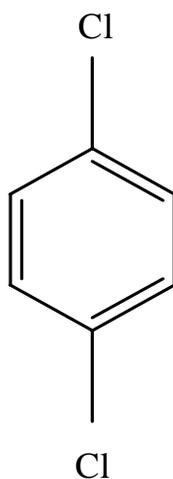


## **Environmental Fate of Paradichlorobenzene**

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## **Introduction**

Paradichlorobenzene (p-DCB, PDB; 1,4-DCB) is a volatile chlorinated hydrocarbon one of three isomers consisting of two chlorine atoms substituted onto a benzene ring. It is produced by chlorination of benzene in the liquid phase with a catalyst, and is typically quantified in environmental media using gas chromatography with flame ionization, electron capture detection, or via gas chromatography/mass spectrometry (Oliver et al., 1982).

p-DCB was first produced commercially in the United States (U.S.) in 1915. p-DCB is a neutral, colorless, crystalline solid used primarily as an insecticidal fumigant against clothes moths (moth balls), molds/mildews, carpet beetles, and cake deodorant for garbage receptacles and restrooms. Estimates of use are from 35-40% for moth control, 35-55% as a space deodorant, and the balance for remaining uses (ATSDR, 1998).

All three DCBs are widely used with p-DCB entering the environment as it releases into the air from space deodorants, toilet deodorizers, and moth repellants. The other two isomers 1,2 and 1,3-dichlorobenzene (1,2-DCB; 1,3-DCB) are liquids and are used primarily as solvents and chemical intermediates. They are not as widely detected in the environment as p-DCB. United States Environmental Protection Agency (U.S. EPA) estimated in 2003 that a total of 99,993 pounds (44 metric tons) of p-DCB was released into the environment from 21 processing facilities. Estimated fractions of p-DCB as contaminants to the environment included 85,463 lbs (39 metric tons) release into air, 815 pounds (0.4 metric tons) released to water, 270 lbs (0.1 metric tons) released to land, and 10,408 lbs (5 metric tons) released via underground injection. This total does not include all production facilities in the U.S. and reflects only the largest producers (U.S. EPA TRI, 2003).

p-DCB has not been registered for agricultural uses in California since 1993. Historical agricultural uses in the U.S. for p-DCB have included control for peach tree borer and tree-boring insects of apricots, cherries, nectarines, plums, and peaches, ants, root aphids, wire-worms, potato weevil, and minor uses for underground rodent control, fumigant control for stored honeybee combs, bird repellent, and mold in tobacco seeds. p-DCB is also used in the manufacture of other organic chemicals in plastics, dyes and pharmaceuticals. Trade names for p-DCB include Paramoth, Para crystals, Di-Chloricide, Paradi, Paradow, Perisia-Perazol, Evola, Parazene, Santochlor, Dichloride, p-Chlorophenyl chloride, p-Dichlorobenzene, and Paracide (IPCS, 2001). It is also used in the production of the polymer (poly(p-phenylene sulfide)).

## **Physico-Chemical Properties**

p-DCB (Figure 1) is volatile, and when exposed to air slowly sublimates from a solid to a vapor. The vapor is the exposure route that kills the intended target insect, mold, or mildew. p-DCB has low water solubility, moderate vapor pressure, and a moderate

octanol/water partition coefficient (Table 1). p-DCB is transformed and degraded via atmospheric photo-oxidation; volatilization; partitioning to soil; sediment and biota; and aerobic degradation (CEPA, 1993; Howard et al., 1989; Howard et al., 1991).

Chlorobenzenes in general are known to be chemically stable and their chemical degradation in the environment is limited when micro-organisms are not present for degradation. Environmental fate of dichlorobenzenes has been well characterized in the past three decades. There are no natural sources for dichlorobenzenes in the environment.

The U.S.EPA identified p-DCB as a priority pollutant (U.S. EPA, 2007). Of the 1,662 hazardous waste sites in the U.S. proposed for inclusion in the U.S. EPA National Priorities List 330 sites were identified with p-DCB and other DCBs as contaminants (ATSDR, 2005).

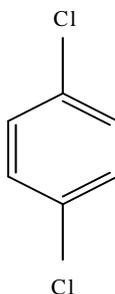
<b>Table 1. Physical Chemical Properties of Paradichlorobenzene</b> chemical abstracts number 106-46-7	
<b>Molecular Formula:</b>	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>
<b>Molecular Weight:</b>	147.02 g/mole
<b>Physical State:</b>	Colorless solid
<b>Odor:</b>	Mothball-like odor threshold 0.18 ppm
<b>Melting Point:</b>	53 degrees C (127 degrees F)
<b>Boiling Point:</b>	174 degrees C/760 mm Hg
<b>Henry's Law Constant<sup>1</sup>:</b>	1.92x10 <sup>-3</sup> atm m <sup>3</sup> /mol
<b>Koc value<sup>2</sup>:</b>	434 (estimated)
<b>Water solubility<sup>3</sup></b>	70 mg/L at 20 degrees C, 90.6 mg/L at 25 degrees C
<b>Vapor Pressure:</b>	1.76 mm Hg at 25 degrees C; volatile, sublimes readily
<b>Relative vapour density</b>	(air = 1): 5.08
<b>Relative density of vapour air-mixture @ 20 degrees C</b>	(air = 1): 1.01
<b>Log K<sub>ow</sub> (octanol/water partition coefficient):</b>	3.52
<b>Solubility:</b>	81 mg/L at 20 C
<b>Flash Point:</b>	66 degrees C

<sup>1</sup> Henry's Law Constant Reference: Mackay, D. and Shiu, W.Y. 1981. J. Phys. Chem. Ref. Data 10, 1175-1199.

<sup>2</sup> Solubility Reference: Yalkowsky, S.H., Dannenfelser, R.M.: Aquasol Database of Aqueous Solubility. Version 5: College of Pharmacy, University of Arizona Tucson, AZ. 1992.

<sup>3</sup> Koc Value Reference: EPI Suite property estimation v. 3.12. Syracuse Research Corporation/ U.S. EPA Office Pollution Prevention and Toxics.

**Figure 1. Chemical Structure of Para-dichlorobenzene (1,4-dichlorobenzene)**



### **Environmental Fate**

#### **Degradation Pathways**

The main environmental degradation pathway for dichlorobenzenes is oxidative dechlorination leading to the formation of hydroxylated aromatic compounds comprised of mostly phenols, followed by ring fission, and ultimate mineralization to carbon dioxide and water (IPCS, 1991).

Some photodegradation occurs when dichlorobenzenes are irradiated with sunlight although absorption of light is weak above 290 nanometers and decomposition is slow. Dechlorination is the main photochemical reaction for dichlorobenzenes exposed to light (IPCS, 1991).

It has been observed that microorganisms degrade dichlorobenzenes in various substrates (soil, water, sediment, and sewage sludges). More highly chlorinated chlorobenzenes are more resistant to this breakdown pathway compared to less chlorinated congeners (p-DCB, 1,3-DCB, and 1,2-DCB). Garrison and Hill (1972) demonstrated this by finding that mono-dichlorobenzene, 1,2-DCB and p-DCB were completely volatilized in less than one day from solutions containing mixed cultures of aerobic organisms, but 2% of 1,2,4-trichlorobenzene remained after 80 hours.

#### **Atmospheric Fate**

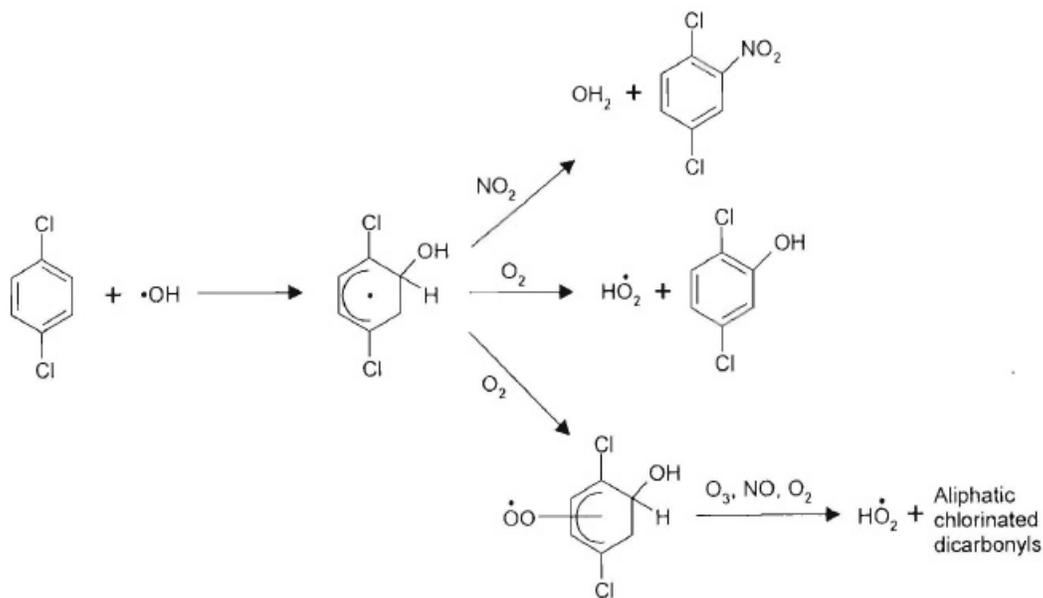
p-DCB is moderately volatile, and the reaction with photochemically produced hydroxyl radicals in the atmosphere yields a half-life for indirect photooxidation of 31 days. Reactions with hydroxyl radicals occur in the atmosphere to breakdown p-DCB to produce nitrochlorobenzene, chlorophenol, and aliphatic dicarbonyl product that are further degraded by photolysis (INCHEM, 2004). The breakdown of p-DCB in air is shown in Figure 2. It is present at low concentrations in the atmosphere but the short half-

life of p-DCB is not suspected of contributing to ground level ozone, depletion of stratospheric ozone, or global warming (CEPA, 1993; Boutonnet, 2004). Mackay et al. (1992) proposed a mean half-life of p-DCB in the atmosphere of about three weeks based on photo-oxidation and advection processes.

Direct photolysis of p-DCB was reported by and additional investigation to study the transformation of p-DCB in pure water resulted in photohydrolysis to 4-chlorophenol, with the additional products hydroquinone and hydroxybiphenyls resulting from secondary reactions detected by fluorescence (Meunier et al., 2001).

In addition to air studies, 1,4-dichlorobenzene was detected in seven rainwater samples collected in Portland, Oregon at levels of 3.0-7.0 ppt (Ligocki et al., 1985) and in rainwater in the United Kingdom at levels of 0.01-0.005 ppb (Fielding et al., 1981). DCBs have also been detected in Antarctic snow (Laniewski et al., 1998; Zoumis et al., 2001) suggesting transport through the atmosphere over long distances.

**Figure 2. The Decomposition of p-Dichlorobenzene in Air**  
**(Department of Health and Human Services, 2005)**



## **Outdoor Urban Air Fate**

Outdoor air releases of p-DCB have been estimated at 70 to 90% of the total U.S. production and emanations from the use of toilet deodorizers, garbage deodorant, and moth control agents. These releases have resulted in significant exposure to humans (IARC, 1982).

Urban air concentrations of six selected volatile aromatic chlorinated compounds were measured at Hiyoshi in Yokohama, Japan from November 1994 to October 1997 using an automated gas chromatographic (GC) system over a two-day period (Yamamoto et al., 2000). Mean 1-hr concentrations of p-dichlorobenzene ranged from 0.07 to 0.42 ppb.

Other sources of dichlorobenzene are related to manufacturing of pesticides and industrial processes. Ambient mean air concentrations of 0.03-4.19 ppb were detected in New Jersey above six abandoned hazardous waste sites and were attributed to volatile emanations. Flue gas effluents from a municipal refuse-fired steam boiler in Virginia contained  $4.4 \mu\text{g}/\text{m}^3$  of dichlorobenzene isomers, and a refuse driven power plant in Ohio resulted in  $7.8 \text{ ng}/\text{m}^3$  ( $1.3 \times 10^{-3}$  ppb) of dichlorobenzene isomers in the resulting emissions (ATSDR, 1988).

## **Indoor Air**

The main mode of exposure for humans of p-DCB is indoors due to the use of air fresheners and products to control clothes moths. Shah and Heyerdahl (1988) found the mean indoor air concentrations of p-DCB at 2,121 sites at 3.988 ppb. In personal air monitoring (breath samples) of 1,650 persons the average concentration was 0.416 ppb. Indoor air concentrations in 54 homes monitored in California showed overnight concentrations of p-DCB ranging from 0.07 to 0.47 ppb (Wallace, 1988). Threshold limit values for an 8-hour time-weighted-average for p-DCB are 10.0 ppb (ATSDR, 2005).

In Canada, a nationwide study of indoor air concentrations of 26 Volatile Organic Compounds (VOCs) was conducted in 1991 (CEPA, 1993). Mean concentrations of p-DCB were 5.96 ppb in winter, 2.5 ppb in spring, 1.76 ppb in summer, and 2.5 ppb in the fall. These concentrations were attributed to the use of household products and moth repellent crystals. The concentrations of p-DCB were highest in the winter months when moth crystals were present consistently over a few weeks, temperatures were lower, and ventilation was low. In an Ottawa, Canada study p-DCB was detected in 81% of 75 randomly selected dwellings with a mean concentration of 0.029 ppb (ATSDR, 2005).

Environmental exposures were using data from the U.S. EPA total exposure assessment methodology (TEAM) studies to estimate exposure to nine volatile organic compounds VOC's across U.S. cities (Rappaport, et al., 2004). Median 24-hour personal air (indoor) concentrations for p-DCB were calculated to be 0.291 ppb and outdoor air concentrations were found at 2.23 ppb (average of high and low concentrations). In Los Angeles, California mean personal air concentrations were found at 0.530 ppb (winter), and 0.219

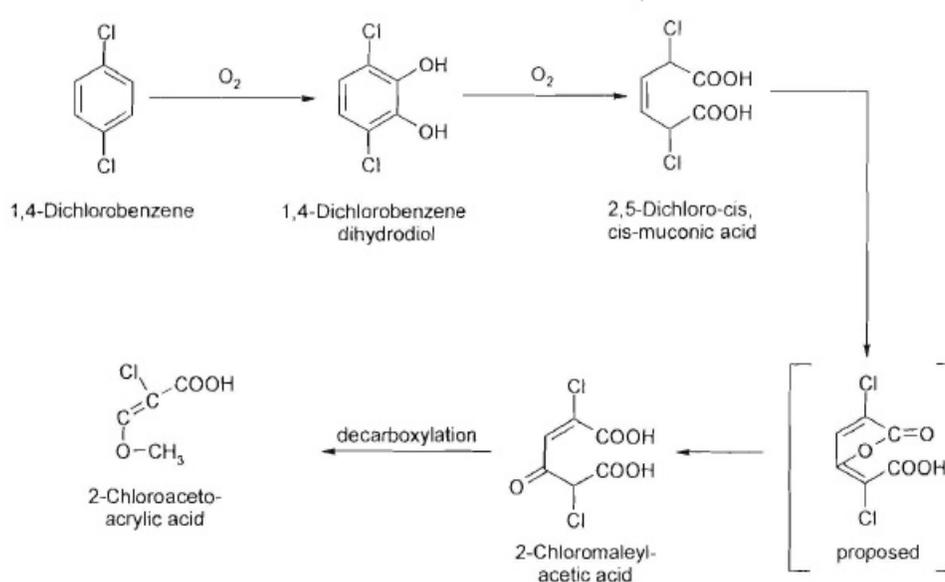
ppb in summer. In New Jersey, mean personal air concentrations were 1.17 ppb in winter and 0.711 ppb summer.

### **Environmental Fate in Soil**

Volatilization from soil surfaces is an important fate and transport mechanism of dichlorobenzenes in soil (Mackay et al., 1992; Callahan, et al., 1979). Degradation of p-DCB in soil occurs from biodegradation processes from certain types of soil bacteria under aerobic conditions (Oltmanns, et al., 1988). Chemical degradation processes such as hydrolysis, oxidation, or direct photolysis on soil surfaces are not expected to readily breakdown p-DCB. There is a positive correlation between the degree of chlorination of chlorobenzenes and adsorption on organic matter. Experimental results have shown that retention of chlorobenzenes increases with the organic content of soils. A half-life in soil for p-DCB of approximately eight months was estimated (Mackey et al., 1992) and four weeks to six months (Howard, 1991).

When released to soil, p-DCB can be moderately to tightly adsorbed and slowly biodegrades under aerobic conditions. Microbial degradation of monochloro-1,2-dichloro-, 1,4-dichloro-, and 1,2,4-trichlorobenzene in soil slurries was reported by Brunsbach et al. (1994). Indigenous soil microbes degraded monochlorobenzene when incubated at 27 degrees C in slurries with 29% suspended solids. The other chlorobenzenes persisted during an incubation period of one month. The addition of *Pseudomonas aeruginosa* microbe strain to a titre of  $1 \times 10^5$  cells/g soil led to rapid and complete degradation of 0.8 mM growth substrate with p-DCB within 30 hours. In addition, the strain was able to degrade 1,2-dichloro- and 1,2,4-trichlorobenzene with stoichiometric release of chloride in the presence of acetate, ethanol, monochloro- or p-DCB. In mixtures of chlorobenzenes the co-metabolism of 1,2-dichloro- and 1,2,4-trichlorobenzenes occurred until the growth substrates monochloro- and p-DCB were degraded. The degradation was faster in the slurries of garden soil containing 8% organic carbon than in soil with the lower content of 2.6% (Brunsback et al., 1994). p-DCB can also occur in soil due to lindane degradation (ATSDR, 2005).

**Figure 3. The Decomposition of 1,4-Dichlorobenzene in Soil and Water**  
 (Department of Health and Human Services, 2005)



### Environmental Fate in Groundwater

Leaching through soil does occur (Elder et al., 1981) mostly from industrial or contaminated sites and p-DCB has been detected in groundwater in the U.S. and throughout various countries in the world. In groundwater, 19 of 685 monitoring locations in New Jersey from 1977-1979 had detections of p-DCB. The highest concentration was at 995 ppb. In the U.S. states of Colorado, Texas, and Arizona positive concentrations of dichlorobenzene were also detected in groundwater sources (U.S. EPA, 1983).

Between 1985 and 1995, United States Geological Survey (USGS) collected groundwater samples as part of the National Water Quality Assessment Program (NAWQA). p-DCB was detected in 1.8% of the urban well samples with a median concentration of 1.0 ppb and detections ranging from 0.3-50.0 ppb. p-DCB was detected in 0.2% of the rural well samples with a median concentration of 1.5 ppb. Detections were in the range of 0.6-8.0 ppb. Between 1985-1999 USGS monitored 1,926 rural private wells and p-DCB was only detected in one sample at 1.2 ppb. Other detections of p-DCB were made in 29 alluvial wells beneath Denver, Colorado with a maximum of 1.7 ppb (Bruce, 1996). A New Jersey study found 995 ppb in a groundwater investigation (Stackelberg et al., 2001).

In a well study in Bitterfield (Saxony-Anhalt) region in Germany, it was observed that the reductive dechlorination of p-dichlorobenzene takes place very slowly in a chlorobenzene contaminated groundwater aquifer under anaerobic conditions. Under

aerobic conditions the indigenous micro-organisms are able to breakdown and mineralize monochlorobenzene and p-DCB (Dermietzel et al., 1999).

### **Environmental Fate in Surface Water**

The Henry's Constant of p-DCB is  $1.92 \times 10^{-3}$  atm m<sup>3</sup>/mol making it readily volatile from water (Mackay et al., 1981). Figure 3 diagrams the breakdown of 1,4-DCB in water. In a model river, 1 meter in depth, with a current of 1 meter per second, and a wind velocity of 3 meters per second at 20 degrees C, the calculated half-life was 4.3 hours. In a similar model for a lake scenario (1 meter deep, 0.05 meter/second water current and 0.5 meter/second wind velocity) a half-life of 117.4 hours was calculated (Lyman et al., 1982).

1,4-DCB has been detected in surface water in the U.S. and various locations around the world. Surface water detections have been mostly attributed to improper chemical disposal, direct manufacturing sources, chemical waste dumps, and from use as urinal block deodorizers that contribute to sewage water contamination (Spectrum, 2007; ATSDR, 2005; Oliver, 1982). A maximum contaminant level (MCL) of 0.005 ppb was established by the California Department of Health Services in 1988. This level is more stringent than the federal MCL of 0.075 ppb (CalEPA, 1997).

Leaching from hazardous waste disposal areas has occurred and resulted in contamination of adjacent surface water and ground water wells in Niagara Falls, New York (New York, 1983). p-DCB was detected in drinking water samples from three cities near Lake Ontario, Canada in 1980 at 0.013 ppb. Mean concentrations of 45.0, 4.0, and 10.0 ppt were detected in Lake Ontario, Lake Huron, and Grand River, Canada respectively during 1980. In New Jersey, surface water monitoring resulted in positive concentrations of p-DCB in 26 out of 463 surface water locations from 1977-1979 (Spectrum, 2007).

Extensive monitoring in the Great Lakes area and analysis of Lake Ontario sediment cores has shown persistence of p-DCB since before 1940. p-DCB was detected in 100% of 91 samples analyzed from the Great Lakes. Mean concentrations ranged from 0.28 ppt in Lake Huron to 1.5 ppt in Lake Ontario. In three cities surrounding Lake Ontario, p-DCB was detected in drinking water supplies in the 1980's at 0.013 ppb (CEPA, 1993). p-DCB was also detected in the cities of Miami, Philadelphia, and Cincinnati. p-DCB was found in nine of 945 treated water supplies utilizing groundwater sources across the U.S. with concentrations ranging from 0.60-0.74 ppb. In the area of Love Canal in Niagara Falls, New York dichlorobenzene isomers were found at levels of 10-800 ng. Between 1981 and 1983 the Niagara River had concentrations of p-DCB from 8.7-110 ppt with a mean average concentration of 24 ppt. Average concentrations on the Niagara River between September and October 1982 were 48 ppt (CEPA, 1993).

In one study, 139 streams in 30 states were monitored and 25.9% of the samples yielded concentrations of p-DCB from 0.09-4.3 ppb (Kolpin et al., 2002). In a monitoring

program of surface and raw drinking water in Alberta, Quebec, Nova Scotia, New Brunswick, Prince Edward Island, and Newfoundland conducted from 1987-1989 concentrations of p-DCB were detected from 0.57 to 130 ppt (Environment Canada, 1992).

### **Environmental Fate in Sediment**

p-DCB can accumulate in sediments when anaerobic conditions exist. Sediments in water bodies are the most concentrated environmental sink for chlorobenzenes (Zoumis et al., 2001). When p-DCB partitions to the organic fractions of bottom sediments, it can persist for long periods of time (Oliver et al., 1982, 1984). p-DCB was reported in soil core sediment samples from Lake Ontario. It is estimated that chlorobenzenes have accumulated in the sediment phase of the lake for a period of 80 years increasing from 0.4-15.0 ppb during 1898-1904, 18.0-1,100 ppb from 1959-1967, and 6-110 ppb from 1980-1981 (Oliver, 1989). An estimated mean half-life was approximately 2 years for p-DCB in the first one centimeter of sediment (Mackay et al., 1992).

A mitigation study conducted in the Mulde reservoir in Saxony, Germany demonstrated remobilization of sediment bound p-DCB (Zoumis et al., 2001). The study also showed that the mobility of chlorobenzenes increased with a corresponding decrease in the number of chlorine atoms. Remobilization of contaminants in sediment can occur due to flooding, oxidation of anoxic sediments by bioturbation, changes in geochemical parameters (such as pH, oxidation), and degradation of contaminants to a more mobile form. In the case of p-DCB in the Mulde reservoir, concentrations were found at 19.9 ppb in the sediment, 2,217 ppt in the overlying water, and 3,964 ppt in the pore water.

USGS reported concentrations of p-DCB at <100 µg/kg in streambed sediment samples from 14 river sites in the New England Coastal Basin as part of the USGS National Water-Quality Assessment Program (USGS, 2002). p-DCB was reported in sediment at 3.6 mg/kg in the Calcasieu River estuary in Louisiana (ATSDR, 1998). Oliver and Nicol (1984) found p-DCB concentrations in sediments from 13 sites in Lake Superior, 42 sites in Lake Huron, 5 sites in Lake Erie, and 11 sites in Lake Ontario. Mean 1,4-DCB concentrations were 5.0 ppb and ranged from non-detectable to 10.0 ppb in Lake Superior, 26.0 ppb in Lake Erie, 38.0 ppb in Lake Huron, and 560 ppb in Lake Ontario. Deep core sediment collected also had 1,4-DCB concentrations down to 7 cm in depth, with the highest detections of 230 ppb at the 3-4cm depth at Lake Ontario (ATSDR, 1998).

1,4-DCB concentrations in sediment were reported at the outfall of a marine municipal sewage discharge in Victoria, Canada. Concentrations were as high as 1,710 ppb dry weight decreasing in distance from the outfall. The source of the contamination was attributed to the use of toilet block deodorizers (CEPA, 1993; Chapman et al., 1996).

## Wastewater

Effluent sources of p-DCB have been found to contribute to surface water detections (USGS, 2005). The Tres Rios Demonstration Treatment Wetlands near Phoenix, Arizona receive effluent from a wastewater treatment plant and were sampled for organic and inorganic chemicals from 1998-2000. There were detections of p-DCB in water samples collected up to 0.25 ppb.

Wetland-treated leachate water at a municipal solid waste landfill site in Central Florida was analyzed for chlorobenzenes. p-DCB was detected at concentrations from 0.04-0.13 ppb. Groundwater contained p-DCB at concentrations from 0.08-10.71 ppb (Chen et al., 1995).

p-DCB has been detected in various wastewater treatment effluents in Canada including a mean mass daily loading value of 143 g/day being discharged into the Strait of Georgia in the Vancouver area between March and December 1987 (Fanning et al., 1989). It was concluded in a study of water supplies in three cities in Ontario, Canada (Oliver et al., 1982) that p-DCB detections were probably from urinal deodorant blocks. Concentrations in the study ranged from 8.0-20 ppt with a mean of 13 ppt. p-DCB was also detected in raw and treated water in Quebec, Canada in May 1985 and February and July 1986 (CEPA, 1993).

In 1976, a concentration ranging from 0.4-100 ppb was found in finished effluent waters during Southern California municipal wastewater sampling. In July 1978 and November 1980, concentrations were reported in finished effluent water from the Los Angeles County municipal wastewater treatment plant. Dichlorobenzenes isomers have been detected in leachates from municipal waste sites in Minnesota and Ontario, Canada (CEPA, 1993).

Sewage sludges used on agricultural lands can contribute to p-DCB contamination (Wang et al., 1995). In Woburn, England, dichlorobenzene-tainted sewage sludge was used on agricultural land from 1941-1961. p-DCB soil concentrations ranged from 7.76-71.8 ppb (mean, 29.8; median, 25.5 ppb). They also reported that soil concentrations of other chlorobenzene congeners decreased over time while p-DCB concentrations increased. The researchers concluded that the increase was due to seasonal pesticide applications of organochlorine pesticides since p-DCB has been found as an impurity.

In Michigan, 204 sewage sludges were analyzed for 73 organic compounds. Concentrations of p-DCB ranged from 0.04-633 mg/kg dry weight and mean and median concentrations of 12.0 and 2.02 ppm (Jacobs et al., 1983).

A study was conducted about the transfer of chlorobenzenes to carrots grown in low and high rate sewage sludge amended soil containing chlorobenzenes (Wang et al., 1994). The investigators reported 10.0 and 7.4 ppb in the low rate sewage-amended soil and 38.0 and 30.0 ppb in the high rate sewage amended soil. Concentrations of p-DCB in carrot

foliage were 22.0 ppb for the low rate sewage amended soil and 60.0 and 45.0 ppb in the high rate amended soil. Conclusions from the study were that foliar uptake is an important bioaccumulation pathway for dichlorobenzenes.

### **Ecotoxicity**

High log octanol-water partition coefficient (log  $K_{ow}$ ) values of 3.43-3.53 suggests bioconcentration occurs in aquatic organisms (Hansch et al., 1995). In one study exposed guppies had a bioconcentration of 1800 (Spectrum, 2007). Additionally, bioconcentration factors from 370-720 for *Oncorhynchus mykiss* (rainbow trout) exposed to p-DCB under laboratory conditions (Calamari et al., 1982). Table 2 is a summary of ecotoxicity acute study values and Table 3 contains results for chronic studies for p-DCB (Boutonnet et al., 2004).

**Table 2. Acute ecotoxicity results for p-dichlorobenzene**

Species	Test duration hours (h) days(d)	Criterion (LC50/EC50 NOEC)	Concentration (mg/L)	Reference
<b>Freshwater</b>				
<i>Pimephales promelas</i>	96h	LC50	4.2	Carlson & Kosian (1987)
<i>Pimephales promelas</i>	96h	LC50	30.0	Curtis and Ward (1981)
<i>Pimephales promelas</i>	96h	LC50	3.6	Mayes (1983)
<i>Brachydanio rerio</i>	96h	LC50	2.1	Roederer (1990)
<i>Brachydanio rerio</i>	14d	NOEC	0.44	Roederer (1990)

**Table 2 Continued. Acute ecotoxicity results for p-dichlorobenzene.**

<b>Species</b>	<b>Test duration hours (h) days(d)</b>	<b>Criterion (LC50/EC50 NOEC)</b>	<b>Concentration (mg/L)</b>	<b>Reference</b>
<b>Freshwater</b>				
<i>Brachydanio rerio</i>	24h	LC50	4.25	Calamari (1983)
<i>Oncorhynchus mykiss</i>	24h	LC50	1.18	Roederer (1990)
<i>Jordanella floridae</i>	96h	LC50	4.5	Smith (1991)
<i>Poecilia reticulata</i>	14d	LC50	4.0	Canton (1985)
<i>Lepomis macrochirus</i>	96h	LC50	4.3	Buccafusco (1981)
<b>Freshwater Invertebrates</b>				
<i>Daphnia magna</i>	48h	LC50	2.2	Canton (1985)
<i>Daphnia magna</i>	14d	EC50 (reproductive effects)	0.93	Calamari (1982)
<i>Daphnia magna</i>	24h	EC50	1.6	Calamari (1982)
<i>Daphnia magna</i>	24h	EC50	3.2	Kuehn (1989)
<i>Daphnia magna</i>	48h	LC50 NOEC	11.0 0.68	LeBlanc (1980)
<b>Marine</b>				
<i>Cyprinodon variegatus</i>	96h	LC50	7.4	Heitmueller (1981)
<b>Saltwater</b>				
<i>Artemia salina</i>	24h	LC50	14.0	Abernethy (1986)
<i>Palamonetes pugio</i>	96h	LC50	60.0	Curtis and Ward (1981)
<i>Mysidopsis bahia</i>	96h	EC50	1.99	U.S. EPA (1978)

**Table 3. Chronic ecotoxicity study results for p-dichlorobenzene.**

Species	Test duration hours (h) days(d)	Criterion (LC50/EC50 NOEC)	Concentration (mg/L)	Reference
<b>Freshwater</b>				
<i>Daphnia magna</i>	28d	NOEC	0.22	Calamari (1982)
<i>Daphnia magna</i>	21d	NOEC	0.3	Kuehn (1989)
<i>Jordanella floridae</i>	28d 10d	NOEC NOEC	>0.35 0.20-0.23	Smith (1991)
<i>Oncorhynchus mykiss</i>	60d	NOEC	>0.122	Carlson and Kosian (1987)
<i>Brachydanio rerio</i>	28d	NOEC	1.0	Adema and De Ruiter (1987)
<b>Freshwater</b>				
Species	Test duration hours (h) days(d)	Criterion (LC50/EC50 NOEC)	Concentration (mg/L)	Reference
<b>Aquatic Plants</b>				
<i>Selenastrum capricornutum</i>	96h	EC50	1.6	Calamari (1982)
<i>Scenedesmus pannonicus</i>	72h	EC50	31.0	Canton (1985)
<i>Scenedesmus subspicatus</i>	48h	EC50	28.0	Kuehn and Pattard (1990)
<i>Scenedesmus subspicatus</i>	48h	EC50	38.0	Kuehn and Pattard (1990)
<i>Cyclotella meneghiniana</i>	48h	EC50	34.3	Figuroa and Simmons (1991)
<i>Ankistrodesmus falcatus</i>	4h	EC50	20.0	Wong (1984)
<b>Saltwater</b>				
<i>Skeletonema costatum</i>	96h	EC50	59.1	U.S. EPA

Water flea (*Daphnia magna*) has been identified as the most sensitive species to p-DCB (Table 3). Canton et al. (1985) reported a 48-hr LC<sub>50</sub> of 2.2 ppb, and Calamari et al., (1983) reported a 24 hr IC<sub>50</sub> (immobilization) of 1.6 ppb. Inhibition of growth and photosynthesis effects in freshwater algae (*Selenastrum capricornutum*) occurred at concentration of 1.6 ppb and 5.2 ppb (Calamari et al., 1982, 1983).

In a study measuring the effect of exposure to chlorobenzenes on growth rates of juvenile crabs (*Portunus pelagicus*) (Mortimer et al., 1995) concluded that at concentrations less than those that are acutely toxic to juvenile crabs, extended exposure to aqueous chlorobenzene solutions resulted in reduced growth rates.

Chironomid midge larvae (*Chironomus decorus*) were the subject of a study to observe the bioavailability of sediment bound DCBs (Knezovich et al., 1988). Sediments with high (14.5%) and low (3.6%) organic matter were used in the study. They observed that bioconcentration increased with increasing chlorination. Most of the uptake of chlorobenzenes occurred in the interstitial water.

Lake and rainbow trout from the Great Lakes have been documented to contain levels from 1.0-4.0 ppb p-DCB (Oliver, 1982). In the Calcasieu River estuary, Louisiana p-DCB in catfish ranged from non-detect to 0.17 to 0.47 ppm (Pereira, 1988). Concentrations of p-DCB in Atlantic croakers, blue crabs, spotted sea trout, and blue catfish from the Calcasieu River estuary were 0.24, 0.60, 0.90, and 2.5 ppm, respectively (ATSDR, 1995). Concentrations of p-DCB in amphipods and oligochaetes collected in Lake Ontario in 1981 were reported to be 370 and 630 ng/g (dry weight) (Fox, 1983).

In a marine mesocosm study Wakeham et al. (1983) reported a half-life of 18 days at 8-16 °C. Half lives ranging from 1.1 to 25 days were found at different sampling locations in Narragansett Bay coastal waters (EPA, 1985).

### **Biodegradation of p-Dichlorobenzene**

Various experiments have been performed worldwide demonstrating the capability of different strains of bacteria to effectively biodegrade chlorobenzenes. Specific requirements for bacterial degradation to occur include favorable physicochemical conditions, presence of the proper strain of bacteria, bioavailability of the targeted harmful chemical, micro/macronutrients, cosubstrates, and electron acceptors. Biodegradation has been investigated in soil, groundwater aquifers, and sediments of waterbodies.

In Bitterfeld, Saxonia Anhalt, Germany a chlorobenzene contaminated aquifer was subjected to several remediation technologies, one of which was based on the aerobic degradation of chlorobenzene with hydrogen peroxide as an oxygen-releasing compound in the presence of nitrate (Vogt et al., 2004). The degradation pathway is initiated by a dioxygenase attack and ortho cleavage of the 3-chlorocatechol formed and was determined to be the critical step in the metabolism of chlorobenzenes by bacteria. It was found that 3-chlorocatechol inhibit catechol-2-3-dioxygenase, the enzyme reaction necessary for degradation. In low oxygen situations 3-chlorocatechol accumulates. Oxygen was the limiting factor for mineralization to take place from biodegradation in the groundwater aquifer. Five bacterial strains (*Acidovorax facilis* B517, *Cellulomonas turbata* B529, *Pseudomonas veronii* B547, *Pseudomonas veronii* B549, and

*Paenibacillus polymyxa* B550) were isolated on chlorobenzene as their sole source of carbon and energy. The experiment demonstrated that in chlorobenzene contaminated water remediation situations with bacteria require knowledge of the complete pathway for the bioremediation to be successful.

A second study (Wenderoth et al., 2003) performed in the Bitterfeld, Leipzig, Germany region tested bioremediation strategies with bioaugmentation and biostimulation of various strains of bacteria in a quaternary aquifer contaminated with chlorobenzenes. Both strategies were successful in rapid degradation of chlorobenzenes in the groundwater aquifer. In the biostimulation assays, oxygen and nitrate were used as electron acceptors and when combined with specialized aerobic degraders lead to the fastest degradation.

A wetland soil experiment (Lee et al., 2003) further proved that microbial populations can directly access sorbed contaminant and that desorption-resistant p-DCB can be readily accessed by bacteria. The experiment proved that aged, sorbed contaminants are bioavailable and subject to environmental biodegradation.

### **Summary**

p-DCB is a volatile, mobile but non-persistent chemical that is ubiquitous in the environment due to its widespread use. The primary uses are as an insecticidal fumigant for domestic pests such as clothes moths and has little use as an agricultural pesticide in field situations. Although p-DCB is relatively widespread in aquatic systems most reported detections are below acute toxicity levels for aquatic organisms. The highest concentrations in surface water systems tend to occur near sewage treatment plants and are attributable to widespread use as toilet deodorant blocks. p-DCB has been detected in ground water but is biodegradable. Due to the volatility of p-DCB and its attendant capacity for atmospheric transport it has been found everywhere around the globe including remote polar areas. Bioaccumulation in sediments and food crops does occur and has led to contamination of aquatic species used for food consumption and is present in the human and animal food chain. Air, water, sediment, aquatic species, and humans are subject to p-DCB exposure throughout the world where environmental releases occur.

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