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Materials Balance for Chlorobenzenes

Review Copy

Level I — Preliminary

FINAL REPORT
MATERIALS BALANCE - TASK #4
CHLOROBENZENES

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Prepared for:

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THE FINAL REPORT PRESENTED HEREIN RESULTED FROM A LEVEL I MATERIALS BALANCE STUDY ON CHLOROBENZENES. THE RESULTS WERE BASED ON AN ANALYSIS OF LITERATURE SUPPLIED BY EPA. ALTHOUGH SUPPLEMENTARY INFORMATION UNDOUBTEDLY EXISTS, OBTAINING IT WAS OUTSIDE THE SCOPE OF THIS TASK. THE LEVEL I REPORT IS INTENDED TO SERVE AS A FOCUS OF DISCUSSION AND AS A BASIS FOR FUTURE MATERIALS BALANCE STUDIES; IT IS NOT MEANT TO BE A DEFINITIVE STUDY.

MATERIALS BALANCE LEVELS

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below.

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division as a source of data and references involving readily available information. Most Level I MB's are completed within a 3-6 week period; CID literature searches generally require a 2 week period to complete. Thus the total time required for completion of a Level I materials balance ranges from 5-7 weeks.

Level II:

A Level II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature, (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A Level III study requires generation of new data through monitoring and other means. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and necessary monitoring. The data generated in this type of study are intended to be statistically valid and have known confidence values. The goal is a study upon which regulations or legal proceedings may be based.

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EXECUTIVE SUMMARY

General Description of Chlorinated Benzenes

Chlorinated benzenes are halogenated aromatic compounds. There are twelve compounds in this group and their structures and nomenclature are summarized in Appendix A. Physical properties of the various chlorinated benzenes are shown in Appendix B. While most of the chlorobenzenes are white crystalline solids, mono-, 1,2-di-, 1,3-di- and 1,2,4-trichlorobenzene are liquids. The mono- and dichlorobenzenes each have a distinctive aroma and are flammable. The lower chlorinated benzenes are more volatile than the higher chlorinated benzenes and significant amounts of these compounds may be lost to air. All of the chlorinated benzenes are highly lipid soluble (Investigation of Selected Potential Environmental Contaminants, 1977) and the higher chlorinated benzenes have a tendency to bioaccumulate. In addition, chlorinated benzenes are considered to be insoluble in water. However, some amounts of these substances (e.g., 49 mg monochlorobenzene/100g water at 30°C; Investigation of Selected Potential Environmental Contaminants, 1977) are soluble in water. Due to the fact that these compounds have a higher density than water, any quantities which are not soluble would tend to sink in a still lake.

Production and Primary Uses

Flow diagrams for production and use of various chlorinated benzenes are shown in Figure 1.

Monochlorobenzene production in 1977 was 147,700 kkg. Imports of this compound were 500 kkg. Monochlorobenzene is used consumptively in the production of chloronitrobenzene (35%), diphenyl oxide (10%), rubber intermediates (10%), and DDT (7%). Nonconsumptive uses include the production of adhesives, paints, polishes and waxes and use as an inert process solvent (30%).

o-Dichlorobenzene production and import in 1977 were 21,500 kkg and 500 kkg, respectively. Export of o-dichlorobenzene was estimated at 7300 kkg. o-Dichlorobenzene is used consumptively in the production of dyes (5%) and 3,4-dichloroaniline (65%). Its nonconsumptive uses include solvent use (25%) and use as a pesticide and deodorant ($<5\%$).

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FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)

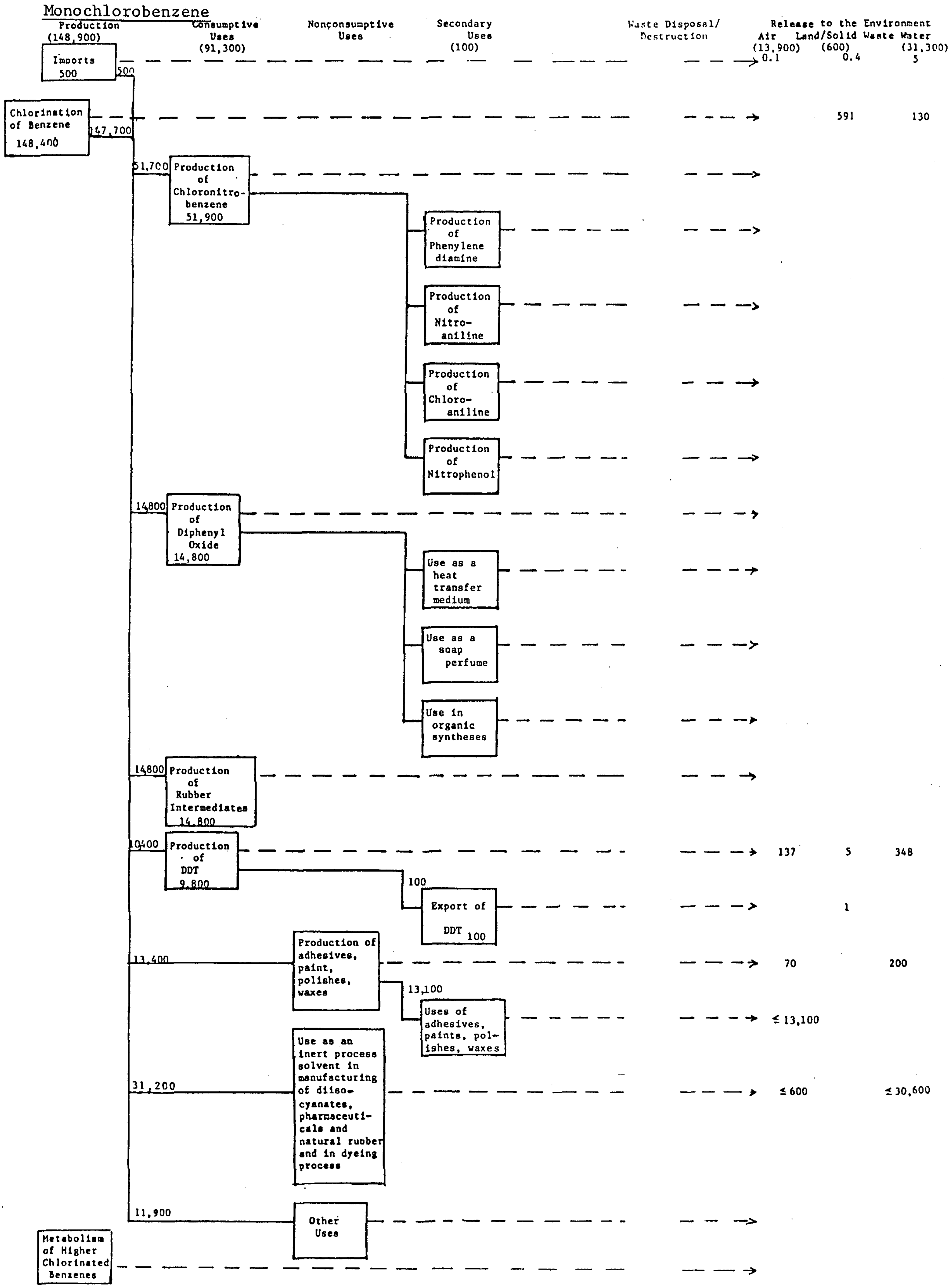


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

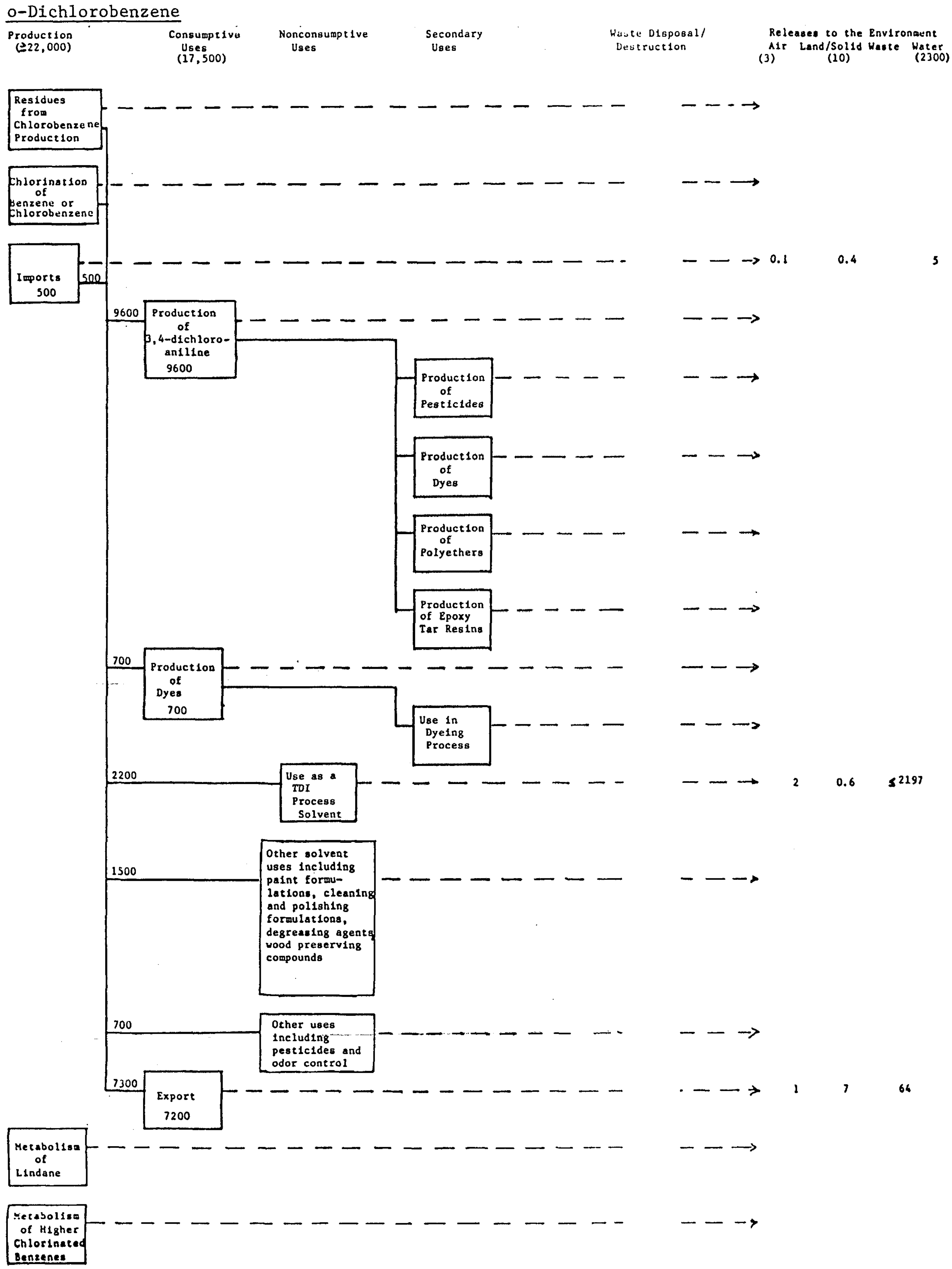
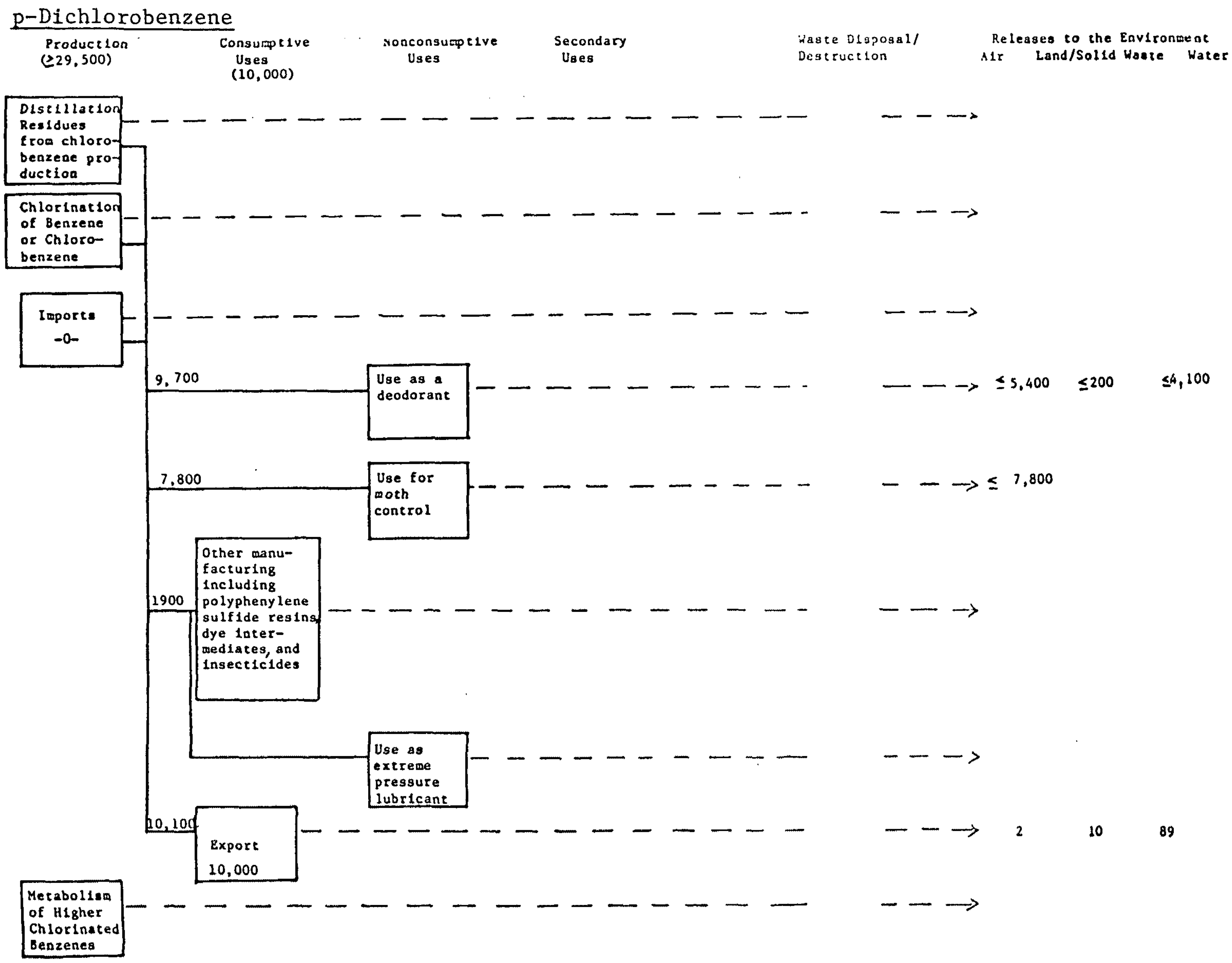


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)



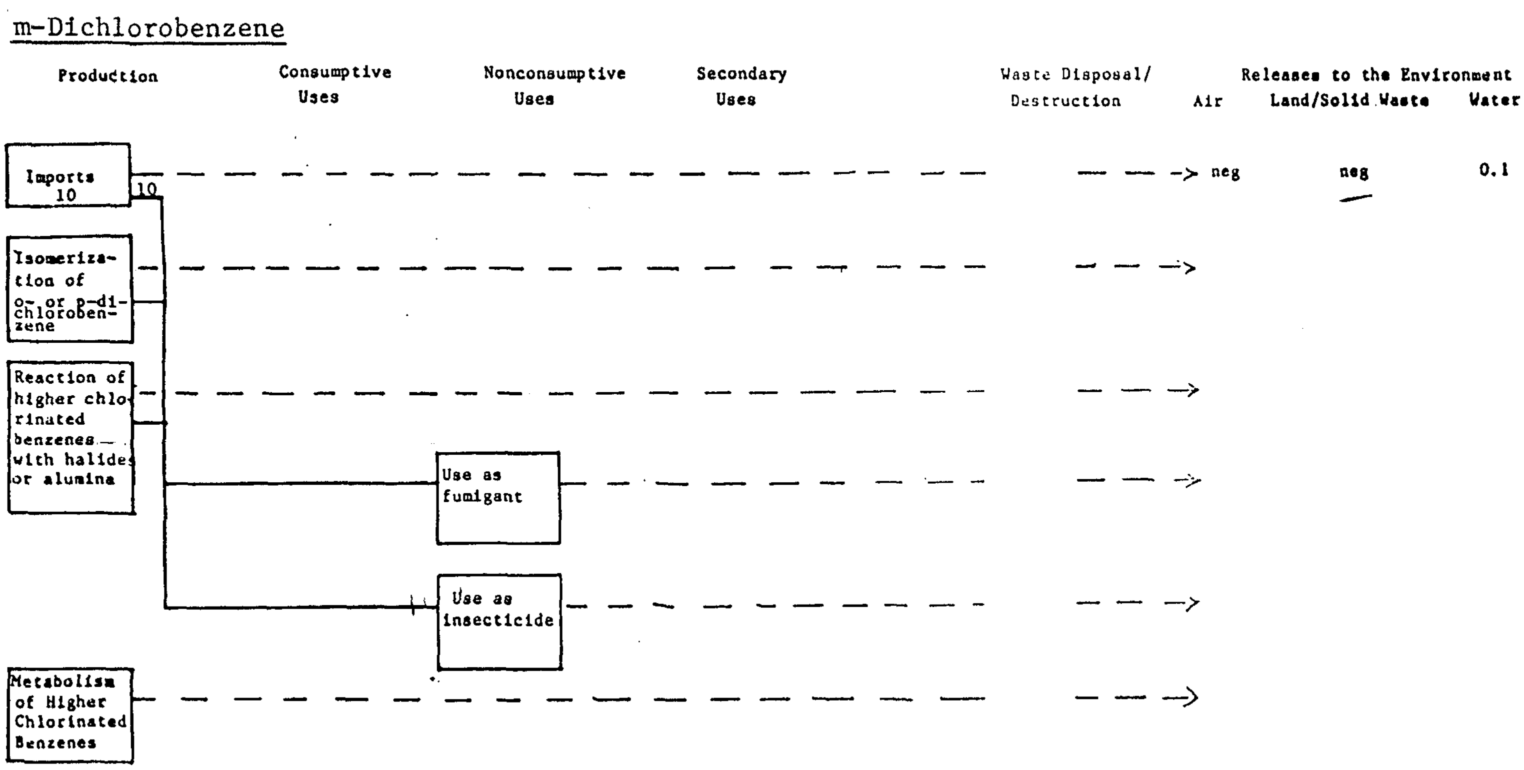


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

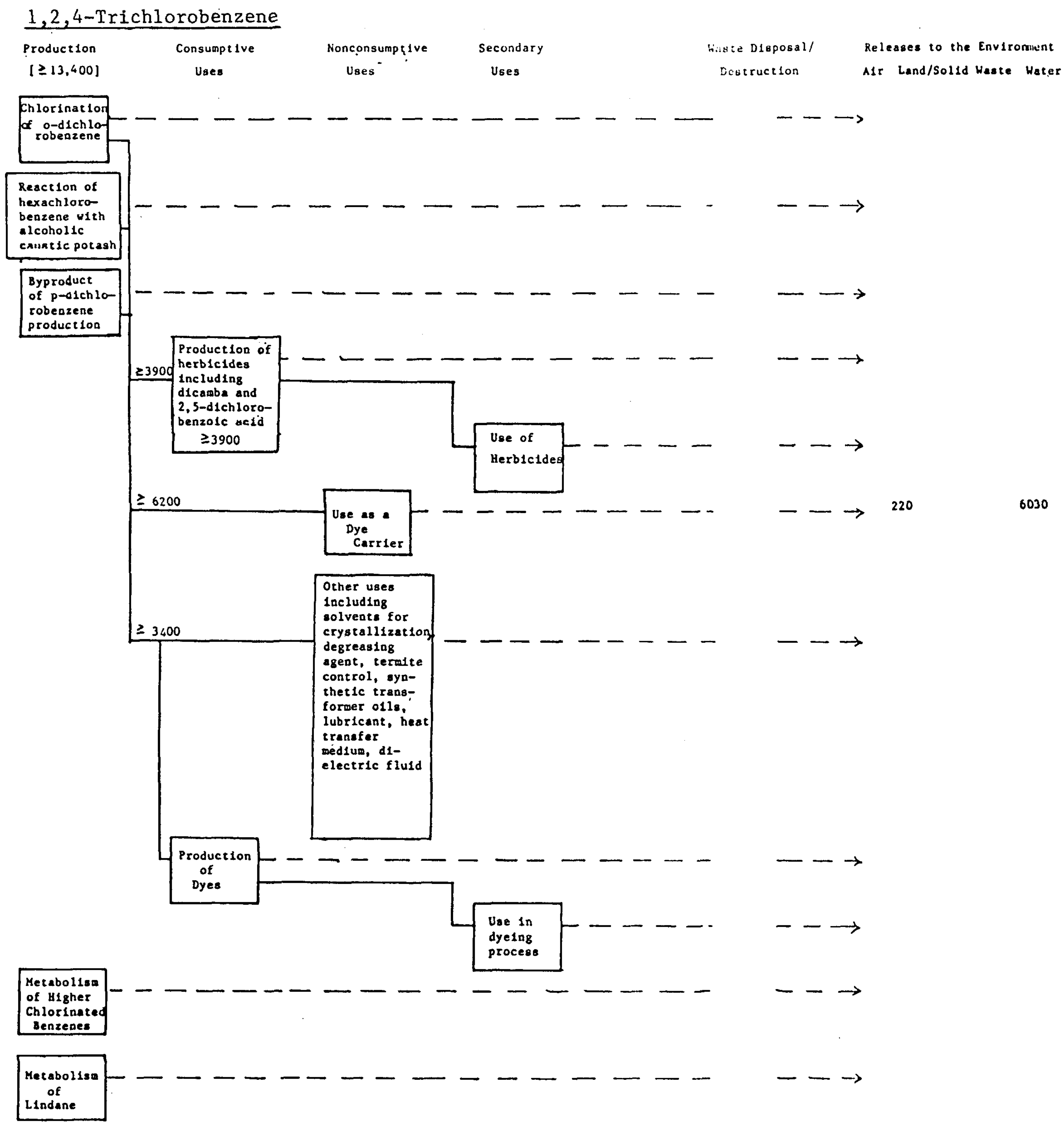
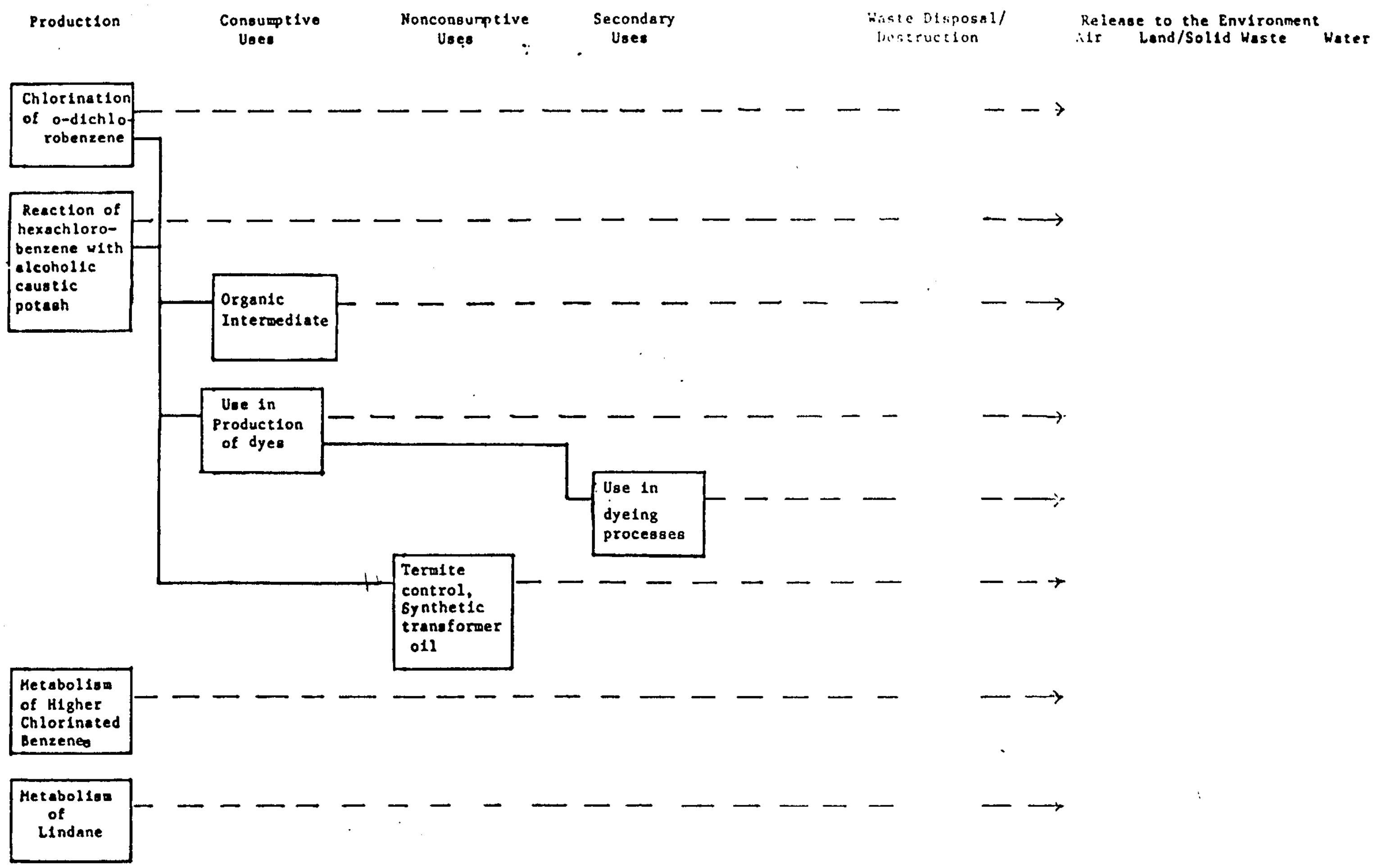


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

1,2,3-Trichlorobenzene



1,3,5-Trichlorobenzene

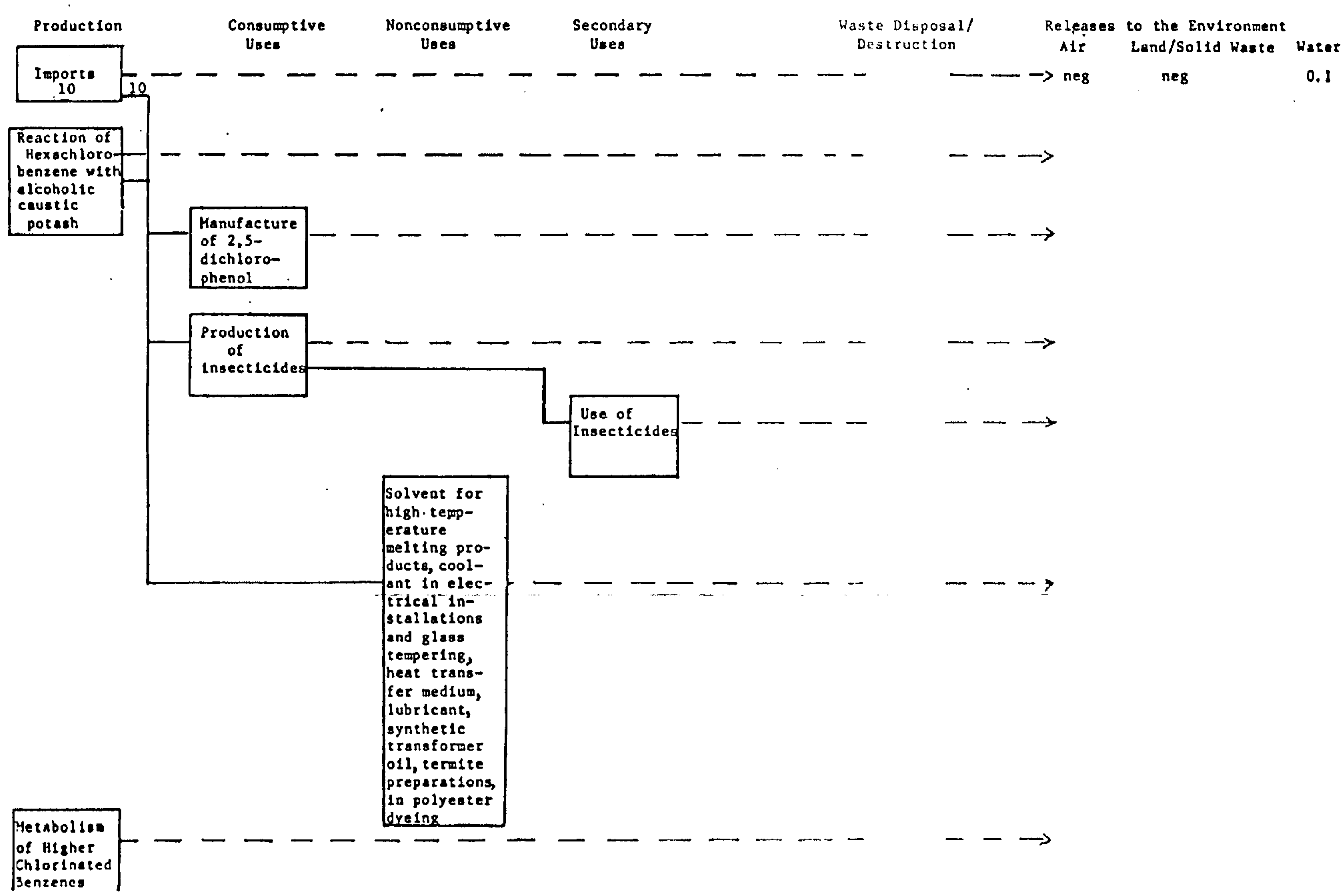
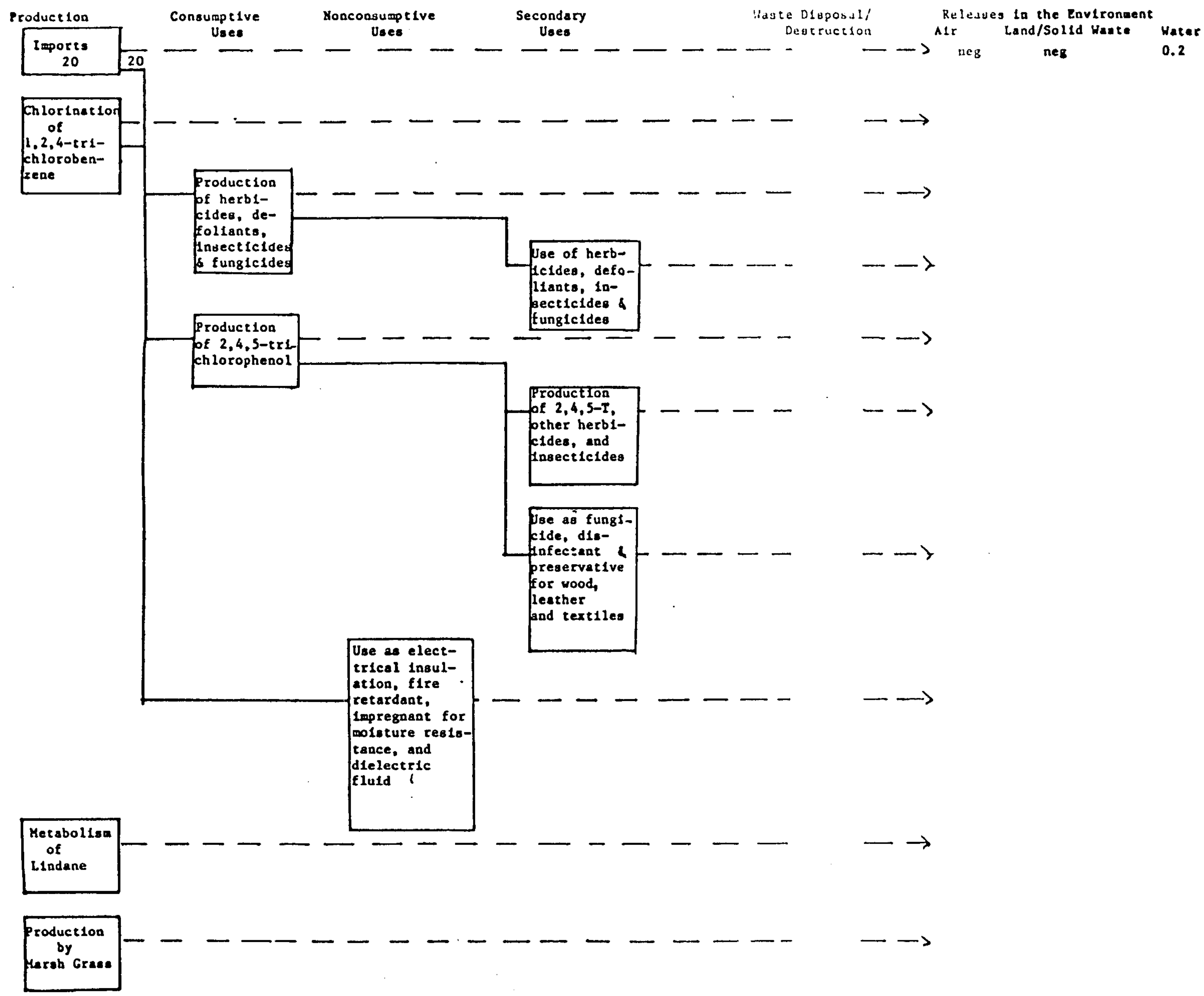


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

1,2,4,5-Tetrachlorobenzene



1,2,3,5-Tetrachlorobenzene

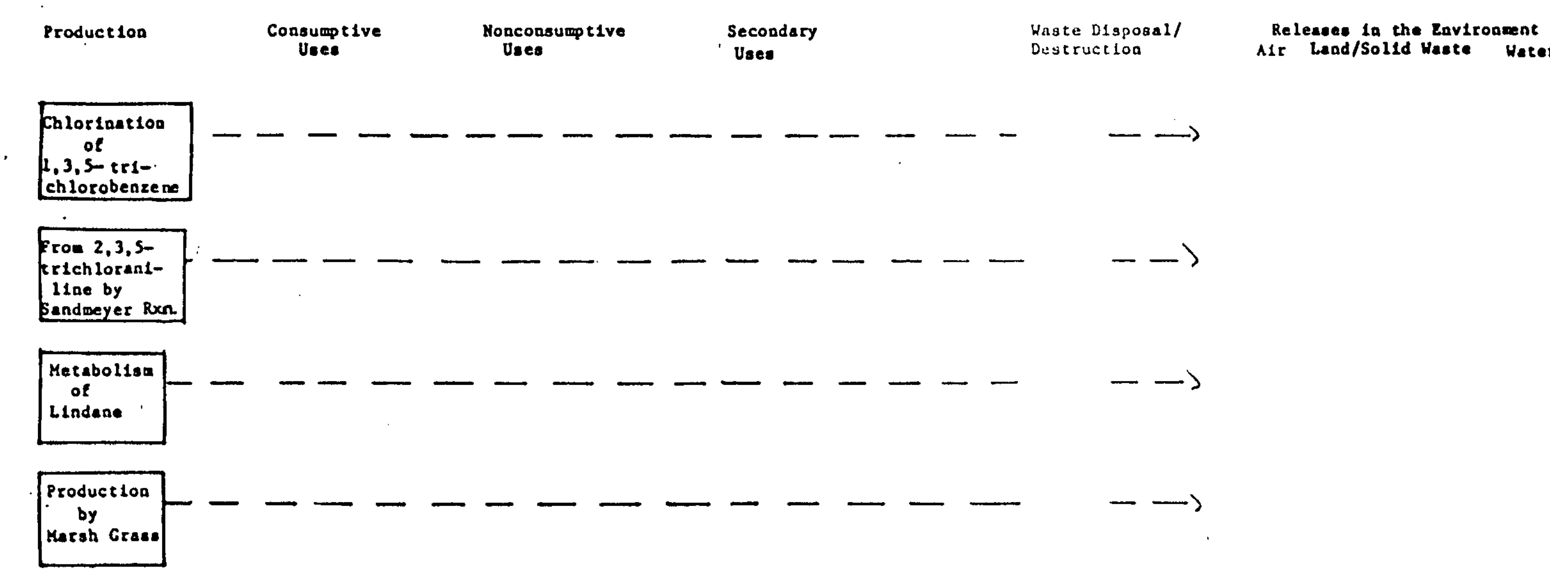
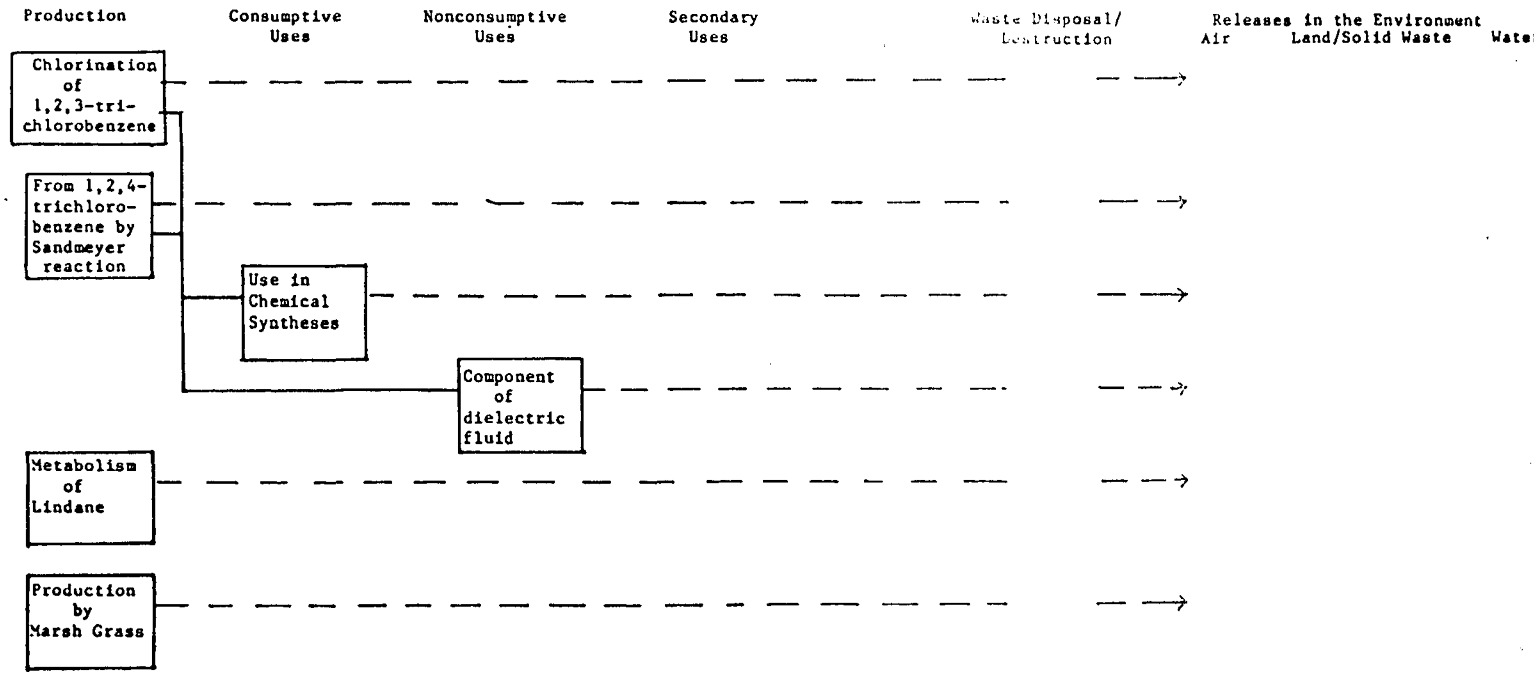


FIGURE 1 FLOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

1,2,3,4-Tetrachlorobenzene



Pentachlorobenzene

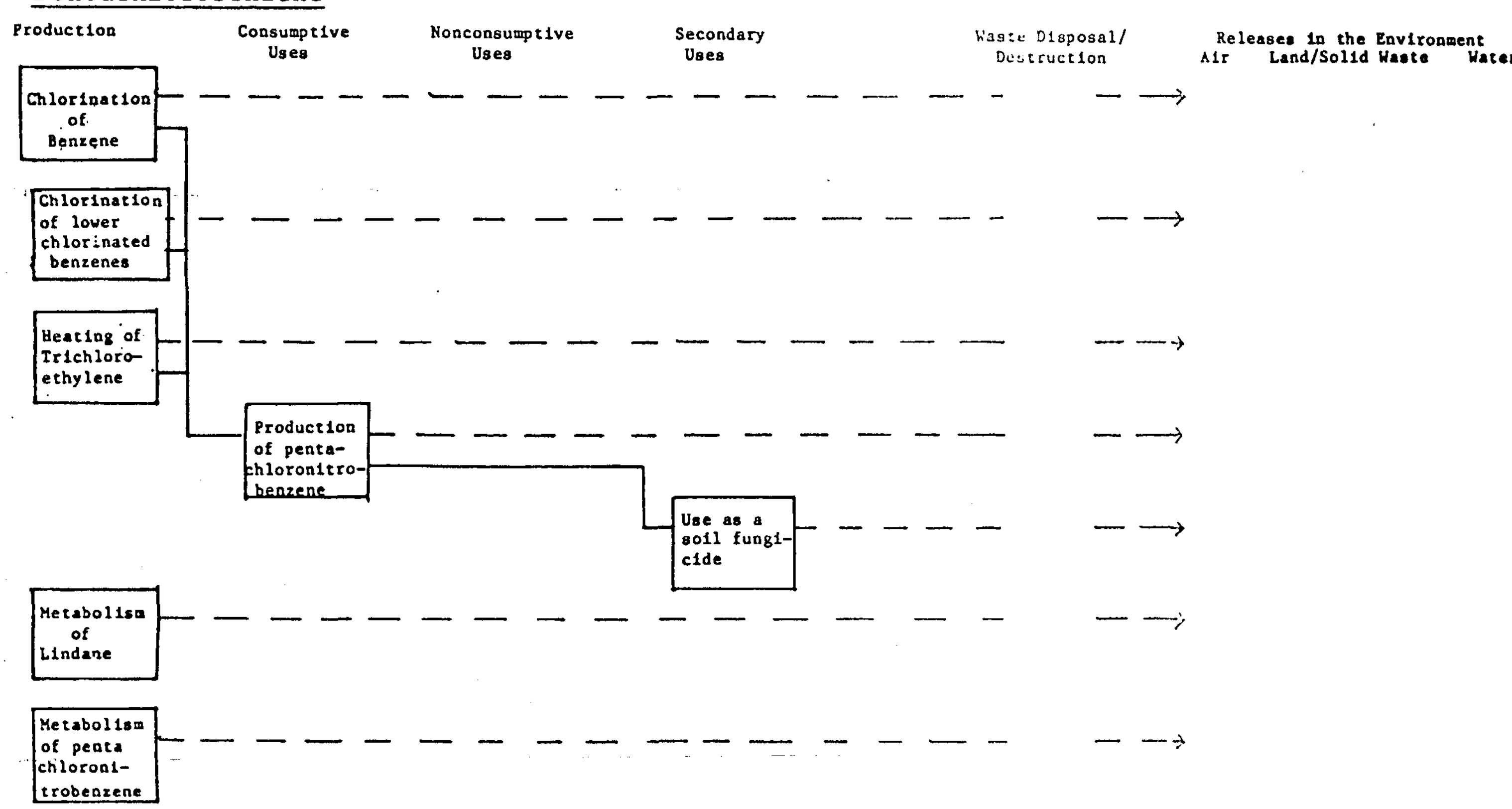
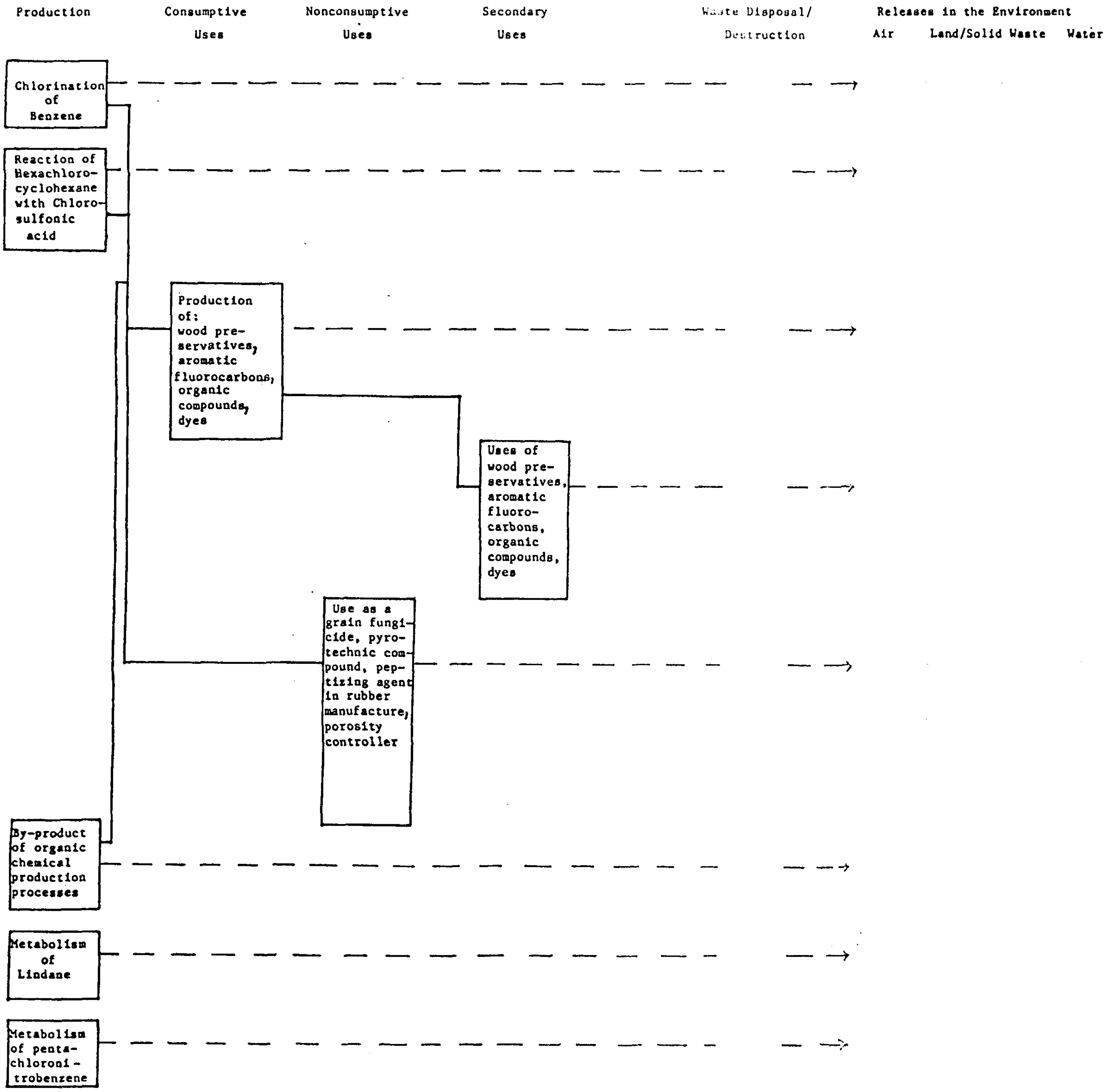


FIGURE 1 FlOW DIAGRAM FOR CHLORINATED BENZENES (kkg)(continued)

Hexachlorobenzene



p-Dichlorobenzene production in 1977 was 29,500 kkg. Its export was estimated at 10,100 kkg. p-Dichlorobenzene is used mainly as a deodorant (50%) and for moth control (40%).

The amounts of m-dichlorobenzene produced are unknown. Imports of this compound in 1977 were 10 kkg. m-Dichlorobenzene is used as a fumigant and insecticide.

Production of 1,2,4-trichlorobenzene in 1977 was estimated to be greater than 13,400 kkg. Import and export figures for 1,2,4-trichlorobenzene are unknown. 1,2,4-Trichlorobenzene is used primarily as a dye carrier (46%) and in the production of herbicides (29%). It also has many minor uses (25%).

Production figures for 1,2,3- and 1,3,5-trichlorobenzene are unknown, as are the quantities exported. Ten kkg of 1,3,5-trichlorobenzene were imported in 1977. 1,2,3-Trichlorobenzene is used in the production of dyes and other organic compounds, in termite control and as a synthetic transformer oil. 1,3,5-trichlorobenzene is used in the production of 2,5-dichlorophenol and insecticides and for a variety of nonconsumptive uses.

Production figures for 1,2,4,5-, 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene are also unknown. Twenty kkg of 1,2,4,5-tetrachlorobenzene were imported in 1977. Uses of 1,2,4,5-tetrachlorobenzene include the production of herbicides, defoliants, insecticides, fungicides, disinfectants and preservatives. It has numerous other uses. Uses of 1,2,3,5-tetrachlorobenzene are unknown. 1,2,3,4-Tetrachlorobenzene is used in chemical syntheses and as a component of dielectric fluids.

Production, import, and export data for pentachlorobenzene is unknown. Pentachlorobenzene is used in the synthesis of pentachloronitrobenzene, a soil fungicide.

Hexachlorobenzene production in 1977 was estimated at 2,700 kkg. Imports and exports are unknown. Hexachlorobenzene is used in the production of wood preservatives, aromatic fluorocarbons, dyes and other organic compounds. Its nonconsumptive uses include use as a grain fungicide, pyrotechnic compound, peptizing agent in rubber manufacture, and porosity controller.

Releases of Chlorinated Benzenes

The total releases of chlorinated benzenes to the environment from their production and use were estimated to be at least 72,000 kkg. Of this amount, the greatest releases appear to be to water (61%), while smaller amounts enter the atmosphere (38%), or are deposited on land (1%). Monochlorobenzene, dichlorobenzene and 1,2,4-trichlorobenzene contributed 46,000 kkg, 20,000 kkg and 6,000 kkg, respectively. Since very little quantitative information was available for the other chlorinated benzenes, it was not possible to estimate their releases. In general, releases from uses appear to be greater than releases during production. This appears to be due to the large number of nonconsumptive uses of the products.

In addition to releases during the production and use of chlorinated benzenes, significant releases of hexachlorobenzene occur due to its formation as a byproduct in the production of chlorinated solvents and pesticides. Releases may occur during formation or use of the chlorinated products, recovery of hexachlorobenzene from byproducts, or disposal of wastes.

Materials Balance for Chlorinated Benzenes

In theory, the amount of chlorinated benzenes produced should balance with the amounts consumed or destroyed (e.g., consumptive uses, export, waste incineration), the amounts stored and the amounts released. However, due to a lack of readily available quantitative information, the materials balances presented in this report do not completely balance. These materials balances do represent our best understanding of the flow of the chlorinated benzenes between production and environmental release, and serve as a basis for further studies.

1.0 INTRODUCTION

This report presents the results of a Level I Environmental Materials Balance for chlorobenzenes. This study has been prepared in response to a task order from the United States Environmental Protection Agency (EPA) Office of Pesticides and Toxic Substances (OPTS). The primary objective of the study is to determine, within the constraints of time and information availability, the quantities of chlorobenzenes annually released to the environment and the sources of these releases.

This study involves twelve compounds: monochlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene. In order to perform this multiple materials balance, these compounds are presented by chemical groupings (e.g., dichlorobenzenes, trichlorobenzenes, etc.) within each chapter.

Chlorobenzenes are halogenated aromatic compounds that are produced by the chlorination of benzene. These compounds are used in the manufacture of organic chemical intermediates, herbicides, pesticides, dyes, and rubber chemicals. Chlorobenzenes are also used as dye carriers, process solvents, pesticides, and deodorizing agents.

2.0 RELEASES FROM MANUFACTURE OF CHLORINATED BENZENES

2.1 OVERVIEW

Chlorobenzene compounds are formed by the substitution of hydrogen atoms on the benzene ring by chlorine. These chlorine atoms, once in place on the ring, influence and direct further substitution of hydrogen by chlorine. Therefore, some isomers are preferentially produced, and some of the higher chlorinated benzenes can be made only by seemingly less direct routes because of this influence. However, only chlorobenzene and o- and p-dichlorobenzene are of great industrial importance, and these compounds are are easily formed (Snell and Ettre, 1970).

2.2 PRODUCTION AND MANUFACTURERS

2.2.1 Quantities Produced

Current production data are available for chlorobenzene and o- and p-dichlorobenzene. Table 2.1 summarizes the production figures for these compounds from 1974 to 1977. Chlorobenzene is produced in much greater quantities then o- and p-dichlorobenzene.

Little information was available on the quantities of other chlorobenzenes being produced. The USITC ceased reporting the production of trichlorobenzenes after 1973 and did not report any production statistics for the higher chlorinated benzenes during the period 1974 to 1977. The USITC will report production statistics for a chemical or group of chemicals when (1) there are three or more producers and none dominate the production, (2) publication of the information would not constitute an unlawful disclosure of confidential information, and (3) the volume of sales or production is greater than 5,000 pounds or the sales value is $5,000 or more (USITC, 1978a, 1977a, 1977b, 1976a). Evidently, reporting production statistics for tri-, tetra-, penta- and hexachlorobenzene would violate one or more of the requirements listed above.

TABLE 2.1 PRODUCTION (kkg)

Compound	1974	1975	1976	1977
chlorobenzene	172,000	138,800	149,300	147,700
o-dichlorobenzene		24,800	22,000	21,500
p-dichlorobenzene		20,800	16,600	29,500

Source: (USITC, 1978a, 1977a, 1977b, 1976a)

Table 2.2 summarizes the available production information for the higher chlorinated benzenes. It is estimated that 13,400 kkg of 1,2,4-trichlorobenzene were produced in the United States in 1977 (see Table 2.2, footnote 1). Comer et al. (1979) notes that the major source of 1,3,5-trichlorobenzene is importation (no production information was available). Hexachlorobenzene is a specialty chemical that is not produced in great quantities and is produced only when needed (Blackwood and Sipes, 1977).

2.2.2 Manufacturers

Most manufacturers of chlorobenzene produce more than one isomer and each plant has the capability to vary production of a particular compound in response to the market demand (Investigation of Selected Potential Environmental Contaminants, 1977). Table 2.3 lists those companies that produced chlorobenzenes in 1977, and which isomers or their mixtures were produced. This table is based on the USITC report for 1977; it may not be a complete list of the producers of chlorobenzenes since small producers are not reported.

Table 2.4 lists other known producers of chlorobenzenes and which isomers they produce. It is uncertain whether these companies produced these chlorobenzenes in 1977. Some companies (Hooker and Transvaal) no longer produce chlorobenzenes. One company, Specialty Organics, is a processor rather than a producer; this company processes mixtures of chlorobenzenes purchased from other companies to produce the separate isomers. Also included in this table are those 1977 producers that were mentioned in the literature as producing or having the capacity to produce isomers that they were not listed as producing in 1977 by the USITC.

The largest producers of chlorobenzene are Dow, Monsanto, Montrose, PPG, and Standard Chlorine. These companies are also the major producers of o- and p-dichlorobenzene. (Investigation of Selected Potential Environmental Contaminants, 1977.) The locations of these and other producers of chlorobenzenes are located on the map in Figure 2.1. The majority of the companies are located in the Midwest and Eastern regions of the United States.

TABLE 2.2 PRODUCTION OF HIGHER CHLORINATED BENZENES (kkg)

Compound	Amount	Year	Source
1,2,4-trichlorobenzene	13,400[1]	1977	
hexachlorobenzene	1,500	1975	Blackwood and Sipes, 1977
	2,700[2]	1977	Saxton and Narkus-Kramer, 1975

1. Production of 1,2,4-trichlorobenzene was estimated as follows:

   a) It was stated that PPG Industries, Inc. produced 300 kkg/yr and that Dow Chemical Co. produced 3600 kkg/yr of 1,2,4-TCB (Comer et al., 1979).

   b) Since Dow Chemical Co. was producing 1,2,4-TCB at approximately 80% of capacity (4500 kkg; Investigation of Selected Potential Environmental Contaminants, 1977), we estimated that other plants were also producing 1,2,4-TCB at 80% capacity.

   c) Plant capacities for Standard Chlorine of Delaware (8200 kkg; Investigation of Selected Potential Environmental Contaminants, 1977) and ICC Industries (3600 kkg; Hydroscience, 1978) were obtained. Production figures for these plants are estimated at:

      Standard Chlorine - (8200 kkg) (0.8) = 6600 kkg.

      ICC Industries - (3600 kkg) (0.8) = 2900 kkg.

   d) Total estimated production for PPG Industries, Dow Chemical Co., Standard Chlorine of Delaware, and ICC Industries is 300 kkg + 3600 kkg + 6600 kkg + 2900 kkg or 13,400 kkg.

   Estimated production of 13,400 kkg is a minimum since these four plants are not the only ones producing 1,2,4-TCB (see Tables 2.3 and 2.4).

2. This is a projected production estimate for 1977.

TABLE 2.3 1977 PRODUCERS OF CHLORINATED BENZENES (PARTIAL LIST)

Company	monochlorobenzene	o-dichlorobenzene	m-dichlorobenzene	o- and p-	p-dichlorobenzene	1,2,3-trichloro-benxene	1,2,4-trichloro-benzene	1,3,5-trichloro-benzene	1,2,3- and 1,2,4-trichlorobenzene	trichlorobenzenes (unspecified)	1,2,3,4-tetra-chlorobenzene	1,2,4,5-tetra-chlorobenzene	1,2,3,5-tetra-chlorobenzene	tetrachlorobenzene (unspecified)	pentachlorobenzene	hexachlorobenzene
Allied Chemical Corp.	x	x			x											
Dow Chemical Co.	x	x			x		x					x				
Monsanto Co.	x	x														
Montrose Chemical Corp. of California	x															
PPG Industries, Inc.	x	x			x				x							
Standard Chlorine of Delaware, Inc.	x	x			x		x		x							
Dover Chemical Corp. (Blackwood and Sipes, 1977)				x	x											x

SOURCE: (USITC, 1978)

TABLE 2.4 OTHER PRODUCERS OF CHLORINATED BENZENES

Company	monochlorobezene	o-dichlorobenzene	m-dichlorobenzene	o- and p-	p-dichlorobenzene	1,2,3—trichloro-benzene	1,2,4-trichloro-benzene	1,3,5-trichloro-benzene	1,2,3- and 1,2,4-trichlorobenzene	trichlorobenzenes (unspecified)	1,2,3,4-tetra-chlorobenzene	1,2,4,5-tetra-chlorobenzene	1,2,3,5-tetra-chlorobenzene	tetrachlorobenzene (unspecified)	pentachlorobenzene	hexachlorobenzene
ICC Industries (Hydroscience, 1978; Investigation of Selected Potential Environmental Contaminants, 1977)	x	x	x		x		x			x					x[3]	
Dover Chemical Corp. (TRW, 1977; Investigation of Selected Potential Environmental Contaminants, 1977)	x														x[3]	
Hooker Chemicals & Plastics[1] (TRW, 1977)	x									x						
Dow Chemical Co. (Hydroscience, 1978; Investigation of Selected Potential Environmental Contaminants, 1977)						x				x				x	x[3]	
Standard Chlorine of Delaware, Inc. (Hydroscience, 1978)							x			x				x		
Monsanto Co. (Hydroscience, 1978)					x											

TABLE 2.4 OTHER PRODUCERS OF CHLORINATED BENZENES (continued)

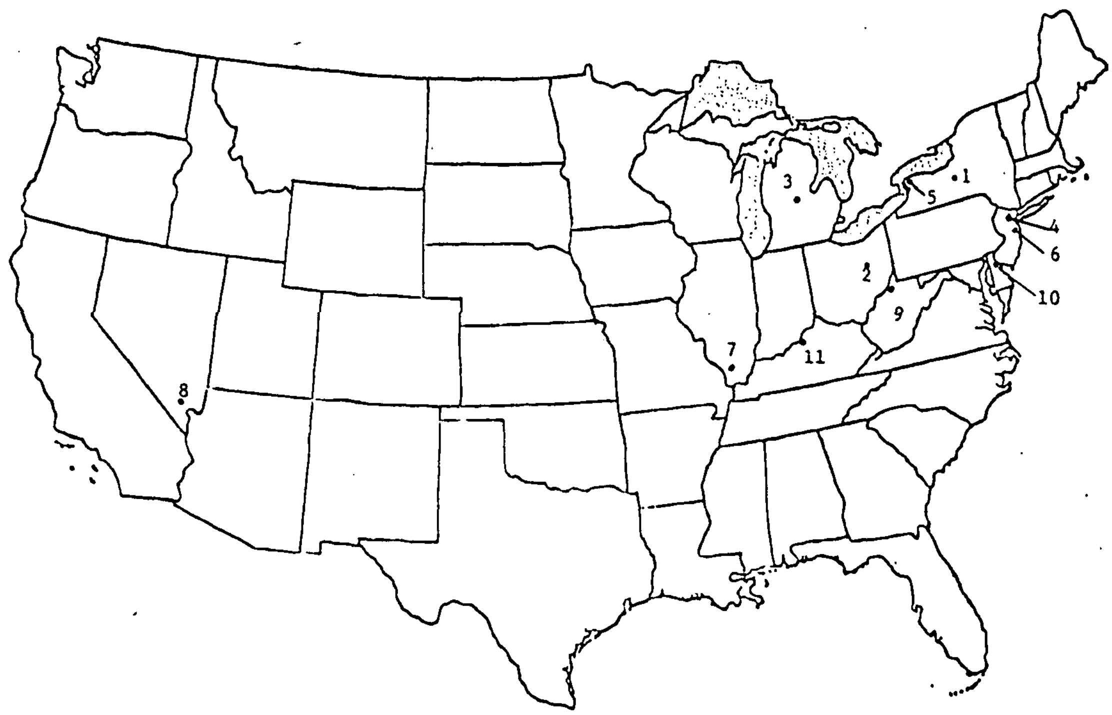
Company	monochlorobezene	o-dichlorobenzene	m-dichlorobenzene	o- and p-	p-dichlorobenzene	1,2,3--trichloro-benzene	1,2,4-trichloro-benzene	1,3,5-trichloro-benzene	1,2,3- and 1,2,4-trichlorobenzene	trichlorobenzenes (unspecified)	1,2,3,4-tetra-chlorobenzene	1,2,4,5-tetra-chlorobenzene	1,2,3,5-tetra-chlorobenzene	tetrachlorobenzene (unspecified)	pentachlorobenzene	hexachlorobenzene
Hummel Chemical Co., Inc. (Blackwood and Sipes, 1977)																x
Kennedy and Klein, Inc. (Comer et al., 1979)								x[2]								
Montrose Chemical Corp. of California (Investigation of Selected Potential Environmental Contaminants, 1977)		x			x											
Stauffer Chemical Co. (Blackwood and Sipes, 1977)																x
Rhodia, Inc. (Blackwood and Sipes, 1977)																x
PPG Industries, Inc. (Investigation of Selected Potential Environmental Contaminants, 1977)						x										
Specialty Organics[4] (Investigation of Selected Potential Environmental Contaminants, 1977)		x			x											

TABLE 2.4 OTHER PRODUCERS OF CHLORINATED BENZENES (continued)

Company	monochlorobezene	o-dichlorobenzene	m-dichlorobenzene	o- and p-	p-dichlorobenzene	1,2,3-trichlorobenzene	1,2,4-trichlorobenzene	1,3,5-trichlorobenzene	1,2,3- and 1,2,4-trichlorobenzene	trichlorobenzenes (unspecified)	1,2,3,4-tetrachlorobenzene	1,2,4,5-tetrachlorobenzene	1,2,3,5-tetrachlorobenzene	tetrachlorobenzene (unspecified)	pentachlorobenzene	hexachlorobenzene
Eastman Kodak (Investigation of Selected Potential Environmental Contaminants, 1977)			x													
Guardian Chemical Co. (Investigation of Selected Potential Environmental Contaminants, 1977)			x													
Transvaal, Inc.[5] (Investigation of Selected Potential Environmental Contaminants, 1977)											x	x				
Aceto Chemical Co. (Investigation of Selected Potential Environmental Contaminants, 1977)															x	
Chemical Procurement Labs, Inc. (Investigation of Selected Potential Environmental Contaminants, 1977)															x	

1. Hooker Chemicals and Plastics no longer produces chlorobenzenes (Journal of Commerce, 1976).
2. 1,3,5-trichlorobenzene is produced as a specialty chemical (Comer et al., 1979).
3. Pentachlorobenzene is produced as a captive byproduct (Investigation of Selected Potential Environmental Contaminants, 1977).
4. Specialty Organics is a processor rather than a manufacturer (Investigation of Selected Potential Environmental Contaminants, 1977).
5. Transvaal, Inc. imports rather than produces chlorobenzenes (Investigation of Selected Potential Environmental Contaminants, 1977).

FIGURE 2.1 LOCATION OF PLANTS MANUFACTURING CHLOROBENZENES



(1) Allied Chemical Corp., Solvay, New York
(2) Dover Chemical Corp., Dover, Ohio
(3) Dow Chemical Co., Midland, Michigan
(4) Hummel Chemical Co., Inc., South Plainfield, New Jersey
(5) ICC Industries, Niagara Falls, New York
(6) Kennedy and Klein, Inc., Red Bank, New Jersey
(7) Monsanto Co., Sauget, Illinois
(8) Montrose Chemical Corp. of California, Henderson, Nevada
(9) PPG Industries, Inc., New Martinsville, West Virginia
(10) Standard Chlorine of Delaware, Inc., Delaware City, Delaware
(11) Stauffer Chemical Co., Louisville, Kentucky

2.3 IMPORTS AND EXPORTS

Table 2.5 summarizes the imports of chlorobenzene compounds from 1972 through 1978. The quantities imported vary from year to year. No information was readily available for those chlorobenzenes that are produced in small quantities and have limited uses (e.g., 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, etc.).

Belgium, France, and West Germany are major exporters of chlorobenzenes to the United States (Investigation of Selected Potential Environmental Contaminants, 1977). However, the majority of the chlorobenzene imports in 1975 came from Poland (SRI, 1977). Only one importer, Transvaal, Inc., is known. This company ceased production of tetrachlorobenzene in favor of its importation from West Germany (Investigation of Selected Potential Environmental Contaminants, 1977).

Dichlorobenzene exports amounted to 500 kkg in 1975 and 1200 kkg in 1976 (SRI, 1977). It is estimated that 17,400 kkg of dichlorobenzene will be exported in 1979 (U.S. Exports, 1979). No information regarding the exports of other chlorobenzene compounds was readily available.

2.4 PRODUCTION METHODS AND PROCESS

The higher chlorinated benzenes are produced with chlorobenzene during the catalytic chlorination of benzene but the amounts are small. Changes in the reaction conditions can maximize or minimize the production of specific chlorobenzenes (Investigation of Selected Potential Environmental Contaminants, 1977). In general, the higher chlorinated isomers are produced via the chlorination of the lesser chlorinated isomers. However, the rate of chlorine substitution will decrease with the degree of chlorination (Investigation of Selected Potential Evnironmental Contaminants, 1977), so it is sometimes necessary to use less direct routes for the production of the more highly chlorinated compounds (e.g., hexachlorobenzene from cyclohexane).

TABLE 2.5 IMPORTS (kkg)

COMPOUND	1972	1973	1974	1975	1976	1977	1978
monochlorobenzene			700	3800	2800	500	400
o-dichlorobenzene	6		700	50	800	500	20
m-dichlorobenzene		1	10		2	10	60
p-dichlorobenzene		2					10
trichlorobenzene-mixed isomers			400		100	3	900
1,2,4-trichlorobenzene			1300				
1,2,5-trichlorobenzene	1	20	10		4	10	
1,2,4,5-tetracholorobenzene		80	700		20	20	600

SOURCES: (Investigation of Selected Potential Environmental Contaminants, 1977; SRI, 1977; USITC, 1979, 1978b, 1977c, 1976b)

3.0 RELEASES FROM USE

3.1 RELEASES FROM CHLOROBENZENE USAGE

The current usage of chlorobenzene is as follows: production of chloronitrobenzenes (35%), use as a solvent (30%), production of diphenyl oxide (10%), production of rubber intermediates (10%), and other uses (including DDT production) (15%) (Hydroscience, 1978). Table 3.1 summarizes these usages and the losses of chlorobenzene to the environment from these usages.

The greatest releases of chlorobenzene are from its use as a solvent. Chlorobenzene is used as a solvent in the production of adhesives, paints, polishes, and waxes; it is also used as an inert process solvent in the manufacture of diisocyanates, pharmaceuticals, and natural rubber, and as a dye carrier in textile dyeing operations (Investigation of Selected Potential Environmental Contaminants, 1977). Although some losses will occur during the production of adhesives, paints, polishes, and waxes (see Table 3.1, footnote 3), we estimate that the majority of the chlorobenzene will be retained in the products and subsequently released to the air through their use. However, as an inert process solvent, chlorobenzene serves as the medium in which a chemical reaction occurs. The product is separated from the solvent, some of the solvent is recovered and recycled, and the remainder is released to water and air. It is estimated that all of the chlorobenzene used as an inert solvent during a year will be released, with the majority (98%) entering the water.

In Table 3.1, footnote 5, it is estimated that 7% of the available chlorobenzene (10,400 kkg) is used in the production of the insecticide dichlorodiphenyltrichloroethane (DDT). Montrose Chemical Corporation is the only producer of DDT in the United States (Midwest Research Institute, 1972). All of the chlorobenzene produced in Montrose's plant in Henderson, Nevada is captively used in the production of DDT (Hydroscience, 1978); the DDT plant is located in Torrance, California and some formulation is done there (Midwest Research Institute, 1972). Other formulators are Helena Chemical and Valley Chemical, Mississippi; Micro Chemical, Louisiana; and Olin Corporation, Arkansas (Midwest Research Institute, 1972). Essentially all the DDT produced in the United States is exported (SRI, 1977).

TABLE 3.1 RELEASES FROM USES OF CHLORINATED BENZENES

PROCESS	AMOUNT USED (kkg)	POINT SOURCES OF RELEASE	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt. (kkg)	Form	Amt. (kkg)	Form	Amt. (kkg)	Form
<u>Monochlorobenzene Use</u>									
Production of chloronitrobenzene	51,900[1]								
Production of Adhesives, Paints, Polishes, Waxes	13,400[2]	Spills	13,100[3] stored in products	70[3]				200[3]	
Use of Adhesives Paints, Polishes, Waxes	13,100[3] stored in products			≤13,100[3]					
Use as an inert process solvent	31,200[2]			≤600[4]				≤30,600[4]	
Production of Diphenyl Oxide	14,800[1]								
Production of Rubber Intermediates	14,800[1]								

TABLE 3.1 RELEASES FROM USES OF CHLORINATED BENZENES (Continued)

PROCESS	AMOUNT USED (kkg)	POINT SOURCES OF RELEASE	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt. (kkg)	Form	Amt. (kkg)	Form	Amt. (kkg)	Form
Production of DDT	10,400[5]	Reactor vent		2[6]					
		Reactor scrubber						19[6]	
		Recycling vents	5[6]	135[6]					
		Acid wastes	to landfill						
		Crystallizer, dryer, flaker liquid						312[6]	
		Spills						5[6]	
		Wash-up and lab						10[6]	
		Formulation and Packaging		negligible[6]				2[6]	
Export of DDT	100[7] as a contaminant	Spills				1[7]			
Other uses	11,900[5]								
<u>o-Dichlorobenzene Use</u>									
Production of 3,4-dichloro-aniline	9,600[9]								
Use as TDI process solvent	2,200[9]	Vents		2[10]					
		Scrubber on vents						20[10]	
		Solvent disposal to water						≤2,177[10]	
		Centrifuge residue	0.6[10] in landfill						

TABLE 3.1 RELEASES FROM USES OF CHLORINATED BENZENES (Continued)

PROCESS	AMOUNT USED (kkg)	POINT SOURCES OF RELEASE	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt. (kkg)	Form	Amt. (kkg)	Form	Amt. (kkg)	Form
Other solvent uses	1,500[6]								
Production of Dyes, including Mordant Red 27, Direct Blue 108, and Direct Violet 54	700[9]								
Other uses, including use as a pesticide and deodorant	700[9]								
Exports	7,300[8]	Spills		1[11]		7[11]		64[11]	
p-Dichlorobenzene Use									
Use as a deodorant	9,700[12]	Toilet bowl garbage	≤200[13] in landfill	≤1,700[13] ≤3,700[13]				≤4,100[13]	
Use for moth control	7,800[12]	Moth balls		≤7,800[14]					

TABLE 3.1 RELEASES FROM USES OF CHLORINATED BENZENES (Continued)

PROCESS	AMOUNT USED (kkg)	POINT SOURCES OF RELEASE	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt. (kkg)	Form	Amt. (kkg)	Form	Amt. (kkg)	Form
Other manufacturing	1,900[12]								
Exports	10,100[8]	Spills		2[15]		10[15]		89[15]	
1,2,4-Trichlorobenzene Use									
Use as a dye carrier	6,200[16]	Vats during dyeing		60[17]					
		Waste water						6000[17]	
		Removal from fabric							
		Alkaline scour						30[17]	
		Heating		160[17]					
Production of herbicides, including dicamba and 2,5-dichlorobenzoic acid	3,900[16]								
Other uses including functional fluids	3,400[16]								

Table 3.1 footnotes:

1. Production of monochlorobenzene in 1977 was reported to be 147,700 kkg (U.S. International Trade Commission, 1978a). Imports of this compound in 1977 were reported at 500 kkg (U.S. International Trade Commission, 1978b). Losses during import were estimated to be 6 kkg (page 2-22). No information on exports of this compound were obtained, and exports are assumed to be 0 kkg. Therefore the amounts of chlorobenzene available for use in this year would be 147,700 kkg + (500 kkg - 6 kkg) ≃ 148,200 kkg of monochlorobenzene.

   Using the percentages of uses of monochlorobenzene stated by Hydroscience (1978), this available chlorobenzene can be broken down into the following amounts used:

Production of chloronitrobenzene	51,900 kkg (35%)
Use as a solvent	44,500 kkg (30%)
Production of diphenyl oxide	14,800 kkg (10%)
Production of rubber intermediates	14,800 kkg (10%)
Production of DDT and other uses	22,200 kkg (15%)

2. Of the 44,500 kkg of monochlorobenzene used as a solvent, we estimated that the larger portion (70%) may be used as an inert process solvent. This estimation is based on the fact that two of these processes, diisocyanate production and textile dyeing, are done on a large scale. The other 30% of monochlorobenzene use would include the formulation of adhesives, paints, polishes, and waxes.

   Inert process solvent = (70%)(44,500) = 31,200 kkg

   Adhesive, paints, polishes, waxes = (30%)(44,500) = 13,400 kkg

3. During the production of adhesives, paints, polishes and waxes, we estimate that 2% of the monochlorobenzene used will be lost to spillage. Of this, we estimate a 1.5% loss to air through evaporation.

   (0.015)(13,400 kkg) = 200 kkg

   (0.005)(13,400 kkg) = 70 kkg

   The remaining monochlorobenzene (13,400 kkg - 270 kkg = 13,100 kkg) is retained in these compounds and will be released to air through their use.

4. At a maximum, all of the chlorobenzene used as an inert process solvent (31,200 kkg) will be released to the environment during use or disposal. Two percent might be expected to be lost to air through volatilization during use, while 98% is estimated to be discarded after use. We assume that the discarded amount is released to water, since we have no other information on solvent disposal.

   (0.02)(31,200 kkg) = 600 kkg

   (0.98)(31,200 kkg) = 30,600 kkg

Table 3.1 footnotes (continued):

5. In 1973 and 1974, DDT production was estimated to account for 7% and 7.5%, respectively, of monochlorobenzene use (Investigation of Selected Potential Environmental Contaminants, 1977; SRI, 1977). Assuming that DDT production has remained at a similar use level (7% of monochlorobenzene production), we estimated that (0.07)(148,200 kkg) or 10,400 kkg of monochlorobenzene is used in the production of DDT (see footnote 1). The remaining 8% of the category "DDT and other uses" (footnote 1) would be attributed to "other uses" of monochlorobenzene. This amount is (0.08)(148,200 kkg) or 11,900 kkg.

6. From analysis of the DDT production process (Figure 3.1), we have estimated the following possible losses during DDT production. These losses are based on knowledge of the high vapor pressure and low water solubility of chlorobenzene.

   a) reactor vent - (0.0002)(10,400 kkg) = 2 kkg to air

   b) reactor vent scrubber - (0.0018)(10,400 kkg) = 19 kkg to recycling pond

   c) vents from recycling - (0.013)(10,400 kkg) = 135 kkg to air

   d) acid wastes - (0.0005)(10,400 kkg) = 5 kkg to landfill

   e) liquid from crystallizer, dryer, flaker - (0.03)(10,400 kkg) = 312 kkg to recycling pond

   f) spills - (0.0005)(10,400 kkg) = 5 kkg to recycling pond

   g) washup and lab - (0.001)(10,400kkg) = 10 kkg to recycling pond

   h) formulation and packaging - (0.0002)(10,400 kkg) = 2 kkg to recycling pond, negligible air release

7. All DDT produced in the U. S. is exported to other countries. If we estimate that 1% of the chlorobenzene used in the production of DDT remains as a contaminant (100 kkg) and that 1% of DDT is spilled during transport out of the country, (10,400 kkg)(0.01)(0.01) or 1 kkg would be expected to be released to land during transport.

8. Exports of dichlorobenzenes from the first 6 months of 1979 were obtained from the U. S. Department of Commerce (September 1979). This amount was 8,700 kkg/6 months or 17,400 kkg/yr. Assuming:

   a) 1979 is comparable to 1977

   b) no meta-dichlorobenzene is exported

   c) amounts of o- and p-dichlorobenzene are exported in the same proportions as they are made - 21,500 kkg o-dichlorobenzene and 29,500 kkg p-dichlorobenzene or 42% ODCB and 58% PDCB (U.S. International Trade Commission, 1978a).

   We would expect exports of o-dichlorobenzene in 1977 to be (17,400 kkg)(0.42) or 7300 kkg and exports of p-dichlorobenzene in 1977 to be (17,400kkg)(0.58) or 10,100 kkg.

9. Quantities of o-dichlorobenzene available for use in 1977 were calculated from amounts produced, imported and exported. These amounts were 21,500 kkg (U.S. International Trade Commission, 1978a), 500 kkg (U.S. International Trade Commission, 1978b) and 7300 kkg (footnote 8), respectively. In addition, 6 kkg of ODCB are lost during import (pg. 2-22).

   21,500 kkg + (500 kkg - 6 kkg) ≃ 22,000 kkg - 7300 kkg = 14,700 kkg

Table 3.1 footnotes (continued):

Using the percentage uses of o-dichlorobenzene stated by Hydrosciences (1978) and SRI (1977), we estimate the following amounts of o-dichlorobenzene use:

Production of 3,4-dichloroaniline	9600 kkg (65%)
Use of TDI process solvent	2200 kkg (15%)
Other solvent uses	1500 kkg (10%)
Dye manufacture	700 kkg (5%)
Other uses (including as pesticide and deodorant)	700 kkg (5%)

10. Amounts of ODCB released during use as a TDI process solvent were estimated using a process schematic for this process (Figure 3.2). These estimates were based upon knowledge of the physical properties of ODCB (e.g. high vapor pressure, low water solubility).

    a) Vents from process - (.001)(2200 kkg) = 2 kkg to air

    b) Scrubbers on vents - (.009)(2200 kkg) = 20 kkg to water

    In addition to these estimates, an estimate of the amount of ODCB landfilled in the centrifuge residue was obtained. Processes Research (1977) reported that 558 kkg of centrifuge residue were produced each year per TDI plant. Since 10 plants are in operation (Directory of Chemical Producers, 1977), we would expect 5580 kkg of centrifuge residue to be produced. Since it was stated that less than several hundred ppm of this centrifuge residue is ODCB (Investigation of Selected Potential Environmental Contaminants, 1977), we estimate (5580 kkg)(100 ppm) or 0.6 kkg of ODCB is released in this residue each year.

    Finally, quantities of TDI solvent not released during use would be disposed of in some way after use. This solvent is probably released to water.

11. Amount of ODCB released during export were estimated at 1% of the amount exported. Of the amount spilled, 88% was estimated to be cleaned up and, therefore, released in water. Ten percent of the spillage might be expected to remain on land, while 2% was estimated to volatilize.

    (7300 kkg)(0.01)(0.02) = 1 kkg to air

    (7300 kkg)(0.01)(0.10) = 7 kkg to land

    (7300 kkg)(0.01)(0.88) = 64 kkg to water

12. Quantities of p-dichlorobenzene available for use in 1977 were calculated from amounts produced and exported. These amounts were 29,500 kkg (U. S. International Trade Commission, 1978), and 10,100 kkg (footnote 8). No import data was obtained.

    29,500 kkg - 10,100 kkg = 19,400 kkg

Table 3.1 footnotes (continued):

Using the percentage uses of p-dichlorobenzene stated by SRI (1977), we estimate the following amounts of p-dichlorobenzene use:

Use as a deodorant	9700 kkg (50%)
Use for moth control	7800 kkg (40%)
Other manufacturing	1900 kkg (10%)

13. PDCB is used as a toilet bowl deodorant and a garbage deodorant. We estimated that the greater use (60%) would be as a toilet bowl deodorant.

Toilet bowl - (0.60)(9700 kkg) = 5800 kkg

Garbage - (0.40)(9700 kkg) = 3900 kkg

In its use as a toilet bowl deodorant, we further estimated that 70% would be released to the water, whereas 30% would volatize into the air.

Water - (0.70)(5800 kkg) = 4100 kkg

Air - (0.30)(5800 kkg) = 1700 kkg

In its use as a garbage deodorizer, we estimated that 95% would be released to the air, while 5% might be landfilled in the garbage.

Air - (0.95)(3900 kkg) = 3700 kkg

Landfill - (0.05)(3900 kkg) = 200 kkg

14. It was estimated that release of p-dichlorobenzene from mothball use would be entirely to air.

15. Releases during export of PDCB were estimated to be similar to releases during export of ODCB (footnote 11).

(10,100 kkg)(0.01)(0.88) = 89 kkg to water

(10,100 kkg)(0.01)(0.10) = 10 kkg to land

(10,100 kkg)(0.01)(0.02) = 2 kkg to air

16. A minimum production figure for 1,2,4-TCB is shown in Table 2.2, footnote 1 (13,400 kkg). Since no import or export figures could be obtained for 1,2,4-TCB, we assume that these quantities are 0 kkg. Therefore, the minimum amount of 1,2,4-TCB available for use is 13,400 kkg.

Using the percentage uses of 1,2,4-TCB stated by Investigation of Selected Potential Environmental Contaminants (1977), the following amounts of 1,2,4-TCB are used:

Table 3.1 footnotes (continued):

Use as a dye carrier	6200 (46%)
Production of herbicides	3900 (29%)
Other uses	3400 (25%)

17. During use of 1,2,4-TCB as a dye carrier, we estimated that 1% of the amount used would be released to the air during the dyeing process. In addition, it was estimated that as much as 3% of the 1,2,4-TCB used might be absorbed by the fiber. Two processes are used to remove 1,2,4-TCB from the fiber - alkaline scour and heating (Schmidlin, 1963). Since heating is used preferably with dye carriers which are readily sublimed, we estimated that this process may remove up to 2.5% of 1,2,4-TCB absorbed by treated fibers. The other 0.5% is probably removed by the alkaline scour technique. Finally, 96% of the 1,2,4-TCB used is estimated to be released in the wastewater from the dyeing operation.

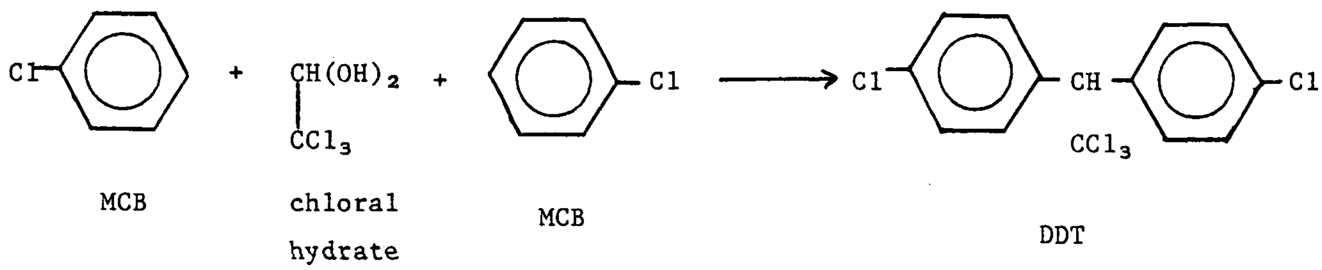
Vats - (0.01)(6200 kkg) = 60 kkg to air

Heating - (0.025)(6200 kkg) = 160 kkg to air

Alkaline scour - (0.005)(6200 kkg) = 30 kkg to water

Wastewater - (0.96)(6200 kkg) = 6000 kkg to water

Figure 3.1 illustrates the manufacturing process for DDT. The condensation of chlorobenzene with chloral hydrate in the presence of sulfuric acid produces DDT, as follows:



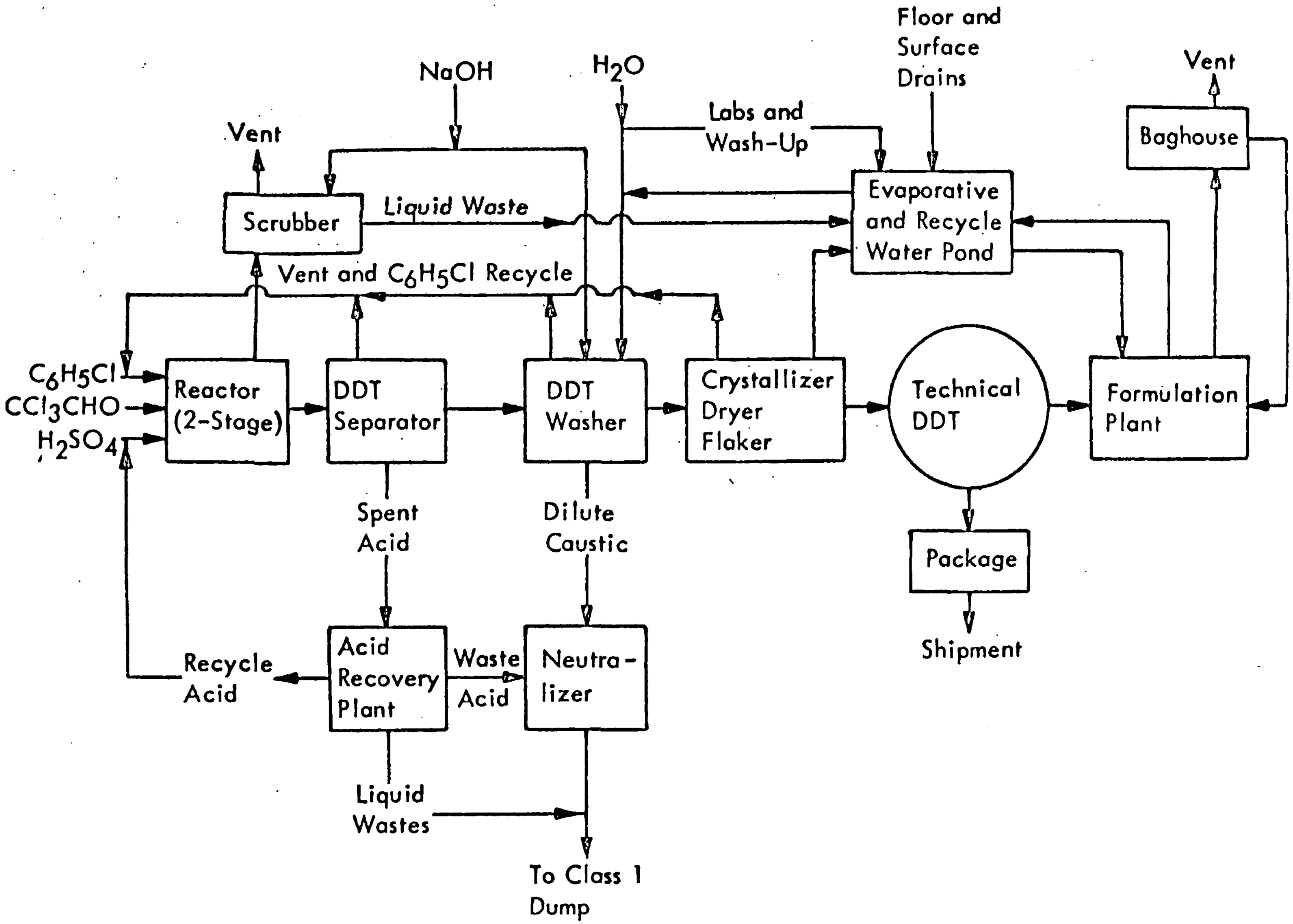
The releases of chlorobenzene during the production of DDT are summarized in Table 3.1 (see footnote 6). It is estimated that the greatest releases to the atmosphere will be from the recycling vents while the greatest releases to the water will be the waste stream from the crystallizer dryer flaker.

DDT is known to contain chlorobenzene as an impurity (Investigation of Selected Potential Environmental Contaminants, 1977), but no information was available regarding the amount of impurity. It is estimated (see Table 3.1, footnote 7) that in one year, 100 kkg of chlorobenzene is retained as an impurity in DDT. Since DDT is exported, the contaminants will only be released in the United States from spills during transport to the port and these are estimated to release 1 kkg of chlorobenzene to the land.

No information regarding the production processes for the manufacture of chloronitrobenzenes, diphenyl oxides, or rubber intermediates from chlorobenzene was readily available. Therefore, no estimates of releases from these processes were made.

The largest area of consumption of chlorobenzene is in the production of chloronitrobenzene. Du Pont and Monsanto have high yields of o- and p-chloronitrobenzene from chlorobenzene (Investigation of Selected Potential Environmental Contaminants, 1977); Monsanto captively uses much of the chlorobenzene it produces to manufacture chloronitrobenzenes (Hydroscience, 1978). Chloronitrobenzenes are intermediates in the production of phenylene diamine, nitroaniline, chloroaniline, and nitrophenol. These compounds are further used to produce dyes,

FIGURE 3.1 PRODUCTION OF DDT (Midwest Research Institute, 1972)



rubber chemicals, and pesticides (Stetcher, 1968; Hahn, 1970; Hancock, 1975). Chlorobenzene may be a contaminant of chloronitrobenzene and would be released during the manufacture of products from chloronitrobenzene or be carried through as a contaminant of these secondary products.

Diphenyl oxide is used as a heat transfer medium, in perfuming soaps, and in organic syntheses. Chlorobenzene will be released in the production of diphenyl oxide, and in the manufacture and use of secondary products from diphenyl oxide contaminated with chlorobenzene.

3.2 RELEASES FROM DICHLOROBENZENE USAGE

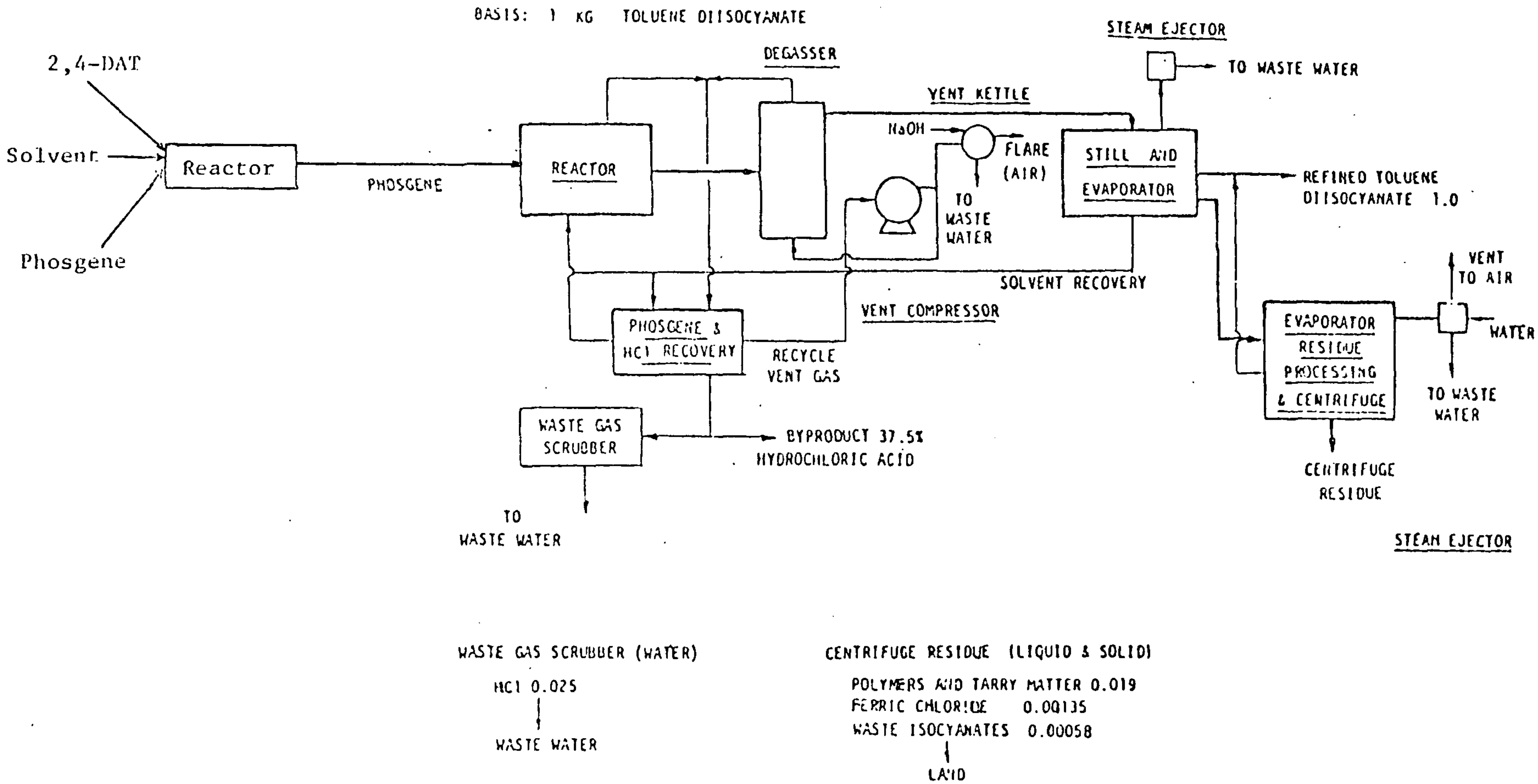
3.2.1 o-Dichlorobenzene

The majority of the ODCB produced in the United States is consumed in the production of 3,4-dichloroaniline (see Table 3.1, footnote 9). No information on the production process was readily available so no estimates of ODCB release during the process were made. 3,4-dichloroaniline is an intermediate in the production of herbicides (propanil, diuron, neburon), dyes, polyethers, and epoxy tar resins (SRI, 1977; Investigation of Selected Potential Environmental Contaminants, 1977). Releases of ODCB will occur during the production of 3,4-dichloroaniline and during the manufacture of products using 3,4-dichloroaniline contaminated with ODCB.

ODCB is used as an inert process solvent in the manufacture of toluene diisocyanate (TDI). During the synthesis of TDI, phosgene is reacted with 2,4-diaminotoluene in an ODCB solution (Investigation of Selected Potential Environmental Contaminants, 1977). Figure 3.2 illustrates the production process for TDI. In the course of one year, all the ODCB used as a solvent will be released to the environment. The majority of the ODCB will be released to the waste stream with the remainder being released to air or landfilled (see Table 3.1, footnote 10).

Approximately 14% of the ODCB available is consumed in the production of dyes and pesticides, and as a solvent. ODCB is an intermediate in the production of the following dyes: Mordant Red 27, Direct Blue 108, and Direct Violet 54.

FIGURE 3.2. TOLUENE DIISOCYANATE MANUFACTURE (Processes Research, 1977)



Other compounds can be used to produce the two direct dyes but Mordant Red 27 can only be produced from ODCB. (SRI, 1977.) Solvent uses include paint formulations, engine cleaning compounds, cleaning and polishing formulations, degreasing agents, and wood-preserving compounds (World Health Organization, 1974). ODCB is registered for use a pesticide against termites, beetles, bacteria, slime, and fungi, however, little is believed to be used at present. ODCB is also used to control the odor in industrial wastewater (Investigation of Selected Potential Environmental Contaminants, 1977). No information on the processes involved in the manufacture of these compounds from ODCB was available. However, ODCB releases will occur during the production of these compounds and ODCB may be present as a contaminant.

A large portion (33%) of the ODCB produced is exported (see Table 3.1, footnote 8). ODCB is released to air, land, and water through spills associated with exportation.

3.2.2 p-Dichlorobenzene

Much of PDCB is used directly as a deodorant for toilets and garbage, and in moth control. The majority of PDCB used in this manner will enter the atmosphere by sublimation (Investigation of Selected Potential Environmental Contaminants, 1977). In its use as a toilet deodorizer, some PDCB will enter the atmosphere but the majority will enter the sewer system (see Table 3.1, footnote 13) (Investigation of Selected Potential Environmental Contaminants, 1977).

Some PDCB is used in the manufacture of polyphenylene sulfide resins, dye intermediates, insecticides, pharmaceuticals, and as an extreme pressure lubricant (World Health Organization, 1974; Investigation of Selected Potential Environmental Contaminants, 1977). Little information on the processes utilized to manufacture these compounds was available. Again, PDCB could be a contaminant of these substances and will be released during their production.

It is estimated that 10,100 kkg of PDCB were exported in 1977 (see Table 3.1, footnote 8). During exportation, PDCB will be released to air, land, and water (the majority to water) from spills (see Table 3.1, footnote 15).

3.2.3 m-Dichlorobenzene

Very little information regarding MDCB is available. Hawley (1977) notes that MDCB is used as a fumigant and an insecticide.

3.3 RELEASES FROM TRICHLOROBENZENE USAGE

3.3.1 1,2,4-Trichlorobenzene

The majority of the 1,2,4-TCB produced in the United States is used as a dye carrier. 1,2,4-TCB is mixed with disperse dye and a leveling agent; this mixture is then applied to the material at 100°C for several hours (Investigation of Selected Potential Environmental Contaminants, 1977). It is estimated that all of the 1,2,4-TCB will be released during this process but that the majority of the releases will occur from the release of the dye solution into the waste stream (see Table 3.1. footnote 17). The carrier that remains on the fabric will be removed by heating or an alkali scour (Investigation of Selected Potential Environmental Contaminants, 1977) and will be released to air and water (see Table 3.1, footnote 17).

The remainder of the 1,2,4-TCB has a variety of uses. 1,2,4-TCB is used in the production of several herbicides (dicamba, 2,5-dichlorobenzoic acid) but little information is available on the manufacturing processes involved. Other uses of 1,2,4-TCB include: a solvent for the crystallization of high melting point products, degreasing agent, termite control agent, dye intermediate, synthetic transformer oil, lubricant, heat transfer medium, and dielectric fluid (Investigation of Selected Potential Environmental Contaminants, 1977; Comer et al., 1979; Third Report of TSCA Interagency Testing Committee, 1979). Again, the manufacturing processes are unknown; 1,2,4-TCB may be present as a contaminant in these products, and it will be released to the environment during the production and use of these compounds.

3.3.2 1,2,3-Trichlorobenzene

1,2,3-TCB has a variety of uses and these are similar to those for 1,2,4-TCB. These uses are: an organic intermediate, termite control agent, synthetic transformer oil, and dye intermediate (Comer et al., 1979; Third Report of TSCA Interagency Testing Committee, 1979). No quantitative information on the production and use of 1,2,3-TCB is available. However, the TSCA Interagency Testing Committee Report (1979) noted that 1,2,3-TCB is released to air and water through agricultural runoff, termite control operations, use as a transformer oil, and its general use in the laboratory.

3.3.3 1,3,5-Trichlorobenzene

No quantitative information is available on the production and use of 1,3,5-TCB. This compound is used as a solvent for high-temperature melting products, a coolant in electrical installations and glass tempering, a heat transfer medium, a lubricant, synthetic transformer oil, in termite preparations, in the manufacture of 2,5-dichlorophenol, in polyester dyeing, and in insecticides (Identification of Organic Compounds, 1975).

3.4 RELEASES FROM TETRACHLOROBENZENE USAGE

3.4.1 1,2,4,5-Tetrachlorobenzene

1,2,4,5-TECB is an intermediate in the production of herbicides, defoliants, insecticides and fungicides (Third Report of the TSCA Interagency Testing Committee, 1979; Investigation of Selected Potential Environmental Contaminants, 1977). All the 1,2,4,5-TECB produced by Dow is reportedly captively consumed in the manufacture of 2,4,5-trichlorophenol which has germicidal properties and is used in the production of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (Hydroscience, 1978; Investigation of Selected Potential Environmental Contaminants, 1977). 2,4,5-trichlorophenol is a fungicide and is used as a disinfectant, a preservative for leather, textiles and wood, and as an intermediate in the production of herbicides (other than 2,4,5-T) and insecticides (Investigation of Selected Potential Environmental Contaminants, 1977).

The only quantitative information available is a 1973 break down of 1,2,4,5-TECB usage. Since the end of the Vietnamese War, the demand for herbicides such as 2,4,5-T has decreased so the 1973 break down is considered to no longer be representative of the usage of 1,2,4,5-TECB.

1,2,4,5-TECB is also used in electrical insulation, as temporary fire-retardant protection in packaging, as an impregnant for moisture resistance, and as a dielectric fluid (Investigation of Selected Potential Environmental Contaminants, 1977; Third Report of the TSCA Interagency Testing Committee, 1979).

3.4.2 1,2,3,4-Tetrachlorobenzene and 1,2,3,5-Tetrachlorobenzene

1,2,3,4-TECB is a component of dielectric fluids and is used in chemical syntheses (Comer et al., 1979; Third Report of the TSCA Interagency Testing Committee, 1979). No quantitative information was available.

1,2,3,5-TECB may have uses similar to the other tetrachlorobenzene isomers but no information was available regarding its actual use (Comer et al., 1979).

3.5 RELEASES FROM PENTACHLOROBENZENE USAGE

Pentachlorobenzene is used as a chemical intermediate. Olin Corporation uses the higher chlorinated benzenes to produce the soil fungicide pentachloronitrobenzene and pentachlorobenzene is present as a contaminant (less than 0.2%). (Investigation of Selected Potential Environmental Contaminants, 1977.) No quantitative information on pentachlorobenzene was available.

3.6 RELEASES FROM HEXACHLOROBENZENE USAGE

Hexachlorobenzene is used in the manufacture of wood preservatives, aromatic fluorocarbons, dyes, and organic compounds. Other uses include: a grain fungicide, a pyrotechnic compound, a peptizing agent in rubber manufacture, and a porosity controller. (Identification of Organic Compounds in Effluents, 1975; Blackwood and Sipes, 1977.) As a fungicide, hexachlorobenzene is used to control wheat bunt and smut fungi of grains; hexachlorobenzene was used in Washington, Oregon, and California as a fungicide in the early 1970's but there is no current information on its use (Blackwood and Sipes, 1977).

Blackwood (1977) notes that the major source of pollution by hexachlorobenzene is from the production of other chemicals (see section 4.0).

3.7 RELEASES FROM MIXED ISOMER USAGE

A mixture of tri-, tetra- and pentachlorobenzene has been used to reduce the attack of gastropods such as snails and oyster drills on commercially important clams and oysters. This product is called Polystream and consists of a minimum of 95% total active tri-, tetra- and pentachlorobenzenes; it is mixed with sand, and applied around oyster and clam beds in order to repel predators (MacKenzie, 1970). Polystream acts by swelling the tissues of certain species of gastropods, and eventually causes death in these organisms (Loosanoff et al., 1960). The compound does not harm the shellfish it is designed to protect, although it has been found that some of the compound remains in the tissues of clams and oysters for a brief period of time following treatment (MacKenzie, 1970). No information was available regarding current usage of Polystream.

There is also a mixture of trichlorobenzenes commercially available. This mixture consists of 85% 1,2,4-TCB, 7.3% 1,2,3-TCB, and traces of di- and tetrachlorobenzenes. This mixture is used as a solvent, a lubricant, and a dielectric fluid (Investigation of Selected Potential Environmental Contaminants, 1977). However, no other quantitative information was available.

4.0 RELEASES FROM INDIRECT PRODUCTION

Several forms of indirect production have been elucidated for chlorinated benzenes. These include the metabolism and degradation of insecticides, the metabolism of chlorinated benzenes, the chlorination of water, the production of tetrachlorobenzene by marsh grass, and the production of hexachlorobenzene as a byproduct in the formation of chlorinated compounds.

The metabolism of the insecticide lindane (1,2,3,4,5,6-hexachlorocyclohexane) has been the subject of several studies. For example, when lindane was topically applied to houseflies, the following percentages of metabolites were formed during metabolism: 0-0.1% 1,2,4-TCB; 0-0.1% 1,2,4,5-TECB; and trace amounts of 1,2,3-TCB, 1,2,3,4-TECB, and PCB (Reed and Forgash, 1970). Rabbits which were orally dosed with ^{14}C-lindane produced 6% ODCB, 0.3% 1,2,4-TCB, and traces of 1,2,3,4-TECB, 1,2,3,5 and/or 1,2,4,5-TECB, and PCB as ether-soluble urinary metabolites (Karapally et al., 1973). In addition, tri and tetrachlorobenzenes were reported as metabolites of lindane in pheasant eggs and chicks and in carrot mold (Third Report of the TSCA Interagency Testing Committee, 1979). Lettuce contained 1,2,3-TCB, 1,2,4-TCB, 1,2,3,4-TECB, PCB and HCB as metabolites (Investigation of Selected Potential Environmental Contaminants, 1977). Since lindane is produced in small quantities ($<$500 kkg/yr. estimated; Midwest Research Institute, 1972), we do not feel that this would be a significant source of chlorinated benzenes in the environment.

Another pesticide which has been shown to produce chlorinated benzenes as metabolites is Terraclor (pentachloronitrobenzene), a soil fungicide. Beagles and rats orally dosed with this pesticide contained low levels of PCB and HCB. In addition, cotton plants grown in soil treated with Terraclor also were shown to contain PCB and HCB (Kuchar et al., 1969). Since production of this compound was also estimated to be low ($<$1400 kkg/yr; Midwest Research Institute, 1972), the production of chlorinated benzenes from this source also is apparently not significant.

In addition to reports on lindane metabolism by biological organisms, the degradation of lindane to trichlorobenzene is also of interest. It has been reported that residues of trichlorobenzene are produced during the baking of bread and breakfast cereals (Third Report of the TSCA Interagency Testing Committee, 1979).

The dehalogenation of higher chlorinated benzenes is a method of indirect production of the lower chlorinated benzenes. For example, Jondorf et al. (1958) reported the production of di- and trichlorobenzenes by the dechlorination of tetrachlorobenzenes in rabbits. This metabolism appeared to be the result of action by bacteria in the rabbit gut. Parke and Williams (1960), studying the metabolism of 1,3,5-TCB, demonstrated that monochlorobenzene is formed during this process. These researchers also found that 10-20% of an oral dose of pentachlorobenzene was converted to lower chlorinated benzenes; however, HCB appeared not to be metabolized. Since these compounds are formed through a metabolic process, the amounts produced are probably small.

Another indirect source of chlorinated benzenes may be the chlorination of water. Chlorination of benzene and chlorobenzene at pH 3 has been reported; however, these compounds do not appear to be chlorinated at higher pHs. Since most water treatment processes take place at pH 5-9, this is generally not considered to be a significant source of chlorinated benzenes (unpublished data, EPA Monitoring and Data Support Division).

An additional source of production of tetrachlorobenzenes appears to be their production by marsh grass (Investigation of Selected Potential Environmental Contaminants, 1977). This may be a significant natural source of chlorinated benzenes.

A final indirect source of chlorinated benzenes is their production as a waste or byproduct of other chemical reactions. Hexachlorobenzene is produced in large amounts during the production of chlorinated solvents and pesticides (Blackwood and Sipes, 1977). Residues from these processes are estimated at 1000 to 3900 kkg/yr. However, quantities of HCB released to the environment are probably lower due to incineration of some wastes. Fourteen types of industrial processes produce HCB as a waste or byproduct. In addition, significant amounts of HCB are present in some products as a contaminant. Table 4.1 shows the estimated amounts of HCB present in industrial wastes, byproducts, and products in 1972. This appears to be a significant source of hexachlorobenzene.

TABLE 4.1 ESTIMATED TOTAL QUANTITY OF HEXACHLOROBENZENE CONTAINED IN U.S. INDUSTRIAL WASTES, BYPRODUCTS, AND PRODUCTS IN 1972 (Blackwood and Sipes, 1977)

Product	U.S. production, 1,000 metric tons	Estimated HCB produced, metric tons	
		High	Low
Perchloroethylene	334	1,590	794
Trichloroethylene	194	204	104
Carbon tetrachloride	453	182	90
Chlorine	8,660	177	73
Dacthal	0.9	45	36
Vinyl chloride	2,040	12	0
Atrazine, propazine, simazine	51	4	2
Pentachloronitrobenzene	1.4	3	1
Mirex	0.4	0.9	0.4
TOTAL	-[a]	2,200	1,100

[a]Not applicable.

5.0 RELEASE SOURCE EVALUATION

The total releases of chlorinated benzenes to the environment from their production and use are at least 72,000 kkg (summation of releases from Tables 2.7 and 3.1). Based on the estimates in Tables 2.7 and 3.1, of the 72,000 kkg released to the environment, 38% (27,000 kkg) enters the atmosphere, 1% (800 kkg enters the land or is landfilled, and 61% (44,000 kkg) enters the water. Monochlorobenzene is produced in the greatest quantities, and contributes 46,000 kkg to the total quantity released. Dichlorobenzenes and 1,2,4-trichlorobenzene contribute 20,000 kkg and 6,000 kkg respectively. Since very little quantitative information was available for the production and usage of the other chlorinated benzenes, it was not possible to estimate their releases.

Comparing the releases for production and use of chlorobenzene and the dichlorobenzenes, it is apparent that the releases from usage are much larger than the releases from production. For chlorobenzene, 700 kkg are released during its production; this is only 2% of the chlorobenzene releases - usage accounts for the remaining 98% (45,000 kkg). This estimate is primarily based on the nonconsumptive (e.g., solvent) uses of chlorobenzene since data on consumptive uses were lacking. However, any releases from consumptive use of chlorobenzene will further increase the usage releases thus diminishing the contribution of production releases. The results are similar for the dichlorobenzenes - 3% (600 kkg) of the releases are from production while 97% (20,000 kkg) of the releases are from nonconsumptive uses.

Since chlorinated benzenes have numerous solvent applications and are used directly as pesticides (e.g., moth control), these are their major sources of environmental release. The uses and releases of chlorinated benzenes in moth control and as deodorizers are fairly widespread throughout the United States. Releases from solvent uses, however, would be concentrated at the manufacturing plants where they are used. Thus, areas where plants using chlorobenzenes as solvents are clustered may be important sources of large environmental releases of chlorobenzenes.

The production sites for chlorinated benzenes may also be important sources of release. Most of the plants that produce mono- and dichlorobenzenes produce the higher chlorinated benzenes as well. These sites would be sources of release for a variety of chlorinated benzenes, and the total quantities of chlorinated benzenes released would be higher than has been estimated. More information on the production of the higher chlorinated benzenes is needed in order to more accurately assess their contribution.

In addition to releases of chlorinated benzenes during manufacture and use of these compounds, releases of hexachlorobenzene as a by-product, contaminant or waste of other organic syntheses appears to be significant. More information on these processes is needed in order to more accurately assess the amounts of hexachlorobenzene released to the environment.

6.0 DATA GAPS

Numerous data gaps were encountered during the preparation of this report. These data gaps were due to incomplete literature on pertinent subjects, the fact that much of the industrial information is confidential, the lack of research in various areas, and the lack of monitoring data within the industrial facilities. Table 6.1 lists the major data gaps for each compound and recommendations of methods for their solution.

The most important areas for which basic data was lacking were production and uses of the chlorobenzene compounds. In the production area, the releases can be better estimated when there is data available on the actual quantities of each chlorobenzene compound produced by each process, what the release factors for each process are, and how the wastes are treated by each manufacturer. For example, in the production of monochlorobenzene, both o-dichlorobenzene and p-dichlorobenzene are produced; however, the quantities recovered and the quantities released are not well-determined in the literature. An analysis of the products from each manufacturing process would indicate which isomers are present and the quantity since all the isomers are formed under similar conditions.

Under the uses of the chlorobenzene compounds, the most serious lack of data was the absence of actual breakdown of the uses as well as the lack of qualitative information on each use. Basic information on the uses needs to be obtained in order to determine the releases from the uses. This information includes specific data on how much of each chlorobenzene compound is used in each area, the nature of each area (consumptive or nonconsumptive), where the products are manufactured, what the products are, and where the products are used. In many cases, an analysis of consumer goods for chlorobenzene impurities or content in indicated.

This study involved twelve compounds, and the data gaps are such that original research and monitoring are indicated to fill them. For these reasons, a Level III materials balance would be required to eliminate the data gaps and to adequately determine the releases of chlorobenzenes to the environment. Approximately 6,000 manhours (or 3 manyears) would be needed to find the data through extensive literature searches, contacts with industry and trade associations, and monitoring studies within the industrial sites.

TABLE 6.1 DATA GAPS AND RECOMMENDATIONS

DATA GAPS	RECOMMENDATIONS
Monochlorobenzene	
A. Production	
1. Complete list of 1977 producers	TSCA non-confidential data on producers; contacts with industry; Chemical Economics Handbook
2. Chlorination of benzene	
a. Which processes (batch or continuous) are used by the various producers	Industry contacts ; Chemical Economics Handbook
b. What additives (e.g., fuller's earth, aluminum chloride) are used to vary amounts of mono- and dichlorobenzene made	Industry contacts
c. Description of the continuous process and releases which occur using the continuous process	Industry contacts; chemical engineering literature
d. Amounts of chlorinated benzenes present in polychlorinated aromatic resinous waste	Laboratory examination of waste; industry contacts
e. Percentage breakdown of o-, p-, and m-dichlorobenzene produced in dichlorobenzene waste	Laboratory examination of waste; industry contacts
3. Imports	
a. Quantity imported	Contacting import agents; detailed information from USITC; Chemical Economics Handbook
b. Route of importation	Contact with industries importing; contact with import agents
c. Releases during import	Industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
4. Amount produced during metabolism of higher chlorinated benzenes	Laboratory research required to assess which organisms metabolize higher chlorinated benzenes and at what rate
B. Uses	
1. Specific rubber intermediates produced from MCB	International Institute of Synthetic Rubber Manufacturers; Rubber Manufacturers Association, Inc.; Manufacturing Chemists Association; chlorobenzene manufacturers; American Chemical Society
2. Specific formulations of adhesives, paints, polishes and waxes made from MCB	Consumer Product Safety Commission; Effluent Guidelines
3. Knowledge of "other uses" of MCB	Survey of consumer products; Effluent Guidelines; extensive literature search; Manufacturing Chemists Association; American Chemical Society

TABLE 6.1 (continued)

4. Production processes for:	
a. Chloronitrobenzene	Faith, Keyes and Clark's Industrial Chemicals; Kirk-Othmer
b. Diphenyl oxide	Faith, Keyes and Clark's Industrial Chemicals; Kirk-Othmer
c. Rubber intermediates	International Institute of Synthetic Rubber Manufacturers; Rubber Manufacturers Association; Inc.; Industrial Process Profiles: Synthetic Rubber Manufacturers
d. Adhesives, paints, polishes, waxes	Effluent Guidelines
e. Pharmaceuticals	NIH Computer Research and Technology Division
f. Natural rubber	Rubber Manufacturing Association
g. Dyeing	Textile trade associations
5. Further knowledge of production processes for:	
a. DDT	Montrose Chemical Corporation
b. Diisocyanates	Diisocyanate manufacturers
6. Releases of MCB which occur from processes in 4 and 5	Contacts in 4 and 5; industrial contacts; Effluent Guidelines
7. Carry-over of MCB impurities in primary products into:	
a. Phenylene diamine b. Nitroaniline c. Chloroaniline d. Nitrophenol	Quality control office of manufacturers of chloronitrobenzene (Dupont, Monsanto) or its products; extensive literature search; laboratory analysis
e. Heat transfer media f. Soaps g. Organic chemicals	Quality control office of manufacturers of diphenyl oxide or its products; extensive literature search; laboratory analysis
h. DDT which is exported	Quality control office of Montrose Chemicals Corporation; literature search; laboratory analysis
i. Diisocyanates j. Pharmaceuticals k. Natural rubber j. Fabrics	Quality control office at manufacturers of these products; literature search; laboratory analysis

TABLE 6.1 (continued)

9. MCB releases from production and/or use of above products	Determine production processes from industry or literature and obtain any release data
10. Export	
a. Amounts exported	Contact with industries exporting; export agencies; Bureau of Census files; Chemical Economics Handbook
b. Export process	Contact with industries exporting; contact with export agents
c. Releases during export	Contact with industry exporting; Dept. of Transportation; Coast Guard; American Association of Railroads; port authorities
11. Storage	Contact with chlorobenzene industry
a. Amounts stored	
b. Amounts released during storage	
m - Dichlorobenzene	
A. Production	
1. Quantities produced	Contact with chlorobenzene manufacturers; USITC; TSCA nonconfidential data on producers
2. Producers	Chemical Economics Handbook; TSCA nonconfidential data on producers; contacts with industry
a. Locations	
b. Capacities	
3. Detailed production process	Contact with chlorobenzene industry; Chemical Economics Handbook
4. Associated releases	Contact with chlorobenzene industry
5. Imports	
a. Origin of Imports	Import agents; USITC; Chemical Economics Handbook
b. Companies that import and from where	Import agents; contact with companies that import; USITC
c. Ports of entry	USITC; import agents; Coast Guard
d. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
6. Indirect Production	Research needed to assess which organisms metabolize higher chlorinated benzenes and the rate of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) quantity produced (amount ingested, yield)	
(2) where it goes	

TABLE 6.1 (continued)

B. Uses	
1. Fumigant and pesticide	Agricultural trade association; contact with industry
a. Amount used in each	
b. Where used	
c. Associated releases	
2. Other uses	Contact with chlorobenzene industry; extensive literature search
3. Exports	
a. Quantity exported	Bureau of Census; Chemical Economics Handbook
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Railroad Association; port authorities; chlorobenzene industry
4. Storage	Contact with chlorobenzene industry
<u>o-Dichlorobenzene</u>	
A. Production	
1. List of actual producers and their capacities and locations	TSCA non-confidential data on producers; Chemical Economics Handbook; contacts with industry
2. Quantity produced during production of chlorobenzene	Contact with chlorobenzene manufacturers; extensive literature search
3. Quantity produced directly	Contact with chlorobenzene manufacturers
4. Releases during production (batch, continuous, direct)	Contact with chlorobenzene manufacturers; chemical engineering literature
5. Imports	
a. Origin of imports	Import agents; USITC; Chemical Economics Handbook
b. Companies that import (and from where)	Import agents; contact with companies that import; USITC
c. Ports of entry	USITC; import agents; Coast Guard
d. Modes of transfer and associated losses	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads

TABLE 6.1 (continued)

6. Indirect Production	Research needed to assess which organisms metabolize compounds and rate of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) Quantity produced	
(2) Where it goes	
b. Metabolism of lindane	
(1) Quantity produced	
(2) Where it goes	
B. Uses	
1. Production Processes and Locations	
a. 3, 4-dichloraniline and its products	Chemical Economics Handbook; Faith Keyes and Clark's Industrial Chemicals; Kirk-Othmer; trade associations for pesticides and dyes; American Chemical Society; industry contacts
b. Dye production - Mordant Red 27 - Direct Blue 108 - Direct Violet 54	Textile associations; literature search; industry contact
c. Other solvent uses - Cleaning and polishing formulations - Paint formulations - Engine cleaning compounds - Degreasing agents - Wood-preserving compounds	Effluent guidelines; literature search; Consumer Products Safety Commission; industry contacts
2. Impurity	
a. 3, 4-dichloroaniline and its products	Industry contacts; extensive literature search; laboratory analysis
b. TDI	Contacts with quality control office at Mobay Chemical Corporation or Dow Chemical Company; laboratory analysis; extensive literature search
c. Dyes	Textile trade associations; laboratory analysis; extensive literature search
3. Method of disposal of solvent from TDI manufacture	Mobay Chemical Corporation, Dow Chemical Company, Olin Corporation
4. Process using dyes contaminated with ODCB	Textile associations; literature search

TABLE 6.1 (continued)

5. Actual products containing ODCB in formulations ("other solvent uses")	Effluent Guidelines
6. Quantity used as pesticide	Agricultural trade associations; extensive literature search; industry contacts
a. What application	
b. Where	
7. Quantity used as wastewater deodorant - where and how much	Contact with chlorobenzene manufacturers; Consumer Products Safety Commission
8. Exports	
a. Destinations	Chemical Economics Handbook; Bureau of Census; export agents; chlorobenzene industry
b. Ports of exit	Bureau of Census; export agents; chlorobenzene industry; Coast Guard
c. Mode of transportation and associated releases	Dept. of Transportation; Coast Guard; American Association of Railroads; port authorities; chlorobenzene industry
d. Which companies export	Contact with chlorobenzene industry
9. Storage	Contact with chlorobenzene indstry
<u>p-Dichlorobenzene</u>	
A. Production	
1. List of actual producers and their capacities and locations	TSCA nonconfidential data on producers; Chemical Economics Handbook; contacts with industry
2. Quantity produced during production of MCB	Contact with chlorobenzene manufacturers; extensive literature search
3. Quantity produced directly	Contact with chlorobenzene manufacturers
4. Releases during production (batch vs. continuous vs. direct)	Contact with chlorobenzene manufacturers; chemical engineering literature
5. Imports	
a. Origin of imports	Import agents; USITC; Chemical Economics Handbook
b. Companies that import and from where	Import agents; contact with companies that import; USITC
c. Ports of entry	USITC; import agents; Coast Guard
d. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads

TABLE 6.1 (continued)

6. Indirect Production	Research needed to assess which organisms metabolize higher chlorinated benzenes and the rate of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) Quantity produced	
(2) Where it goes	
B. Uses	
1. Production Processes and Locations	
a. Polyphenylene sulfide resins	Kirk-Othmer; Faith, Keyes and Clark's Industrial Chemicals; industry contacts; Chemical Economics Handbook
b. Dye intermediates	Textile associations; American Chemical Society; literature search; industry contacts
c. Insecticides	Agricultural trade associations; contact with chlorobenzene industry
d. Pharmaceuticals	NIH Computer Research and Technology Division; contact with chlorobenzene industry
2. Quantities used in #1	Contact with chlorobenzene manufacturers and manufacturers of specific products
3. Impurity in products from #1	Industry contacts; extensive literature search; laboratory analysis
4. What insecticides produced and where used	Agricultural trade associations; contact with chlorobenzene industry
5. What pharmaceutical products	NIH Computer Research and Technology Division; contact with chlorobenzene industry
6. What dye intermediates	Textile trade associations; contact with chlorobenzene industry
7. Quantity PCDB used as garbage deodorant and which products contain it	Consumer product survey; contact with chlorobenzene industry; Consumer Product Safety Commission
8. Toilet deodorant	
a. Quantity used	Contact with chlorobenzene industry; Consumer Product Safety Commission
b. Which products contain it	Consumer Product Safety Commission
c. Releases - air vs. water	Laboratory examination of releases from use

TABLE 6.1 (continued)

9. Extreme pressure lubricant	
a. Quantity used	Contact with chlorobenzene industry
b. Consumptive vs. nonconsumptive use	Manufacturing Chemists Association; industry contacts
c. Associated releases (production and uses)	Industry contacts
10. Exports	
a. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
b. Who exports and to where	Contact with chlorobenzene industry
c. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
d. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
11. Storage	Contact with chlorobenzene industry
<u>1,2,4-TCB</u>	
A. Production	
1. Actual production figure	USITC; TSCA nonconfidential data on producers
2. Producers	Contact with chlorobenzene manufacturers; Chemical Economics Handbook; TSCA nonconfidential data on producers
a. All and locations	
b. Capacities and which process	
3. Quantity produced by each method	Chemical Economics Handbook; contact with chlorobenzene industry
a. Chlorination of ODCB	
b. Hexachlorobenzene	
c. Byproduct of PDCB	
4. Releases associated with each method	Contact with industry
5. Imports	
a. Quantity	USITC; Chemical Economics Handbook
b. Origin of imports	Import agents; USITC; Chemial Economics Handbook

TABLE 6.1 (continued)

c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
6. Indirect Production	Research needed to assess which organisms metabolize these compounds and the rate of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) Quantity produced (yield, amount ingested)	
(2) Where it goes (excreted vs. retained)	
b. Metabolism of lindane	
(1) Quantity produced	
(2) Where it goes	
B. Uses	
1. Production Processes and Locations	American Chemical Society; agricultural trade associations; contact with pesticide industry
a. Herbicides	
- dicamba	
- 2,5-dichlorobenzoic acid	
2. Impurity in products from #1	Quality control office of manufacturers; extensive literature search; laboratory analysis
3. Which herbicides are produced	Contact with chlorobenzene or pesticide manufacturers; agricultural trade associations; American Chemical Society
4. Quantities TCB used for each	Contact with chlorobenzene or pesticide manufacturers
5. Other uses	Contact with chlorobenzene manufacturers; extensive literature search
a. Quantity TCB used in each	
b. Which are consumptive and which are nonconsumptive	
c. Production process for consumptive	
d. Impurity in products	
e. Which nonconsumptive uses are products on the commercial market	
f. Releases associated with each use	

TABLE 6.1 (continued)

6. Process for release of dye solution containing TCB	Textile trade associations; textile industry contacts; extensive literature search
7. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
8. Storage	Contact with chlorobenzene industry
<u>1,2,3-Trichlorobenzene</u>	
A. Production	
1. Quantity produced	TSCA nonconfidential data on producers; USITC; Chemical Economics Handbook; contacts with industry
2. Companies - locations - capacities - process	TSCA nonconfidential data on producers; Chemial Economics Handbook
3. Quantity produced by each process and process details	Contacts with chlorobenzene industry; Chemical Economics Handbook
a. Chlorination of ODCB	
b. Hexachlorobenzene dechlorination	
4. Releases associated with each process	Contacts with industry and extensive literature search
5. Imports	
a. Quantity	USITC; Chemical Economics Handbook; contact with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads

TABLE 6.1 (continued)

6. Indirect Production	Research needed to assess which organisms metabolize these compounds and the rates of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) Quantity ingested	
(2) Yield of reaction	
(3) Where product goes	
b. Metabolism of lindane	
(1) Quantity produced	
(2) Released or retained	
B. Uses	
1. What chemicals produced from 1,2,3-TCB and quantity for each and where	Contacts with chlorobenzene industry; extensive literature search; Chemical Economics Handbook
2. Which dyes produced from 1,2,3-TCB and quantity for each and where	Textile trade associations; contacts with chlorobenzene industry; Chemical Economics Handbook; Colour Index
3. Production processes	
a. Organic chemicals identified in #1	Kirk-Othmer; Faith, Keyes and Clark's Industrial Chemicals; Chemical Economics Handbook
b. Dyes identified in #2	Extensive literature search; contacts with textile industry
4. Impurity	Quality control offices; laboratory analysis; extensive literature search
a. organic chemicals (from #1)	
b. Dyes (from #2)	
5. Quantity used as synthetic transformer oil	Contact with chlorobenzene industry; contact with electrical industry
6. Quantity used in termite control and where used	Contact with chlorobenzene industry; contact with pesticide industry
7. Identify other uses	Contact with chlorobenzene and pesticide industry; extensive literature search; contact with laboratories
a. Pesticide	
b. Laboratory	
8. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry

TABLE 6.1 (continued)

d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
9. Storage	Contact with chlorobenzene industry
<u>1, 3, 5 - Trichlorobenzene</u>	
A. Production	
1. Quantity produced	TSCA nonconfidential data on producers; contact with industry; USITC; Chemical Economics Handbook
2. Companies	TSCA nonconfidential data on producers; Chemical Economics Handbook; contact with industry
a. Location	
b. Capacities	
3. Process description/schematic	Contact with industry; extensive literature research
4. Releases associated with production	Contact with industry; extensive literature search
5. Imports	
a. Quantity	USITC; Chemical Economics Handbook; contact with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
6. Indirect Production	Research needed to assess which organisms metabolize higher chlorinated benzenes and the rate of metabolism
a. Metabolism of higher chlorinated benzenes	
(1) How much produced by this method (quantity ingested, yield of metabolism, where goes)	
B. Uses	
1. Production Processes and Locations	
a. 2,5-dichlorophenol and products	Kirk-Othmer; Faith, Keyes and Clark's Industrial Chemicals; Chemical Economics Handbook
b. Insecticides	Contact with pesticide and chlorobenzene industries

TABLE 6.1 (continued)

2. Impurity	
a. 2,5-dichlorophenol and products	Quality control offices; laboratory analysis; contact with manufacturers
b. Insecticides	Quality control offices; laboratory analysis; contact with manufacturers
3. Identify insecticides produced from 1,3,5-TCB and where used	Contact with chlorobenzene industry; Chemical Economics Handbook
4. Solvent uses	Contact with chlorobenzene industry; Consumer Product Safety Commission; Textile trade associations; contacts with pesticide industry; contacts with electrical industry; extensive literature search
a. Process description	
b. Products containing 1,3,5-TCB	
c. Descriptions of applications	
5. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
6. Storage	Contact with chlorobenzene industry
<u>1,2,4,5-Tetrachlorobenzene</u>	
A. Production	
1. 1977 producers	Chemical Economics Handbook; TSCA nonconfidential data on producers; contacts with industry; USITC
2. Amount of 1,2,4,5-TeCB produced by chlorination of 1,2,4-TCB	Chemical Economics Handbook; contacts with industry
3. Production process and releases from production	Contacts with industry; extensive literature search; Chemical Economics Handbook

TABLE 6.1 (continued)

4. Imports	
a. Quantity	USITC, Chemical Economics Handbook, contacts with industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
5. Indirect production by:	Research needed to assess which organisms metabolize these compounds and the rate of metabolism
a. Metabolism of lindane	
b. Marsh grass	
B. Uses	
1. Current breakdown of amounts used	Contact with chlorobenzene industry; Chemical Economics Handbook
2. Specific herbicides, defoliants, insecticides and fungicides produced	Contact with chlorobenzene and pesticide industries; extensive literature search
3. Production processes for:	Contact with pesticide industry; extensive literature search
a. herbicides	
b. defoliants	
c. insecticides	
d. fungicides	
e. 2,4,5-trichlorophenol	Contact manufacturers (Dow); Kirk-Othmer
4. Releases from these processes	Contact with pesticide industry; contact 2,4,5-trichlorophenol manufacturers; extensive literature search
5. Impurities of 1,2,4,5-TECB in products carried over into:	
a. Use of herbicides, defoliants, insecticides and fungicides	Contacts with pesticide industry; extensive literature search; laboratory analysis
b. Production of 2,4,5-T, herbicides and defoliants	Quality control offices; contact with manufacturers (Dow); laboratory analysis, extensive literature search
6. Releases from above processes	Contacts with industry; extensive literature search

TABLE 6.1 (continued)

7. Releases during the use of 2,4,5-trichlorophenol as a fungicide, disinfectant, wood preservative, leather and textile preservative	Contacts with manufacturers and pesticide industry; extensive literature search
8. Releases during use of 1,2,4,5-TECB as:	Contacts with industry; extensive literature search; Consumer Product Safety Commission; contacts with electrical industry
a. Electrical insulation	
b. Fire retardant	
c. Impregnant for moisture resistance	
d. Dielectric fluid	
9. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agent; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard, Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
10. Storage	Contact with chlorobenzene industry
1,2,3,4-Tetrachlorobenzene	
A. Production	
1. 1977 producers of 1,2,3,4-TECB	TSCA nonconfidential data on producers; Chemical Economics Handbook; contacts with industry
2. Amount of 1,2,3,4-TECB produced from:	Chemical Economics Handbook; contacts with industry
a. Chlorination of 1,2,3-TCB	
b. Sandmeyer reaction on 1,2,3-TCB	
3. Production processes for 1,2,3,4-TECB and releases from these processes	Contacts with industry; extensive literature search; Chemical Economics Handbook
4. Imports	
a. Quantity	Chemical Economics Handbook; USITC; contacts with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC

TABLE 6.1 (continued)

d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
5. Indirect production of 1,2,3,4-TECB by:	
a. Metabolism of lindane	Research required to assess which organisms metabolize lindane and the rate of metabolism
b. Marsh grass	Research needed to assess quantities of TECB produced by marsh grass and amount of marsh grass present
B. Uses	
1. Breakdown of amounts used	Contact with chlorobenzene industry; Chemical Economics Handbook
2. Specific chemicals produced from 1,2,3,4-TECB	Contact with chlorobenzene industry; extensive literature search; Chemical Economics Handbook; American Chemical Society
3. Production processes for these chemicals and releases during production	Contact with manufacturers; Kirk-Othmer; Faith, Keyes and Clark's Industrial Chemicals; Chemical Economics Handbook; chemical engineering literature
4. Carry-over of 1,2,3,4-TECB impurities into secondary products	Quality control offices; laboratory analysis; extensive literature search
5. Releases during production and/or use of secondary products	Contacts with industry; extensive literature search
6. Use as a component of dielectric fluid and releases during use	Contacts with chlorobenzene industry and electrical industry; extensive literature search
7. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook; contact with chlorobenzene industry
b. Destinations	Chemical Economics Handbook; Bureau of the Census; exports agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
8. Storage	Contact with chlorobenzene industry
<u>1,2,3,5-Tetrachlorobenzene</u>	
A. Production	
1. Producers of 1,2,3,5-TECB in 1977	Chemical Economics Handbook; TSCA nonconfidential data on producers; contacts with industry

TABLE 6.1 (continued)

2. Amounts produced from:	Chemical Economics Handbook; contacts with industry
a. chlorination of 1,3,5-TCB	
b. Sandmeyer reaction on 2,3,5-trichloroaniline	
3. Production processes and releases during production	Chemical Economics Handbook; contacts with industry; extensive literature search
4. Imports	
a. Quantity	Chemical Economics Handbook; USITC; contacts with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportion; Coast Guard; port authorities; American Association of Railroads
5. Indirect production by:	
a. Metabolism of lindane	Research required to assess which organisms metabolize lindane and the rate of metabolism
b. Marsh grass	Research required to assess amounts of TECB produced and quantities of marsh grass present
B. Uses	
1. Specific uses of 1,2,3,5-TECB and breakdown of amounts used	Chemical Economics Handbook; contacts with chlorobenzene industry; extensive literature search
2. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook; contact with chlorobenzene industry
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authoritites; chlorobenzene industry
3. Storage	Contact with chlorobenzene industry

TABLE 6.1 (continued)

Pentachlorobenzene	
A. Production	
1. 1977 producers of PCB	Chemical Economics Handbook; TSCA nonconfidential data on producers; contacts with chlorobenzene industry
2. Amounts of PCB produced from:	Contacts with industry; Chemical Economics Handbook
a. Chlorination of benzene	
b. Chlorination of lower chlorinated benzenes	
c. Heating of trichloroethylene	
3. Production processes for PCB and releases from production	Contacts with industry; extensive literature search; Chemical Economics Handbook
4. Imports	
a. Quantity	Chemical Economics Handbook; USITC; contacts with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
5. Indirect production of PCB by:	Research required to assess which organisms metabolize these compounds and the rate of metabolism
a. Metabolism of lindane	
b. Metabolism of PCNB	
B. Uses	
1. Production processes for PCNB and releases of PCB during this process	Kirk-Othmer; Faith, Keyes and Clark's Industrial Chemicals; Chemical Economics Handbook; agricultural trade associations; pesticide manufacturers
2. More accurate account of impurities of PCB in PCNB which may be released during use as a soil fungicide	Quality control office of PCNB manufacturers; extensive literature search
3. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook; contact with chlorobenzene industry
b. Destinations	Chemical Economics Handbook; Bureau of the Census; exports agents; chlorobenzene industry

TABLE 6.1 (continued)

c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
4. Storage	Contact with chlorobenzene industry
<u>Hexachlorobenzene</u>	
A. Production	
1. 1977 producers of HCB	TSCA nonconfidential data on producers; Chemical Economics Handbook; contacts with chlorobenzene industries
2. Amount of hexachlorobenzene produced from:	
a. Chlorination of benzene	Contacts with industry; Chemical Economics Handbook
b. Reaction of hexachlorocyclohexane with chlorosulfonic acid	Contacts with industry; Manufacturing Chemists Association; literature search
c. Recovery of HCB produced as a by-product of organic chemical production processes	Contact with industries that produce HCB as a byproduct; contacts with industries that recover HCB; literature search
3. Processes involved in production of HCB and releases from these processes	Contact with industries that produce HCB as a byproduct or recover HCB; contacts with chlorobenzene industry; extensive literature search; Chemical Economics Handbook
4. Imports	
a. Quantity	Chemical Economics Handbook; USITC; contacts with chlorobenzene industry
b. Origin of imports	Import agents; USITC; Chemical Economics Handbook
c. Companies that import and from where	Import agents; contact with companies that import; USITC
d. Ports of entry	USITC; import agents; Coast Guard
e. Modes of transport and associated releases	Contact with industry importing; Dept. of Transportation; Coast Guard; port authorities; American Association of Railroads
5. Quantities of HCB produced as:	
a. A metabolite of lindane	Research needed to assess which organisms metabolize these compounds and the rate of metabolism (applies to a and b)
b. A metabolite of pentachloronitrobenzene	
c. A by-product of organic chemical production processes	Contact with industries that produce HCB as a byproduct or recover HCB; extensive literature search
B. Uses	
1. Breakdown of amounts used	Chemical Economics Handbook; contacts with chlorobenzene industry; extensive literature search

TABLE 6.1 (continued)

2. Specific wood preservatives, aromatic fluorocarbons, organic compounds and dyes made from HCB	Contacts with chlorobenzene industry; extensive literature search; Manufacturing Chemists Association; textile trade associations
3. Production processes for above compounds and releases from these processes	Contacts with chlorobenzene industry; extensive literature search; textile trade associations; Manufacturing Chemists Association
4. Use of HCB as a:	
a. Grain fungicide	Contact with pesticide and chlorobenzene industries; extensive literature search
b. Pyrotechnic compound	Contact with Manufacturing Chemists Association; contact with chlorobenzene industry; extensive literature search
c. Peptizing agent in rubber	Rubber Manufacturers Association, Inc.; contact with chlorobenzene industry; extensive literature search
d. Porosity controller	Contact with Manufacturing Chemists Association; contact with chlorobenzene industry; extensive literature search
5. Releases during above uses	Contact with industry; extensive literature search
6. Impurities carried over into:	Quality control offices; laboratory analysis; contacts with industry; extensive literature search; textile trade associations; Rubber Manufacturers Association, Inc.
a. Wood preservatives	
b. Aromatic fluorocarbons	
c. Organic chemicals	
d. Dyes	
e. Rubber	
7. Releases during uses of products above	Contact with industry; extensive literature search
8. Exports	
a. Quantity	Bureau of the Census; Chemical Economics Handbook; contacts with chlorobenzene industry
b. Destinations	Chemical Economics Handbook; Bureau of the Census; export agents; chlorobenzene industry
c. Who exports and to where	Contact with chlorobenzene industry
d. Ports of exit	Bureau of the Census; export agents; chlorobenzene industry; Coast Guard
e. Modes of transportation and associated releases	Coast Guard; Dept. of Transportation; American Association of Railroads; port authorities; chlorobenzene industry
9. Storage	Contact with chlorobenzene industry

TABLE 6.1 (continued)

<u>Mixed Isomers</u>

1. Current use of Polystream	Contact Clyde McKenzie and co-authors of reports on Polystream
2. Uses of mixed isomers	Contact Dow Chemical Co.; Standard Chlorine; ICC Industries (producers of mixed isomers)

LITERATURE CITED

Blackwood, T. R. and Sipes, T. G., "Status Assessment of Toxic Chemicals: Hexachlorobenzene," prepared for Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio, November 1977.

Comer, R., Chen, A., and Lee, A., "Trichlorobenzene and Tetrachlorobenzene," JRB Associates, Inc., 1979.

Directory of Chemical Producers, Stanford Research Institute, 1977.

Hahn, A. V., The Petrochemical Industry Market and Economics, McGraw-Hill Book Co., New York, 1970.

Hancock, E. G. (ed.), Benzene and Its Industrial Derivatives, John Wiley and Sons, New York, 1975.

Hawley, G. G. (ed), Condensed Chemical Dictionary, 9th ed., Van Nostrand Reinhold Co., New York, 1977.

Hydroscience, "Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry, Chlorobenzenes Product Report," prepared for Office of Air Quality and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1978.

"Identification of Organic Compounds in Effluents from Industrial Sources," EPA/OTS, EPA 560/3-75-002, April 1975.

"Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes," EPA/OTS, July 1977.

Jondorf, W. R., Parke, D. V., and Williams, R. T., "The Metabolism of Halogenated Benzenes. 1:2:3:4-, 1:2:3:5- and 1:2:4:5-Tetrachlorobenzenes," Biochemical Journal, Vol. 69, pp. 181-189, 1958.

Journal of Commerce, p. 5, May 24, 1976.

Karapally, J. C., Saha, J. C., and Lee, Y. W., "Metabolism of Lindane - ^{14}C in the Rabbit: Ether-Soluble Urinary Metabolites," J. Agr. Food Chem., Vol. 21, No. 5, pp. 811-818, 1973.

Kirk-Othmer Encyclopedia of Chemical Technology, 2nd revised ed., Vol. 5, 1964.

Kuchar, E. J., Geenty, F. O., Griffith, W. P., and Thomas, R. J., "Analytical Studies of Metabolism of Terraclor in Beagle Dogs, Rats, and Plants," J. Agr. Food Chem., Vol. 17, No. 6, pp. 1237-1240, 1969.

Loosanoff, I., MacKenzie, C. L., Jr., and Shearer, L. W., "Use of Chemicals to Control Shellfish Predators," Science, pp. 1522-1523, May 20, 1960.

MacKenzie, C. L., "Control of Oyster Drills, Eupleura Caudata and Urosalpinx Cinerea, with the Chemical Polystream," U. S. Fish and Wildlife Service Fishery Bulletin, Vol. 68, No. 2, pp. 285-297, May 1970.

Midwest Research Institute, "The Pollution Potential in Pesticide Manufacturing," prepared for U. S. Environmental Protection Agency, Office of Water Programs, PB 213-782, June 1972.

Morrison, R. T. and Boyd, R. N., Organic Chemistry, 2nd ed., 1970.

Parke, D. V., and Williams, R. T., "The Metabolism of Halogenobenzenes: (a) Penta- and Hexa-Chlorobenzenes. (b) Further Observations on 1:3:5-Trichlorobenzene," Biochemical Journal, Vol. 74, pp. 5-9, 1960.

Processes Research, Inc., "Alternatives for Hazardous Waste Management in the Organic Chemical Pesticides and Explosives Industry," Cincinnati, Ohio, September 1977.

Reed, W. T. and Forgash, A. J., "Metabolism of Lindane to Organic-Soluble Products by Houseflies," J. Agr. Food Chem., Vol. 18, No. 3, pp. 475-481, 1970.

Saxton, J. C. and Narkus-Kramer, M., "EPA Findings on Solid Wastes from Industrial Chemicals," Chemical Engineering, pp. 107-112, April 28, 1975.

Schmidlin, H. U., Preparation and Dyeing of Synthetic Fibres, Reinhold Publishing Co., New York, 1963.

Snell, F. D. and Ettre, L. S., Encyclopedia of Industrial Chemical Analysis, Wiley Interscience, New York, 1970.

SRI International, " A Study of Industrial Data on Candidate Chemicals for Testing," PB 274-264, EPA/OTS, August 1977.

Stetcher, P. G. (ed.), The Merck Index, 8th ed., Merck & Co., Inc., 1968.

"Third Report of the TSCA Interagency Testing Committee to the Administrator, Environmental Protection Agency," EPA/OTS, January 1979.

TRW, "Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industry," EPA/OSW, 1977.

"U. S. Exports," U. S. Department of Commerce, Bureau of the Census, FT 410/July 1979, issued September 1979.

U. S. International Trade Commission, "Synthetic Organic Chemicals, United States Production and Sales, 1977," Publication 920, U. S. Government Printing Office, Washington, D. C., 1978a.

U. S. International Trade Commission, "Synthetic Organic Chemicals, United States Production and Sales, 1976," Publication 838, U. S. Government Printing Office, Washington, D. C., 1977a.

U. S. International Trade Commission, "Synthetic Organic Chemicals, United States Production and Sales, 1975," Publication 804, U. S. Government Printing Office, Washington, D. C., 1977b.

U. S. International Trade Commission, "Synthetic Organic Chemicals, United States Production and Sales, 1974," Publication 776, U. S. Government Printing Office, Washington, D. C., 1976a.

U. S. International Trade Commission, "Imports of Benzenoid Chemicals and Products, 1978," Publication 990, U. S. Government Printing Office, Washington, D. C., 1979.

U. S. International Trade Commission, "Imports of Benzenoid Chemicals and Products, 1977," Publication 900, U. S. Government Printing Office, Washington, D. C., 1978b.

U. S. International Trade Commission, "Imports of Benzenoid Chemicals and Products, 1976," Publication 828, U. S. Government Printing Office, Washington, D. C., 1977c.

U. S. International Trade Commission, "Imports of Benzenoid Chemicals and Products, 1974," Publication 762, U. S. Government Printing Office, Washington, D. C., March 1976b.

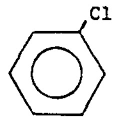
Weast, R. C. (ed.), <u>CRC Handbook of Chemistry and Physics</u>, 58th ed., CRC Press Inc., 1977.

World Health Organization, "International Agency for Research on Cancer Monograph: Evaluation of the Carcinogenic Risk of Chemicals to Man," Vol. 7, 1974.

Unpublished Data, EPA Monitoring and Data Support Division, "Criterion Document, Chlorinated Benzenes (Other than Dichlorobenzenes)," Draft, March 1978.

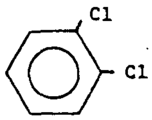
APPENDIX A

STRUCTURES AND NOMENCLATURE OF CHLOROBENZENES



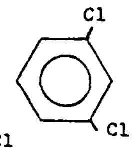
Monochlorobenzene

Chlorobenzene, chlorobenzol, benzene chloride, phenyl chloride



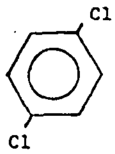
o-Dichlorobenzene

Orthodichlorobenzene, ortho-dichlorobenzene, ortho-dichlorobenzol, 1,2-dichlorobenzene



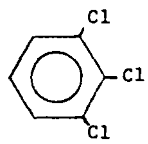
m-Dichlorobenzene

Metadichlorobenzene, meta-dichlorobenzol, meta-dichlorobenzene, 1,3-dichlorobenzene



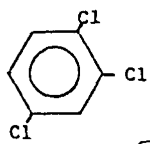
p-Dichlorobenzene

Paradichlorobenzene, para-dichlorobenzene, para-dichlorobenzol, 1,4-dichlorobenzene



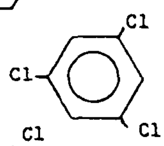
1,2,3-Trichlorobenzene

1,2,3-Trichlorobenzol



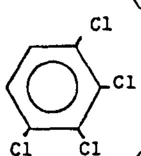
1,2,4-Trichlorobenzene

1,2,4-Trichlorobenzol, uns-trichlorobenzene



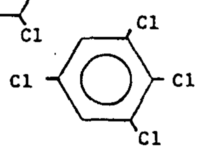
1,3,5-Trichlorobenzene

1,3,5-Trichlorobenzol, sym-trichlorobenzene



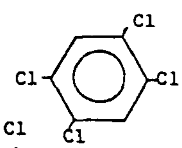
1,2,3,4-Tetrachlorobenzene

1,2,3,4-Tetrachlorobenzol



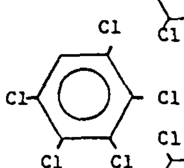
1,2,3,5-Tetrachlorobenzene

1,2,3,5-Tetrachlorobenzol



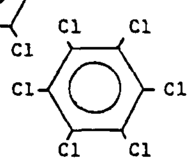
1,2,4,5-Tetrachlorobenzene

1,2,4,5-Tetrachlorobenzol



Pentachlorobenzene

Quintochlorobenzene



Hexachlorobenzene

Source: (Investigation of Selected Potential Environmental Contaminants, 1977)

APPENDIX B

PHYSICAL CHARACTERISTICS OF CHLOROBENZENES

COMPOUND	MOL. WT.	MP(°C)	BP(°C)	DENSITY (g/cm^3)	VAPOR PRESSURE (25°C)	FLASH POINT (°C)	DIELECTRIC CONSTANT(25°C)	SURFACE TENSION (25°C) dynes/cm^3	VISCOSITY (25°C)	REFRACTIVE INDEX	SOLUBILITY WATER
monochlorobenzene	112.56	-45.2	132.0	d_4^{15} 1.117	9 (20°C)	27.8 (open cup)	5.621	32.65	0.756	n_D^{51} 1.5275	insoluble
1,2-dichlorobenzene	147.01	-17.2	179.2	d_4^{25} 1.2973	1.28	71.1 (closed cup)	9.93	36.61	1.0318	$n_D^{20.4}$ 1.5485	insoluble
1,3-dichlorobenzene	147.01	-26.3	172.0	d_4^{25} 1.2799	1.89	--	--	--	--	$n_D^{20.9}$ 1.5457	insoluble
1,4-dichlorobenzene	147.01	53.0	174.5	d_4^{55} 1.2495	0.4	66.7 (closed cup)	2.41	31.4 (60°C) 27.2 (100°C)	--	$n_D^{19.9}$ 1.5267	insoluble
1,2,3-trichloro-benzene	181.45	52.4	218.0	--	0.07	112.8 (closed cup)	--	--	--	--	insoluble
1,2,4-trichloro-benzene	181.45	16.6	213.0	d_4^{25} 1.4634	0.29	98.9 (closed cup)	2.24 (20°C)	38.54	1.8848	n_D^{25} 1.5524	insoluble
1,3,5-trichloro-benzene	181.45	63.0	208.0	--	0.15	107.2 (closed cup)	--	--	--	--	insoluble
1,2,3,4-tetra-chlorobenzene	215.90	47.5	254.0	--	--	--	--	--	--	--	insoluble
1,2,3,5-tetra-chlorobenzene	215.90	51.0	246.0	--	--	--	--	--	--	--	soluble(hot)
1,2,4,5-tetra-chlorobenzene	215.90	138.0	244.0	d_4^{22} 1.858	0.05	155.0 (closed cup)	--	--	--	--	insoluble
pentachlorobenzene	250.34	87.0	276.0	$d_4^{16.5}$ 1.8342	--	--	--	--	--	--	insoluble
hexachlorobenzene	284.79	229.0	326.0	$d_4^{23.6}$ 1.5691	1.09 x 10^{-5}(20°C)	242.2	--	--	--	--	insoluble

Source: (Weast, 1977)

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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4. TITLE AND SUBTITLE Materials Balance - Task #4 - Chlorobenzenes		5. REPORT DATE December 31, 1979
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16. ABSTRACT

The purpose of the Level I materials balance for chlorobenzenes is to evaluate the sources of release of the various chlorinated benzenes to the environment. The major route of commercial production of chlorinated benzenes is the direct chlorination of benzene with chlorine. Chlorinated benzenes are indirectly produced through the metabolism of pesticides, their production by marsh grass and their production as a byproduct of organic chemical production processes. Chlorinated benzenes are used consumptively in the production of many organic chemicals. These include chloronitrobenzene, diphenyl oxide, DDT, 3,4-dichloroaniline, 2,5-dichlorophenol, pentachloronitrobenzene, rubber intermediates, dyes, pesticides, and aromatic fluorocarbons. In addition, chlorinated benzenes have many nonconsumptive uses, including use as a solvent, pesticide, deodorizer, dielectric fluid, coolant, lubricant, heat transfer medium, and synthetic transformer oil. The major sources of release of chlorinated benzenes to the environment appear to be from their various non-consumptive uses. Releases from production and consumptive uses appear to be comparatively minor.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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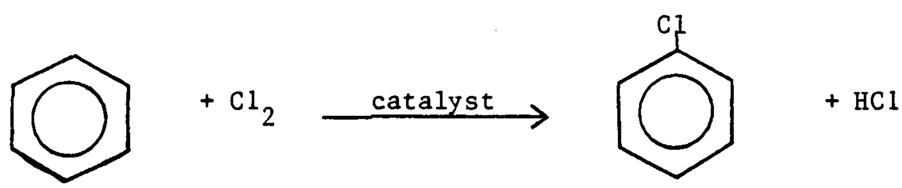
2.4.1 Monochlorobenzene (MCB)

Chlorobenzene is produced by the catalytic chlorination of benzene at an elevated temperature in a batch or continuous process. Sublimed ferric chloride is the most frequently used catalyst but anhydrous aluminum chloride, stannic chloride, iron, and aluminum are also used (Investigation of Selected Potential Environmental Contaminants, 1977; Kirk-Othmer, 1964). The reaction sequence is as follows:

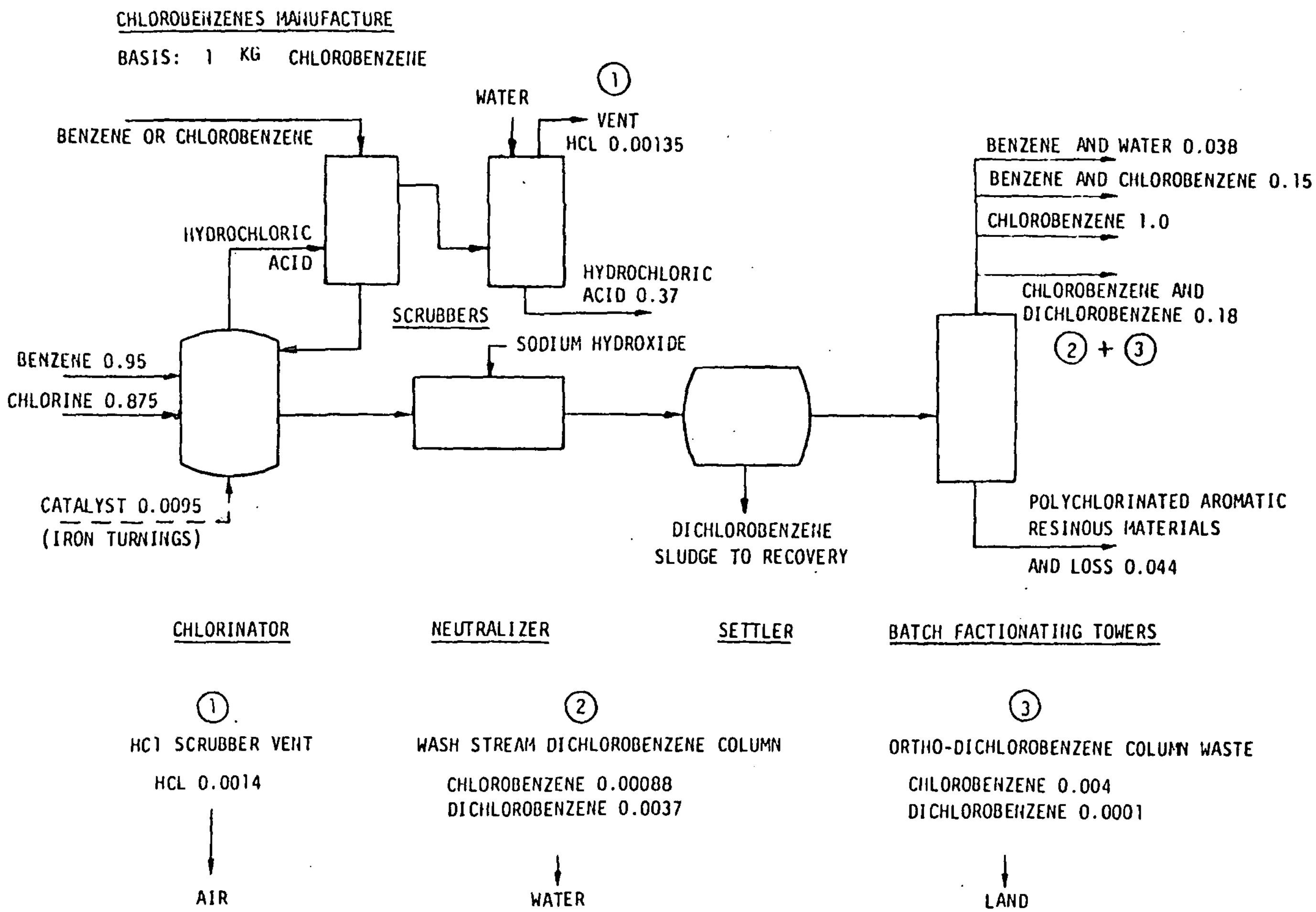


Following chlorination, the crude chlorobenzene (a mixture of chlorobenzene and dichlorobenzenes) is neutralized with dilute sodium hydroxide and separated into sludge and supernatant. The sludge contains dichlorobenzenes which are separated by distillation. The supernatant is fractionally distilled to separate benzene, chlorobenzene, o-dichlorobenzene, and p-dichlorobenzene (TRW, 1977; Hydroscience, 1978).

The batch process, described above, is a three-product process which produces o- and p-dichlorobenzene in addition to chlorobenzene, and is illustrated in Figure 2.2. The quantities of dichlorobenzenes produced can be controlled by various additives; fuller's earth reduces dichlorobenzene formation while aluminum chloride enhances their formation (Investigation of Selected Potential Environmental Contaminants, 1977).

The continuous process for production of chlorobenzene is similar to the batch process but it minimizes the formation of dichlorobenzenes. In the continuous process, the reaction occurs in a series of small vessels, there is a large benzene to chlorine ratio, and once chlorinated, the chlorobenzene is rapidly removed to prevent further chlorination. The yield for this process is 95% (Kirk-Othmer, 1964; Investigation of Selected Potential Environmental Contaminants, 1977).

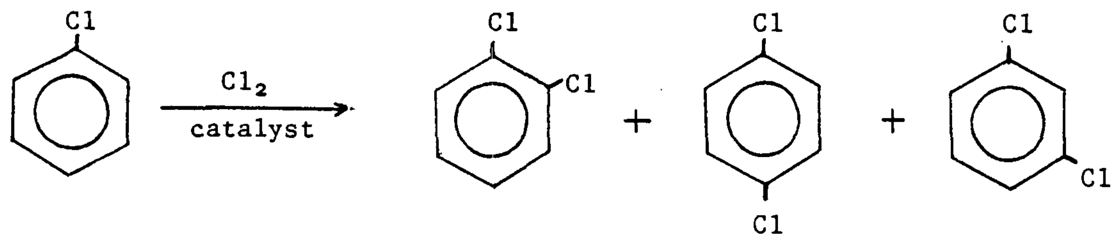
FIGURE 2.2 PRODUCTION OF MONOCHLOROBENZENE (TRW, 1977)



Releases are kg/kg product.

2.4.2 Dichlorobenzene (DCB)

When chlorobenzene is chlorinated, essentially two isomers result, in the following percentages:



ortho (30%) para (70%) meta (trace)

A very small amount of the meta isomer is formed (Morrison and Boyd, 1970).

O- and p-dichlorobenzene are produced primarily from the distillation residues from the manufacture of chlorobenzene. Another method of obtaining the dichlorobenzenes is by chlorination of benzene or chlorobenzene, as illustrated above. The products can be separated by fractional distillation or by crystallization of the para isomer. If the crystals are washed with methanol and heated to 100°C under vacuum suction to remove the alcohol, the ortho isomer can be separated from the crystalline para isomer (Snell and Ettre, 1970).

To produce p-dichlorobenzene, the products from the chlorination of chlorobenzene are further chlorinated. The ortho isomer chlorinates more rapidly than the para isomer to form 1,2,4-trichlorobenzene which is easily separated from the para isomer by fractional distillation. Alternatively, the dichlorobenzene mixture is reacted with chlorosulfonic acid; the ortho isomer forms o-dichlorobenzene sulfonic acid, and the para isomer is easily extracted by distillation (Snell and Ettre, 1970; Kirk-Othmer, 1964).

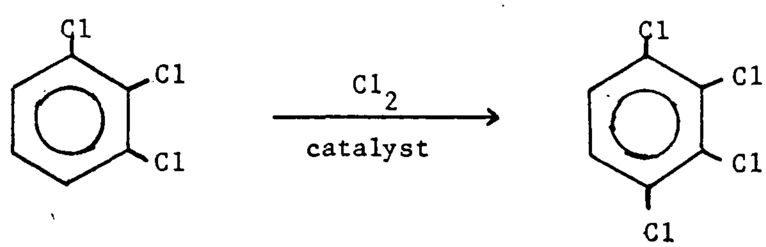
Only trace amounts of the meta isomer are formed from the chlorination of benzene or chlorobenzene. Isomerization of the ortho or para isomers is one method for producing the meta isomer; this reaction occurs at 120°C and 4.48×10^6 pascals with aluminum chloride or hydrochloric acid as the catalyst. M-dichlorobenzene is also formed from hexachlorobenzene or any of the other higher chlorinated derivatives by reaction at 350°-500°C with hydrogen and cuprous halide or alumina (Kirk-Othmer, 1964; Investigation of Selected Potential Environmental Contaminants, 1977).

2.4.3 Trichlorobenzenes (TCB)

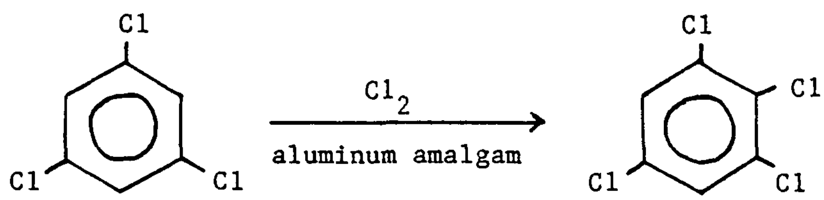
1,2,4-and 1,2,3-trichlorobenzene isomers are synthesized by the catalytic chlorination of o-dichlorobenzene at 25-30°C with ferric chloride as the catalyst (Snell and Ettre, 1970; Kirk-Othmer, 1964; Investigation of Selected Potential Environmental Contaminants, 1977). If hexachlorobenzene is reacted with alcoholic caustic potash, all three isomers (1,2,3-, 1,2,4-, and 1,3,5-) can be obtained (Investigation of Selected Potential Environmental Contaminants, 1977). As previously mentioned, 1,2,4-trichlorobenzene is a byproduct of p-dichlorobenzene production.

2.4.4 Tetrachlorobenzene (TECB)

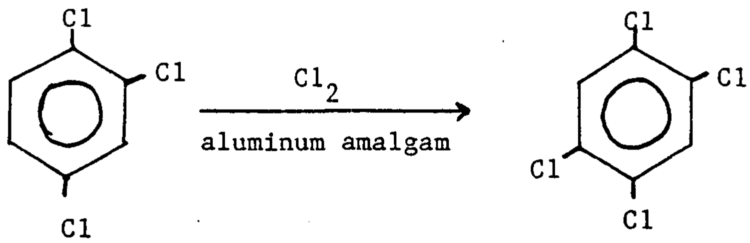
The various tetrachlorobenzenes are synthesized from trichlorobenzene in the following manner (Investigation of Selected Environmental Contaminants, 1977; Kirk-Othmer, 1964):



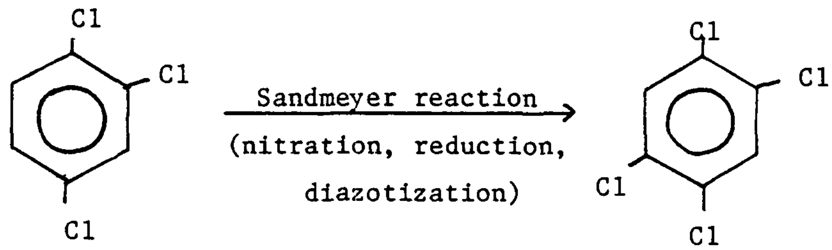
1,2,3-trichlorobenzene 1,2,3,4-tetrachlorobenzene



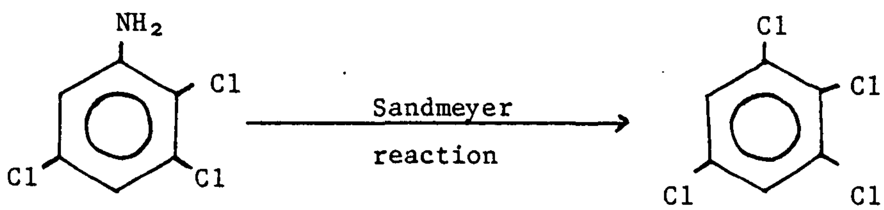
1,3,5-trichlorobenzene 1,2,3,5-tetrachlorobenzene



1,2,4-trichlorobenzene 1,2,4,5-tetrachlorobenzene



1,2,4-trichlorobenzene 1,2,4,5-tetrachlorobenzene



2,3,5-trichloroaniline 1,2,3,5-tetrachlorobenzene

The crystallization of these tetrachlorobenzenes is aided by residual hydrogen chloride formed as a byproduct of the chlorination of benzene or chlorobenzenes. The 1,2,3,4,5-TECB crystals are filtered, centrifuged or decanted, and washed with methanol, ethanol, liquid chlorobenzenes or acetone. Up to half of the 1,2,4,5-TECB produced is still retained in the supernatant, and will precipitate upon cooling. 1,2,4,5-TECB can be separated from a mixture of tri-, penta-, and other tetra- isomers by fractional crystallization in an acid solution, according to the Kissling method (Investigation of Selected Potential Environmental Contaminants, 1977).

2.4.5 Pentachlorobenzene (PCB)

The chlorination of benzene in the presence of ferric chloride at 150 to 200°C, or chlorination of the lower chlorobenzenes produces pentachlorobenzene. This process is illustrated in Figure 2.3. Of the tetrachlorobenzenes used to produce pentachlorobenzene, 1,3,4,5-TECB chlorinates most rapidly while the 1,2,4,5-TECB reaction rate is slowest (Investigation of Selected Potential Environmental Contaminants, 1977). When trichloroethylene is heated to 700°C, a mixture of pentachlorobenzene and small amounts of other compounds result (Kirk-Othmer, 1964).

2.4.6 Hexachlorobenzene (HCB)

Hexachlorobenzene is produced from benzene or hexachlorocyclohexane. The chlorination of benzene in the presence of ferric chloride and excess chlorine at 150-200°C yields hexachlorobenzene, hydrochloric acid, and lesser chlorinated chlorobenzenes. Hexachlorocyclohexane catalytically reacts with chlorosulfonic acid or sulfuryl chloride to form hexachlorobenzene. The catalyst is ferric chloride and the reaction proceeds at a temperature of 130-200°C (Blackwood and Sipes, 1977). These processes are illustrated in Figure 2.3. Blackwood and Sipes (1977), however, note that most of the hexachlorobenzene in this country is recovered as a byproduct from other organic chemical production processes rather than being produced directly (see section 4.0).

2.4.7 Impurities

As previously mentioned, the production of one chlorobenzene compound will result in the simultaneous production of lesser and more highly chlorinated derivatives. These additional compounds will be present as impurities in the final product. Table 2.6 summarizes the impurities found in the major commercial grades of chlorinated benzenes. Many of the impurities are present in small quantities but others (depending on the commercial grade involved) are present in significant amounts. These impurities are of interest because they will be released to the environment during the use of a specific chlorobenzene.

FIGURE 2.3 PRODUCTION OF HIGHER CHLORINATED BENZENES

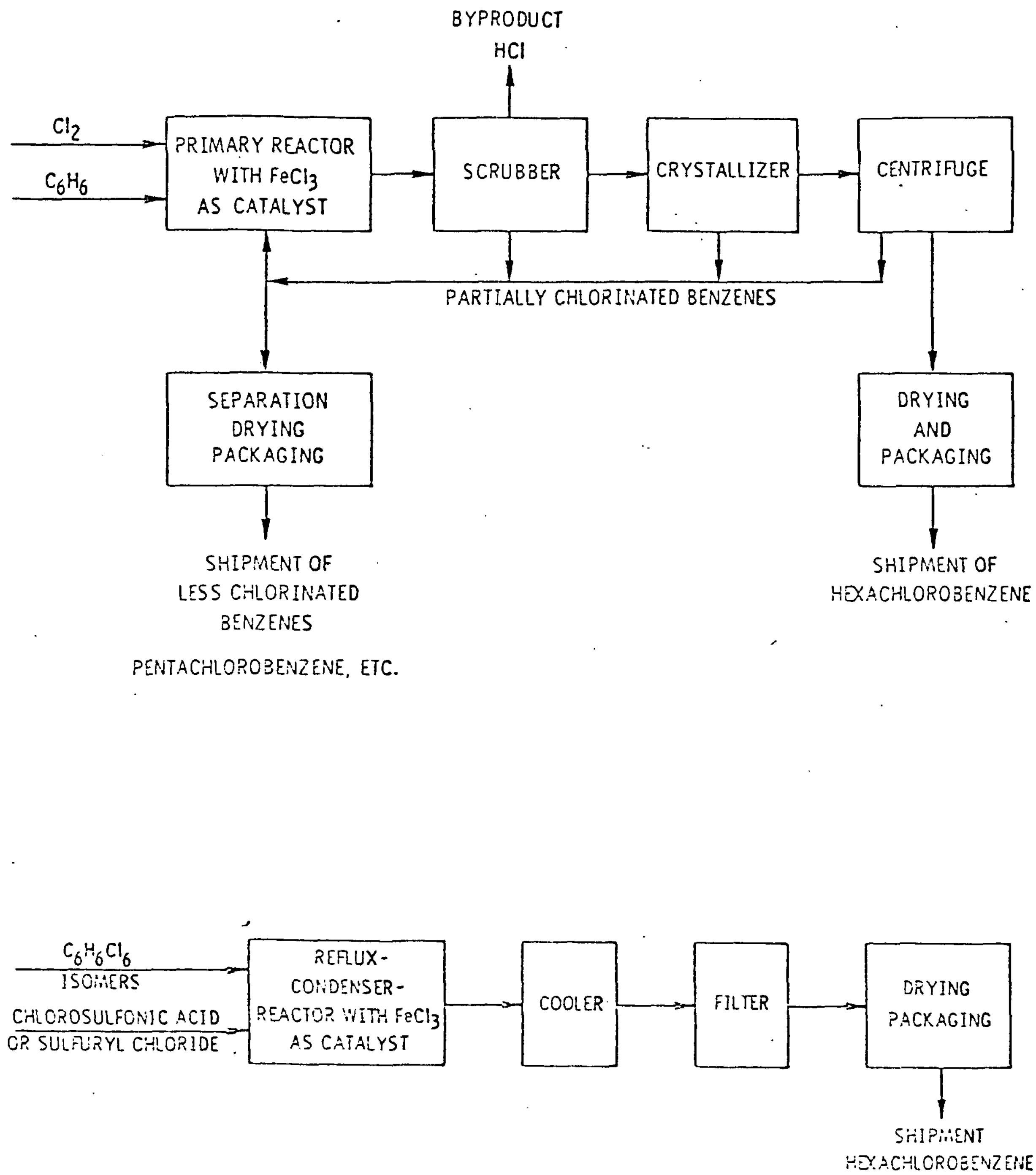


TABLE 2.6 IMPURITIES OF COMMERCIALLY IMPORTANT CHLORINATED BENZENES

(Investigation of Selected Potential Environmental Contaminants, 1977)

Chemical	%	chloro-benzene	1,2-di-chlor-benzene	1,3-di-chloro-benzene	1,4-di-chloro-benzene	tri-chloro-benzene	tetra-chloro-benzene	penta-chloro-benzene	hexa-chloro-benzene
chlorobenzene	99.9		x		x				
	90		x		x				
1,2-dichlorobenzene	99			x					
	75-85	x		0-5	15-25	x			
	82.7	0.07		0.5	15.4	x			
	80	x		2	17	1.6			
	60-75	x		x	25-40	x			
1,4-dichlorobenzene	99.95		x			x			
	99.5	x	x	x					
	96	x	x	x					
	65	x	35	x					
1,2,4-trichloro-benzene	100					x			
	99					x			
1,2,4,5-tetrachloro-benzene	97					x	x	x	
pentachlorobenzene	-						x		x
hexachlorobenzene	90-99						x	9%	

Key: x = present but amount is unknown

2.5 RELEASES FROM PRODUCTION

There are two methods for the manufacture of chlorobenzene: the batch process and the continuous process. Both methods are used commercially, but no data were available regarding the quantities produced by each method. Table 2.7 summarizes the releases of chlorinated benzenes to land and water from the manufacturing process. These calculations are based on the production schematic for the batch process (Figure 2.2), and the assumption that all the chlorobenzene is produced via the batch process.

The polychlorinated aromatic resinous waste constitutes the majority of the waste (84%) from the batch process. No specific description of this waste is available, but it probably contains chlorinated benzenes. This waste will be discharged to the land.

Chlorobenzene and dichlorobenzene constitute the remaining 16% of the waste. This waste will be discharged to land (47%) and water (53%). Of this 16%, 56% (720 kkg) is monochlorobenzene and 44% (560 kkg) is dichlorobenzene. The dichlorobenzene present is presumably o- and p-dichlorobenzene.

The paucity of information on the production processes (and the quantities produced) for di-, tri-, tetra-, penta-, and hexachlorobenzene precluded estimation of losses during their production. However, the amounts of o- and p-dichlorobenzene believed to be produced during the production of monochlorobenzene are noted in Table 2.7.

2.6 RELEASES FROM IMPORTS

A certain amount of chlorinated benzene would be expected to be released during shipment of these chemicals into the United States. We estimate that 1% of the chlorinated benzenes imported would be lost due to spillage. Ninety percent of this amount might be expected to be cleaned up and would be released to water. Approximately 2% of the amount of monochlorobenzene or dichlorobenzene would be expected to volatilize due to the high vapor pressure of these compounds. Another 8% would be lost to land. Using this estimate, we would expect that 5 kkg monochlorobenzene, 5 kkg o-dichlorobenzene, 0.2 kkg 1,2,4,5-tetrachlorobenzene, 0.1 kkg m-dichlorobenzene and 0.1 kkg 1,3,5-trichlorobenzene would be lost to water during import. In addition, monochlorobenzene or o-dichlorobenzene losses to air would be 0.4 kkg, while losses to water would be 0.1 kkg. Losses of the other chlorinated benzenes to air and land appear to be negligible.

TABLE 2.7 RELEASES DURING PRODUCTION OF CHLOROBENZENES

PROCESS	AMOUNT OF PRODUCED (kkg)	POINT SOURCES OF RELEASES	QUANTITIES STORED	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Chlorobenzene Batch Process	147,700[1] Chlorobenzene	Wash stream from dichlorobenzene column							
		• chlorobenzene						130[2]	
		• dichlorobenzene						546[2]	
		Dichlorobenzene column waste							
		• chlorobenzene				591[2]			
		• dichlorobenzene				15[2]			
		Polychlorinated aromatic resinous material waste (probably contains some chlorinated benzenes)				6500[2]			
	8,900[3] o-dichlorobenzene								
	28,100[3] p-dichlorobenzene								

Table 2.7 Footnotes:

1. In 1977, 147,700 kkg of monochlorobenzene were produced in the United States (USITC, 1978a).

2. The losses of chlorobenzene, dichlorobenzene, and polychlorinated materials during the production of chlorobenzene were calculated using the information from the production schematic (Figure 2.2).

   a) Dichlorobenzene Column Wash Stream - to water
      (0.00088 kg MCB/kg MCB produced)(147,700 kkg) = 130 kkg
      (0.0037 kg DCB/kg MCB produced)(147,700 kg) = 546 kg

   b) O-Dichlorobenzene Column Waste - to land
      (0.004 kg MCB/kg MCB produced)(147,700 kg) = 591 kkg
      (0.0001 kg DCB/kg MCB produced) (147,700 kkg) = 15 kkg

   c) Polychlorinated Aromatic Resinous Materials - to land
      (0.044 kg/kg MCB produced)(147,700 kkg) = 6,500 kkg

3. The batch process for MCB production simultaneously produces o- and p-dichlorobenzene. The yield is approximately 80% MCB, 5% ODCB, and 15% PDCB (Investigation of Selected Potential Environmental Contaminants, 1977). To calculate the amount of ODCB and PDCB produced per kilogram of MCB produced, the following assumptions are made: (a) all the chlorobenzene produced is made via the batch process; and (b) the reaction conditions are such that the yield will be 80% MCB, 5% ODCB, and 15% PDCB. If 1 kg MCB is the 80% yield, then the total chlorinated benzene yield is 1.25 kg. The remaining 0.25 kg consists of 0.19 kg PDCB (15% of the total) and 0.06 kg ODCB (5% of the total).

   The amounts of PDCB and ODCB produced via the batch process for chlorobenzene are calculated as follows:

   (0.19 kg PDCB/kg MCB)(147,700 kkg MCB) = 28,100 kkg PDCB

   (00.06 kg ODCB/kg MCB)(147,700 kkg MCB) = 8,900 kkg ODCB