presently, most manufacturers utilize vacuum stripping to remove 1,4-dioxane before the formulation of ethoxylated surfactants in consumer cosmetics and household products (EU, 2002). There is no documented information regarding natural sources or occurrences of 1,4-dioxane. Thus, it appears that all sources of this substance are anthropogenic. However, 1,4-dioxane occurs in various foods at low concentrations, and it is not known for certain whether its presence in food items reflects natural production or contamination of other substances in food as a chemical impurity (EU, 2002). If its presence in food is the result of it being a chemical impurity, the suspected source is ethoxylated food additives, such as polysorbates (NICNAS, 1998). In summary, 1,4-dioxane may enter the environment through wastewater and air effluents at the sites where it is produced, processed, used and *via* unintentional formation.

*Fate:* Given its estimated Henry's law constant of  $4.88 \times 10^{-6} \text{ atm}\cdot\text{m}^3 \text{ mol}^{-1}$  (Howard 1990), 1,4-dioxane is expected to be moderately volatile from water surfaces, as well as moist soils (Park et al., 1987; Thomas, 1990; EU, 2002). The volatilization half-life from a model river was estimated to be five days, while the volatilization half-life from a model lake was estimated to be 56 days (U.S. EPA, 2005). Others have suggested

**Table 1. Canadian Water Quality Guidelines for 1,4-Dioxane for the Protection of Aquatic Life ( $\text{mg L}^{-1}$ )**

|            | Long-Term Exposure | Short-Term Exposure |
|------------|--------------------|---------------------|
| Freshwater | NRG                | NRG                 |
| Marine     | NRG                | NRG                 |

NRG = no recommended guideline

that discharges of 1,4-dioxane to surface water should result in mass transport from water to air *via* volatilization because of the value for Henry's Law constant (GDCH, 1991a). However, both level one and

level two MacKay fugacity models, as modelled by ATSDR (2004) and The Sapphire Group, Inc. (2007), respectively, indicate that at equilibrium, 91-92% of 1,4-dioxane will partition to water, with the remainder partitioning to air. Others have also suggested that molecular diffusion to air will be slow (NICNAS, 1998). Based upon estimated aqueous aerobic biodegradation, Howard et al. (1991) provided half-lives for 1,4-dioxane in surface water with a range of one to six months, and in ground water with a range of two to 12 months. The estimated half-life of 1,4-dioxane in water ranged from 67 days to over nine years, based on measured photo-oxidation rates and by reaction with hydroxyl radicals in water (NICNAS, 1998). As there are no hydrolysable groups on this compound, and since ethers are generally resistant to hydrolysis, 1,4-dioxane would not be expected to undergo significant hydrolysis in the environment (NICNAS, 1998).

1,4-dioxane appears to be stable in water. It is highly water soluble (HSDB, 2003). Since 1,4-dioxane does not absorb light in the environmental spectrum (*i.e.*, >290 nm), 1,4-dioxane is not expected to undergo direct photolysis in water, although it may undergo indirect photolysis by reaction with aqueous hydroxyl radicals near the water surface (HSDB, 2003; ATSDR, 2004). The half-life for this reaction is estimated at 336 days at neutral pH (Anbar and Neta, 1967). 1,4-dioxane is also resistant to biodegradation in water under ambient conditions (ATSDR, 2004; EU, 2002; HSDB, 2003). It also does not readily undergo biodegradation in conventional waste water treatment systems (ATSDR, 2004). There is some evidence that acclimated microbial cultures may be capable of degrading 1,4-dioxane under certain conditions, such as the presence of co-substrates, nutrient enhancement, and elevated temperatures (Roy et al., 1994; 1995; Zenker et al., 1999, 2000; Kelley et al., 2001; Parales et al., 1994).

**Bioaccumulation:** The log octanol/water partition coefficient ( $\log K_{ow}$ ) available for 1,4-dioxane ranges from -0.49 (GDCH, 1991b) to -0.27 (Howard, 1990) indicating that its affinity for lipids is low and there is a low potential for concentration in aquatic organisms. The results of an experimental bioconcentration study reported very low Bioconcentration Factor (BCF) values (0.2 to 0.7) for 1,4-dioxane (Japan Chemical Industry Ecology-Toxicology and Information Center, 1992). Therefore, bioconcentration, bioaccumulation, and biomagnification are unlikely to be significant processes for 1,4-dioxane in aquatic systems (HSDB, 2003; ATSDR, 2004).

**Method Detection Limits:** WHO (2005) reports that 1,4-dioxane can be analyzed by various analytical techniques with detection limits as low as  $1.0 \times 10^{-4}$  mg L<sup>-1</sup>. The Laboratory Services Branch with the Ontario Ministry of the Environment analyzes for 1,4-Dioxane by purge and trap capillary gas chromatography/quadropole mass spectrometry. The method detection limit is  $5.0 \times 10^{-4}$  mg L<sup>-1</sup> (R. Salemi 2008, pers. com.), however this method is not accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL).

**Ambient concentrations:** Samples of groundwater within the vicinity of various landfills in Canada between 1983 and 1986 contained less than 0.001 mg L<sup>-1</sup> of 1,4-dioxane (GDCH, 1991a). The maximum concentration of 1,4-dioxane detected in groundwater was 0.500 mg L<sup>-1</sup> detected underneath a landfill in Canada (GDCH, 1991a). The National Water Quality Monitoring Office of Environment Canada provided 1,4-dioxane concentration data measured in surface waters from eastern Canada (C. Lochner 2008, pers. com.). All of the surface water samples (n=29 in New Brunswick, n=41 in Newfoundland, n=31 in Nova Scotia) were below the detection limit of 0.5 mg L<sup>-1</sup>. No other ambient surface water concentrations of 1,4-dioxane in Canada were available.

**Toxicity-modifying factors:** No information on the effect of water quality parameters on the aquatic toxicity of 1,4-dioxane was available.

**Toxicity:** Based on the available data, it appears that vertebrates are generally more tolerant of both short-term and long-term exposures when compared to invertebrates. Toxicity ranges exhibited by aquatic organisms exposed to 1,4-dioxane are displayed in Figure 1.

In fresh waters, short-term severe effect toxicity concentrations (24 to 96h LC<sub>50</sub>s) for fish exposed to 1,4-dioxane ranged from 4,269 mg L<sup>-1</sup> for the bluegill sunfish (*Lepomis macrochirus*) (Brooke, 1987) to 13,000 mg L<sup>-1</sup> for the fathead minnow (*Pimephales promelas*) (GDCH, 1991b). In the case of invertebrates, only two severe effect concentrations were derived from the literature, a 96h LC<sub>50</sub> of 2,274 mg L<sup>-1</sup> for the scud (*Gammarus pseudolimnaeus*) (Brooke, 1987) and a 24h LC<sub>50</sub> of 4,700 mg L<sup>-1</sup> for the water flea (*Daphnia magna*) (Bringmann and Kuhn, 1977). The lowest acute effect concentration for invertebrates was a 48h immobilization EC<sub>50</sub> of 163 mg L<sup>-1</sup> for the water flea (*Ceriodaphnia dubia*) (GDCH, 1991b).

Long-term ( $\geq 7$ d exposures for fish and invertebrates,  $\geq 24$ h exposures for aquatic plants and algae) effect concentrations ranged from a 32d NOEC of 145 mg L<sup>-1</sup> for embryo-larval fathead minnow (*Pimephales promelas*) (GDCH, 1991b) to a 28d LOEC of 6,933 mg L<sup>-1</sup> for medaka (*Oryzias latipes*) (Johnson et al., 1993). For invertebrates, only two studies on the long-term effects of 1,4-dioxane were reported in the dataset, both for the water flea *Ceriodaphnia dubia*. These were a 7d NOEC and LOEC of 635 and 1,250 mg L<sup>-1</sup>, respectively (Dow, 1995).

Only two studies on the effects of 1,4-dioxane on aquatic plants were provided in the dataset. An 8d Toxicity Threshold (TT) of 575 and 5,600 mg L<sup>-1</sup> were reported for the blue-green algae (*Microcystis aeruginosa*) and the green algae (*Scenedesmus quadricauda*), respectively (Bringmann and Kuhn, 1977).

**Water Quality Guideline Derivation:** Neither a short-term nor long-term freshwater Canadian water quality guideline for the protection of aquatic life (CWQG-PAL) could be developed for 1,4-dioxane because the minimum data requirements were not met (CCME, 2007). The minimum dataset for a type B2 guideline was missing one long-term toxicity study on a salmonid. The minimum data set for a type A, or B1 CWQG-PAL was missing a salmonid study as above, plus one study on an aquatic or semi-aquatic invertebrate. There were enough data for a short-term type A CCME CWQG-PAL, however the CCME Water Quality Task Group decided that short-term guidelines would not be developed in the absence of a long-term guideline for the following reason. Since short-term water quality guidelines are not fully protective (see following paragraph), there was reluctance to publish short-term guidelines without the context of fully protective long-term guidelines.

**Short-term Freshwater Quality Guideline:** Short-term exposure guidelines are derived using severe effects data (such as lethality) of defined short-term exposure periods (24-96h). These guidelines identify estimators of severe effects to the aquatic ecosystem and are

intended to give guidance on the impacts of severe, but transient, situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/nonpersistent substances). Short-term guidelines *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term guidelines are levels which *do not* protect against adverse effects.

**Long-term Freshwater Quality Guideline:** Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods ( $\geq 7$ d exposures for fish and invertebrates,  $\geq 24$ h exposures for aquatic plants and algae).

**Marine Water Quality Guideline:** Marine toxicity data was not evaluated to see if there was sufficient data available to derive a short-term or long-term marine water quality guideline for 1,4-dioxane.

**Guidelines of Other Agencies:** The Ontario Ministry of the Environment (OMOE) has developed an interim Provincial Water Quality Guideline (PWQG) for 1,4-dioxane of 58 mg L<sup>-1</sup>. This interim PWQG was developed using Ontario's Water Quality Guideline development process (OMOE 1992). A full PWQG could not be derived because the minimum data requirements, as outlined in OMOE (1992), were not met. The interim PWQG was derived using the lowest effect concentration found in the literature (fathead minnow 96-h EC<sub>50</sub> of 9,340 mg L<sup>-1</sup>) which was divided by an uncertainty factor of 160. The size of the uncertainty factor reflects the availability of appropriate data (quality and quantity) as well as the potential of the material to bioaccumulate. Additional chronic toxicity studies for invertebrates and vertebrates as well as freshwater macro-phytes and algae are needed to fulfill the minimum data requirements for developing a full PWQG.

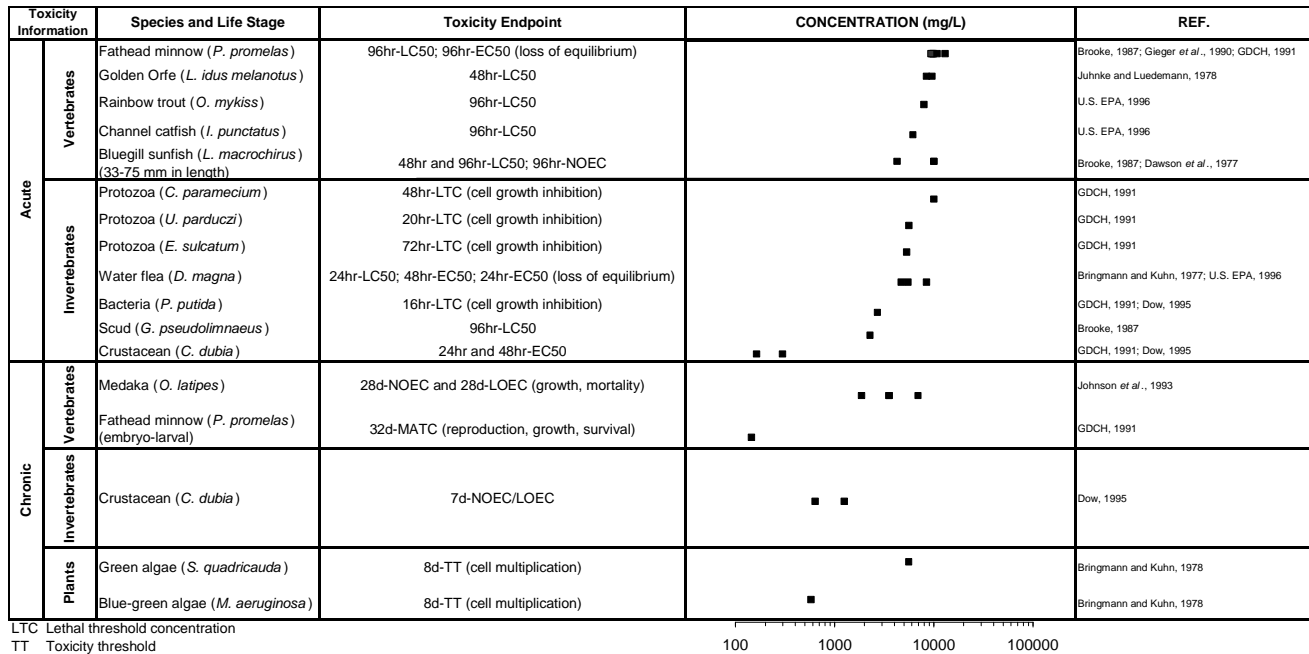


Figure 1. Toxicity Ranges Exhibited by Aquatic Organisms Exposed to 1,4-Dioxane.

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