5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Chlorinated benzenes are produced typically by reacting liquid benzene with gaseous chlorine in the presence of a catalyst at moderate temperature (unspecified) and atmospheric pressure (IARC 1999; Rossberg et al. 2002). This reaction yields a mixture of chlorobenzene isomers with varying degrees of chlorination. A maximum dichlorobenzene yield of 98% is obtainable in a batch process in which 2 moles of chlorine is used per mole of benzene (mass ratio approximately 1.8:1) in the presence of ferric chloride and sulfur monochloride (IARC 1999). 1,2- and 1,4- DCB are the major DCB isomers formed in this process, with 1,2:1,4 ratios dependant on the type of catalyst used (Table 5-1). 1,3-DCB is also formed, but in much smaller quantities (Krishnamurti 2001). The DCB isomers are typically separated by crystallization and distillation.

Production of 1,4-DCB in the United States has risen from approximately 15 million pounds (6,800 metric tons) in 1981 to approximately 72 million pounds (32,600 metric tons) in 1993 (IARC 1999). The production volume of 1,4-DCB reported by manufacturers in 1998 and 2002 was within the range of greater then 50 million pounds to 100 million pounds (>23,000–45,000 metric tons) (EPA 2002e). The historical rate of growth of this chemical from 1989–1998 was 1.1 percent per year (CMR 1999).

Production of 1,2-DCB in the United States fell from approximately 54 million pounds (24,700 metric tons) in 1975 to approximately 35 million pounds (15,800 metric tons) in 1993 (IARC 1999). The production volume of 1,2-DCB reported by manufacturers in 1998 was within the range of >50 million pounds to 100 million pounds (>23,000–45,000 metric tons) (EPA 2002e). In 2002, companies reported production within the range of <10 million pounds to 50 million pounds (<5,000–23,000 metric tons) (EPA 2002e). The historical rate of growth of this chemical from 1986–1995 was 0.7 percent per year (CMR 1996).

Production of 1,3-DCB in the United States was <1 million pounds (500 metric tons) in 1983 (IARC 1999). The production volume of this chemical reported by manufacturers was within 10 thousand pounds to 500 thousand pounds (5–200 metric tons) during reporting year 1986, >1 million pounds to 10 million pounds (500–5,000 metric tons) during reporting year 1990, and >500 thousand pounds to

Table 5-1. Influence of Catalysts on the Ratio 1,4-:1,2-Dichlorobenzene

Catalyst	Proportion of 1,4-dichlorobenzene (in percent) in the dichlorobenzene fraction	Ratio 1,4- : 1,2-di-chlorobenzene
$MnCl_2 + H_2O$	ca. 50	1.03
$SbCl_5$		1.5
$FeCl_3$ or Fe	ca. 59	1.49–1.55
Metallosilicon organic compounds	61–74	1.56–2.8
$AlCl_3$ – $SnCl_4$		2.21
$AlCl_3$ – $TiCl_4$		2.25
Fe – S – PbO	ca. 70	
$FeCl_3$ – diethyl ether		2.38
Aluminum silicate-hexamethylene-diamine		2.7
$FeCl_3$ – S_2Cl_2	ca. 76	
$FeCl_3$ – divalent organic sulfur compounds	ca. 77	3.3
L-type zeolite	ca. 88	8.0
$TiCl_4$ (chlorinating agent is $FeCl_3$)		20–30

Source: Rossberg et al. 2002

1 million pounds (>200–500 metric tons) in reporting years 1994 and 1998 (EPA 2002e). Production volume data were not listed for reporting year 2002.

1,4-DCB is the most important of the three DCB isomers commercially (Elovaara 1998). However, the high 1,2- to 1,4-DCB ratio has traditionally created an isomer imbalance in the DCB market (CMR 1999). Decreasing demand for 1,2-DCB in recent years has resulted in an increased economic disadvantage for the companies producing these chemicals.

1,4-DCB and 1,2-DCB are currently produced by 2 U.S. companies at 2 different locations: Solutia Inc., in Sauget, Illinois and PPG Industries, Inc., in Natrium, West Virginia (SRI 2005). Current annual 1,4-DCB production capacity for Solutia Inc. and PPG Industries, Inc. are 39 and 40 million pounds (17,700 and 18,100 metric tons), respectively (SRI 2005). Total annual production capacity for this isomer has fluctuated during the last 2 decades. The annual production capacity was 119 (54,000), 132 (59,900), 371 (168,000), 144 (65,000), 145(66,000), 154(70,000), and 79 (35,800) million pounds (metric tons) in 1983, 1988, 1995, 1997, 1999, 2001, and 2003 respectively (SRI 1984, 1988, 1995, 1997, 1999, 2001, 2003). Current annual 1,2-DCB production capacity for Solutia and PPG are 13 and 20 million pounds (5,900 and 9,000 metric tons), respectively (SRI 2005). The annual production capacity for the 1,2- isomer was 78 (35,000), 81 (37,000), 81 (37,000), 76 (34,000), 80 (36,000), 83 (38,000), and 33 (15,000) million pounds (metric tons) in 1983, 1988, 1995, 1997, 1999, 2001, and 2003 respectively (SRI 1984, 1988, 1995, 1997, 1999, 2001, 2003).

Tables 5-2, 5-3, and 5-4 list the facilities in each state that manufacture or process 1,2-, 1,3-, and 1,4-DCB, respectively. These tables give the intended use and the range of maximum amounts of each DCB isomer that are stored on site. The data listed in Tables 5-2 through 5-4 are derived from the Toxics Release Inventory (TRI03 2005). Only certain types of facilities were required to report (EPA 1997b). Therefore, this is not an exhaustive list.

5.2 IMPORT/EXPORT

In 1978, about 1.09×10^4 kg (24,030 pounds) of 1,4-DCB were imported into the United States (HSDB 2005; NTP 1989). Import volumes of 1,4-DCB were 867,441 kg (1.9 million pounds), 1,113,676 kg (2.5 million pounds), 996,649 kg (2.2 million pounds), 3,283,759 kg (7.2 million pounds), and 3,019,233 kg (6.7 million pounds) for 1990, 1991, 1992, 1993, and 1994, respectively. U.S.

Table 5-2. Facilities that Produce, Process, or Use 1,2-Dichlorobenzene

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	3	1,000	999,999	6, 11, 12
AR	12	100	49,999,999	2, 3, 6, 7, 10, 12
AZ	1	1000	9,999	11
CA	15	100	9,999,999	2, 3, 7, 8, 9, 11, 12
CO	1	1,000	9,999	7
CT	2	1,000	99,999	12
DE	6	1,000	9,999,999	1, 3, 4, 6, 7, 9
FL	2	10,000	99,999	7, 11
GA	3	1,000	99,999	7, 8
IL	3	1,000	9,999,999	1, 4, 12
IN	8	100	999,999	2, 3, 7, 10, 12
KS	3	100	99,999	12
KY	2	10,000	999,999	1, 3, 6
LA	12	100	999,999	1, 5, 6, 10, 12
MA	8	100	999,999	7, 10, 11, 12
MI	4	0	9,999	7, 8, 9, 12
MN	1	1,000	9,999	12
MO	6	100	99,999,999	7, 9, 12
MS	5	0	999,999	1, 3, 9, 11, 12
NC	12	100	999,999	2, 3, 6, 7, 10, 11, 12
NE	2	10,000	999,999	12
NH	1	0	99	12
NJ	22	1,000	9,999,999	2, 3, 6, 7, 8, 9, 10, 12, 14
NY	8	1,000	999,999	10, 11, 12
OH	8	1,000	9,999,999	3, 7, 9, 10, 11, 12
OK	1	1,000	9,999	12
OR	2	10,000	99,999	8, 12
PA	9	0	999,999	3, 7, 10, 11, 12
RI	4	1,000	99,999	7, 8, 10
SC	6	100	999,999	6, 10, 11, 12
TN	3	10,000	999,999	10, 11
TX	31	100	9,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13
VA	2	10,000	999,999	12
WI	3	10,000	999,999	9, 10
WV	6	100,000	49,999,999	1, 4, 10, 11

Source: TRI03 2005 (Data are from 2003)

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Table 5-3. Facilities that Produce, Process, or Use 1,3-Dichlorobenzene

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AR	1	1,000	9,999	12
CA	1	100	999	12
DE	7	100	9,999,999	1, 3, 4, 5, 6, 13
IL	5	1,000	9,999,999	1, 4, 5, 12, 13
IN	1	100	999	12
KY	1	10,000	99,999	1, 3, 6
LA	4	1,000	999,999	1, 5
MI	2	100,000	999,999	2, 3, 6
MO	3	100	99,999	6, 12
MS	1	100	999	12
NJ	3	100	999,999	3, 6, 10, 12
OH	2	1,000	99,999	12
SC	1	10,000	99,999	6
TX	7	0	99,999	1, 5, 11, 12, 13
WV	3	100,000	9,999,999	1, 4, 5, 13

Source: TRI03 2005 (Data are from 2003)

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Table 5-4. Facilities that Produce, Process, or Use 1,4-Dichlorobenzene

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AR	6	1,000	99,999	1, 2, 6, 7, 12, 13
CA	2	100	999	3, 4, 9, 12
DE	2	1,000,000	49,999,999	1, 3, 4, 6
FL	4	10,000	99,999	4, 7, 9
GA	9	1,000	999,999	7, 8, 9, 12
IL	8	0	9,999,999	1, 2, 3, 4, 7, 9, 11, 12, 14
IN	6	100	99,999	7, 8, 11, 12
KS	8	100	999,999	7, 9, 12
KY	3	1,000	99,999	2, 4, 12
LA	8	0	999,999	1, 5, 6, 13
MA	5	1,000	999,999	2, 3, 7, 11
MI	2	1,000	99,999	2, 5
MO	4	100	999,999	1, 5, 8, 12
NC	5	100	999,999	2, 3, 6, 11, 12
NE	1	10,000	99,999	12
NJ	12	1,000	999,999	2, 3, 4, 7, 8, 9, 12
NY	1	100	999	2, 4
OH	13	1,000	999,999	1, 2, 3, 4, 7, 8, 9, 10, 11, 12
OK	4	1,000	99,999	2, 3, 6, 8
PA	6	100	99,999	3, 7, 9, 10, 11, 12
SC	2	10,000	99,999	6, 12
TX	12	0	49,999,999	1, 2, 3, 5, 6, 7, 12, 13
UT	1	1,000	9,999	12
VA	1	1,000	9,999	12
WV	1	1,000,000	9,999,999	1, 4

Source: TRI03 2005 (Data are from 2003)

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

imports of 1,2-DCB were 6,300 kg in 1972 and 1,230,000 kg in 1975 (HSDB 2005). U.S. imports of 1,3-DCB were 56,600 kg in 1983 (HSDB 2005). More recent import data for the DCB isomers were not available.

In 1972, U.S. exports of 1,4-DCB were reported to be $4.5x10^6$ kg (9.9 million pounds) (HSDB 2005). Exports of 1,4-DCB have expanded through the 1980s at about 1–2% per year due to the growth in production of polyphenylene sulfide (PPS) resin overseas (HSDB 2005; NTP 1989). In 1990, the United States exported about 25% (about 33 million pounds) of its 1,4-DCB production volume (CMR 1990). Export volumes of 1,4-DCB were 11,925,179 kg (24.1 million pounds), 11,185,034 kg (24.7 million pounds), 10,651,337 kg (23.5 million pounds), 13,390,545 kg (29.5 million pounds), and 11,078,150 kg (24.4 million pounds) for 1990, 1991, 1992, 1993, and 1994, respectively. 1,4-DCB exports during 1994–1997 averaged 25 million pounds (11,000 metric tons) (CMR 1999). U.S. exports of 1,2-DCB averaged 14 million pounds (6,000 metric tons) per year during 1991–1995 (CMR 1996). Export data for 1,3-DCB were not available.

Based on a 1993 production volume value of 72 million pounds (32,600 metric tons), an import value of 7 million pounds (3,000 metric tons), and an export value of 30 million pounds (14,000 metric tons), the total amount of 1,4-DCB available for use in U.S. commerce in 1993 was 49 million pounds (22,000 metric tons). Based on a 1993 production volume value of 35 million pounds (15,800 metric tons) and an export value of 14 million pounds (6,000 metric tons), the total amount of 1,2-DCB remaining in the United States in 1993 was 21 million pounds (10,000 metric tons) assuming that imports of this chemical during that year were negligible. It should be noted, however, that not all of the 1,2-DCB that is produced is expected to be available for use since large quantities of this chemical are more likely to be disposed of when it is produced as a byproduct in the production of 1,4-DCB. Although reported export values for 1,2- and 1,4-DCB show that considerable amounts of these chemicals have been sent to other countries in previous years, the production volumes for these chemicals have been consistently higher suggesting that more than half of the amounts produced each year have remained in the United States.

5.3 USE

For the past 20 years, 1,4-DCB has been used principally (25–55% of all uses) as a space deodorant for toilets and refuse containers, and as a fumigant for control of moths, molds, and mildews. In recent years, the use of 1,4-DCB in the production of polyphenylene sulfide (PPS) resin has increased steadily (25–

50% of its total use). 1,4-DCB is also used as an intermediate in the production of other chemicals such as 1,2,4-trichlorobenzene (approximately 10%). Minor uses of 1,4-DCB include its use in the control of certain tree-boring insects and ants, and in the control of blue mold in tobacco seed beds (CMR 1999; HSDB 2005).

1,2-DCB is used primarily as a precursor to 3,4-dichloroaniline herbicides. Other uses of 1,2-dichloroaniline include its use as a solvent, in the synthesis of dyes, and in odor control products (CMR 1996; HSDB 2005).

1,3-DCB has been used in the production of herbicides and insecticides as well as in the production of pharmaceuticals and dyes (IARC 1999).

5.4 DISPOSAL

Wastes containing DCBs are considered hazardous if they meet certain criteria specified by law. Hazardous wastes are subject to the handling, transport, treatment, storage, and disposal regulations as promulgated under the Resource Conservation and Recovery Act (HSDB 2005; IRPTC 1985). Regulations governing the treatment and disposal of wastes containing DCBs are detailed in Chapter 8.

Incineration by appropriate means is the recommended method for the disposal of waste 1,4-DCB (HSDB 2005). 1,4-DCB may be disposed of by making packages of the chemical in paper or other disposable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device or by dissolving the chemical in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device (IRPTC 1985). Halogenated compounds may be disposed of by incineration provided they are blended with other compatible wastes or fuels so that the composite contains <30% halogens. Liquid injection, rotary kiln, and fluidized bed incinerators are typically used to destroy liquid halogenated wastes. Temperatures of at least 2,000–2,200 °F are necessary. Residence times of seconds are required for liquids and gases, while hours are required for solids (HSDB 2005). 1,2-DCB is produced in large quantities as a byproduct during the production of 1,4-DCB. Unused supplies may be disposed of or released directly into the environment.

No data were located regarding historic disposal trends or the amounts of 1,2-, 1,3-, or 1,4-DCB disposed of by different means.