

Canadian Water Quality Guidelines for the Protection of Aquatic Life

PHTHALATE ESTERS

DEHP DBP DOP

he three phthalate esters included in this fact sheet are di(2-ethylhexyl) phthalate (DEHP), di-*n*-butyl phthalate (DBP), and di-*n*-octyl phthalate (DOP) (CAS numbers 117-81-7, 84-74-2, 117-84-0, and molecular weights 390.6, 278.4, 390.6, respectively). Information concerning the uses and production of the phthalate acid esters DEHP, DBP, and DOP in Canada is limited by confidentiality restrictions. Pierce et al. (1980) provide a more extensive review of Canadian production and processing of phthalate esters as a group.

DEHP is one of the most widely used plasticizers in Canada (Environment Canada 1983). Out of 18 000 t of DEHP supplied in 1984, 30% was used in the production of polyvinyl chloride (PVC) film and sheet, and 15% was used to produce PVC flexible profiles. The remaining 55% was used in various products, including PVC pipe and fittings, wire, cable, coated fabrics, molding, siding, PVC flooring and other uses of PVC and resins. Adhesives and consumer products account for 70% of the use of DBP in Canada, while plastisols account for another 30% (Martec Limited 1979). Use and production information was not found on DOP.

DEHP, DBP, and DOP were monitored in surface and drinking waters in Quebec, Ontario, and Alberta (CCME 1993). Canadian surface water samples were reported to range from 0.29 to $300 \,\mu g \cdot L^4$ for DEHP, from 0.04 to $14 \,\mu g \cdot L^4$ for DBP, and from 0.02 to $7 \,\mu g \cdot L^4$ for DOP (Mayer et al. 1972; Brownlee and Strachan 1977; Ewing et al. 1977; NAQUADAT/ENVIRODAT 1991). DOP levels of up to $55 \,\mu g \cdot L^{-1}$ were reported in water samples taken from an effluent plume of a Lake Superior pulp mill (Brownlee and Strachan 1977), while other effluents from an industrial facility in Alberta contained DBP residues up to $64 \,\mu g \cdot L^{-1}$ (NAQUADAT/ENVIRODAT 1991).

Environmental fate processes of phthalic acid esters are driven mainly by their hydrophobicities and ability to partition and adsorb to organic phases. Sorption to terrestrial soils plays an important role in reducing the mobility of these chemicals and may significantly delay their entry into groundwater and aquatic systems. The most significant environmental loss processes for phthalates occurs through biodegradation. Abiotic processes, including volatilization, hydrolysis, and photolysis, are of minor environmental importance (CCME 1993).

Biological decomposition is a significant degradation pathway of phthalates in the environment. DEHP can be used as a sole carbon source by several microbes in pure culture studies and has been found to degrade in soil, water, and activated sludge (Richards and Shieh 1986).

The half-life of DEHP (measured as loss of parent compound) at a concentration of $20~\text{mg}\cdot\text{L}^{-1}$ in distilled water treated with acclimated sewage was 5.25 d and ranged from 4.55 to 6.77 d, with 86% mineralization being observed over a 28-d period (Sugatt et al. 1984). DBP in wastewaters ($20~\text{mg}\cdot\text{L}^{-1}$) had a half-life of 15.4 d, and losses of up to 57% (as CO_2) were reported after 28 d (Sugatt et al. 1984).

Studies using DEHP have demonstrated steady state BCFs ranging from 112 to 518 in zooplankton (*Daphnia magna*) exposed for 21 and 1 d, respectively (Macek et al. 1979). Benthic organisms had BCFs that ranged from 350 in the midge larvae *Chironomus plumosus* to 3996 in the amphipod *Gammarus pulex* after exposure to DEHP for 7 and 10 d, respectively (Mayer and Sanders 1973; Thuren and Woin 1991). The BCFs for DEHP in fish appear to be highly variable and ranged from 42 in rainbow trout to 2600 in channel catfish over exposure durations of 94 and 1 d, respectively (Stalling et al. 1973; Mehrle and Mayer 1976).

For DBP, a single study on *D. magna* resulted in a BCF of 400 after 7 d, and BCFs in benthic organisms ranged from 430 in the mayfly *Hexagenia bilineata* to 1400 in the amphipod *G. pseudolimneaus* following exposures of 7 and 14 d, respectively (Mayer and Sanders 1973; Thuren and Woin 1991). Only one study on freshwater fish was found; it yielded BCFs ranging from 580 to 2080 in the fathead minnow after 11 d (Call et al. 1983).

Table 1. Water quality guidelines for phthalate esters for the protection of aquatic life (CCME 1993).

Aquatic life	Guideline value (μg·L ⁻¹)						
	DEHP	DBP	DOP				
Freshwater	16*	19*	NRG [†]				
Marine	NRG^{\dagger}	NRG^{\dagger}	NRG^\dagger				

^{*}Interim guideline.

[†]No recommended guideline.

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for phthalate esters for the protection of aquatic life were developed based on the CCME protocol (CCME 1991)

Freshwater Life

DEHP

Only one study on the phytotoxicity of DEHP was found in the literature. Duckweed (*Lemna gibba*) exposed to DEHP for 7 d had an EC_{50} (growth) of 2060 mg·L⁻¹ (Davis 1981).

In acute studies with invertebrates, the most sensitive species was the zooplankton D. magna, with 48-h LC₅₀s of 2.0 mg·L⁻¹ (Adams and Heidolph 1985) and 11 mg·L⁻¹ (LeBlanc 1980). In chronic studies, D. magna was the most sensitive species tested, with a 21-d LOEL (reproduction) of $0.003~\text{mg}\cdot\text{L}^{-1}$ (Mayer and Sanders, 1973). These data were ranked unacceptable, however, because of low control fecundity and because DEHP levels at the beginning and the end of the test were not reported (Federal Register 1990). In other chronic studies using D. magna as a test, SMATCs ranged from 158 to 811 µg·L⁻¹ (Brown and Thompson 1982; Knowles et al. 1987). Springborn Bionomics (1984a) exposed D. magna to DEHP concentrations ranging from 0.024 to $0.38 \text{ mg} \cdot L^{-1}$ for 21 d. Exposure to $0.16 \text{ mg} \cdot L^{-1}$ significantly reduced survival after both 14 and 21 d of treatment.

Definitive acute toxicity data for vertebrates were available for three fish species and two amphibians. In rainbow trout (*Oncorhynchus mykiss*), a 96-h LC₅₀ of 540 mg·L⁻¹ was reported (Hrudey et al. 1976). Birge et al. (1978) exposed the eggs of channel catfish (*Ictalurus punctatus*), leopard frogs (*Rana pipiens*), Fowler's toads (*Bufo fowleri*), and redear sunfish (*Lepomis microlophus*) to DEHP and reported 72-h LC₅₀s ranging from 1.21 to 77.20 mg·L⁻¹. Although the test chemical was reported as DOP in the Birge et al. (1978) studies, according to M. Kercher (1992, Water Resources Institute, University of Kentucky, Lexington, Kentucky, pers. com.), the experiment actually used DEHP.

Mehrle and Mayer (1976) exposed fathead minnows to DEHP concentrations ranging from 0.0019 to 0.062 mg·L⁻¹ for 56 d and reported no adverse effects related to growth or survival. The same study also

Toxi inform		Species	Toxicity endpoint		Co	ncentrat	tion (µg	·L ⁻¹)	
Acute Invertebrates	Vertebrates	O. mykiss I. punctatus L. microlophus	96-h LC ₅₀ 72-h LC ₅₀ 72-h LC ₅₀						
	Invertebrates	D. magna D. magna	48-h LC ₅₀ 48-h LC ₅₀			•			
nic	Vertebrates	-	168-d LOEC 8-d LC ₅₀ 8-d LC ₅₀ 8-d LC ₅₀			8			
Chronic	Invertebrates	D. magna D. magna D. magna D. magna	21-d LOEL MATC MATC 21-d LOEL			•			
Ca	ınadia	n Water Quality G 16 μg·L ⁻¹	uideline						
	ty end rimary	points: y • critical		10¹ ♠ (10 ² Canadian	10 ³ Guidel	10 ⁴	105	10

Figure 1. Select freshwater toxicity data for DEHP.

exposed rainbow trout embryo-larvae from 12 d before hatching until 90 d after hatching and reported that hatchability was not affected by DEHP concentrations ranging from 0.005 to 0.054 mg·L⁻¹. A significant increase in sac-fry mortality (20%) was reported 5 d after hatching in treatment groups receiving 0.014 mg·L⁻¹ DEHP. There were no significant effects on mortality compared to controls when the exposure was continued beyond 24 d. DeFoe et al. (1990) treated rainbow trout embryo-larvae with DEHP from 72 h after fertilization until 90 d after hatching. They reported no adverse effects on egg hatchability, survival, or growth occurred to rainbow trout eggs exposed to 0.052 mg·L⁻¹ for 90 d. These results failed to support those of Mehrle and Mayer (1976). Eggs of channel catfish, redear sunfish, largemouth bass (Micropterus salmoides), and rainbow trout had chronic LC₅₀s ranging from 0.69 to 149 mg·L⁻¹ (Birge et al. 1978, 1979). In amphibians, Birge et al. (1978) reported LC₅₀s of 3.88 and 4.44 mg·L⁻¹ for eggs of the Fowler's toad and leopard frog exposed to DEHP for 8 d.

The available acceptable toxicity data indicate that the most sensitive freshwater organism was *D. magna*. The data of Mayer and Sanders (1973) and Mehrle and Meyer (1976), which had more sensitive endpoints, were ranked as unacceptable and, therefore, could not be used for guideline derivation. The interim water quality guideline for DEHP for the protection of freshwater life is 16 μg·L⁻¹. It was derived by multiplying the 21-d LOEC of 0.16 mg·L⁻¹ (survival) for chronically exposed *D. magna* (Springborn Bionomics 1984a) by a safety factor of 0.1 (CCME 1991).

DBP

One study on the phytotoxicity of DBP was found in the literature. Springborn Bionomics, Inc. (1984b) examined the effects of DBP on the growth rate of the green alga *Selenastrum capricornutum* and reported an EC₅₀ of 0.75 mg·L⁻¹.

Invertebrate acute toxicity values ranged from a 48-h LC_{50} of $0.76~mg\cdot L^{-1}$ to a 24-h LC_{50} of $17~mg\cdot L^{-1}$ for the midge larvae (*C. plumosus*) and *D. magna*, respectively (Streufert et al. 1980; Kühn et al. 1989). In chronic invertebrate studies, Springborn Bionomics, Inc. (1984b) studied the effects of DBP on survival and reproduction of *D. magna* and reported a 21-d EC_{50} of $1.5~mg\cdot L^{-1}$. Similarly, a 15-d NOEL and LOEL of 0.56 and $1.8~mg\cdot L^{-1}$, respectively, were reported for reproductive inhibition of *D. magna* (McCarthy and Whitmore 1985). Other studies reported similar *D. magna* 21-d EC_{50} and 21-d EC_{50} (reproduction) values of $1.92~and~1.64~mg\cdot L^{-1}$ (DeFoe et al. 1990).

Mayer and Ellersieck (1986) reported 96-h LC₅₀ data for a number of fish species including yellow perch (*Perca flavescens*), channel catfish, rainbow trout, bluegill sunfish (*Lepomis macrochirus*), and fathead minnows ranging from 0.35 to 3.96 mg·L⁻¹. Other acute toxicity data on fish ranged from 0.85 to 1.2 mg·L⁻¹ for 96-h and 24-h LC₅₀ tests on fathead minnows and bluegills (EG&G Bionomics 1983; DeFoe et al. 1990). In chronic studies, Ward and Boeri (1991) reported a LOEL (mortality) of 190 μg·L⁻¹ and a SMATC of 400 μg·L⁻¹ for rainbow trout in a 99 d. study. Other studies reported reduced hatching success and embryo survival of fathead minnows at DBP concentrations of 1000 μg·L⁻¹ in 20-d tests. Also reported was a 20-d NOEL for fathead minnow hatching and survival of 560 μg·L⁻¹ (McCarthy and Whitmore 1985).

The most sensitive acceptable chronic study was a 99-d LOEL of 190 µg·L⁻¹ based on mortality in rainbow trout by Ward and Boeri (1991). The interim water quality guideline for DBP for the protection of freshwater life is 19 µg·L⁻¹. It was derived by multiplying the 99-d LOEC of 190 µg·L⁻¹ based on mortality (Ward and Boeri 1991) for rainbow trout by a safety factor of 0.1 (CCME 1991).

DOP

Only two toxicity studies for DOP were found in the literature. DeFoe et al. (1990) exposed fathead minnows to the *ortho* isomer of DOP and reported a 96-h LC₅₀ of 0.045 µg·L⁻¹. McCarthy and Whitmore (1985) examined the effect of a 21-d DOP exposure on the reproductive

Toxicity information		Species	Toxicity endpoint	Concentration (µg·l			μg·L ⁻¹)	
te	brat	O. mykiss L. macrochirus P. promelas L. macrochirus	96-h LC ₅₀ 96-h LC ₅₀ 96-h LC ₅₀ 24-h LC ₅₀					
Acute	Plants Invertebrates	C. plumosus D. magna S. capricornutum	48-h LC ₅₀ 24-h LC ₅₀ EC ₅₀			_	•	
Chronic	ertebrates	O. mykiss O. mykiss P. promelas	99-d LOEL MATC 20-d LOEL		•			
	tebrai	D. magna D. magna D. magna D. magna	21-d EC ₅₀ 15-d LOEL 21-d LC ₅₀ 21-d EC ₅₀					
		n Water Quality G 19 μg·L ⁻¹	20		l	ı	ı	
Toxicity pri		•		10¹ ♠	10 ² Canadian (10 ³	10^{4}	1

Figure 2. Select freshwater toxicity data for DBP.

success of *D. magna*. A NOEL of 0.320 mg·L⁻¹ and a LOEL of 1.0 mg·L⁻¹ were reported. DOP had no effect on the survival of embryos or larvae of fathead minnows at 3.2 mg·L⁻¹ during 28-d exposures. However, hatching was decreased by 35% at 10 mg·L⁻¹. It is difficult to interpret these data because the DOP concentrations used in these studies exceeded the water solubility of the compound.

There were insufficient data to recommend a Canadian water quality guideline for DOP.

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