Toxic Substances

&EPA

Materials Balance Chloroform

Review Copy

Level I — Preliminary

FINAL REPORT

LEVEL I MATERIALS BALANCE

CHLOROFORM

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
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EXECUTIVE SUMMARY

This Level I materials balance reports on emissions due to the production and use of chloroform using 1978 for the data base. Estimates of environmental releases were based on emission estimates in the literature, industrial contacts, and engineering judgment based on the physical properties of chloroform. We were able to make reasonable assumptions regarding environmental releases.

Figure I shows the overall flow of chloroform from production through use, and the corresponding points of environmental release. Figure II quantifies the releases of chloroform to air, water, and land, and the quantities destroyed.

In 1978, an estimated 158,500 kkg of chloroform were produced by two processes: methane chlorination and chlorination of methyl chloride produced by hydrochlorination of methanol. Approximately 77 percent of the chloroform was produced by methyl chloride chlorination, and 23 percent by methane chlorination. In 1978, total chloroform production was 71 percent of capacity.

Total air emissions from process vents, storage and handling, fugitive emissions, and secondary emissions were 216 kkg (or 422 kkg assuming uncontrolled conditions). Other process losses were 9.5 kkg released to water and 5.8 kkg released to land. An additional 177 kkg were lost during transit. Total process and transit emissions amounted to 0.3 to 0.5 percent of the total chloroform produced; 16.4 kkg of chloroform were identified as being incinerated from the methyl chloride chlorination process. The quantity of wastes incinerated from the methane chlorination process could not be identified.

Significant indirect sources of chloroform include production of vinyl chloride monomer; treatment of potable water, municipal wastewater, cooling waters, pulp and paper wastes; the combustion of gasoline; and degradation of trichloroethylene. These indirect sources were estimated to contribute 12,800 kkg of chloroform in 1978. Vinyl chloride monomer production, treatment of pulp and paper, and cooling water were the most significant indirect sources, contributing 21 percent, 49 percent, and 19 percent of the total, respectively. Chloroform releases to air from indirect production were estimated to be 9,730 kkg, or 76 percent of the total chloroform produced indirectly. Another 620 kkg (5 percent) of chloroform were released to water, and 18 percent, or 2,290 kkg, were incinerated. The remaining 200 kkg was disposed of in landfills.

The large environmental releases of chloroform from indirect production are in marked contrast to the releases from direct production; whereas direct production emitted only about 0.2 percent of the total produced, almost all of the chloroform produced indirectly was emitted to the environment.

Figure I Environmental Flow Diagram for Chloroform

DIRECT PRODUCTION OF CHLOROFORM

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- CARBON TETRACHLORIDE STILL BOTTOMS
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- ATMOSPHERIC DECOMPOSITION OF TRICHLOROETHYLENE
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- EXTRACTION SOLVENT FOR PHARMACEUTICALS
- REAGENT GRADE LABORATORY SOLVENT
- INDUSTRIAL SOLVENT
- DYES AND TEXTILES
- PESTICIDE / FUMIGANT
- FLUOROCARBON MANUFACTURE
  - FLUOROCARBON RESINS
  - REFRIGERANTS
- EXPORTS

IMPURITY IN CARBON TETRACHLORIDE
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  - RESINS (TEFLON)
  - REFRIGERANTS
- FUMIGANTS
- MINOR USES
- STOCKPILES

Environmental Materials Balance for Chloroform (1978) — flow diagram and data table.

Flow diagram columns: Production (179,000) → Consumptive Use (150,600) → Nonconsumptive Use (14,600) → Secondary Products Contaminants

Production sources:
- Methyl Chloride Chlorination (122,400 kkg)
- Methane Chlorination (36,100 kkg)
- Imports (7,670 kkg)
- Stockpiles (0)
- Vinyl Chloride Monomer (2,680 kkg)
- Chlorination of Potable Water (912 kkg)
- Chlorination in Municipal Treatment Systems (91 kkg)
- Chlorination of Cooling Water (2,460 kkg)
- Bleaching of Paper Pulp (6,700 kkg)
- Auto Exhaust**
- Photodecomposition of Trichloroethylene**
- Other Indirect Sources

Consumptive Use: CFC-22 Production, Exports, Pharmaceuticals, Pesticides, Laboratory Use, Stockpiles

Nonconsumptive Use: CFC-22 Resins, CFC-22 Refrigerant, Methyl Chloride, Methylene Chloride, Perchloroethylene, Carbon Tetrachloride

Secondary Products / Contaminants (with quantities):
- Methyl Chloride: Storage/Handling, End-Use
- Methylene Chloride: Storage/Handling 0.0014, Paint Remover 1.280, Metal Cleaning 0.860, Aerosols 0.305, Urethane Foam 0.350, Other/Exports 0.975
- Carbon Tetrachloride: Storage/Handling 0.029, CFC-11/CFC-12 44.0, Fumigants 1.98, Other 1.92, Stockpiles 2.6

Destroyed/Retained in Products/Storage 2,360	Air 10,887 A / 11,093 B	Water 670	Landfill 590
16.4	312 A* / 483 B*	7.3	5.8
0.072	0	0	0
0	190	0	0
0.025	0.005	0	0
?	81 A* / 116 B*	2.2	0
0	0	0	0
0	Neg.	0	0
0.17	?	?	?
0	0.0014	0	0
0	0.96	0.192	0.128
0.017	0.65	0.105	0.088
0	0.726	0	0.079
0.137	0.196	0	0.017
0.76	0.157	0.027	0.026
0	0.0018	0	0
0	0.029	0	0
44	0.067	0	0.0006
0.18	1.9	0	0
0.12	1.8	0	0
2.6	0	0	0
0	0	0	0
?	570	46	384
4.2	37.8	0	0
?	Probably Large	Probably Large	?
0	?	?	?
2,290	190	0	200
0	820	92	0
0	32	9	0
0	2,340	120	0
0	6,300	400	0
0	May be Large	0	0
0	May be Large	0	0

*Includes transportation losses (177 kkg)
A - Controlled   B - Uncontrolled

Materials Balance[1] Equation:

Chloroform Produced (179,000 kkg) = Consumptive Use (150,600 kkg) + Non-Consumptive Use (14,600 kkg) + Quantity Destroyed/Retained in Products (2,360 kkg) + Emissions to Air (10,900 kkg; Controlled) + Releases to Water (670 kkg) + Amount Landfilled (590 kkg)

** May be large.   [1]Balance inexact due to rounding off.

Figure II.   Environmental Materials Balance for Chloroform (1978) (Units: kkg/yr)

The major use of chloroform is as a feedstock for the production of chlorodifluoromethane (CFC-22). Ninety percent of the chloroform produced domestically, or 143,000 kkg, was estimated to be used in CFC-22 production. Air emissions have been estimated at 190 kkg, or 0.13 percent of the total chloroform consumed for this process. No releases of chloroform to water or land were identified.

CFC-22 is used to produce refrigerants (40 percent) and CFC-22 resins (60 percent). By assuming 1 ppm of chloroform in CFC-22, 0.072 kkg of chloroform was estimated to be destroyed during CFC-22 manufacture, 0.025 kkg to be retained in refrigerants, and 0.005 kkg to be released to air from use of refrigerants.

The remaining 10 percent of the chloroform was used nonconsumptively, or was stockpiled. Nonconsumptive uses include pharmaceutical extractions, use as a fumigant, and use as a laboratory chemical. Several literature sources suggested that chloroform is also used as an industrial solvent, and in the textile and dye industries; however, numerous industrial contacts made for this study indicated that use of chloroform for these purposes is minimal, if any.

About 1,000 kkg of chloroform were used for drug extractions in 1978. This amounts to 0.6 percent of the chloroform produced. Of the chloroform used by the pharmaceutical industry, 57 percent was emitted to air, 5 percent was released to water, and 38 percent was landfilled.

Only 42 kkg of chloroform were used as a fumigant in 1978. The majority of this (90 percent) was emitted directly to air, and 10 percent was retained on the grain.

The remaining 13,600 kkg of chloroform were used for laboratory purposes, were stockpiled, or were used as an industrial solvent. Available information was insufficient to quantify the amount of chloroform used for each of these purposes.

The final source of chloroform releases is as a contaminant of other chloromethanes produced concurrently with chloroform in the methane chlorination process and the methyl chloride chlorination process. The total amount of chloroform present as an impurity in carbon tetrachloride, methylene chloride, and methyl chloride was estimated to be 54.4 kkg. Potentially significant sources of chloroform from the storage, handling, and use of these chloromethanes include: 1.8 kkg to air from use of carbon tetrachloride as a fumigant; 0.96 kkg to air from the use of paint removers containing methylene chloride; 0.73 kkg to air from the use of methylene chloride in aerosol products; and 0.65 kkg to air from the use of methyl chloride in metal cleaning. All other uses of chloromethanes emit less than 0.25 kkg of chloroform.

1.0 INTRODUCTION

This report presents the results of a Level I Materials Balance for Chloroform. The study has been conducted 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 chloroform released annually to the environment and the sources of these releases.

By definition, a Level I materials balance involves a survey of readily available information. This information is supplied mainly by the Management Support Division of OPTS, and is supplemented by JRB in-house information and information readily available by phone calls. In a Level I study, many assumptions and estimations must be made in accounting for all releases of the chemical to the environment. The results of the study are based on all the assumptions presented, and represent the best analysis of the readily available data.

2.0 PRODUCTION

2.1 DIRECT PRODUCTION

There are currently five U.S. corporations producing chloroform in seven plant locations. The locations of these plants are shown in Figure 2.1. Chloroform is produced commercially by the methane chlorination process or by hydrochlorination of methanol followed by methyl chloride chlorination. In the former process, chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride. In the methyl chloride process, carbon tetrachloride is a byproduct produced in small quantities and methylene chloride is a coproduct (Hobbs and Stuewe 1979a).

Since chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride, production ratios may vary. In general, chloroform production can be increased by increasing the chlorine/methane ratio and varying operating temperatures (Versar 1977).

In 1978, 158,500 kkg of chloroform were produced in the United States. This represents 71 percent of the production capacity. As the production figures in Table 2.1 indicate, chloroform production decreased by 14 percent in 1975, but increased by 3 percent between 1976 and 1977, and by nearly 9 percent from 1977 to 1978.

Table 2.1 Production of Chloroform, 1974 to 1978

Year	kkg
1978	158,500
1977	136,900
1976	132,500
1975	118,000
1974	137,000

Source: USITC 1976, 1977a, 1977b, 1978, 1979

Table 2.2 summarizes the chloroform production capacity of the seven U.S. plants as well as their production capacity for the other chloromethanes. Chloroform production capacity by the methyl chloride chlorination process accounts for 77 percent of the total capacity while the methane chlorination process accounts for only 23 percent of total chloroform capacity. This process is only economically competitive with methyl chloride chlorination when there is a cheap source of methane or natural gas and chlorine.
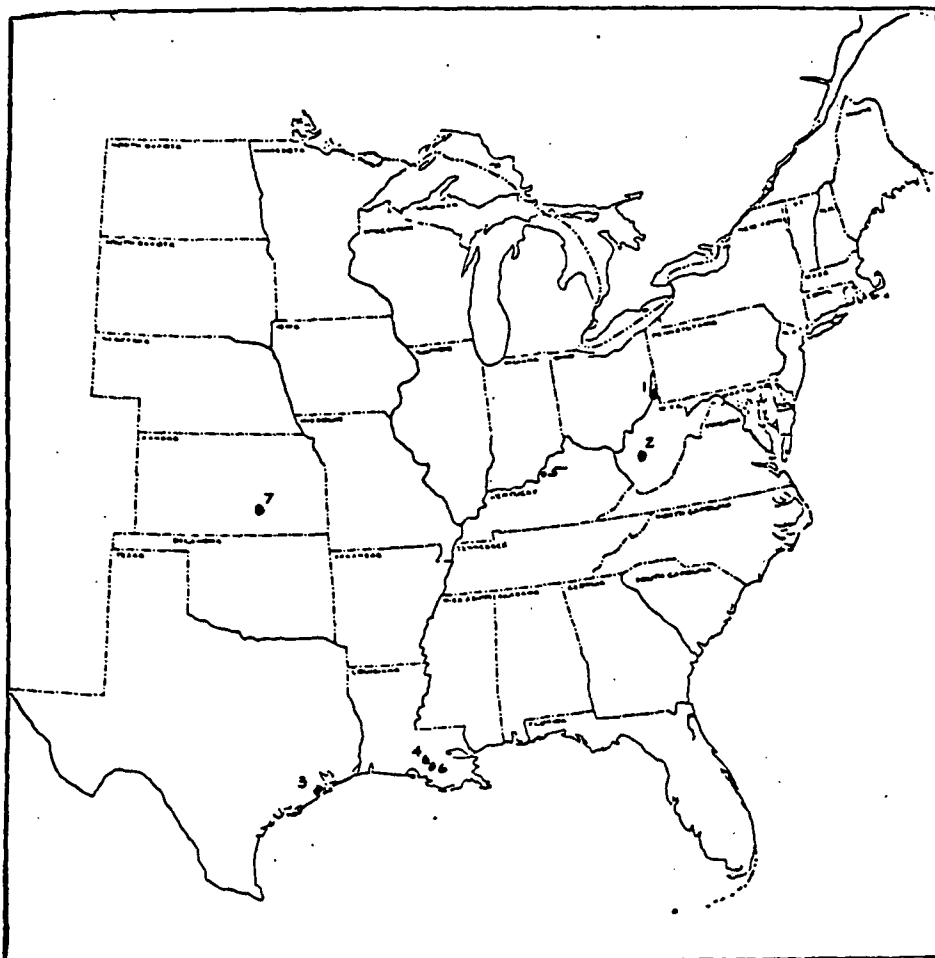
1. Allied Chemical, Moundsville, WV
2. Diamond Shamrock, Belle, WV
3. Dow Chemical, Freeport, TX
4. Dow Chemical, Plaquemine, LA

5. Stauffer, Louisville, KY
6. Vulcan, Geismar, LA
7. Vulcan, Wichita, KS

Figure 2.1   Locations of U.S. Plants Producing Chloroform
            Source: Hobbs and Stuewe 1979

Table 2.2 Chloroform and Chloromethane Capacity for Seven U.S. Plants

Plant	Chloroform Capacity (10^3 kkg)	Methyl Chloride Capacity (10^3 kkg)	Methylene Chloride Capacity (10^3 kkg)	Carbon Tetrachloride Capacity (10^3 kkg)	Total Capacity (10^3 kkg)	Process
Allied Chemical (Moundsville, WV)	13.3 0.7	10.5 0.5	22 1	4 0.2	52.2	Methyl Chloride Chlorination Methane Chlorination
Diamond Shamrock (Belle, WV)	18	11	45	1.5	75.5	Methyl Chloride Chlorination
Dow Chemical (Freeport, TX)	45	32	91	33	201	Methane Chlorination
Dow Chemical (Plaquemine, LA)	45	68	86	4	203	Methyl Chloride Chlorination
Stauffer (Louisville, KY)	34	7	27	1	69	Methyl Chloride Chlorination
Vulcan (Geismar, LA)	21		36	1	58	Methyl Chloride Chlorination
Vulcan (Wichita, KS)	40.5 4.5		45 5	2 1	98	Methyl Chloride Chlorination Methane Chlorination
TOTAL	222.0	129.0	358.0	47.7	756.7	

Source: Hobbs and Stuewe 1978, 1979a

2.1.1 Chloroform Production by Methanol Hydrochlorination Followed by Methyl Chloride Chlorination

Figure 2.2 shows a flow schematic for the hydrochlorination of methanol followed by methyl chloride chlorination, and points where environmental releases occur. Appendix B includes a detailed process description. In this process, methyl chloride is produced by the hydrochlorination of methanol. This reaction is then combined with the continuous chlorination of methyl chloride to produce methylene chlorine and chloroform along with carbon tetrachloride as a by-product.

Total production capacity for plants producing chloroform by methyl chloride chlorination in 1978 was estimated to be 172,000 kkg (Hobbs and Stuewe 1978). No estimate was available on the quantity of chloroform produced by this process. Since total production was 71 percent of capacity in 1978, it was assumed that the methane chlorination process and the methyl chloride chlorination process each produced 71 percent of potential capacity. The amount of chloroform produced in 1978 by methyl chloride chlorination was therefore estimated as 122,000 kkg. This estimate is considered accurate to $\pm 10\%$.

The production figure of 122,000 kkg does not include chloroform losses from production, storage, and transportation. JRB estimates that at the most, approximately 400 kkg of chloroform are lost during these operations, and we have therefore estimated total production at 122,400 kkg.

2.1.1.1 Air Emission

There are five sources of air emissions from the methyl chloride chlorination process: the inert gas purge vent, the methylene chloride and chloroform condenser vents, fugitive emissions, storage and handling losses, and secondary emissions (see Figure 2.2).

A. Inert Gas Purge Vent

The chlorine feed to the methyl chloride chlorination reactor contains inert gases which must be vented. However, chloroform has not been identified as a constituent of this stream (Hobbs and Stuewe 1978).

B. Methylene Chloride and Chloroform Distillation Column Vents

Condenser vents in the distillation operation are required to prevent pressure from building up inside the condensers during normal operation.

Hydroscience calculated emission factors for volatile organic compounds (VOC) for the condenser vents based on information provided for the Vulcan Chemical plant (Hobbs and Stuewe 1978). The emission factor for the methylene chloride condenser was estimated to be 0.019 kg of total VOC/kkg of chloromethanes and that for the chloroform condenser was estimated to be 0.0056 kg of total VOC/kkg of chloromethanes. It was assumed that 30 percent of the total chloromethane
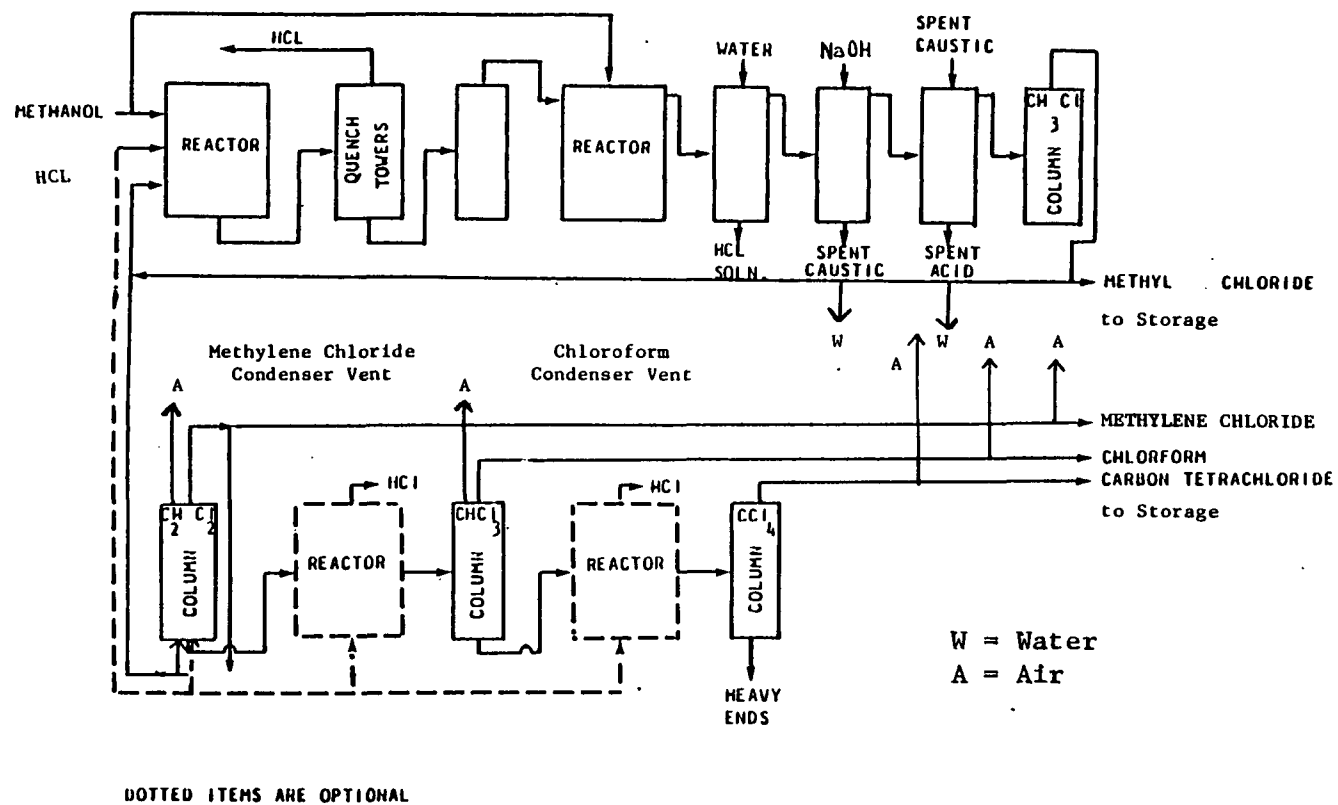
Figure 2.2 Production of Chloroform from Methyl Chloride Chlorination
Source: Hobbs and Stuewe 1978

product is chloroform (Hobbs and Stuewe 1978), and that the percentage distribution of VOC from the condenser vents was as follows (Lant 1978):

	Methylene chloride condenser vents (%)	Chloroform condenser vents (%)
Methylene chloride	72	73
Chloroform	26	26
Carbon tetrachloride	2	1

Using this information, the emission rates for chloroform are calculated as follows.

$$\left(\begin{array}{c}\text{Emission factor}\\ \text{for total VOC}\end{array}\right) \left(\begin{array}{c}\text{Percent chloro-}\\ \text{form in VOC}\end{array}\right) = \begin{array}{c}\text{Emission factor}\\ \text{for chloroform}\end{array}$$

Methylene chloride condenser vent:

$$(0.019 \text{ kg/kkg}) \quad (0.26) \quad = \begin{array}{c}0.0050 \text{ kg chloroform/}\\ \text{kkg chloromethanes}\end{array}$$

Chloroform condenser vent:

$$(0.0056 \text{ kg/kkg}) \quad (0.26) \quad = \begin{array}{c}0.0015 \text{ kg chloroform/}\\ \text{kkg chloromethanes}\end{array}$$

These emission factors are based on total chloromethane production, rather than on the production of chloroform only. Emissions associated with production of methyl chloride, methylene chloride, and carbon tetrachloride are presented in Section 3.3. About one-third of the total chloromethane capacity is for chloroform (Table 2.2). The emission factor for chloroform production alone is thus assumed to be one-third of the total VOC emissions.

$$\left(\begin{array}{c}\text{Chloroform}\\ \text{produced}\end{array}\right) \left(\begin{array}{c}\text{Combined emission}\\ \text{factor}\end{array}\right) \left(\begin{array}{c}\text{Percent}\\ \text{chloroform in}\\ \text{chloromethanes}\end{array}\right) = \begin{array}{c}\text{Chloroform}\\ \text{released from}\\ \text{condenser}\\ \text{vents}\end{array}$$

$$\left(\begin{array}{c}122{,}400\\ \text{kkg}\end{array}\right) \left(\begin{array}{c}0.0065 \text{ kg chloroform/}\\ \text{kkg total chloromethanes}\end{array}\right) \quad (0.33) \quad = 0.26 \text{ kkg}$$

No rationale was given in the Hydroscience report for the way emission factors were determined. The estimates are assumed to be accurate to +30%. This uncertainty accounts for variability in emission factors at other plants besides Vulcan, and for variability in operating conditions. When the uncertainty estimate of +10% for the quantity of chloroform produced by methyl chloride chlorination is taken into account, our overall uncertainty estimate for chloroform releases is +38%.

C. Fugitive Emissions

Fugitive emissions in a typical chloromethane plant result from process fluid leaks from plant equipment including pump seals, compressor seals, pipeline valves, and pressure relief valves.

The number of equipment components typically used in a chloromethane plant with a capacity of 45-180 x 10^3 kkg and the rates of fugitive losses from each component are shown in Table 2.3. Controlled emissions differ from uncontrolled emissions in that major leaks have been repaired.

Table 2.3 Sources of Fugitive Emissions and Typical Rates of Emissions

Component	Number of components	Uncontrolled emissions (kg/day/unit)	Uncontrolled emissions (kg/day/unit)
Pumps	30 + 30 backup	1.5	0.16
Process valves	1,000	0.068	0.006
Relief valves	15	1.1	0.1
Compressors	2	3.9	1.0

Source: Hobbs and Stuewe 1978

By utilizing information presented in Table 2.3 plus the following equation, total fugitive emissions (chloroform plus other constituents) are estimated for the six plants using the methyl chloride process. This estimated total is based on 260 days/year of operation.

$$\begin{pmatrix} \text{Release rate} \\ \text{per unit} \\ \text{per day} \end{pmatrix} \begin{pmatrix} \text{Number of} \\ \text{units} \end{pmatrix} \begin{pmatrix} \text{Number of} \\ \text{operating} \\ \text{days} \end{pmatrix} \begin{pmatrix} \text{Number of} \\ \text{plants} \end{pmatrix} = \begin{array}{c} \text{Total} \\ \text{fugitive} \\ \text{losses} \end{array}$$

For example, uncontrolled releases from pump valves equal:

(1.5 kg/day/seal)   (60)   (260)   (6)   =   140 kkg

Total controlled and uncontrolled fugitive emissions are summarized below:

	Uncontrolled emissions (kkg)	Controlled emissions (kkg)
Pump seals	140	15
Process valves	110	9
Pressure relief valves	26	2
Compressors	12	3
Total	288	29

These estimates are considered accurate to $\pm 35\%$ to account for variations in release rates per unit and in the number of components in chloromethane plants.

Since detailed flow diagrams of the chloromethane plants could not be obtained, it is not possible to calculate the percentage of chloroform in fugitive emissions. Nevertheless, an estimate was based on the volatility of feed and product compounds and the process operating conditions.

The composition of fugitive emissions is estimated to be:

Compound	Mole percent	Molecular weight	Weight percent
HCl	35	36.0	25
Methanol	25	32.0	16
Methyl chloride	20	50.5	20
Other VOC	20	98.9	39

Plant capacities listed in Table 2.2 indicate that production of chloroform, methylene chloride, and carbon tetrachloride average 32, 65, and 3 percent of the total, respectively. Assuming that fugitive losses of chloroform included in "other VOC" are in proportion to the total quantity of chloroform produced, the quantity of chloroform in fugitive emissions is estimated as follows:

$$\left(\begin{array}{c}\text{Total fugitive}\\\text{emissions}\end{array}\right) \left(\begin{array}{c}\text{Weight percent}\\\text{of "other VOC"}\end{array}\right) \left(\begin{array}{c}\text{Weight percent}\\\text{of chloroform}\\\text{in VOC}\end{array}\right) = \begin{array}{c}\text{Total Chloroform}\\\text{in fugitive}\\\text{emission}\end{array}$$

Uncontrolled Conditions:

(288 kkg)   (0.39)   (0.32)   =   35.9 kkg

Controlled Conditions:

(29 kkg)   (0.39)   (0.32)   =   3.6 kkg

Controlled and uncontrolled emissions are considered separately in the overall materials balance.

Our estimate for the quantity of chlorform in fugitive emissions under controlled conditions is considered accurate to +20%. When combined with the uncertainty estimate of +35% for total fugitive emissions, the overall uncertainty is +53%. Factors contributing to this uncertainty include the variability in the age and number of process components, which affect fugitive losses; uncertainty related to amount of chloroform in fugitive releases; and the extent to which fugitive emissions are controlled.

D. Storage and Handling

Storage tanks for both crude and finished chloromethanes can be a source of evaporative losses. The American Petroleum Institute (API) has developed an empirical formula based on field testing which correlates evaporative losses with several factors related to storage, such as tank volume, paint condition, and liquid level (USEPA 1977).

In the following section, chloroform releases from storage and handling will be estimated using the empirical formula. Fixed roof storage tanks are the minimum requirement for storage and it is assumed in the calculations that follow that all tanks are fixed roof tanks.

(1) Determination of Breathing Losses

Assuming that all six plants producing chloroform by the chlorination of methyl chloride operate at about 71 percent of capacity, the product storage requirements for chloroform will approximate the quantities shown below:

	Estimated production (10^3 kkg)	Volume for storage (10^3 ℓ)
Allied Chemical	9.4	6,270
Diamond Shamrock	12.8	8,500
Dow Chemical	31.9	21,300
Stauffer	24.1	16,100
Vulcan (LA)	14.9	9,900
Vulcan (KS)	28.8	19,200
Total	122.0	81,300

It was assumed that the plants would maintain tanks at about 50 percent of capacity. Tank sizes and turnover rates were estimated using data supplied by USEPA (Hobbs and Stuewe 1978) and Vulcan (Leonard 1978) (see Appendix B). Table 2.4 shows the tank sizes and tank turnover rates used in calculating releases from storage and

Table 2.4 Summary of Breathing Losses from Chloroform Storage

Tank volume		Number of tanks	Percent of capacity	Turnover rates /yr	Recovery method	Breathing losses per tank (kkg/yr)	Total breathing losses (kkg/yr)[a]	
(gallons)	(liters)						controlled	uncontrolled
7,000	26,250	12	50	125	None	0.56	6.8	6.8
16,000	60,000	2	50	125	None	1.75	3.5	3.5
50,000	187,500	6	50	20		4.6	27.5	27.5
100,000	375,000	2	50	20	Refrig. vapor recovery	3.7	7.3	29.3
461,000	1,728,750	2	50	20	" "	13.7	27.3	109.9
							72.4	177.0

[a]Controlled and uncontrolled emissions are considered separately in the final materials balance.

handling. Using the API empirical formula (USEPA 1977), storage emissions can be calculated as follows:

$$LB = (2.21) \ 10^{-4} M \left[\frac{P}{14.7-P} \right]^{0.68} D^{1.73} \ H^{0.51} \ T^{0.5} Tp C Kc$$

where

LB = fixed roof breathing losses (lb/day)

M = molecular weight = 119

P = true vapor pressure at bulk liquid conditions (psia) = 3.259

D = tank diameter; variable (see Appendix B)

H = average vapor space height, variable (see Appendix B)

T = average ambient temperature change from day to night; assume $20^{\circ}F$

Tp = paint factor; assume 1

C = adjustment factor for small diameter tanks - variable

Kc = crude oil factor = 1

Appendix B details calculations for breathing losses from tanks of each size. Table 2.4 summarizes breathing losses based on the empirical formula. It was assumed that the tanks of largest volume (375×10^3 and $1,729 \times 10^3$ liters) have refrigerated vapor recovery systems and that the smaller volume tanks have no controls. Vapor recovery systems are generally 60-90 percent efficient in recovering chloromethanes. An efficiency of 75 percent was assumed for these estimates. As shown in Table 2.4 total breathing losses from storage are estimated to be 72.4 kkg/year with refrigerated vapor recovery systems. Without the refrigerated vapor systems, chloroform storage losses would be 176 kkg/year, or 1.43 kg/kkg. This estimate is in reasonably good agreement with an estimate made by Hydroscience for uncontrolled emissions from chloroform storage (Hobbs and Stuewe 1978). This study estimated an emission factor of 1.7 kg/kkg for all chloromethanes. Using this estimate and that of 122,000 kkg of chloroform stored, total chloroform losses would be 207 kkg/year. It is highly unlikely, however, that there are no vapor recovery systems, at least on the larger storage tanks.

Our estimate of 72.4 kkg of controlled emission is considered accurate to +40%, -20%. This range allows for uncertainties related to storage conditions and the use of vapor recovery systems. When this uncertainty estimate is combined with that of +10% for the quantity of chloroform stored, the overall uncertainty is +54%, -39%.

(2) Working Losses

Working losses were similarly estimated using an empirical formula derived from API (USEPA 1977). The expression to estimate these losses is:

$$LW = 2.4 \times 10^{-2} \; M \; P \; K_n K_c$$

where

    LW = fixed roof working losses (lb/10^3 gal)

    M = molecular weight = 119

    P = true vapor pressure at bulk liquid conditions = 3.259 psia

    K_n = turnover factor; variable

    K_c = crude oil factor = 1

Appendix B details the calculations for working losses from storage tanks assuming tank volume and turnover rates shown in Table 2.5. JRB estimates for working losses are also summarized in Table 2.5.

Table 2.5 Summary of Estimates for Working Losses

Tank volume		Number of tanks	Turnover per year	Working Losses (kkg/yr)[a]	
(gallons)	(liters)			controlled	uncontrolled (no vapor recovery)
7,000	26,250	12	125	6.5	6.5
16,000	60,000	2	125	3.7	3.7
50,000	187,500	6	20	12.7	12.7
100,000	375,000	2	20	2.1	8.4
461,000	1,728,500	2	20	9.7	39.0
				34.7	70.3

[a]Controlled and uncontrolled conditions are considered separately in the final materials balance.

An estimated 34.7 kkg of chloroform/year are lost during handling. This corresponds to an emission rate of 0.28 kg/kkg. Without refrigerated vapor recovery systems for the larger tank, handling emissions would be 69.3 kkg or 0.57 kg/kkg produced. In contrast, Hydroscience estimated controlled working losses at 0.36 kg/kkg (Hobbs and Stuewe 1978). For this materials balance, JRB's estimate of controlled losses will be used. This estimate is assigned an uncertainty of +30%, -0% to account for the

possibility that the Hydroscience estimate is more accurate. Since the estimated uncertainty for the quantity of chloroform in storage is +10%, the overall uncertainty estimate is +40%, -10%.

2.1.1.2 Releases of Chloroform to Land/Secondary Emissions

Secondary VOC emissions result during handling and disposal of process waste liquids and residues. Incineration of carbon tetrachloride still bottoms is the major source of secondary emissions in the methyl chloride chlorination process. The residue is produced at a rate of 1.02 kg/kkg of chloroform, and is estimated to be 18.4 percent chloroform by weight (Lant 1978). From these factors and the 1978 production figure for chloroform (122,400 kkg), the total quantity of chloroform in the carbon tetrachloride residue is estimated as 23 kkg.

No information was available on the fate of these wastes. JRB assumed that 75 percent of the still bottoms are incinerated, and that the incinerator operates at 95 percent efficiency. The quantity of chloroform incinerated was thus estimated as 17.3 kkg. Of this amount approximately 0.86 kkg was released to the air and 16.4 kkg were landfilled. Presumably, the remaining still bottoms (5.8 kkg) are landfilled. The method by which these wastes are contained is not known.

Our estimate for the quantity of chloroform in carbon tetrachloride residues is accurate to only +25%. The estimate was based on data from one plant only; the quantity of residue produced will undoubtedly vary from one plant to the next. The estimates for the quantities incinerated and landfilled are considered accurate to +15% and +50%, respectively. When combined with the uncertainty estimate of +25% for the total quantity of chloroform in the residue, our overall error ranges are +39% and +72% for the quantities incinerated and landfilled, respectively.

2.1.1.3 Emissions of Chloroform to Water

There are three potential sources of chloroform releases to wastewater during chloroform production: the spent caustic water, the spent acid waste, and the indirect contact cooling water.

A. Indirect Contact Cooling Water

Indirect contact cooling water used during production of chloroform may be contaminated by minor spills and leaks. One process was reported to use 5,800 ℓ/kkg of chloroform produced (Lant 1978). The cooling water from one process was estimated to be contaminated with 1,000 mg of chloroform/ℓ (Lant 1978). However, comparison of emissions from this plant and those from other plants using the methyl chloride chlorination process showed emissions from this facility to be very high due to the age of this plant. We assume, on an average, that cooling water is contaminated with 100 mg of chloroform/ℓ. The total

chloroform released from spills and leaks to cooling water can be estimated as follows:

$$\begin{pmatrix} \text{Total} \\ \text{production} \\ \text{of chloroform} \end{pmatrix} \begin{pmatrix} \text{Cooling water/} \\ \text{kkg chloroform} \end{pmatrix} \begin{pmatrix} \text{Chloroform in} \\ \text{Cooling Water} \end{pmatrix} = \begin{matrix} \text{Total chloroform} \\ \text{released to} \\ \text{cooling water} \end{matrix}$$

$$(122{,}400 \text{ kkg}) \quad (5{,}800 \text{ } \ell/\text{kkg}) \quad (10^{-7} \text{ kkg}/\ell) \quad = \quad 70 \text{ kkg}$$

It is assumed that 90 percent or 63 kkg of the chloroform is evaporated to air and the remaining 10 percent or 7 kkg remains in the water.

This estimate is not considered more accurate than +75%, -50%. When combined with the uncertainty estimate of +10% for the quantity of chloroform produced by methyl chloride chlorination, the overall uncertainty estimate is +90%, -56%. Releases of chloroform from spills and leaks are intermittent and vary from one plant to the next. The nature of this wastewater makes it difficult to quantify chloroform losses to cooling water.

B.. **Spent Acid and Spent Caustic**

Gruber and Ghassemi estimated that approximately 0.04 kg of chloroform/kkg of total chloromethanes is released to the spent acid and spent caustic streams. This release factor was not based on plant data and is therefore not considered very reliable. However, in the absence of better data, this factor is used to give an approximation of emissions. Since the emission factor is based on total chloromethanes produced rather than on chloroform only, the following equation corrects for this by multiplying by the ratio of chloroform to total chloromethanes.

$$\begin{pmatrix} \text{Total} \\ \text{chloroform} \\ \text{produced} \end{pmatrix} \begin{pmatrix} \text{Emission factor} \\ \text{kg } CHCl_3/\text{kkg} \\ \text{chloromethane} \end{pmatrix} \begin{pmatrix} \text{Percent} \\ \text{chloroform in} \\ \text{chloromethanes} \end{pmatrix} = \begin{matrix} \text{Total} \\ \text{chloroform} \\ \text{released} \end{matrix}$$

$$(122{,}400 \text{ kkg}) \quad (0.04) \quad (0.33) \quad = \quad 1.6 \text{ kkg}$$

Because these waste streams are small, the chloroform will be diluted to low concentration. It is assumed that about 80 percent or 1.3 kkg will evaporate and 20 percent or 0.3 kkg will remain in the water. Our uncertainty estimates for the percentages released to air and remaining in water are +10% and +30%, respectively. Our uncertainty estimate for total chloroform released to spent caustic and spent acid wastes (1.6 kkg) is +75%. When the uncertainty of +10% for total chloroform produced is taken into account, the overall uncertainties are +110%, -100% for air and +125%, -100% for releases to water.

2.1.1.4 Summary of Environmental Releases

Figure 2.3 summarizes the multimedia releases of chloroform from the methyl chloride chlorination process. If fugitive emissions and

Incinerated
16.4 kkg

176.0 kkg (Controlled)
348.5 kkg (Uncontrolled)

Air (process losses)

Chloroform
Production by
Methyl Chloride
Chlorination
(122,400)

Water   7.3 kkg

Air   136. kkg
               (Transportation Losses)

Landfill   5.8 kkg

∿122,000 kkg
Product*
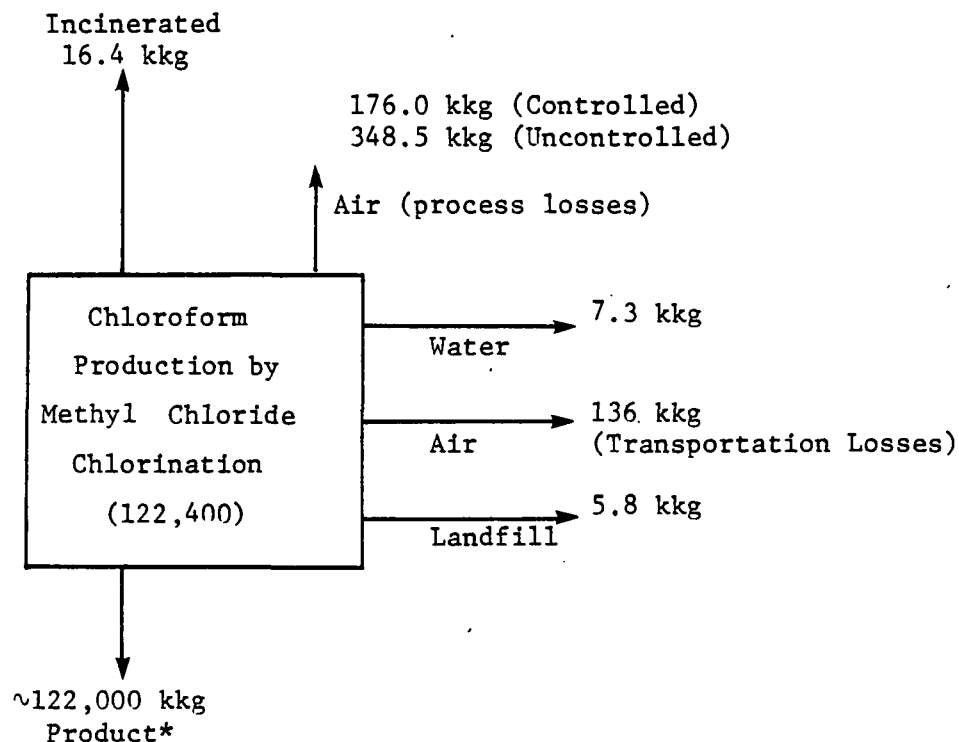
*The quantity of product available will depend on the extent
 fugitive, storage, and working emissions are controlled.
 Although air emissions are shown for both controlled
 and uncontrolled conditions, controlled conditions are
 probably more representative of losses.

Figure 2.3   Summary of Multimedia Release of Chloroform from the
             Methyl Chloride Chlorination Production Process

storage and working losses are assumed to be controlled, as previously discussed, the process releases a total of 189 kkg of chloroform or approximately 0.2 percent of the total produced. Of the chloroform released, 93 percent is emitted to air or is evaporated from water, 4 percent is discharged to water, and 3 percent is landfilled. An additional 16.4 kkg is destroyed by incineration.

If fugitive, storage, and working emissions were not controlled, the process would release a total of 360 kkg, with more than 96 percent of the emissions going to air.

Figure 2.3 includes the transportation losses derived in Section 2.1.3.

2.1.2 Methane Chlorination Process

Chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride by the thermal chlorination of methane. A detailed description of this process is presented in Appendix B. A simple flow diagram illustrating points of environmental release is shown in Figure 2.4.

The Dow Chemical plant at Freeport, Texas, is the only plant using the methane chlorination process exclusively. Allied Chemical uses chlorination of methane for about 5 percent of its total production and the Vulcan plant at Geismar produces an estimated 10 percent of its output by methane chlorination (Hobbs and Stuewe 1979a). The total chloroform production capacity for this process is approximately 50,200 kkg.

Production figures for 1978 were not available for the methane chlorination process. Since total chloroform production is estimated to operate at 71 percent of capacity, it is assumed that methane chlorination and methyl chloride chlorination each operated at 71 percent capacity in 1978. Total chloroform produced by methane chlorination is thus estimated as 36,000 kkg, 23 percent of total chloroform production. This estimate is considered accurate to ±30%.

Estimating process emissions at about 100 kkg, total production is assumed to be 36,100 kkg.

2.1.2.1 Air Emissions

Air emissions from the chlorination of methane come from the following sources:

- Inert gas purge vent for methane recycling
- Drying bed regeneration vent
- Distillation area emergency inert gas vents
- Fugitive emissions
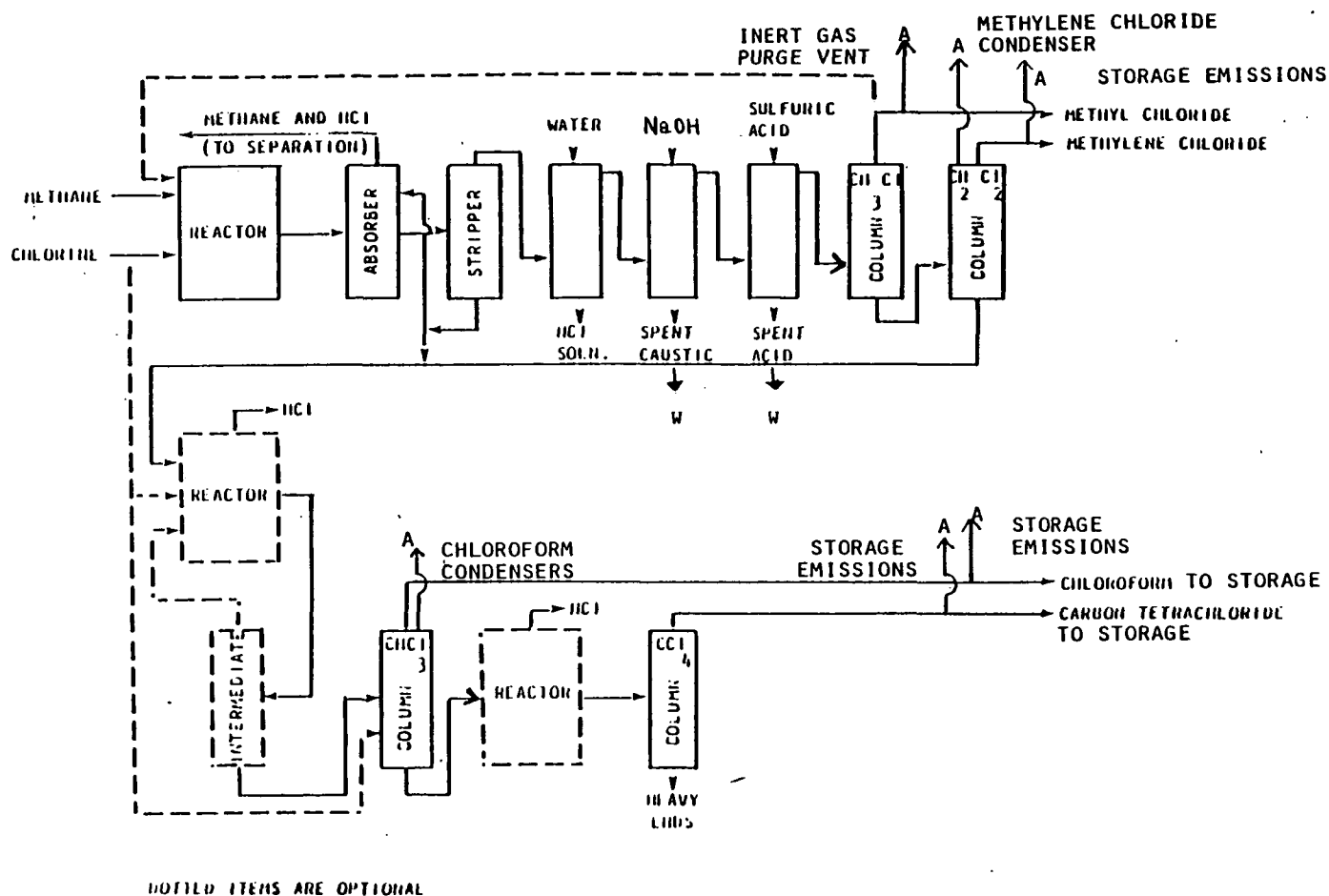- Storage and handling
- Secondary emissions

2-16

Figure 2.4   Production of Chloroform from Methane and Chlorine
Source: Hobbs and Stuewe 1979a

The Hydroscience report (Hobbs and Stuewe 1979a) was the only source of data on emissions from the chlorination of methane. The emission factors in this report were based on information supplied by Dow Chemical.

A. Inert Gas Purge Vent for Methane Recycling

Inert gases enter the process with feeds to the chlorination chamber, and remain with the unreacted methane throughout the methane purification step. A portion of the recycled methane stream is vented to prevent a buildup of inert gases. It is estimated that 2.10 kg of chloromethanes are released per kkg of chloromethanes produced. The stream composition indicates that the vent stream is 0.01 mole percent chloroform, or 0.0033 kg of chloroform/kkg of chloromethanes.

Since the emission factor is based on total chloromethanes, we have multiplied by the fraction of chloroform in total chloromethanes produced (about 25 percent) to determine emissions associated with chloroform production only.

$$\begin{pmatrix} \text{Chloroform} \\ \text{produced} \end{pmatrix} \begin{pmatrix} \text{Emission factor} \\ \text{chloroform/} \\ \text{chloromethanes} \end{pmatrix} \begin{pmatrix} \text{Fraction} \\ \text{chloroform in total} \\ \text{chloromethanes} \end{pmatrix} = \begin{matrix} \text{Chloroform emitted} \\ \text{from inert gas} \\ \text{purge vent} \end{matrix}$$

$$(36,100 \text{ kkg}) \quad (0.0033 \text{ kg/kkg}) \quad\quad (0.25) \quad\quad = \quad\quad 0.03 \text{ kkg}$$

The industrial source for this emission factor did not give error bounds on this estimate. We assume the emission factor to be accurate to +50%, -25%. The uncertainty factors for total chloroform produced from this process is ±30%. The overall uncertainty is thus +80%, -55%.

B. Drying Bed Regeneration Vent

Chloroform has not been identified as a constituent of this stream.

C. Distillation Area Emergency Gas Vent

Venting of distillation area equipment prevents buildup of pressure in the condensers. Emissions during emergency venting were estimated to be 0.061 kg/kkg of chloromethanes (Hobbs and Stuewe 1979a). The composition of the uncontrolled emissions is reportedly:

Component	Mole Percent
Chlorine	40
HCl	34.6
VOC	22.4
Air	3

When these constituents are expressed as percentage by weight, VOC make up about 34 percent of the total emissions. Assuming that chloroform comprises 25 percent of the VOC then the emission factor for the gas vent is 0.005 kg/kkg of chloroform produced. Total releases of chloroform from venting of distillation area condensers are estimated from this emission factor and chloroform production of 36,000 kkg as 0.19 kkg.

Neither the method for estimating the emission factor nor the uncertainty of this estimate was given. We assume the estimate to be accurate to +50%, -25%. With an uncertainty estimate of ±30% for total chloroform produced, our overall uncertainty is +80%, -50%.

D. Fugitive Emissions

As indicated in Section 2.1.1, estimates of fugitive emissions from process fluid leaks are based on average daily losses for controlled and uncontrolled emissions for the petroleum refinery industry. These fugitive emission factors for chloromethanes are shown in Table 2.6. The number of process valves, compressors, and other components has been estimated for a chloromethane plant with a capacity of $45-180 \times 10^{-3}$ kkg (Hobbs and Stuewe 1978). This estimate is only a rough approximation and only accounts for fugitive losses associated with the Dow plant at Freeport, Texas. Without detailed process descriptions, fugitive emissions cannot be estimated for the Allied plant at Moundsville, West Virginia, or the Vulcan plant at Geismar, Louisiana, since production capacities are so small.

Table 2.6 summarizes the number of equipment components, the average controlled and uncontrolled emissions per unit, and the total fugitive emissions from each component. Emissions were calculated assuming a 260 day work year, using the following equation:

$$\begin{pmatrix} \text{Total number} \\ \text{of components} \end{pmatrix} \begin{pmatrix} \text{Average loss/} \\ \text{component/day} \end{pmatrix} \begin{pmatrix} \text{Number of} \\ \text{work days} \end{pmatrix} = \begin{array}{c} \text{Total fugitive} \\ \text{losses/components} \end{array}$$

The data presented in Table 2.6 indicate that the total uncontrolled fugitive emissions equal 47.4 kkg/year, and total controlled fugitive emissions equal 5.6 kkg. These estimates are thought to be accurate to ±30%.

Table 2.6 Summary of Emission Factors for Fugitive Emissions of Chloromethanes from Various Equipment Components

	Total no. of units	Uncontrolled losses (kg/day/unit)	Controlled losses (kg/day/unit)	Total uncontrolled emissions[a] (kkg/yr)	Total controlled emissions[a] (kkg/yr)
Pump seal	60	1.5	0.16	23.4	2.5
Compressor	2	3.9	1.0	2.0	0.5
Process valve	1,000	0.068	0.006	17.7	1.6
Pressure relief valve	15	1.1	0.1	4.3	0.4
TOTAL				47.4	5.0

[a]Uncontrolled and controlled emission are considered separately in the overall materials balance.

Source: Hobbs and Stuewe 1979a

Since a quantitative breakdown of the composition of gases in fugitive emissions was not available, the composition was estimated based on vapor pressure of the gases and process operating conditions. Emissions are estimated to have the following composition:

	Mole percent	Molecular weight	Weight percent
Methane	30	16	2.9
Chlorine	5	70	25.4
Hydrogen chloride	30	36	13.2
Methyl chloride	20	50	18.3
Other VOC	15	103	37.4

An estimate of chloroform in other VOC was made by assuming that this category consisted only of carbon tetrachloride, methylene chloride, and chloroform and that the concentrations were proportional to the quantities of each produced. The estimated percentages are:

Methylene chloride	56 percent
Chloroform	31 percent
Carbon tetrachloride	13 percent

The total quantity of chloroform in fugitive emissions is estimated from the total fugitive emissions (47.4 kkg uncontrolled; 5.0 kkg controlled), the fraction of other VOC in these emissions (0.374), and the fraction of chloroform in other VOC (0.31). These chloroform emissions are thus estimated as 5.5 kkg for uncontrolled conditions and 0.58 kkg for controlled conditions. It is likely that fugitive emissions are controlled.

The overall uncertainty for controlled emissions is ±50%. This uncertainty is attributed to the likelihood that the number of equipment components varies from the values shown in Table 2.6, and to uncertainty related to the composition of fugitive emissions.

E. Emissions from Storage and Handling

Emissions from storage and handling are estimated using an empirical formula developed by API which correlates evaporative losses with several factors related to storage (USEPA 1977). It was assumed that all tanks are of the fixed roof type and that refrigerated vapor recovery systems are used for tanks with a volume of 375,000 liters or greater. Efficiency of a refrigerated vapor recovery system varies from 60-90 percent for chloromethanes. An efficiency of 75 percent was assumed for these calculations.

Assumptions regarding storage tank size and factors which affect storage emissions were based on data included in Appendix B and Table 2.7, which shows the assumed tank volumes, number of tanks, and turnover rates. Our estimates for breathing and working losses are also shown in the table.

Table 2.7 Summary of Chloroform Storage Variables and Chloroform Breathing and Working Losses

Tank volume (gal)	Tank volume (ℓ)	Number of tanks	Approximate percent of capacity	Turnover rate	Recovery method	Breathing losses (kkg/yr)[a]		Working losses (kkg/yr)[a]	
						controlled	uncontrolled	controlled	uncontrolled
300,000	1,125,000	1	50	20	Refrigerated vapor recovery	6.7	26.7	3.2	12.7
16,000	60,000	1	50	125	None	1.7	1.7	1.9	1.9
7,000	26,250	5	50	125	None	2.8	2.8	4.1	4.1
TOTAL						11.2	31.2	9.2	18.7

[a]Controlled and uncontrolled emissions are considered separately in the overall materials balance.

Breathing losses were determined using the following equation:

$$LB = 2.21 \times 10^{-4}\ M \left[\frac{P}{14.7-P}\right]^{0.68} D^{1.73}\ H^{0.51}\ T^{0.5}\ TpCKc$$

where

LB = fixed roof working losses (lb/day)

M = molecular weight - 119

P = true vapor pressure at bulk conditions (psia) - 3.259

D = tank diameter (see Appendix B)

H = average vapor space height (see Appendix B)

T = ambient temperature change from day to night - assume $20^{\circ}F$

Tp = paint factor - assume 1

C = adjustment factor for small diameter tanks - variable

Kc = crude oil factor = 1

Appendix B details the calculations for breathing losses by use of this empirical formula. As Table 2.7 and Appendix B indicate, the total chloroform storage losses with vapor recovery are estimated at 11.2 kkg. This corresponds to an emission factor of 0.31 kg/kkg of chloroform produced. Without refrigerated vapor recovery the emission factor would be 0.9 kg/kkg of chloroform. This estimate is somewhat lower than that of 1.35 kg/kkg made by Hydroscience (Hobbs and Stuewe 1979a) for uncontrolled fugitive losses. Although the overall materials balance considers both controlled and uncontrolled emissions, the controlled conditions are more likely. Our estimate of 11.2 kkg of chloroform released during storage with vapor recovery is considered accurate to +75%, -25%. This uncertainty takes into account the possibility that the Hydroscience estimate is more accurate and the uncertainty related to the extent to which vapor recovery systems are used.

F. Working Losses

Working losses were also estimated using an empirical formula developed by API (USEPA 1977). The formula is:

$$LW = 2.4 \times 10^{-2}\ MPKnKc$$

where

LW = fixed roof working losses (lb/10^3 gal)

M = molecular weight = 119

P = true vapor pressure at bulk liquid conditions = 3.259 psia

Kn = turnover factor - variable

Kc = crude oil factor

The turnover factor is a function of the turnover rate shown in Table 2.7. The calculations for working losses based on the empirical formula are detailed in Appendix B. Table 2.7 summarizes working losses. Assuming controlled conditions (i.e. vapor recovery), an estimated 9.2 kkg of chloroform were lost due to handling in 1978. This corresponds to an emission factor of 0.26 kg/kkg. Without the use of refrigerated vapor recovery, the emission factor would be 0.52 kg/kkg and emissions would be about 18.7 kkg. This is significantly higher than the estimate of 0.36 kg/kkg made by Hydroscience for handling emissions from this process (Hobbs and Stuewe 1979a). The accuracy of our estimate for controlled emissions is considered +75%, -25% to take into account the uncertainties related to the use and efficiency of vapor recovery systems, the number of tanks, and tank turnover.

G. Secondary Emissions

Secondary emissions result during the handling and disposal of process liquids. Potential sources for secondary emissions include:

- Incineration of carbon tetrachloride incineration bottoms

- Waste caustic from scrubbers

- Sulfuric acid waste from the dryer of the methyl chloride product stream.

Quantitative estimates of these emissions could not be made.

2.1.2.2 Releases to Water

Because of similarities between the methyl chloride and the methane chlorination processes, it is assumed that the wastewater streams in the former process are present in the latter. These indirect streams are contact cooling water and wastewaters containing spent caustic and spent acid.

A. Indirect Cooling Water

Only one estimate was available on the amount of cooling water used in chloromethane production (Lant 1978). We assume that similar quantities, 5,800 ℓ/kkg of chloroform, are generated in all chloromethane plants, although this amount is probably quite variable. We further assume that cooling water is contaminated by spills and leaks, producing chloroform concentrations of 100 mg/ℓ. Contaminant levels of 1,000 mg/ℓ were reported for one process, but because of the age of this plant, this value was not considered representative. For chloroform production of 36,000 kkg, these factors give an estimate of 21 kkg of chloroform released to cooling water. JRB assumes that 90 percent (18.9 kkg) of the chloroform is readily evaporated and the remaining 10 percent (2.1 kkg) is released to water. This estimate of 21 kkg is considered accurate to +75%, -50% to account for variation in chloroform contaminant levels, (which have not been monitored) and in amount of cooling water per kkg of chloroform. Since the uncertainty for the quantity of chloroform produced is $\pm$30%, the overall uncertainty estimate is +110%, -76%.

B. Wastes Containing Spent Caustic and Spent Acid

Gruber and Ghassemi (1975) estimated release of chloroform to waste-water from spent caustic and spent acid at 0.04 kg/kkg of total chloro-methanes. The derivation of this release rate is not described, and it is thought to be a rough estimate at best. Assuming that 25 percent of the chloromethanes is chloroform, total chloroform releases to waste-water from chloroform production can be estimated:

$$\begin{pmatrix} \text{Total chloroform} \\ \text{produced} \end{pmatrix} \begin{pmatrix} \text{Emission factor} \\ \text{chloroform/} \\ \text{chloromethanes} \end{pmatrix} \begin{pmatrix} \text{Fraction} \\ \text{chloroform in} \\ \text{chloromethanes} \end{pmatrix} = \begin{array}{c} \text{Total} \\ \text{chloroform} \end{array}$$

| (36,100 kkg) | (0.04 kg/kkg) | (0.25) | = | 0.36 kkg |

JRB assumed that at the dilute concentrations present in these waste streams, 80 percent of the chloroform (0.3 kkg) will be evaporated and 20 percent (0.1 kkg) will remain in water.

Our estimates of the percentages of chloroform released to air and water are considered accurate to +10%, -30%, respectively. Our esti-mate of 0.36 kkg for total chloroform releases is considered accurate to +75%. When the uncertainty of +30% for total chloroform produced is taken into account, the overall uncertainties are +152%, -100% for air and +150%, -100% for water.

2.1.2.4 Summary of Environmental Releases

Figure 2.5 summarizes the environmental releases of chloroform from the methane chlorination process under both controlled and uncon-trolled conditions. Process emissions under controlled emissions are estimated to be 42.6 kkg, or less than 0.2 percent of the total produc-tion. Of the chloroform emitted, 95 percent is released directly to air or evaporated from wastewater and the remaining 5 percent is discharged to water. An unidentified amount is incinerated during destruction of carbon tetrachloride still bottoms.

2.1.3 Transportation Losses

Transporting chloroform from the production sites to the end-use sites causes losses from loading and transit. No information is available on transportation practices. However, several reasonable assumptions can be made to estimate these losses.

2.1.3.1 Loading Losses

Loading is the primary source of evaporative losses during trans-portation. These losses occur when hydrocarbon vapors residing in the empty cargo tanks are displaced to the atmosphere by liquids being loaded. Emissions from loading can be estimated using the following expression (USEPA 1977):

```
                                        40.4 kkg (Controlled)*
                                        74.8 kkg (Uncontrolled)
                  ?                     Air (Process losses)
        Incinerated

              ┌─────────────────┐
              │   Chloroform    │          2.2 kkg
              │ Production from │   Water ────►
              │    Methane      │         (Transportation losses)
              │  Chlorination   │   Air ────►        41
              │    Process      │          0 kkg
              │  (36,100 kkg)   │   Land ────►
              └─────────────────┘
                       │
                       ▼
                 ᴧ36,000 kkg
```
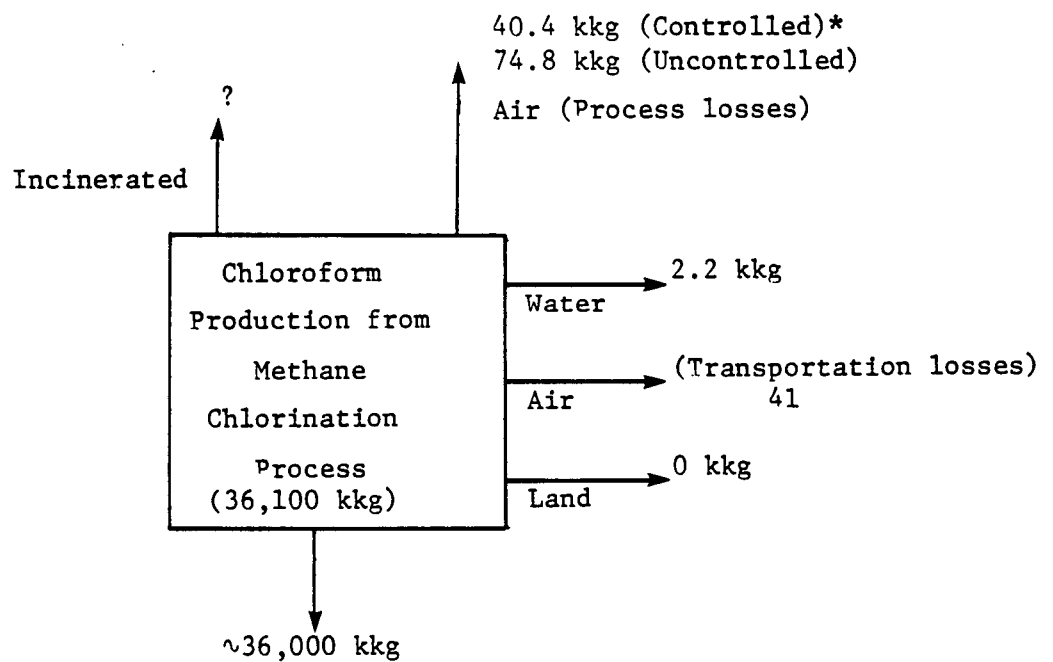
*Controlled conditions: Vapor recovery systems associated
with large storage tanks and control of fugitive emissions
by repair of major leaks. Although both controlled and
uncontrolled conditions are shown, controlled conditions
are more likely.

Figure 2.5   Summary of Multimedia Releases of Chloroform
             from Methane Chlorination Process

$$LL = 12.46 \ \frac{SPM}{T}$$

where

    LL = Loading losses, $lb/10^3$ gal

    M = Molecular weight = 119

    P = True vapor pressure = 3.2 psia

    T = Bulk temperature liquid - assume $530^{\circ}R$

    S = Saturation factor - assume 1.45 for tank cars
                                                0.5 for barges
                                              0.2 for marine vessels

The saturation factor reflects the concentration of chloroform vapor in the tank atmosphere. It depends upon the type of loading. JRB assumes that splash loading is used, which results in higher evaporative losses than the alternative, submerged loading.

We also assumed that in addition to the chloroform exported, 20 percent of the chloroform produced was transported by barge, and the remainder by tank trucks or cars.

Then, for tank cars:

$$L = \frac{(12.46)(1.45)(3.2)(119)}{530} = 13.0 \ lb/10^3 \ gal \ or \ 1.6 \ kg/10^3 \ \ell$$

The quantity of chloroform loaded on tank trucks and cars is estimated by subtracting the quantity exported, the quantity assumed to be transported by barge, and the quantity produced by Allied Chemical (which is used consumptively on-site) from the total chloroform produced (values in kkg converted to liters by use of the density, 1.481 g/ml):

$$\begin{pmatrix} \text{Total} \\ \text{chloroform} \\ \text{produced} \end{pmatrix} - \underbrace{\left[(\text{Exports}) + \begin{pmatrix} \text{Domestically used} \\ \text{chloroform} \\ \text{transported} \\ \text{by barge} \end{pmatrix} + \begin{pmatrix} \text{Estimated} \\ \text{production} \\ \text{by Allied} \end{pmatrix} \right]}_{\substack{\text{Total chloroform transported} \\ \text{by trucks and cars}}} =$$

$$(106 \times 10^6 \ \ell) - \left[(5.3 \times 10^6 \ \ell) + (20.0 \times 10^6 \ \ell) + (6.3 \times 10^6 \ \ell) \right] =$$

$$74.4 \times 10^6 \ \ell$$

Total chloroform losses from loading are estimated from the loss factor and the total quantity transported as 119 kkg.

The uncertainty of this estimate is ±50%. USEPA (1977) estimates the uncertainty at ±30% when all variables in the equations are known. Since certain assumptions were made to estimate temperature and the saturation factor, there is added uncertainty in our estimate.

Chloroform losses from loading of barges and marine vessels can be similarly estimated using the appropriate saturation factors of 0.5 for barges and 0.2 for ocean vessels. Using the equation for loading losses, the chloroform release factors are calculated as 0.5 kg/10^3 ℓ for loading barges and 0.2 kg/10^3 ℓ for loading marine vessels. The quantities transported by these methods were given in the above equation as 20.0 x 10^6 ℓ for barges and 5.3 x 10^6 ℓ for marine vessels (exports). From these amounts and the respective loss factors, the releases are calculated as 10 kkg for loading barges and 1 kkg for marine vessels. These estimates are also considered accurate to ±50%.

2.1.3.2 Transit Losses

An additional source of emissions associated with transportation is transit losses. Small quantities of chloroform are expelled from cargo tanks due to temperature and barometric pressure changes. Losses are assumed to be the same from tank cars, barges, and marine vessels. Assuming the cargo reaches the destination in about 1 week, transit losses can be estimated using the equation:

$$LT = 0.1 \ PW$$

where

LT = Transit losses, lb/week-10^3 gal

P = True vapor pressure = 3.2 psia

W = Density of condensed vapor = 12.5 lb/gal

LT = 0.1 (3.2)(12.5) = 4 lb/week-10^3 gal or 0.5 kg/week-10^3 ℓ

Assuming that 1 week is the average transit time, the total transit losses of chloroform are estimated as follows:

$$\left[\text{Total quantity produced} - \left[\left(\begin{array}{c}\text{Production}\\\text{at Allied}\end{array}\right) + \left(\begin{array}{c}\text{Quantity}\\\text{exported}\end{array}\right) + \left(\begin{array}{c}\text{Loading}\\\text{losses}\end{array}\right)\right]\right] \times$$

$$\left(\begin{array}{c}\text{Release factor}\\\text{for transit}\end{array}\right) = \begin{array}{c}\text{Total Chloroform Losses}\\\text{from Transit}\end{array}$$

$$\left[(106{,}000 \times 10^3 \ \ell) - (6{,}300 \times 10^3 \ \ell + 5{,}300 \times 10^3 \ \ell + 154 \times 10^3 \ \ell)\right] \times$$

$$(0.5 \ \text{kg}/10^3 \ \ell) = 47 \ \text{kkg}$$

This estimate is considered accurate to ±30%, provided all shipments reach their destination in about a week (USEPA 1977). Because of the uncertainty in transit time, we estimate these emissions to be accurate to ±50%.

Total transportation losses are equal to the sum of loading losses from barges (10 kkg), tank cars or trucks (119 kkg), and marine vessels (1 kkg), plus transit losses (47 kkg), or 177 kkg. The overall uncertainty of this estimate is +50%.

2.2 IMPORTS

In 1978, 7,680 kkg of chloroform were imported (U.S. Bureau of the Census 1979b). This quantity is equivalent to less than 5 percent of the domestic production. Information was not available on quantities imported prior to 1978 and, therefore, trends regarding chloroform imports are not discussed.

2.3 STOCKPILES

Although no information is available on stockpiles as a source of chloroform, it is not likely that any stockpiled chloroform was used in 1978. On the contrary, it is more likely that large quantities of domestically produced chloroform were placed in stockpiled reserves in 1978. This is discussed in Section 3.2.

2.4 INDIRECT PRODUCTION

This section discusses indirect sources of chloroform production from both natural sources and as a byproduct in other chemical production processes.

2.4.1 Formation of Chloroform During Production of Vinyl Chloride Monomer

Chloroform is a byproduct of the manufacture of vinyl chloride monomer (VCM) (McPherson et al. 1979; Shiver 1976). A balanced production process employs oxychlorination and the direct chlorination of ethylene to form 1,2-dichloroethane (EDC) followed by its cracking to VCM (see Figure 2.6). The light ends from the EDC distillation column can contain 10 percent by weight chloroform (Shiver 1976). This calculation was based on analysis of a typical VCM waste stream, and we assume an analytical error of +5%. In 1975, production of VCM and light ends were reported as 1,910,000 and 162,00 kkg respectively (Shiver 1976). From these values, light ends are estimated to amount to 0.85 percent of VCM production (Shiver 1976). The sources of these production figures are unknown, and we assume an uncertainty of +10%.

Using the percentage of light ends and the 1978 production figures for VCM as reported by the International Trade Commission (USITC 1979), 3,150,000 kkg (+10%), the quantity of light ends can be estimated as 26,775 kkg (+10%). From the estimated quantity of light ends and their reported chloroform content of 10 percent, the total amount of chloroform contained in the light ends is estimated as 2,680 kkg (+65%, -45%).

2.4.1.1 Air Emissions

Light ends are either incinerated, used as feedstock for other processes, or landfilled, with the majority being incinerated (Shiver
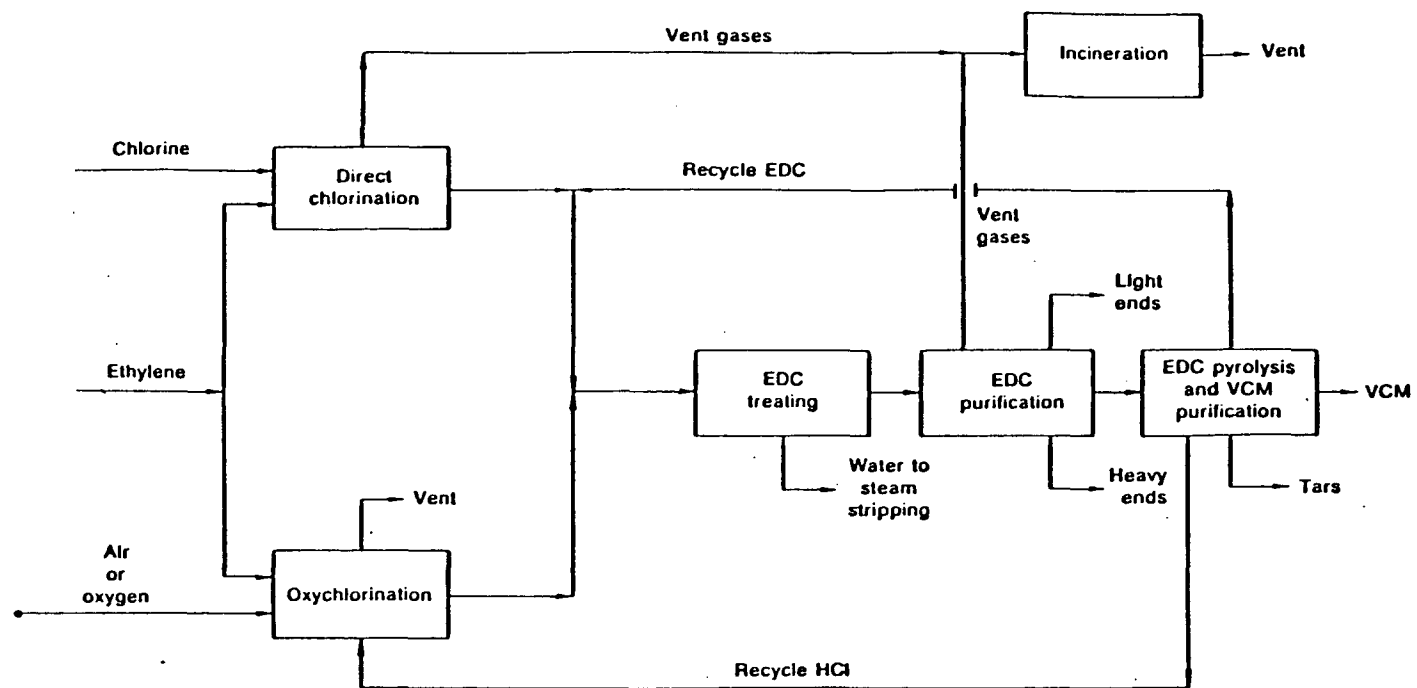
Figure 2.6   VCM Production Process
           Source: McPherson et al. 1979

1976). We assume that 90 percent (+5%) of the light ends are incinera-
ted, based on the industrial information available (Shiver 1976).
Assuming a 95 percent (+5%) emission control efficiency during incinera-
tion, which includes emissions during handling and transport of waste
ends, emissions to the atmosphere can be calculated as follows:

$$\begin{pmatrix} 1 - \text{Efficiency} \\ \text{of incineration} \end{pmatrix} \begin{pmatrix} \text{Fraction} \\ \text{incinerated} \end{pmatrix} \begin{pmatrix} \text{CHCL}_3 \text{ in} \\ \text{light ends} \end{pmatrix} = \begin{array}{c} \text{Estimated CHCl}_3 \\ \text{released to} \\ \text{atmosphere during} \\ \text{incineration} \end{array}$$

$$(1 - 0.95) \qquad (0.9) \qquad (2,680 \text{ kkg}) = \qquad 120 \text{ kkg}$$
$$(+246\%, -100\%)$$

The remaining 268 kkg (+148%, -72%) of the chloroform contained in
the light ends are either landfilled or used as feedstock. We assume,
as the case with maximum releases, that all of this is landfilled. We
further assume that 25 percent (+5%) is released annually from landfill
due to damaged or rusting containers. In this case, an estimated 67
kkg of chloroform (+199%, -80%) would be released from landfills to the
atmosphere annually.

2.4.1.2 Water Emissions

The VCM production process will produce an aqueous waste from
washers and caustic scrubbers. The quantity of this waste stream and
the amount of chloroform contained in it are unknown.

2.4.1.3 Land Emissions

We estimated that 268 kkg of chloroform contained in the light
ends are landfilled. Of this amount, 75 percent, or 200 kkg (+130%,
-71%), is estimated to remain in landfills. Material in landfills
is not considered a release to land but is considered to be in storage
until released. Figure 2.7 summarizes the multimedia releases of
chloroform from VCM production.

2.4.2 Chlorination of Organic Precursors in Water

An important source of indirect, noncommercial production of
chloroform is the aqueous reaction of chlorine with various organic
compounds in municipal drinking water supplies, municipal sewage,
industrial waste and process streams, industrial cooling water, and
most natural waters. The organic precursors to trihalomethane (THM)
formation are natural humic substances present in virtually all source
waters, rivers, lakes, reservoirs, and well water (Stevens et al. 1976).
The products of vegetative decomposition, these humic materials con-
stitute the organic coloring of natural waters; they are complex fulvic
and tannic substances generally classified as aromatic polyhydroxy-
methoxycarboxylic acids (Morris and McKay 1975). The major mechanism
for formation of chloroform and other THM's via the chlorination of
organic matter in water supplies appears to be the classic haloform
reaction (Morris and McKay 1975). This is commonly a base-catalyzed
series of halogenation and hydrolysis reactions between chlorine and
organics containing the acetyl group or compounds oxidizable to the

Air

120

2412 → Incineration

Light Ends 2680
from VCM Production →
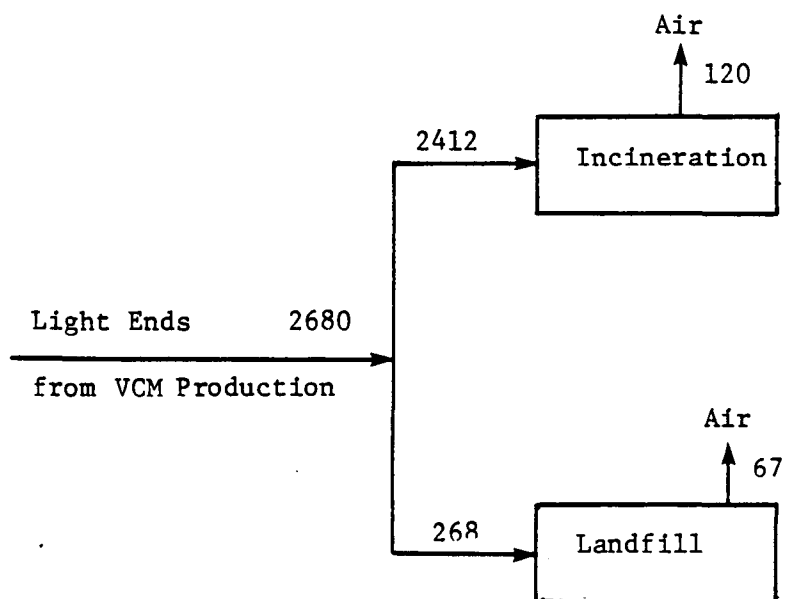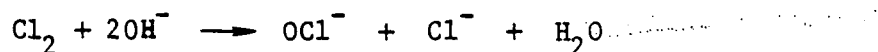
Air

67

268 → Landfill

Figure 2.7 Multimedia Releases of Chloroform from Production of VCM

acetyl group which occur in alkaline aqueous solution. When dispersed
in water at pH greater than 5, the chlorine is instantaneously and
completely hydrolyzed to chloride and hypochlorite (OCl^-) ions accord-
ing to the reaction:

$$Cl_2 + 2OH^- \longrightarrow OCl^- + Cl^- + H_2O$$

When considering potential interactions with organic compounds in
water, hypochlorite is the reactive form of chlorine. In the haloform
reaction, the three hydrogens of the original compound's acetyl group
are successively replaced by chlorine (or other halogen); then the
carbon bond to the carbonyl group is split, giving rise to a haloform
and a carboxylic acid (Morris and McKay 1975). The net reactions may
be written:

$$CH_3COR + 3 HOCl \longrightarrow CCl_3COR + 3H_2O$$

$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH$$
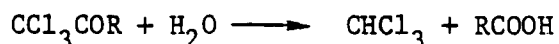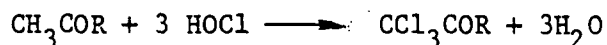
Formation of THM's via this mechanism is enhanced by increases in both
temperature and pH (Stevens et al. 1978).

Chloroform may be produced indirectly, therefore, whenever chlorine
is introduced into waters containing humic acids. It is also possible
that chlorination of other specific organic structures may contribute
significantly to chloroform formation. Potential sources of indirect
chloroform production include disinfection of municipal drinking water
supplies and sewage via chlorination, chlorination of industrial waste
streams and process streams containing precursor organics, and chlori-
nation of industrial cooling waters to control biofouling within heat
transfer systems.

2.4.2.1 Chlorination of Municipal Water Supplies

In recent years the occurrence and formation of chloroform in
potable water supplies have been investigated intensively, but no
comprehensive study has been performed to precisely quantity the
amounts of chloroform generated annually through municipal chlorination
practices.

In 1975, USEPA conducted the National Organics Reconnaissance
Survey (NORS) for halogenated organics in the drinking water of 80
U.S. cities. Results of the survey showed that untreated raw water
concentrations of chloroform were generally less than 0.1 µg/ℓ, but
samples of finished drinking water contained concentrations of chloro-
form ranging from less than 0.2 to 311 µg/ℓ, with a median value of
21 µg/ℓ (Symons et al. 1975). In the same year, the EPA Region V
Organics Survey analyzed raw water and finished water samples collec-
ted at 83 locations throughout the Midwest. Chloroform was detected
in raw water supplies at a mean concentration of less than 1.0 µg/ℓ
and in finished drinking waters at concentrations ranging from less
than 1.0 to 366 µg/ℓ. Combining data from the Region V survey with
the NORS findings yields a median value of approximately 20 µg/ℓ for

chloroform concentrations detected in treated waters (Symons 1976). The data from these two surveys represent the analysis of 165 water samples collected from February through April 1975. It is important to note that 80 percent of the utilities surveyed used surface water sources, although only 20 percent of the U.S. community water utilities use surface sources of water. Many utilities using groundwater sources do not practice chlorination (Symons 1976). However, J. Carrell Morris, Professor of Sanitary Chemistry at Harvard University, states that the 80/20 breakdown is probably accurate with respect to volumes of surface versus groundwater (respectively) treated on a national basis (Morris 1980).

In the NORS study, the nine utilities having the highest levels of chloroform in treated water had an average yield of chloroform equivalent to 2.0 percent of the total chlorine dose applied. The average yield of chloroform at the nine highest sites in the Region V Survey was 2.7 percent of the total chlorine dose. Symons (1976) has concluded that high concentrations of chloroform result when surface water or shallow groundwater with a high total organic carbon content and high chlorine demand is dosed with sufficient chlorine to produce a high free chlorine residual, especially if the water is somewhat basic (pH 7-10). Alan Stevens of the Water Supply Division of EPA's Municipal Environmental Research Laboratory states that the chlorination of municipal water supplies typically yields THM concentrations of approximately 3 percent of the total chlorine applied, but that the yield probably ranges from 0.5 to 5.0 percent depending on variations in parameters such as pH, temperature, contact time, and concentrations of precursor organics in the source water being chlorinated (Stevens 1980).

Representatives of the American Water Works Association (AWWA) (DeBoer 1980), the Chlorine Institute (Doyle 1980), and recognized experts in the field of chlorine chemistry and water treatment -- Robert L. Jolley of Oak Ridge National Laboratory (Jolley 1980), James M. Symons and Alan Stevens of EPA's Municipal Environmental Research Lab (Symons 1980, Stevens 1980), and J. Carrell Morris, Professor of Sanitary Chemistry at Harvard University (Morris 1980) -- have indicated that no calculations have been performed to determine the amounts of chloroform produced annually through municipal water chlorination practices. Two sources in the readily available literature have estimated the quantities of chloroform produced annually through water chlorination, by use of broad assumptions. Versar, Inc. (1977) used 20 $\mu g/\ell$ as the average increase in chloroform concentration as a result of chlorination (based on EPA's Region V Organics Survey and NORS monitoring data) and, assuming estimated annual nonconsumptive use of water in the United States at 4.1×10^{14} ℓ, calculated that approximately 8,200 kkg of the compound are formed annually through water chlorination. This figure may have an associated uncertainty range as great as $\pm 90\%$. Also, "nonconsumptive" water use includes municipal wastewaters (sewage) which are known to yield much lower amounts of chloroform than drinking water supplies when chlorinated (Jolley 1980). Consequently, the Versar estimate is probably too high.

Lowenbach and Schlesinger Associates (1979) used the same basic methodology, but assumed a 30 µg/ℓ average chloroform concentration. They estimate that 12,000 kkg of chloroform are discharged annually from the chlorination of municipal drinking water. Again, the validity of this estimate depends on the validity of their basic assumptions. A chloroform concentration of 30 µg/ℓ is probably too large to use as a national average since groundwater sources, when chlorinated, are known to yield much smaller concentrations of chloroform than surface water sources, and groundwater sources constitute a significant percentage of the nation's community water supplies (Symons 1976). Therefore, the Lowenbach and Schlesinger estimate is probably also too high.

There are two basic methods available for estimating the quantities of chloroform produced annually during water chlorination. One method, used by both Versar and Lowenbach and Schlesinger Associates, consists of multiplying the volume of water chlorinated annually by the expected concentration of chloroform in the treatment plant effluent distributed into the municipal water system. John De Boer of AWWA states that the average national production of water treatment plants is on the order of 150 gallons of water per capita per day (De Boer 1980). This is close to the figure of 148 gallons per capita per day estimated for national water consumption in 1980 (Metcalf and Eddy, Inc. 1972). The AWWA estimate is based on the typical output of approximately 50,000 community public water supply systems across the nation. It does not include small-scale water supplies which may be treated at hotels, motels, weighing stations, or other establishments not supplying water continually. The current U.S. population is approximately 2.2×10^8. Therefore, the total annual national output of water treatment plants is estimated as follows:

$$
\begin{pmatrix} \text{Average daily per capita} \\ \text{production of water} \\ \text{treatment plants} \end{pmatrix} \begin{pmatrix} \text{Estimated} \\ \text{U.S.} \\ \text{population} \end{pmatrix} \begin{pmatrix} \text{Days per} \\ \text{year} \end{pmatrix} = \begin{matrix} \text{Total annual} \\ \text{output} \end{matrix}
$$

$$
(150 \text{ gal}) \quad (2.2 \times 10^8) \quad (365) \quad = \quad 120{,}450 \times 10^8 \text{ gal/year}
$$

$$
= \quad 4.56 \times 10^{13} \text{ ℓ/year}
$$

Assuming that monitoring data derived from the two 1975 surveys are representative for chloroform concentrations in treated water throughout the nation, then 20 µg/ℓ can be used as a national average for chloroform produced in treated municipal water supplies. The estimated total amount of chloroform produced annually through drinking water chlorination is therefore estimated as 91.2×10^7 g or 912 kkg per year. This figure represents an approximate upper limit on the annual production of chloroform through drinking water chlorination, since many public water utilities have altered their chlorination practices in recent years to reduce THM formation in water supplies. This has been done in order to meet the EPA drinking water limit of 100 ppb for THM's. Current practices include pretreatment to remove precursor organics (coagulation, sedimentation, filtration), posttreatment to remove THM's after their formation (carbon adsorption, aeration), or use of alternative

disinfectants such as chlorine dioxide and ozone. The uncertainty range associated with the value for chloroform produced through chlorination is approximately +10%, -50%.

The second method for estimating indirect chloroform production through water chlorination is to apply the percentage yield of chloroform in treated waters to the amounts of chlorine annually used at municipal water treatment plants for disinfection purposes. It has been noted earlier that a 3 percent yield of THM's such as chloroform, bromodichloromethane, dibromochloromethane, and bromoform is typical based on the total chlorine dose applied to a given volume of source water. Russell J. Foster, Commodities Specialist on chlorine with the Bureau of Mines, has data indicating that approximately 515,000 short tons (467,000 kkg) of chlorine were consumed in "water and sanitary services" in 1977 (Foster 1980). Unfortunately, no breakdown is available on the amounts used in municipal water treatment versus municipal wastewater (sewage) treatment. It is also possible that this figure includes use of chlorine in industrial cooling water treatment. Therefore, use of this chlorine consumption figure yields an upper estimate (+5%, -80%) for the quantity of THM produced in 1977: 14,000 kkg.

Chloroform typically constitutes 90 percent or more of total THM formed via chlorination of surface water supplies (Hoehn et al. 1977). Therefore, approximately 12,600 kkg of chloroform were generated in water treatment works in 1977. Again, this number represents an estimated upper limit on combined chloroform production from two sources — drinking water and wastewater chlorination — and may include a third source, cooling water chlorination.

For this materials balance, the figure derived from the first estimation method, 912 kkg, will be used as the estimated total annual production of chloroform through the chlorination of municipal water supplies.

Environmental releases of chloroform produced in this manner will occur through leaks of chloroform-contaminated water from the municipal water distribution system (through water mains, service pipes, and household plumbing), through domestic, commercial, industrial and agricultural consumption of the water, and through treatment of that portion of municipal water destined to enter the sewer system and travel to municipal wastewater works. Chloroform is a volatile compound known to evaporate quite readily from water to air. The National Academy of Sciences (NAS 1978a,b) reports that 90 percent of chloroform usually evaporates within an hour. The various consumptive patterns for chloroform-contaminated municipal water tend to disperse and aerate the liquid, and it is expected that chloroform in municipal water will largely evaporate to the atmosphere rather than settle into waterways or be adsorbed onto sediments. It is therefore assumed that 90 percent (+5%) of the chloroform produced through chlorination of municipal water supplies, or 820 kkg (+45 kkg), will be released to the atmosphere. The remaining 10 percent (+5%), or 92 kkg (+45 kkg) will remain in solution and be released to waterways as potable water is used; an unknown portion of this amount will become bound onto soil particles or river sediments.

2.4.2.2 Chlorination of Municipal Sewage

Jolley (1980) has shown that disinfection of municipal sewage via chlorination results in the formation of numerous chlorinated organic compounds, but these do not include THM (Morris and McKay 1975). Chlorine reacts largely with ammonia in sewage to form chloramines. These do not react further with the organic constituents of sewage to produce significant quantities of halogenated methanes (Hoehn et al. 1977). Because municipal sewage does not contain the high concentration of the humic precursors contained in natural source waters, and the maintenance of a high free chlorine residual is not an important consideration in treating wastewaters, the formation of chloroform through sewage chlorination will be minimal (Jolley 1980).

Nevertheless, monitoring data from a typical sewage treatment plant show an increase of 2 to 3 $\mu g/\ell$ in chloroform concentrations detected in chlorinated effluent compared to the levels found in untreated influent (NAS 1978a,b). In general, about 60 to 80 percent of the per capita consumption of water, or 100 gallons per capita per day (assuming 70 percent), will become sewage (Metcalf and Eddy 1972). All of this water is assumed to be chlorinated before discharge from the wastewater treatment plant (the second chlorination of this water, which was chlorinated before use). Assuming an upper limit of 3.0 $\mu g/\ell$ increase in chloroform after chlorination, then the estimated total amount of chloroform produced annually through wastewater treatment is calculated:

$$\begin{pmatrix} \text{Increase in} \\ \text{chloroform} \\ \text{after} \\ \text{chlorination} \end{pmatrix} \begin{pmatrix} \text{Average} \\ \text{volume} \\ \text{of sewage} \\ \text{generated} \end{pmatrix} \begin{pmatrix} \text{U.S.} \\ \text{population} \end{pmatrix} \begin{pmatrix} \text{Days} \\ \text{per} \\ \text{year} \end{pmatrix} = \begin{array}{l} \text{Total annual} \\ \text{production of} \\ \text{chloroform through} \\ \text{wastewater treatment} \end{array}$$

$$(3.0 \times 10^6 \text{ g}/\ell) \ (379 \ \ell/\text{capita-day}) \ (2.2 \times 10^8) \ (365) = 91 \text{ kkg/year}$$

This figure represents a gross approximation of the annual production of chloroform in wastewater treatment, with an estimated uncertainty of ±50%.

Treated wastewater effluents in which chloroform has been formed are generally discharged directly to natural waterways, although in some instances (particularly in the western United States) the effluent may be used in crop irrigation systems. In either case, chloroform present in sewage effluent will be released primarily to the atmosphere as it volatilizes from water to air. Again, it is assumed that 90 percent (±5%), or 82 kkg (±56 kkg) of the chloroform produced through sewage chlorination will be released to the atmosphere. The remaining 10 percent (±5%) or 9 kkg (±4 kkg) of chloroform constitutes a release to water; some unknown portion of this amount may become bound onto soil and sediments.

2.4.2.3 Chlorination of Cooling Waters

Chlorine is the principal biocide used for antifoulant treatment of cooling systems in electric power-generating plants (Jolley et al. 1978). The chlorination of waters to prevent intake screen and

condenser fouling in both once-through and closed-cycle (cooling tower) systems results in the formation of THM compounds including chloroform (Jolley et al. 1978). No laboratory or field studies have been performed to determine the expected yields of THM from cooling water chlorination. However, Jolley (1978) has estimated total annual chloroform production based on a study of three power plant cooling systems (two cooling towers, one once-through) used in Tennessee. Based on a Federal Power Commission (FPC) estimate of total United States electric power production (340,000 MW in 1977), Jolley projects that 100 to 200 tons of chloroform (90-180 kkg) are produced each year through the chlorination of cooling waters at electric power plants. Jolley notes that this estimate is probably too low because the three cooling systems he studied are not representative of typical power plant operations.

Another estimate for chloroform production in cooling waters can be derived assuming that the yield of THM through cooling water chlorination is equivalent to 3 percent of the total applied chlorine dose as was the case for waters chlorinated in municipal water treatment plants. This approximation is based on the likelihood that source waters used for cooling purposes contain the same types and concentrations of THM precursors (humic acids) as do source waters used for municipal drinking water supplies. The total amount of chlorine applied annually to cooling waters at electric power plants has been estimated at 50,000 to 100,000 tons, 100,000 tons, and 100,000 to 200,000 tons by three different sources in recent years (Hamilton 1978). Hamilton points out that these widely varying estimates are based on projected usage; he presents figures derived from FPC records which show that the total amount of chlorine applied annually to cooling waters at steam electric plants averaged approximately 26,000 tons (23,600 kkg) from 1969 through 1974. This total does not include chlorine applied as calcium or sodium hypochlorite, and has undoubtedly increased since 1974 with several new fossil and nuclear power plants coming onstream. For the purposes of this materials balance, it is assumed that 100,000 tons (approximately 91,000 kkg) of chlorine were applied to power plant cooling waters in 1977. Assuming a 3 percent yield of THM, of which chloroform constitutes 90 percent, then the estimated amount of chloroform produced in this manner in 1977 is calculated to be 2,400 kkg. This estimate has a probable uncertainty range of +20%, -50%.

It is likely that approximately 95 percent (+5%) of this total, or 2,340 kkg (+120 kkg), will evaporate to the atmosphere through cooling tower stacks, or as cooling tower "blowdown" or once-through system waters are discharged to receiving waters. This total also includes an unknown portion of the chloroform which will evaporate from recycled cooling water within the power plant. The remaining 120 kkg (+120 kkg) of chloroform (5 percent of the total) will remain in spent cooling waters released directly to natural waterways.

Cooling towers and once-through cooling systems are also used to remove heat from many other industrial processes or from large pieces of machinery that generate substantial quantities of waste heat, such as commercial air conditioning plants (Stratton and Lee

1975). However, no information on these specific industries or the quantities of chlorine they use in treating cooling waters was presented in the readily available literature.

2.4.3 Industrial Sources

2.4.3.1 Pulp and Paper Industry

The pulp and paper industry is recognized as a significant source of chloroform releases to the environment (NAS 1978a,b). The chlorine bleaching of wood pulp fiber in the production of white paper may yield major quantities of chloroform. Monitoring of paper mill effluents discharged to the Mobile River in Alabama revealed chloroform concentrations of 270 to 1,700 $\mu g/\ell$ (NAS 1978a,b).

Lowenbach and Schlesinger Associates (1979) estimate that 1.4 kkg of chloroform are discharged annually to surface waters in paper mill effluents. This calculation assumes an average chloroform concentration of 1,000 $\mu g/\ell$ and a total annual industry discharge of 1.4 million kkg. However, chloroform releases from this source were calculated to be as high as 300,000 kkg annually, assuming a 6 percent conversion of total chlorine used to chloroform produced in the bleaching process (Lowenbach and Schlesinger Associates 1979).

Because of the high concentration of humic precursors in wood pulp, J. Carrell Morris of Harvard University has estimated the chlorine-to-chloroform conversion efficiency to be approximately 50 percent greater than that expected from the chlorination of municipal source waters (3 percent), or 4.5 percent (Morris 1980). The total quantity of chlorine used in the paper products industry in 1977 is reported to be 1.38 million tons, or 1.25 million kkg (Foster 1980). It is assumed that this quantity was consumed entirely in the bleaching of wood pulp and, further, that this total includes both chlorine and sodium hypochlorite, the two bleaching agents used most extensively by the industry. Assuming a 4.5 percent conversion rate, then the estimated total quantity of chloroform produced through the bleaching of paper pulp in 1977 is calculated as 562,500 kkg. The probable uncertainty range associated with this figure is ±90%. The validity of assuming a fixed chlorine-to-chloroform conversion rate is suspect, and the reported total quantity of chlorine consumed in the pulp and paper industry represents a gross estimate based on industry reports.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted an effluent monitoring survey of 11 pulp mills with bleach plants in 1977. These mills are thought to be representative of pulp bleaching operations nationwide in terms of quantities and types of chlorine used for bleaching, types of wood pulp bleached, and effectiveness of aerated stabilization ponds used to treat effluents. The NCASI study found that an average of 0.74 pound of chloroform was generated in mill effluents per ton of pulp bleached (Blosser 1980). Approximately 20 million tons of wood pulp are bleached annually (Gellman 1980); this figure comprises 17.5 million tons of Kraft or sulfate pulp, 1.5 million tons of sulfite pulp, and 1.5 million tons of high purity dissolving pulp. Applying the NCASI findings for

average chloroform production to this figure yields an estimate of 14.8×10^6 lb/year or 6,700 kkg/year for the total quantity of chloroform generated annually through the bleaching of wood pulp at paper mills. For this materials balance, this figure will be used as the estimated total quantity of chloroform produced annually from pulp bleaching operations.

The NCASI study found that, on the average, there was a 94 percent reduction in chloroform as the mill effluent passed through treatment (aerated lagoons) before discharge to natural waterways. This reduction is due largely to vaporization of chloroform from solution to the atmosphere (NCASI 1977). Hence, of the 6,700 kkg of chloroform produced annually through pulp bleaching, about 94 percent ($\pm 5\%$), or 6,300 kkg (± 330 kkg), will vaporize to the atmosphere as paper mill effluents are treated. The remaining 400 kkg (± 330 kkg) of chloroform will remain in treated effluents discharged to surface waters. The average concentration of chloroform detected in treated effluents from the mills surveyed by NCASI was 100 ppb (Blosser 1980).

2.4.3.2 Other Sources

Other possible industrial sources of indirect chloroform production include effluents from chlorinated rubber manufacturing and the chlorination of wastewaters from the textile industry, the food processing industry (e.g., fruit and vegetable washing and canning), and breweries (USGAO 1977). Estimates of indirect chloroform production from only one of these industries are found in the readily available literature. Lowenbach and Schlesinger Associates (1979) estimate chloroform discharge to the environment from chlorinated rubber manufacturing to be on the order of 20 kkg per year. This calculation is based on several general assumptions and undoubtedly has a great degree of uncertainty associated with it. However, JRB has no additional data upon which to base a separate calculation of such releases.

2.4.4 Combustion of Leaded Gasoline

Analysis of undiluted samples of automobile exhaust has shown the presence of ppb levels of chloroform resulting from the combustion of leaded gasoline (Harsch et al. 1977). Samples of exhaust from a 1975 Pinto equipped with a catalytic converter and operated on non-leaded gasoline contained much lower levels of chloroform -- less than 100 ppt (by volume) -- than did exhaust gases from a 1972 Rambler running on leaded gasoline (6-7 ppb). Harsch suggests that the combustion of leaded gasoline may contribute significantly to elevated levels of chloroform that have been detected in samples of urban air in the State of Washington. The precise mechanism for chloroform formation due to gasoline combustion is not reported in the literature, nor are the estimated total quantities of chloroform produced in this manner. It has been suggested that the use of chlorinated compounds as gasoline additives (e.g., ethylene dichloride) is the source of chloroform detected in auto exhaust (Lowenbach and Schlesinger Associates 1979).

A reasonably good estimate of annual chloroform releases from auto exhausts cannot be made because of inadequate data. However, JRB has made the following rough estimate of releases of chloroform from combustion of gasoline. In 1977, an estimated 9.56×10^4 kkg of ethylene dichloride were used as a lead scavenger compound added to leaded gasoline to provide cleaner burning of anti-knock compounds in the engine (JRB Associates 1979). Assuming that combustion of this compound in leaded gasoline is the sole source of chloroform detected in automobile exhaust, and that typical yields of chloroform from this source are as great as 1 percent of the ethylene dichloride combusted, then the amount of chloroform indirectly produced through the combustion of leaded gasoline in 1977 is calculated to be 956 kkg. This quantity represents an environmental release of chloroform to the atmosphere.

The accuracy of this estimate depends upon the validity of the assumption that ethylene dichloride is the source of chloroform detected in automobile exhaust. A 1 percent yield of chloroform from the degradation of ethylene dichloride during gasoline combustion is probably too high an estimate; consequently, 956 kkg is thought to represent an upper limit on the amount of chloroform so produced. The uncertainty range for this estimate is +5%, -90%.

2.4.5 Other Indirect Sources

Other possible sources of indirect chloroform production include the thermal decomposition of plastics and foams, atmospheric degradation of tri- and tetrachloroethylene, combustion of tobacco products treated with chlorinated pesticides, biological production in red marine algae, and the reaction of chlorinated pollutants with humic substances in natural waters. The quantitative contribution of chloroform from these sources cannot be evaluated without further basic research into these areas (NAS 1978a,b).

The pyrolysis of rigid urethane foams at 500°C has been reported to yield chloroform as a volatile degradation product (NAS 1978a,b). However, the thermal decomposition of plastics is not considered a significant source of chloroform in the environment (Lowenbach and Schlesinger Associates 1979).

Halogenated ethylenes are subject to attack in the atmosphere by hydroxyl radicals to yield dichloroacetyl chloride, photolysis of which leads to formation of chloroform and phosgene. Conditions simulating tropospheric irradiation of trichloroethylene have lead to efficient production of chloroform in laboratory studies (Lowenbach and Schlesinger Associates 1979). Photochemical conversion of trichloroethylene in the troposphere may therefore represent a significant source of indirect chloroform production, especially since atmospheric releases of trichloroethylene have been estimated to be on the order of hundreds of thousands of kkg annually. Estimates of such releases, however, vary by a factor of 700 percent. Farmer et al. (1979) have estimated the total releases of trichloroethylene to the atmosphere to be approximately 90,000 kkg in 1977. Assuming a 0.5 percent conversion efficiency to chloroform in the troposphere, then 450 kkg of chloroform were produced via this mechanism in 1977.

This figure represents a very crude estimate, with an associated uncertainty range as great as +700%, -90%. Photooxidation of tetrachloroethylene appears to be a less directly source of atmospheric chloroform (Lowenbach and Schlesinger Associates 1979).

A 1972 study of cigarette smoke detected chloroform that was derived from tobacco fumigated with p,p'-DDT. This pesticide fumigant is no longer used in the United States (NAS 1978a,b). Cigarette smoke is considered an insignificant source of chloroform production.

The National Academy of Sciences (NAS 1978a,b) cites biological production in species of red marine algae as another natural source of chloroform; however, no data are available for use in estimating such production. It is also possible that chlorine derived from pesticides and herbicides in agricultural runoff and various industrial discharges reacts with humic percursors in natural waters to produce significant quantities of chloroform. More basic research and monitoring data are required before such indirect sources of chloroform production can be accurately evaluated.

2.5 OVERALL SUMMARY OF ENVIRONMENTAL RELEASES FROM PRODUCTION

Table 2.8 summarizes our estimates for the quantities of chloroform produced and the environmental releases from each production source. The data indicate that indirect production is the major route for environmental release. The pulp and paper industry contributes nearly 54 percent of the total chloroform emitted to air, and releases from cooling water account for another 19 percent. In contrast, even if direct production releases are uncontrolled, these processes release only 4.1 percent of the chloroform emitted. A similar situation is observed for releases to water; the pulp and paper industries release nearly 63 percent of the total, and cooling waters release another 19 percent. In contrast, direct production processes release only about 2 percent of the total chloroform emitted to water.

Table 2.8 Summary of Environmental Releases from Chloroform Production

Process	Total chloroform produced (kkg)	To air (kkg)	To air (% of total)	To water (kkg)	To water (% of total)	To landfill (kkg)	To landfill (% of total)	Incinerated (kkg)	Incinerated (% of total)
Methyl chloride chlorination	122,400	176^a 347^b	1.5	7.3	1.2	5.8	3	16.4	1
Methane chlorination	36,100	40.4^a 74.8^b	0.4	2.2	0.4	0	0	?	?
Transportation	177	177	1.5	0	0	0	0	0	0
VCM	2,680	187	1.6	1.6	0.3	200	97	2,290	99
Municipal water supply	912	820	7.1	92.0	14.6	0	0	0	0
Municipal wastewater	91	82	0.7	9.0	0.1	0	0	0	0
Cooling water	2,460	2,340	20.3	120.0	19	0	0	0	0
Pulp and paper	6,700	6,300	54.6	400.0	63.2	0	0	0	0
Leaded gasoline	965	965	8.4	0	0	0	0	0	0
Trichloroethylene	450	450	3.9	0	0	0	0	0	0
TOTAL	173,400	$11,500^a$ $11,700^b$		632		206		2,307	

a = controlled case   b = uncontrolled case

3.0 USES OF CHLOROFORM

3.1 CONSUMPTIVE USES

Chloroform is used consumptively in the production of chlorodifluoromethane. This process accounts for 90 percent of the total domestic chloroform production. Exports, which are considered a consumptive use, amounted to 5 percent of 1978 chloroform production. The remaining 5 percent is used nonconsumptively, and is discussed in Section 3.2.
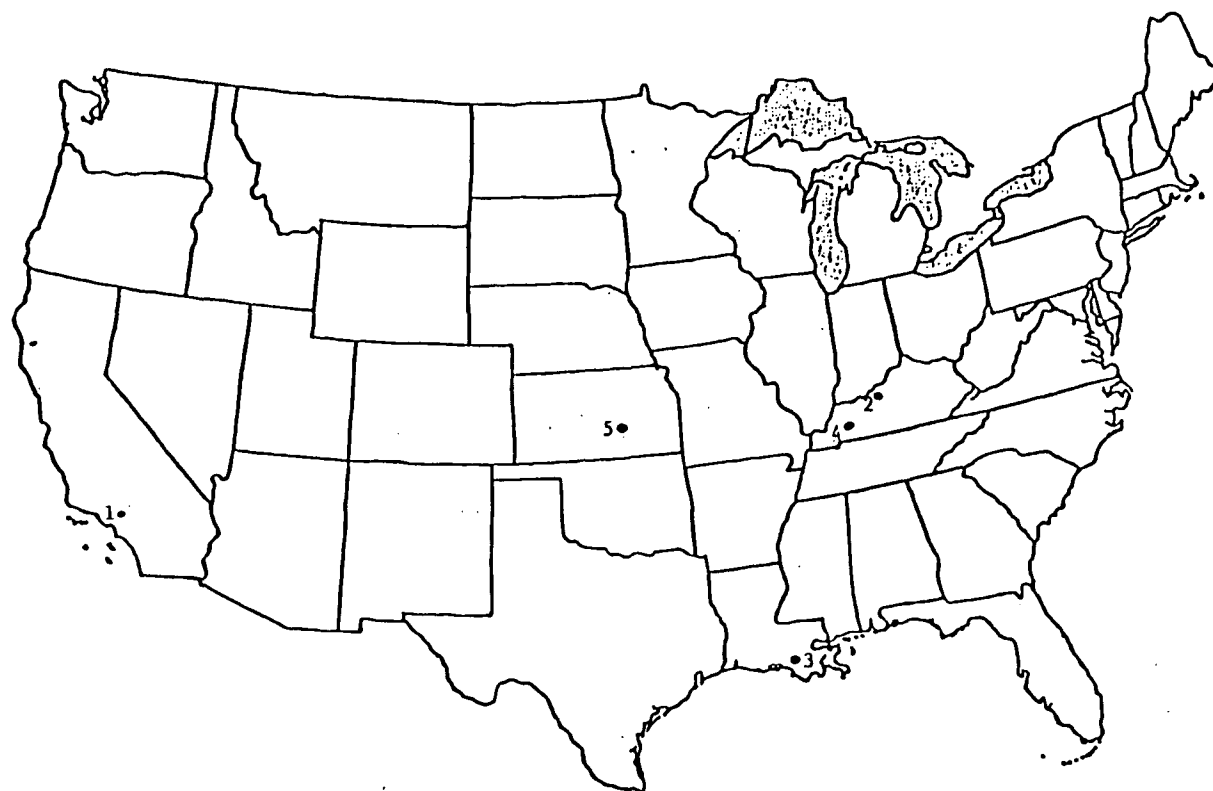
3.1.1 Chlorodifluoromethane

3.1.1.1 Production of Chlorodifluoromethane

Chloroform is used primarily as feedstock for the production of the chlorinated fluorocarbon (CFC) chlorodifluoromethane ($CHClF_2$), commonly known as CFC-22. (The du Pont product is called F-22 after the trade name Freon.) There are five domestic producers of CFC's: du Pont, Allied Chemical, Kaiser Aluminum and Chemical, Pennwalt, and Racon. The locations of U.S. plants producing CFC-22 are shown on the map in Figure 3.1.

Of the 158,500 kkg of chloroform domestically produced, 80-90 percent is used to manufacture CFC-22. Wolf (1979) estimates 90 percent of 1977 production was used for this purpose. EPA's product data report on organic chemical producers estimated that 90 percent of 1978 production was used for CFC-22 manufacture (Radian Corp. 1979). This value was also reported by Dow (Farber 1980), Allied Chemical (Boberg 1980), and Chemical Marketing Reporter (1979). However, reported CFC-22 production figures for 1978 indicate that only 81 percent of the chloroform produced was required for this purpose (USITC 1979). Mannsville (1978a) also estimated that 80 percent of chloroform production was used for this purpose in 1978. However, as discussed in Section 3.2, many former nonconsumptive uses of chloroform have been discontinued; one manufacturer, Allied Chemical, reports that products formulated with chloroform are no longer in the market. Because nonconsumptive usage has apparently declined in recent years, JRB$_3$will use the higher of the available estimates (90 percent or 142.7 x 10^3 kkg) for consumptive usage of chloroform in the manufacture of CFC-22.

Process block diagrams for the production of CFC-22 are shown in Appendix C. The processes used by du Pont (Smith 1978b) and Allied (Hobbs and Stuewe 1978), although similar, differ at stages which the coproduct dichlorofluoromethane (CFC-23) is separated from CFC-22. In du Pont's process, CFC-23 is distilled from CFC-22 and each gas is cleaned separately. Allied inverts these steps by cleaning the combined product gases prior to distillation. The process used by du Pont also vents noncondensables from both CFC-22 and CFC-23 to the atmosphere while Allied's process recycles the CFC-22 noncondensables back into the process. The major difference related specifically to chloroform is the presence of a condenser unit on the chloroform storage tank at du Pont. This unit is lacking at Allied. The rates of chloroform loss to the atmosphere are 0.036 percent at du Pont

1. Allied Chemical, El Segundo, CA.
2. E. I. du Pont, Louisville, KY.
3. Kaiser Aluminum and Chemical, Gramercy, LA.
4. Pennwalt Corp., Calvert City, KY.
5. Racon, Inc., Wichita, KA.

Figure 3.1   U.S. Producers of Chlorodifluoromethane (CFC-22)

(Smith 1978b) and 0.26 percent at Allied (Boberg 1980, Pitts 1978).
No specific data are available on the processes employed at Penwalt,
Racon, or Kaiser.

Production capacity for CFC-22 apart from other CFC's is not
available. Because of the similarity in the processes used to produce
CFC-22 from chloroform and CFC-11/12 from carbon tetrachloride, many
of the production facilities are flexible. They may be used to pro-
duce either of these chlorofluorocarbons as needed. The production
capacity for CFC-22 must be derived from data on total production
capacity. Total CFC capacity must first be reduced by that used for
CFC-113/114. The remaining capacity is for CFC-11 (CCl_3F), CFC-12
(CCl_2F_2), and CFC-22. Judgments on the relative production of these
chlorofluorocarbons are used to apportion the remaining capacity to
the specific products.

Total production capacity was estimated at 650×10^3 kkg for 1976
(Burt 1980). Due to the mandated reductions in fluorocarbon propellant
use, Allied, du Pont, and Pennwalt have reduced capacity. Union Car-
bide exited from production, but still resells CFC products (Mannsville
1978b). These reductions apparently did not affect CFC-113/114, since
production figures for 1976-1978 for miscellaneous fluorocarbons did
not change appreciably (USITC 1977b, 1978, 1979). Wolf (1979) estima-
ted total CFC capacity and a breakdown by specific products and manu-
facturers for 1977. These data are shown in Table 3.1. According to
Wolf (1979) and Burt (1980), 45.4×10^3 kkg of CFC-113/114 are pro-
duced by du Pont, and Allied's capacity is half that much. Du Pont's
total CFC-22 capacity is reported to be 54.5×10^3 kkg (Wolf 1979).
The capacity apportionment of CFC-22 for Pennwalt and Kaiser was esti-
mated to be 25 percent and that for Racon, 50 percent.

JRB believes the ratio of CFC-22 to CFC-11/12 in the product
mix of flexible plants has been understated. Table 3.2 gives USITC
production figures for CFC-11, CFC-12, and CFC-22 for 1975-1978.
Although total production has been decreasing, that of CFC-22 has
been increasing. JRB estimates that both dedicated and flexible
capacity are 413×10^3 kkg for CFC-11, CFC-12, and CFC-22 and that
CFC-22 accounts for 28 percent of production. In our calculations,
we have assigned 30 percent of the capacity to CFC-22. This appor-
tionment is shown in Table 3.3.

3.1.1.2   Environmental Releases of Chloroform During the Production
          of CFC-22

Releases of chloroform during the production of CFC-22 are from
chloroform storage, fugitive process emissions, and controlled process
emissions from condenser vents, catalyst disposal, and gas scrubbers.
The amount of chloroform available for each process is the apportioned
amount reduced by storage losses. The resultant chloroform is conver-
ted to CFC-22 and CFC-23 and process losses are then computed.

Air emissions from the production processes for CFC-22 are esti-
mated to be 150 kkg $\pm 20\%$. There are no quantifiable releases of
chloroform to water or land from fluorocarbon manufacture.

Table 3.1   1976 and 1977 Estimated Production Capacity of Chlorinated
Fluorocarbons (10^3 kkg)

	Total 1976[a]	CFC Capacity 1977 (est.)[b]	CFC-113/114 1977 (est.)	CFC-11/12 1977 (est.)	CFC-22 1977 (est.)
du Pont	315.5	272.4	45.4	172.5	54.5
Allied	140.7	108.9	22.7	66.7	19.5
Pennwalt	52.2	27.2	--	20.4	6.8
Kaiser	36.3	36.3	--	27.2	9.1
Racon	15.9	22.7	--	11.3	11.4
Union Carbide	90.8	--	--	--	--
TOTAL	651.4	467.5	68.1	298.1	101.3

[a]Burt 1980

[b]Wolf 1979

Table 3.2   Annual Production of CFC-11, CFC-12, CFC-22 (10^3 kkg)

	1975	1976	1977	1978
CFC-11	122.58	116.22	96.47	87.94
CFC-12	178.42	178.42	162.67	148.50
CFC-22	59.93	77.18	81.45	91.98
TOTAL	360.93	371.82	340.59	328.42

Source: USITC 1977a,b, 1978, 1979

Table 3.3 Estimated 1978 Production Capacity for CFC (10^3 kkg)

	Total Capacity[a]	CFC-113/114[a]	CFC-11/12[b]	CFC-22[b]	Percent of CFC-22 Capacity
DuPont	272.4	45.4	159.0	68.0	54.9
Allied	122.6	22.7	69.9	30.0	24.2
Pennwalt	27.2	--	19.0	8.2	6.6
Kaiser	36.3	--	25.4	10.9	8.8
Racon	22.7	--	15.9	6.8	5.5
TOTAL	481.2	68.1	289.2	123.9	100.0

Source: (a) Wolf 1979

(b) JRB Estimate

A. Process Which Condenses Vapors from Chloroform Storage

According to the quantities derived in the previous section, the process used by du Pont accounts for 55 percent of CFC-22 production and is assumed to consume 55 percent, or 78.5×10^3 kkg, of chloroform.

Smith (1978b) reported the vent stream exits from the condenser on the chloroform storage tank at a rate of 0.165 kkg/100 kkg and contains 6.26 percent chloroform by volume. This calculation was based on vapor pressure data at a temperature of -5°C. On a weight basis, this vent stream contains 22.5 percent chloroform calculated as follows:

$$\frac{(\text{Volume \% CHCl}_3)(\text{Vapor Density CHCl}_3)}{\left(\begin{array}{c}\text{Volume \%}\\\text{CHCl}_3\end{array}\right)\left(\begin{array}{c}\text{Vapor Density}\\\text{CHCl}_3\end{array}\right) + \left(\begin{array}{c}\text{Volume}\\\text{\% Air}\end{array}\right)\left(\begin{array}{c}\text{Vapor Density}\\\text{Air}\end{array}\right)} = \begin{array}{c}\text{Weight}\\\text{\%}\\\text{CHCl}_3\end{array}$$

$$\frac{(6.26\% \times 4.36 \text{ g/}\ell)}{(6.26\% \times 4.36 \text{ g/}\ell) + (93.74\% \times 1.02 \text{ g/}\ell)} = 22.5$$

The chloroform releases from storage are then given by:

$$\left(\begin{array}{c}\text{CHCl}_3\\\text{used in}\\\text{production}\end{array}\right) \quad (\text{Loss rate}) \quad \left(\begin{array}{c}\text{CHCl}_3\\\text{concentration}\\\text{in vent stream}\end{array}\right) = \begin{array}{c}\text{CHCl}_3\\\text{releases}\\\text{from storage}\end{array}$$

$$(78.5 \times 10^3 \text{ kkg}) \quad (0.165 \times 10^{-2} \text{ kkg/kkg}) \quad (.225) \quad = \quad 29.1 \text{ kkg}$$

The loss rate and stream composition are each assumed to be accurate to ±10%.

Production of CFC-22 (with small amounts of CFC-23) is equal to the net chloroform usage multiplied by the ratio of the molecular weight of CFC-22 to that of chloroform.

$$\left(\begin{array}{c}\text{CHCl}_3 \text{ input} -\\\text{CHCl}_3 \text{ loss}\end{array}\right) \quad \left(\frac{\text{MW CFC-22}}{\text{MW CHCl}_3}\right) \quad = \quad \text{CFC-22 produced}$$

$$(78{,}500 \text{ kkg} - 29 \text{ kkg}) \quad (86.45/119.39) \quad = \quad 56.8 \times 10^3 \text{ kkg}$$

No data were available on fugitive emissions from CFC-22 manufacture. However, an emission rate of 1.46 percent has been estimated for CFC-11/12 (Smith 1978a) and since the process for CFC-22 is similar to that for CFC-11/12, the same emission factor will be used. In addition, CFC-11/12 are reported to contain less than 2 ppm carbon tetrachloride (NAS 1978a,b) and therefore, JRB has assumed a 1 ppm level for residual chloroform in CFC-22. Fugitive emissions from the production of 56,800 kkg of CFC-22 would then be 0.83 kkg. The fact that fugitive emissions were stated for CFC 11/12 (Smith 1978a) and not for CFC-22 (Smith 1978b), could indicate that emissions of CFC-22 are quite low. Bearing this in mind, JRB views the 0.83 kg value as an upper limit, and JRB estimates the uncertainty as -50%.

Following the fluorination reaction, the product gas stream goes to a distillation column where CFC-23 is separated from CFC-22. Each gas is alkali-scrubbed prior to collection, and there is a vent to the atmosphere at the end of each stream. No data were available on the rate of CFC-23 production for the du Pont process. We have Allied Chemical's values of 9.6×10^{-3} kkg/kgg of CFC-22 for a production rate of 22.7 kkg/day; at 18.2 kkg/day, CFC-23 is produced at a rate of 8.9×10^{-3} kkg/kkg (Hobbs and Stuewe 1978). For purposes of this study, we will use the upper value and assume an uncertainty of $\pm 20\%$.

The quantities of CFC-22 and CFC-23 produced can be computed from the production ratio of CFC-23/CFC-22 and the ratio of fluorocarbon formed per unit weight of chloroform. The later values are given by molecular weight ratios.

$$\left(\begin{array}{c} CFC-22 \\ produced \end{array}\right)\left(\frac{MW\ CHCl_3}{MW\ CFC-22}\right) + \left(\begin{array}{c} CFC-22 \\ produced \end{array}\right)\left(\begin{array}{c} CFC-22/23 \\ production \\ ratio \end{array}\right)\left(\frac{MW\ CHCl_3}{MW\ CFC-23}\right) = \begin{array}{c} CHCl_3 \\ consumed \end{array}$$

$$(CFC-22)\left(\frac{119.39}{86.48}\right) + (CFC-22)\ (9.6 \times 10^{-3})\left(\frac{119.39}{70.03}\right) = 78.5 \times 10^3\ kkg$$

Using this equation, the quantity of CFC-22 produced is calculated as 56.2×10^3 kkg. The amount of chloroform required to produce this quantity of CFC-22 is calculated as follows:

$$\left(\begin{array}{c} CFC-22 \\ produced \end{array}\right)\ \left(\frac{MW\ CHCl_3}{MW\ CFC-22}\right) = CHCl_3\ required$$

$$(56.2 \times 10^3)\left(\frac{119.39}{86.48}\right) = 77.6 \times 10^3\ kkg$$

The amount of chloroform available for conversion to CFC-23 is the total chloroform available minus that used for CFC-22, or 0.9×10^3 kkg. The CFC-23 equivalent is:

$$\left(\begin{array}{c} CHCl_3 \\ available \\ for\ CFC-23 \end{array}\right)\left(\frac{MW\ CFC-23}{MW\ CHCl_3}\right) = CFC-23\ produced$$

$$(0.9 \times 10^3\ kkg)\left(\frac{70.03}{119.39}\right) = 550\ kkg$$

Smith (1978b) estimates the vent stream from the CFC-23 condensation process to contain 85 percent CFC-23 by weight. The flow rate is estimated at 0.3 kg/100 kg of CFC-23 produced. Assuming that the CFC-23 contains 1 ppm chloroform, the air emissions are calculated as follows:

$$\left(\begin{array}{c} Production \\ of\ CFC-23 \end{array}\right)\left(\begin{array}{c} Emission \\ rate \end{array}\right)\left(\begin{array}{c} CFC-23 \\ concentration \end{array}\right)(CHCl_3/CFC-23) = \begin{array}{c} Air\ emissions \\ of\ chloroform \end{array}$$

$$(550\ kkg) \quad (0.3 \times 10^{-2}) \quad (.85) \quad (10^{-6}) = \begin{array}{c} 1.40\ g \\ (negligible) \end{array}$$

The air emissions from the CFC-22 condenser vent can be computed similarly from an emission generation factor of 0.19 kkg/100 kkg of CFC-22 and 70 percent CFC-22 content in the vent stream:

$$\begin{pmatrix} \text{Production} \\ \text{of CFC-22} \end{pmatrix} \begin{pmatrix} \text{Emission} \\ \text{rate} \end{pmatrix} \begin{pmatrix} \text{CFC-22} \\ \text{concentration} \end{pmatrix} (CHCl_3/CFC\text{-}22) = \begin{matrix} \text{Air Emis-} \\ \text{sions of} \\ CHCl_3 \end{matrix}$$

$$(56.2 \times 10^3 \text{ kkg}) \quad (.19 \times 10^{-2}) \quad (0.70) \quad (10^{-6}) = \begin{matrix} 75 \text{ g} \\ \text{(negligible)} \end{matrix}$$

The catalyst used for liquid phase fluorination of either carbon tetrachloride or chloroform is a mixture of antimony chlorides and tri-chlorofluoromethane (CCl_3F) (Gruber 1977). A typical composition is 60-70 percent CCl_3F with the remainder being $SbCl_5$ and $SbCl_3$ in a 10:1 ratio. A 1-kg catalyst charge is equivalent to 1 kg of product per hour (Gruber 1977). Approximately twice a year the spent catalyst containing about 10 percent feedstock is replaced (Gruber 1977). Smith (1978b) reports that du Pont ships the spent material from the plant for catalyst regeneration. The specific process is unknown, but two potential processes have been identified by EPA (Gruber 1977). In one, the spent catalyst is dechlori-nated. The other process is a series of distillations in which CFC's, feedstock, and $SbCl_5$ are recovered and the tars generated by the distil-lation of $SbCl_5$ are sent to a landfill.

According to Gruber (1977), a quantity of catalyst equal to 0.02 percent of the CFC production requires regeneration annually. The quantity of chloroform in the catalyst is calculated as follows:

$$(\text{Total CFC produced}) \begin{pmatrix} \text{Fraction of} \\ \text{spent} \\ \text{catalyst} \end{pmatrix} \begin{pmatrix} CHCl_3 \\ \text{fraction in} \\ \text{catalyst} \end{pmatrix} = \begin{matrix} CHCl_3 \\ \text{in} \\ \text{catalyst} \end{matrix}$$

$$(56.2 \times 10^3 \text{ kkg} + 0.55 \text{ kkg}) \quad (0.02 \times 10^{-4}) \quad (0.1) = 11.35 \text{ kg}$$

If 10 percent of the chloroform in the catalyst was released as air emissions, the quantity would be 1.14 kg.

Smith (1978b) also reports that wastewater from the scrubber at du Pont is treated with lime and settled prior to disposal in an open ditch that directs effluents to a plant water treatment facility. du Pont contends the organic content of the waste stream is negligible. This, in fact, may be true. For the similar CFC-11/12 process (Smith 1978a), the presence of some organic components was reported, but that of the feedstock carbon tetrachloride was not. It may be that levels of carbon tetrachloride are too low to be detected or that analysis for feedstock components was not performed. Since the CFC-11/12 production process, similar to that for CFC-22, is not reported to produce an appreciable amount of carbon tetrachloride in this wastewater stream, JRB assumed that the chloroform content in the analogous waste stream for CFC-22 production is also low (1 ppm). Because of the assumption and lack of available data on the solubility of chloroform in salt solutions, JRB has made no estimate of water-borne releases of chloro-form. This information may be obtainable in a Level II effort.

B. Process in which Vapors from Chloroform Storage Are Not Condensed

The remaining 45 percent of the chloroform used for CFC-22 manufacture (64.2×10^3 kkg) is assumed to be made by the process used by Allied Chemical. This process recycles noncondensables rather than venting them and there is apparently no condenser on the chloroform storage tank (Pitts 1978). A loss rate of 2.54 kg/kkg has been reported (Pitts 1979b). Losses from storage may be calculated as 160 kkg. The uncertainty in this calculation is estimated to be $\pm 25\%$.

Fugitive emissions are assumed to be 1.46 percent with a residual chloroform concentration of 1 ppm, as was the case with the du Pont process.

$$\begin{pmatrix} CHCl_3 \\ consumed \end{pmatrix} \begin{pmatrix} \dfrac{MW\ CFC\text{-}22}{MW\ CHCl_3} \end{pmatrix} \quad (\text{Emission rate}) \quad \begin{pmatrix} CHCl_3\ Con\text{-} \\ centration \end{pmatrix} =$$

Fugitive emissions

$$(64{,}200 - 160\ kkg) \quad (86.48/119.39) \quad (1.46 \times 10^{-2}\ kkg/kkg) \quad (10^{-6}) =$$

$$0.67\ kg$$

As previously stated, the uncertainty in the fugitive emission value is estimated to be -50%.

The relative production rates of CFC-23 to CFC-22 have been estimated at 9.6×10^{-3} kkg/kkg at 22.7×10^3 kkg/day and 8.9×10^{-3} kkg/kkg at 18.2 kkg/day (Pitts 1978). JRB estimates the uncertainty to be $\pm 20\%$ at the higher production rate.

$$\begin{pmatrix} CFC\text{-}22 \\ produced \end{pmatrix} \begin{pmatrix} \dfrac{MW\ CHCl_3}{MW\ CFC\text{-}22} \end{pmatrix} + \begin{pmatrix} CFC\text{-}22 \\ produced \end{pmatrix} \begin{pmatrix} CFC\text{-}23/ \\ CFC\text{-}22 \\ ratio \end{pmatrix} \begin{pmatrix} \dfrac{MW\ CHCl_3}{MW\ CFC\text{-}23} \end{pmatrix} = \begin{matrix} CHCl_3 \\ consumed \end{matrix}$$

$$(CFC\text{-}22) \begin{pmatrix} \dfrac{119.39}{86.48} \end{pmatrix} + (CFC\text{-}22)\ (9.6 \times 10^{-3}) \begin{pmatrix} \dfrac{119.39}{70.03} \end{pmatrix} = \begin{matrix} 64.1 \times 10^3 \\ kkg \end{matrix}$$

The quantity of CFC-22 produced is 45.9×10^3 kkg, which consumes 63.3×10^3 kkg of chloroform. The remaining chloroform, 0.8×10^3 kkg, is converted to 470 kkg of CFC-23.

Allied reports their current practice is to landfill spent catalyst (Pitts 1978). Assuming that catalyst usage is 0.02 percent of CFC produced, and that the chloroform level is 10 percent, 9.3 kg of chloroform are landfilled annually. At a 10 percent leakage rate, 0.9 kg would be released as air emissions.

The total chloroform release due to CFC-22 manufacture is the sum of the individual releases and losses.

du Pont process storage loss	29.1	kkg
du Pont process fugitive emissions	+ 0.00083	
du Pont process condenser vent emissions	+ 0.0000764	
du Pont process catalyst regeneration	+ 0.01135	
Allied process storage loss	+ 160	
Allied process fugitive emissions	+ 0.00067	
Allied process catalyst disposal	+ 0.0009	
Total chloroform releases	190	kkg

3.1.1.3 Environmental Releases of Chloroform During the Use of CFC-22

One available reference that discussed chloromethane impurities in CFC's indicated that residual carbon tetrachloride in CFC-11/12 was less than 2 ppm (NAS 1978a,b). Since the production process for CFC-22 is similar to that for CFC-11/12, JRB has assigned a value of 1 ppm for residual chloroform in CFC-22 for the purposes of this study. Even this level may be high. According to industry sources, chloroform content in CFC used as refrigerant must be extremely low due to the possible corrosion potential from traces of water and chloroform (Boberg 1980, Evers 1980). The total CFC-22 production is 102×10^3 kkg. At an estimated chloroform concentration of 1 ppm, there would be 102 kg of residual chloroform in CFC-22.

CFC-22 is used as a chemical intermediate in the production of a variety of fluorocarbons such as Halon fire extinguishants and Teflon PFTE. According to Boberg (1980), any residual chloroform present will be reacted along with the CFC-22. Estimated use of CFC-22 for refrigerants was 80 percent in 1973 (Council on Environmental Quality 1975), 55 percent in 1974 (Lowenheim and Moran 1975), and 30 percent in 1978 (Radian Corp. 1979). For purposes of this balance, we will use 40 percent for refrigerant/air conditioner use and 60 percent for fluorocarbon products. The following assumptions are made about refrigerant usage (Evers 1980):

- Ten percent is used in hermetically sealed refrigeration systems, of which 10 percent are discarded. Of the discarded systems, 10 percent leak.

- Twenty-five percent is used in hermetically sealed air conditioners, of which 2 percent leak during repair.

- Ten percent is used in charged refrigeration systems, with a 1 percent loss during charging, and a 5 percent loss during repair.

- Fifty-five percent is used in charged air conditioning systems, including autos. There is a 1 percent loss during charging, and a 20 percent loss due to leaks.

Using these assumptions, our estimates for releases of chloroform from the end uses of CFC-22 are shown in Table 3.4. Figure 3.2 is a diagram of multimedia releases of chloroform from CFC-22 use. Total losses of 5.2 kg could be understated by as much as 150 percent depending on use patterns and frequency of repair.

Table 3.4   Release of Chloroform Due to CFC-22 Use

Use	Percentage of use	$CHCl_3$ content (kg)	Destroyed	Loss rate[c]	Loss (kg)
Sealed refrigerator[a]	4	4.1	--	1%[b]	0.04
Sealed air conditioner[a]	10	10.2	--	2%	0.20
Charged refrigerator[a]	4	4.1	--	6%	0.25
Charged air conditioner[a]	22	22.4	--	21%	4.7
Fluorocarbon precursor	60	61.2	61.2	--	--
TOTAL	100	102.0	61.2		5.19

[a]Use pattern based on Council on Environmental Quality 1975.

[b]10 percent of the 10 percent discarded refrigerators leak.

[c]Based on Evers 1980.

3.1.2 Exports

In 1978, the United States exported 7,900 kkg of chloroform (U.S. Bureau of Census 1979a). This is approximately 5 percent of the total chloroform produced. This amount was a 13 percent reduction from exports in 1977. Information was not available on exports prior to 1977 and therefore trends cannot be discussed.

3.2 NONCONSUMPTIVE USES OF CHLOROFORM

In 1978 approximately 15,600 kkg of chloroform were used for non-consumptive purposes or were stockpiled. Nonconsumptive uses of chloroform reported in the literature include use in extraction, in pharmaceuticals as a solvent, in lacquers and floor polishes as a solvent, in artificial silk manufacture, as an intermediate for pesticides and dyes, and as a fumigant ingredient (Radian Corp. 1979, Sittig 1979, Kirk-Othmer 1970). Several industrial and government contacts were made to determine the extent to which chloroform is currently being used.

0.061 kkg
Destroyed During
Fluorocarbon
Manufacture

0.005 kkg
Emitted
to Air

CFC-22 Use

60% Fluorocarbon

40% Refrigerant

and

Air Conditioners

0.102 kkg
Chloroform in
CFC-22

0 kkg
Release to Water

0 kkg
Release to Land

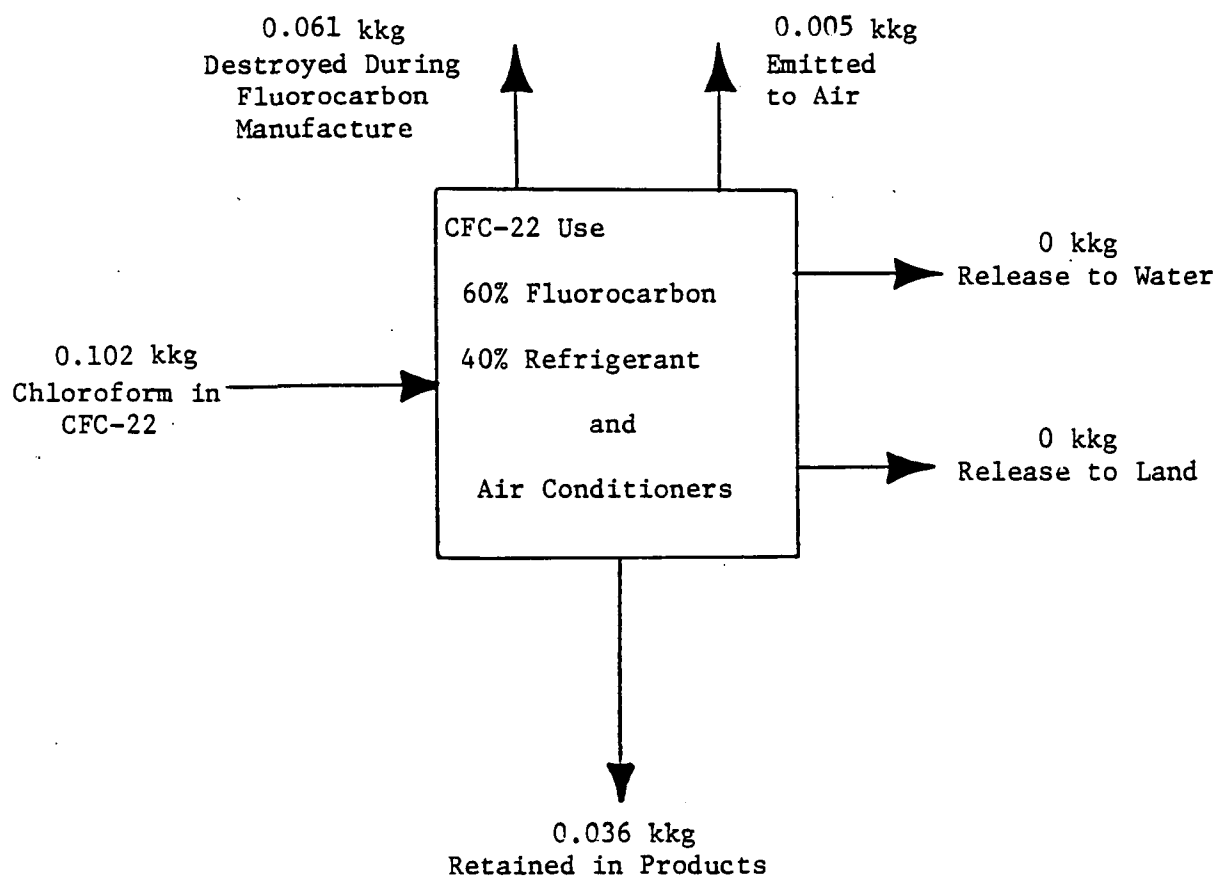0.036 kkg
Retained in Products

Figure 3.2   Multimedia Releases of Chloroform from the Use of CFC-22

The discussion that follows indicates that many of the uses cited in the literature no longer apply to chloroform. Where chloroform was identified as still in use, the quantities are generally small.

3.2.1 Use of Chloroform in the Pharmaceutical Industry

Several sources identified the pharmaceutical industry as a major use of chloroform. The FDA indicated, however, that since chloroform was banned as an active and inactive ingredient in drugs and toiletries in 1976, its use has decreased markedly and is currently limited to extraction procedures (DeGuano 1980). A representative of Squibb indicated that chloroform may also be used as a wetting agent, although Squibb does not use the solvent at all (Schwadron 1980). No literature was found on use of chloroform as a wetting agent. Shering-Plough indicated that methylene chloride and, to a much lesser extent, chloroform are the major halogenated solvents used in extraction procedures (Henley 1979).

In 1975, the pharmaceutical industry purchased approximately 1,100 kkg of chloroform for the preparation of ethical drugs (derived from USEPA 1978a). Although the ban on the use of chloroform as an active or inactive ingredient was not yet in effect, none of the chloroform purchased was used as a drug ingredient. It is reasonable to assume that the chloroform was being used for extractions and that the ban did not significantly affect the purchase of chloroform. We have assumed that 1,000 kkg were purchased in 1978 for drug extractions.

The estimates for the disposition of chloroform waste, listed below and shown in Figure 3.3, are based on information supplied by the Pharmaceutical Manufacturers Association (USEPA 1978c).

Air emissions	570 kkg
Sewer	46 kkg
Contract hauled (assumed landfilled)	350 kkg
Disposed in landfill or deepwell	34 kkg

No uncertainty estimates were available for the quantity of chloroform purchased or for the amounts disposed by each method. We have assumed that the estimate of 1,000 kkg used in extractions is accurate to ±20%, and that quantities disposed of by various methods are accurate to ±35%.

3.2.2 Use of Chloroform in Pesticide Production

The use of chloroform in the production or formulation of pesticides is limited. Chloroform has not been identified as an intermediate in the production of any pesticides (Melnikov 1971, USEPA 1972, SRI 1976, Parsons 1977). However, chloroform's anesthetic and toxic properties are useful in improving the effectiveness of fumigant mixtures (NAS 1978a,b), and chloroform has been registered with the EPA for use as a
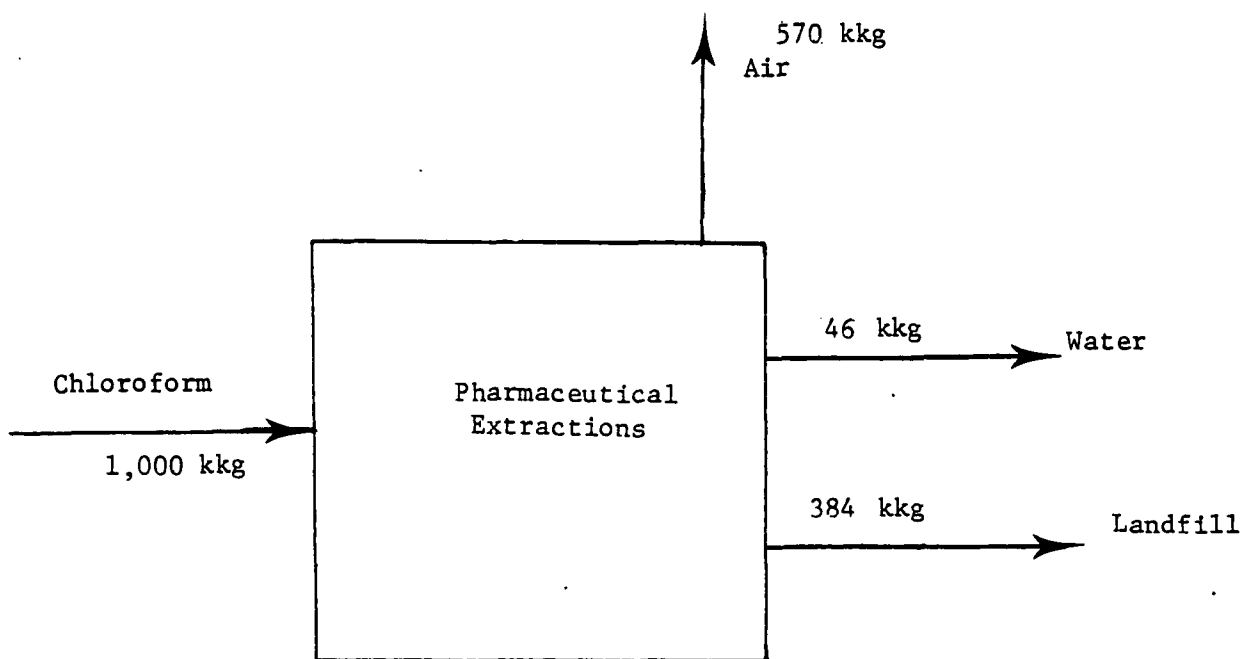
Figure 3.3 Multimedia Releases of Chloroform from Drug Extractions

commodity fumigant (USEPA 1972). This includes application of fumigants for the protection of harvested crops and food products in storage, and prevention of insect, rodent and other vermin infestation in mills, warehouses, grain elevators, railcars, shipholds, and other storage areas. The use of chloroform in fumigants was reported to be 35 kkg in 1976 (Versar 1977). This value is based on an aggregate of data submitted by several companies to the EPA Office of Pesticides. We assigned an uncertainty of +10% to this value to account for possible variability or unreported usage of chloroform in fumigants.

To project consumption to 1978 we assumed that usage of chloroform in fumigants increased 10 percent (+1%) annually, which is the general trend for other major fumigants (SRI 1976). The amount of chloroform used in fumigants in 1978 was estimated as 42 kkg.

Estimates from the grain industry indicate that the amount of stockpiled fumigant is 10 percent (+1%) of the total amount consumed. Assuming that this estimate will apply to fumigants containing chloroform, then the amount stockpiled in 1978 is 4.2 kkg (+24%, -21%). The remaining 37.8 kkg (+11%) were applied to grain.

Air emissions of chloroform will occur when the fumigated grain is exposed to the atmosphere. Grain storage areas are vented to allow shifting the grain for refumigation due to moisture accumulation or infestations. Emissions will also occur when grain is removed from storage areas for loading and transit. We assume that all of the applied chloroform is emitted to the atmosphere.

Figure 3.4 shows the multimedia releases of chloroform that is used in fumigants.

3.2.3 Use of Chloroform as an Industrial Solvent

The use of chloroform as an industrial solvent appears to be decreasing rapidly, primarily due to restrictions imposed by OSHA guidelines (Davenport 1980). The declining use of chloroform was verified by several contacts. Textile Chemical Company, a large mid-Atlantic regional distributor, reported that only two 200-liter drums were sold during 1978, a decrease of about 90 percent from previous periods (Davenport 1980). Ashland Chemical (1980), a national supplier specializing in industrial solvents, reported that they purchase small drum quantities on an intermittent basis. Eastman Organic Chemicals (1980) reported no sales other than those to laboratories. Johnson's Wax (1980) indicated chloroform is not used in any of their formulations nor is chloroform used as a solvent in paints and coatings. The U.S. Consumer Product Safety Commission confirmed that chloroform has minimal use as a solvent in consumer products (Simpson 1980).

3.2.4 Use of Chloroform in the Textile and Dye Industries

Although several literature sources identified chloroform as being used in the textile and dye industries, JRB has found, through numerous contacts, that this use is extremely limited. Only seven of 418 respondents to an Effluent Guidelines questionnaire for these industries
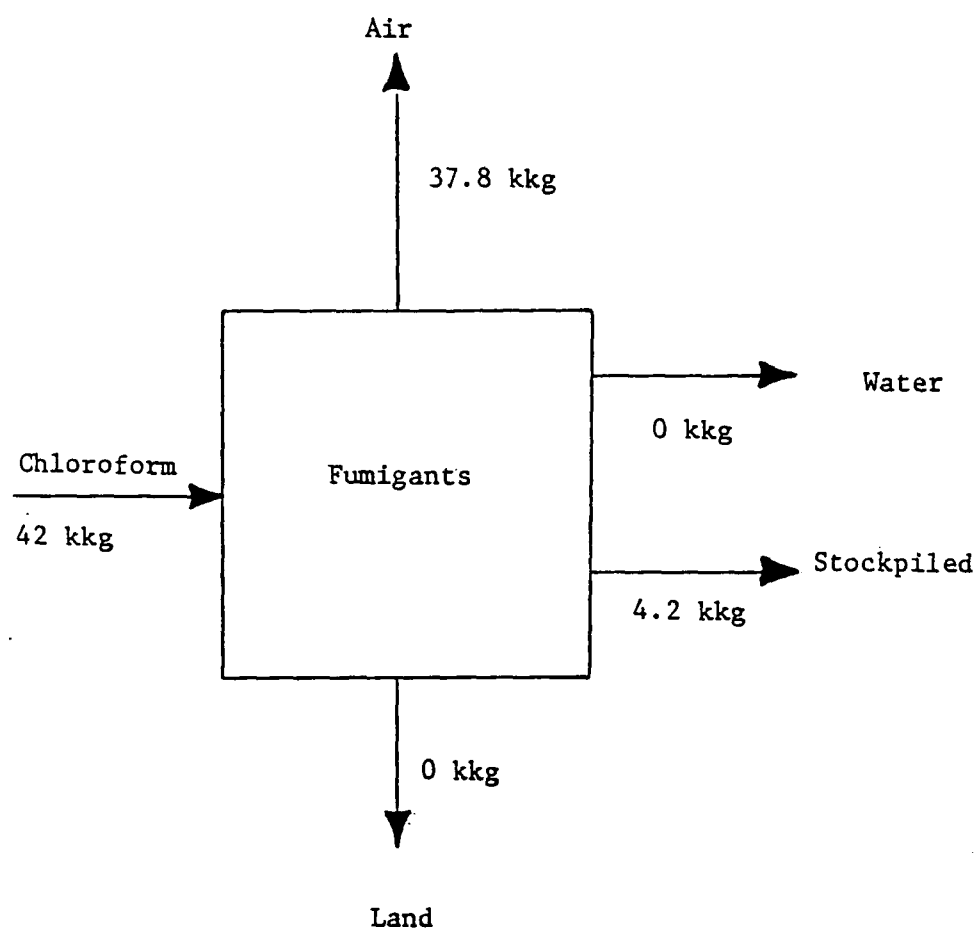
Figure 3.4   Multimedia Releases of Chloroform from the Use of Fumigants

were known or suspected of using chloroform (Buzzell 1980). These survey results support our conclusion that chloroform has limited use in these industries.

One industry source (Bochner 1980) mentioned that chloroform might be used as a solvent for the alkylation of quaternary dyes, but stated that any specifics would be proprietary information. JRB has been unable to confirm this usage. A study by Monsanto Research Corporation reported finding chloroform in the raw waste of 12 to 29 textile plants (USEPA 1978a). The levels of chloroform ranged from 5 to 500 $\mu g/\ell$. The origin of the chloroform could not be determined (Samfield 1980). Sources knowledgeable about the textile and dye industry were contacted, but little additional information was obtained. West Point Pepperill indicated no known use other than two government-required quality control tests (Robert 1980). Hydroscience (Barnhardt 1980) and Sverdrup Corporation (Buzzell 1980) both report no known use in the textile industry. According to Moser (1980), an extension specialist in dye chemistry at North Carolina State University, the use of chloroform as a solvent for dyes is expensive. Perchloroethylene would be a preferred solvent. Neither he nor any other staff members contacted by Livingood (1980) at N.C. State could identify any chloroform uses in the textile industry.

3.2.5 Laboratory Use and Stockpile

Chloroform is currently being used in hospital, industrial, and R&D laboratories. Major laboratory uses include spectrophotometric work, density determinations, and solvent uses (Eastman Organic Chemicals 1980). Several distributors, including J.T. Baker, Mallincrodt, and Eastman Organic Chemicals, were contacted to obtain quantitative information on chloroform used for laboratory purposes, but this information is considered proprietary.

JRB has estimated an upper limit on the quantity of chloroform used for laboratory purposes or stockpiled in 1978. This quantity is estimated as follows:

Sources	(kkg)	
CHCl$_3$ produced	158,500	
Imports	7,670	
	165,670	

Known distribution	(kkg)	
Losses during production	248	(controlled conditions)
Transportation losses	177	
CFC-22 production	142,700	
Exports	7,900	
Used for pharmaceuticals	1,000	
Used for fumigants	42	
	152,067	

$$\begin{array}{ccccc} & & & & \text{Quantity} \\ (\text{Sources}) & - & (\text{Known distribution}) & = & \text{unaccounted} \\ & & & & \text{for} \\ \\ (165{,}670) & - & (152{,}067) & = & 13{,}600 \end{array}$$

The 13,600 kkg unaccounted for was estimated to be the upper limit on the quantity used for laboratory purposes or stockpiled. Small quantities may also be used for other miscellaneous uses such as in the textile industry.

3.3 SECONDARY PRODUCT CONTAMINANTS

As indicated in Section 2.1, chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride in the methane chlorination process; and with methylene chloride and by-product carbon tetrachloride by the further chlorination of methyl chloride.

These products are subsequently separated by distillation but remain contaminated with chloroform at low concentrations.

3.3.1 Releases of Chloroform Contaminant of Methyl Chloride

Methyl chloride is produced by the catalytic chlorination of methane or hydrochlorination of methanol. The latter reaction,

$$HCl + CH_3OH \longrightarrow H_2O + CH_3Cl$$
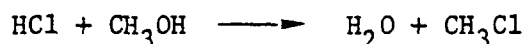
yields only methyl chloride whereas direct chlorination of methane yields all of the chloromethanes:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$
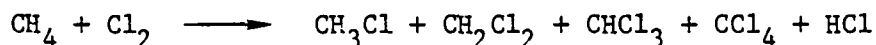
The methane chlorination process results in low levels of product contamination. Chloroform levels in methyl chloride produced from this process are on the order of 5-10 ppm (Boberg 1980).

Table 3.5 shows that of the 14 plants producing methyl chloride, only the Dow plant in Freeport, Texas, uses the methane chlorination process exclusively; Allied Chemical and the Vulcan plant in Wichita, Kansas, use this process for a small percent of their total production (Hobbs and Stuewe 1979a). The production capacity for methyl chloride in the methane chlorination process is 32,500 kkg. JRB estimates that production by this process is, at most, 70 percent of capacity, or 22,800 kkg.

Assuming chloroform contaminant levels of 7.5 ppm, total chloroform content of methyl chloride is estimated as 170 kg. This estimate is considered accurate to ±75% to allow for uncertainties related to chloroform contaminant levels and the quantity of methyl chloride produced by the methane chlorination process.

Table 3.5 Methyl Chloride Capacity in 14 U.S. Plants

Plant	1977 Capacity (10^3 kkg)	Process
Allied Chemical, Moundsville, WV	11^a	Methanol hydrochlorination and methane chlorination
Continental, Westlake, LA	45	Methanol hydrochlorination
Diamond Shamrock, Belle, WV	11^a	Methanol hydrochlorination
Dow, Freeport, TX	32^a	Methane chlorination
Dow, Plaquemine, LA	68^a	Methanol hydrochlorination
Dow Corning, Carronton, KY	9	Methanol hydrochlorination
Dow Corning, Midland, MI	7	Methanol hydrochlorination
du Pont, Niagara Falls, NY	36^a	Methanol hydrochlorination
Ethyl Corp., Baton Rouge, LA	45	Methanol hydrochlorination
General Electric, Waterford, NY	23	Methanol hydrochlorination
Stauffer, Louisville, KY	7^a	Methanol hydrochlorination
Union Carbide, Institute, KY	23	Methanol hydrochlorination
Vulcan, Geismar, LA	b	Methanol hydrochlorination
Vulcan, Wichita, KS	b	Methanol hydrochlorination
Total	317	

(a) Production varies with amount of methyl chloride separated as product and amount used for additional chlorination.

(b) All production used for methylene chloride and chloroform.

Source: Hobbs and Stuewe 1979a

There are no losses of chloroform resulting from the storage of methyl chloride at the production sites since methyl chloride is stored under pressure.

The major chemical uses of methyl chloride are in the production of tetramethyl lead, silicones, and methyl arsenate herbicides (Radian Corp. 1979). It appears that methanol derived methyl chloride is used in these applications and chloroform contamination would not be expected. Dow Corning, General Electric, and Ethyl Corporation probably use methyl chloride directly. Vulcan uses all of their production as feedstock for methylene chloride and chloroform. One nonchemical use of methyl chloride from the methane chlorination process is as a catalyst carrier at low temperatures in the production of butyl rubber (Mannsville 1978b). No specific process or consumption information could be obtained regarding this use.

3.3.2 Releases of Chloroform Contaminant of Methylene Chloride

Methylene chloride is produced concurrently with chloroform by the chlorination of methane, by hydrochlorination of methane, or by hydrochlorination of methanol followed by methyl chloride chlorination. The processes are discussed in Section 2.1.

Table 3.6 summarizes the quantities of methylene chloride utilized for various end uses in 1977 and the quantities of chloroform contaminant derived by assuming an impurity concentration of 15-20 ppm (Boberg 1980). The total chloroform contaminant is 4.28 kkg. The accuracy of the contaminant level is estimated at +30%.

3.3.2.1 Releases of Chloroform During Storage and Handling of Methylene Chloride

Releases of chloroform can occur during the storage and handling of methylene chloride. To estimate these emissions, we have used the emission factors derived in Section 2.1. Storage conditions for methylene chloride and chloroform are not expected to be significantly different, and these emission factors are considered to be accurate with an uncertainty range of +25%. The emission factor for storage is 0.59 kg/kkg, which gives an estimated chloroform release of 2.5 kg.

This overall estimate for chloroform released during storage is considered accurate to +60%, -50% to allow for the uncertainties related to storage conditions for methylene chloride, chloroform contaminant levels in methylene chloride, and the emission factor estimated in Section 2.1.

For working losses, the estimated emission factor is 0.33 kg/kkg. The corresponding estimate for chloroform emission during handling is 1.4 kg. This estimate is considered accurate to +40%. As was the case for breathing losses, there are uncertainties related to storage conditions, chloroform contaminant levels, and the emission factor.

Table 3.6 Quantitative Breakdown of Methylene Chloride End Uses and Corresponding
Chloroform Contaminant Levels

End Uses	Methylene chloride[a] (kkg)	Chloroform contaminant, based on 15 ppm (kg)	Chloroform contaminant based on 20 ppm (kg)	Chloroform contaminant average, 17.5 ppm (kg)
Paint remover	73,000	1,095	1,460	1,280
Metal degreasing	49,000	735	980	860
Aerosol propellant	46,000	690	920	805
Blowing agent	20,000	300	400	350
Exports	44,000	660	880	770
Other	12,000	180	240	210
Total		3,660	4,880	4,275

[a]1977 estimates (SRI 1979)

3.3.2.2 Releases of Chloroform from Methylene Chloride-Based Paint Removers

Thirty percent of the methylene chloride produced in 1977 was used in paint removers (SRI 1979). For an average chloroform contaminant concentration of 17.5 ppm, the quantity of chloroform in these paint removers is estimated in Table 3.6 as 1.28 kkg. This estimate is considered accurate to ±20% due to uncertainties related to the amount of paint removers containing methlylene chloride and chloroform contaminant levels in these products.

Multimedia environmental releases of chloroform from paint removers depend upon the method of application and the type of product. Paint removers range in viscosity from liquids to semigels and may be applied by dip, spray, or brush methods. Frequently the solvent and softened paint-film mixtures are rinsed off the surface with water. Although most of the solvent evaporates, there are losses to water and land from the use and disposal of these products. Because of its high volatility, JRB estimates that 75 percent of the solvent is emitted directly to air, 15 percent is disposed of in water as used solvent, and 10 percent is disposed of to land, mostly as residue in used containers. Based on these assumptions, losses of chloroform from use of these paint removers are estimated as 960 kg to air, 192 kg to water, and 128 kg to land.

Our percentage estimates for chloroform disposal are considered accurate to ±15% for land and water and ±5% for air. When combined with our uncertainty estimate of ±20% for total chloroform released from these products, our overall uncertainty esimates for releases to air, water, and land are ±25%, ±30%, and ±34%, respectively.

Figure 3.5 summarizes the multimedia environmental releases of chloroform from use of these products.

3.3.2.3 Releases of Chloroform from Use of Methylene Chloride in Metal Degreasing

Halogenated solvents are used widely in the metal cleaning industry because of their high solvency power and nonflammable nature. Approximately 49,000 kkg of methylene chloride were used in metal cleaning in 1977 (SRI 1979). The quantity of chloroform released from the use of methylene chloride in metal cleaning was estimated in Table 3.6 as 860 kg.

There are varying estimates in the literature on the percentage of methylene chloride used for cold cleaning versus vapor degreasing. A survey conducted by Dow suggested that 54 percent was used for vapor degreasing and 46 percent for cold cleaning (Dow Chemical Co. 1976). The Office of Air Quality Planning and Standards claims that the breakdown is 23 percent for vapor degreasing and 77 percent for cold cleaning (Bollinger and Schumaker 1977). Since the Dow estimates were based on an industrial survey, these results are considered more reliable.

Air

▲

960 kkg

```
                    ┌─────────────┐
Chloroform          │    Paint    │
──────────▶         │   Removers  │  ──────────▶  Water
1,280 kkg           │             │              192 kkg
                    └──────┬──────┘
```
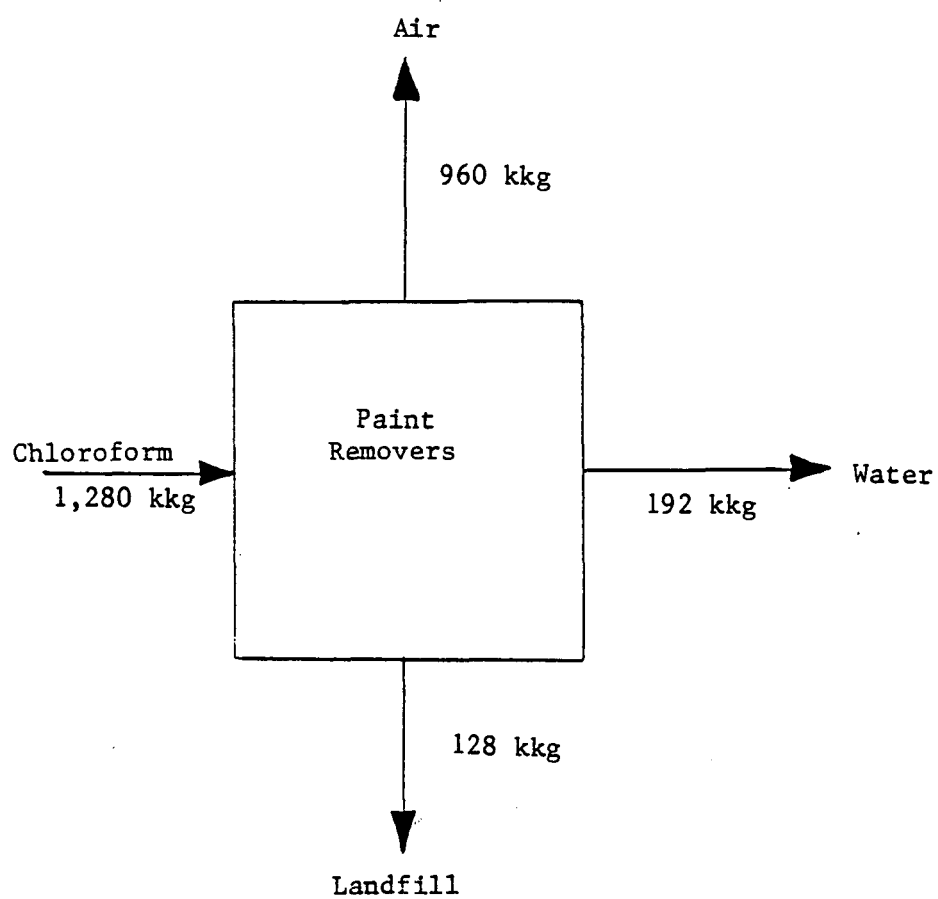
128 kkg

▼

Landfill

Figure 3.5 Multimedia Releases of Chloroform from Use of Paint
Removers Containing Methylene Chloride

Based on the Dow survey, multimedia releases of chloroform from the use of methylene chloride are estimated as follows:

$$\left(\begin{array}{c}\text{Percent of}\\\text{release}\end{array}\right)\left(\begin{array}{c}\text{Total chloroform}\\\text{released from}\\\text{metal cleaning}\end{array}\right)\left(\begin{array}{c}\text{Percent methylene}\\\text{chloride for}\\\text{vapor degreasing}\end{array}\right)=\begin{array}{c}\text{Chloroform}\\\text{released to}\\\text{individual}\\\text{media}\end{array}$$

Emissions to air:	80% x 860 kg x 0.54 =	372 kg
Incinerated:	2% x 860 kg x 0.54 =	9 kg
Discharged:	10% x 860 kg x 0.54 =	46 kg
Landfilled:	8% x 860 kg x 0.54 =	37 kg
	Total	= 464 kg

Cold Cleaning

Emissions to air:	70% x 860 kg x 0.46 =	278 kg
Incinerated:	2% x 860 kg x 0.46 =	8 kg
Discharged:	15% x 860 kg x 0.46 =	59 kg
Landfilled:	13% x 860 kg x 0.46 =	51 kg
	Total	= 396 kg

Combined Emissions (Cold Cleaning and Vapor Degreasing)

Emissions to air:	650 kg
Incinerated:	17 kg
Discharged:	105 kg
Landfilled:	88 kg

Figures 3.6 and 3.7 summarize the environmental releases of chloroform from use of methylene chloride by the metal cleaning industry.

The estimate of 860 kg of chloroform released from the combined use of methylene chloride in vapor degreasing and cold cleaning is considered accurate to ±20%. The factors contributing to our error range include the uncertainties for the quantity of methylene chloride used in metal cleaning and the contaminant levels. Our estimates for the percentage releases are thought to be accurate to ±10% for air and incineration, and ±30% for water and land. Using these individual uncertainties our overall uncertainty estimates for air, water, land, and incineration are ±32%, ±48%, ±46%, and ±29%, respectively.

3.3.2.4   Releases of Chloroform from Use of Methylene Chloride in Aerosols

In 1977, 46,000 kkg of methylene chloride were used in aerosol products. As estimated in Table 3.6, these products contained 17.5 ppm or 805 kg of chloroform. We estimate the accuracy of this number at ±30% to allow for uncertainties related to the amount of methylene chloride used in aerosols and the chloroform concentration.
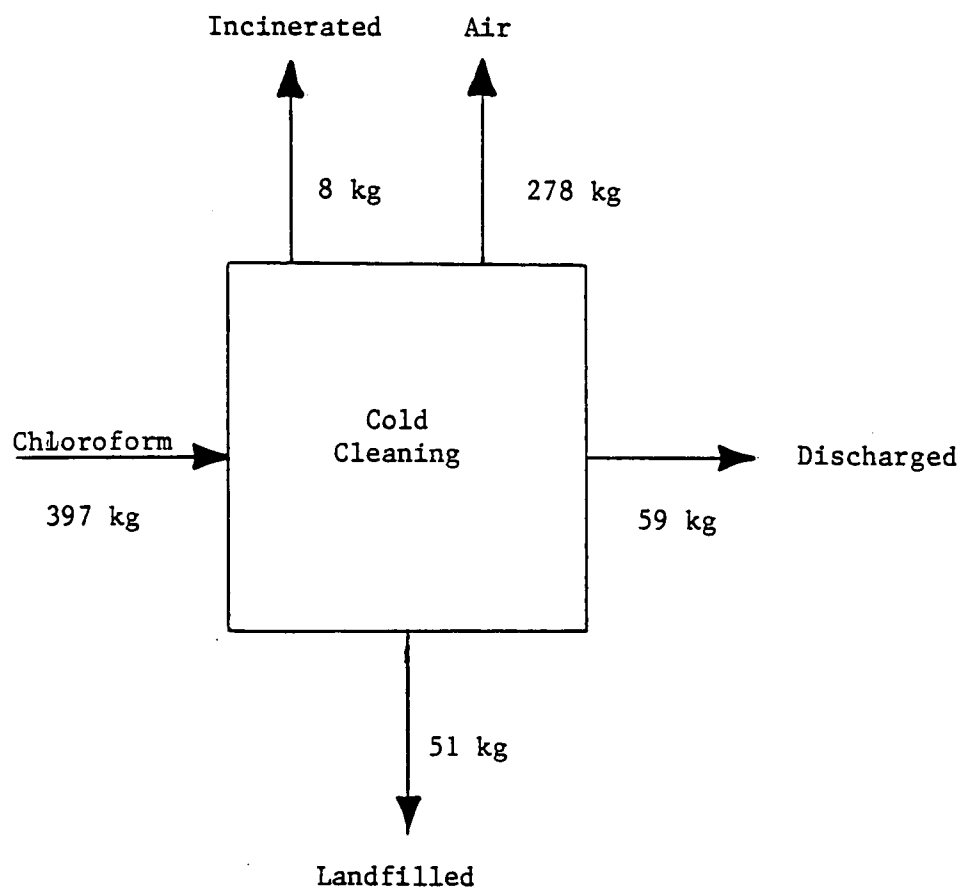
Figure 3.6   Multimedia Releases of Chloroform from Use of Methylene
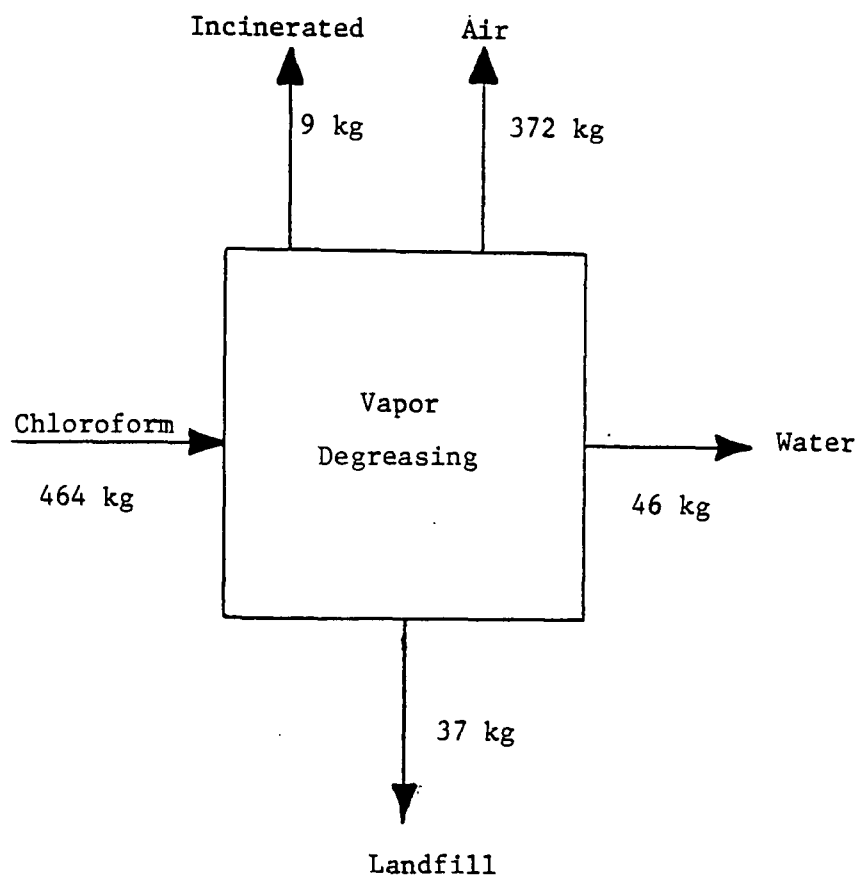Chloride in Cold Cleaning

Figure 3.7 Multimedia Releases of Chloroform from Use of Methylene
Chloride in Vapor Degreasing

A quantitative breakdown of chloroform releases from various types of aerosol products for automotive and household use, etc. can be estimated from the number of aerosol cans in each product category (Kirk-Othmer 1970, USCPSC 1979). Figure 3.8 shows the percentage and total quantity of chloroform released from each product category.

Multimedia releases of chloroform were estimated by assuming that 2 to 3 percent is emitted to air during formulation of aerosols, 10 percent of the chloroform in aerosol products is landfilled as residual in used cans, and the remaining chloroform is emitted during use. An estimated 20 kg were emitted to air during production; of the remaining 785 kg, 79 kg were disposed to land and 706 kg were emitted to air during use. JRB's percentage estimates are believed accurate to within +5% for air and +25% for land. When combined with an estimated uncertainty of +20% for the amount of chloroform in these aerosol products, our overall uncertainties for air and land emissions are +25% and +43%, respectively. Figure 3.9 summarizes the total releases of chloroform from the use of aerosol products containing methylene chloride.

3.3.2.5 Releases of Chloroform from Methylene Chlorine-Based Blowing Agents for Urethane Foam

In 1977, 20,000 kkg of methylene chloride were used in urethane foam blowing (SRI 1979). At a chloroform contaminant level of 17.5 ppm, the quantity of chloroform released from the manufacture and use of urethane foam is estimated as 350 kg (Table 3.6).

In calculating environmental releases of chloroform from urethane foam, it is assumed that 2 percent of the chloroform impurites (7 kg) are released to air during the manufacturing process. It is further assumed that urethane foams are used in open and closed systems in approximately equal portions (Council on Environmental Quality 1975). Virtually 100 percent of the chloroform present in open systems (172 kg) will be released to air. Losses of chloroform from the use of urethane foam in closed systems will be negligible except for an assumed 10 percent of the products in which leaks occur. This will result in 17.2 kg of chloroform being released to the air. It is also assumed that an additional 10 percent of these systems containing 17.2 kg of chloroform are discarded in landfills and the remaining 80 percent which contain an estimated 137 kg of chloroform are contained in products in use. These releases are summarized in Figure 3.10.

The estimate of 350 kg of chloroform contaminant in methylene chloride used as a foam blowing agent is considered accurate to +20% to account for uncertainty regarding the chloroform levels in methylene chloride and the quantity of methylene chloride used for this purpose. Our estimates for the percentages released to air, to land, and retained in closed systems are considered accurate to +20%, +30%, and +30%, respectively. The overall uncertainty estimates for quantities of chloroform are +39% for air, +47% for land, and +47% for products.

20 kg to air
during production

805 kg   785 kg

Chloroform in methylene
chloride-based aerosol
products

27%
212 kg   Household products   (under CPSC jurisdiction)

4%
31 kg   Automotive products

13%
102 kg   Coatings and finishes

51%
400 kg   Personal care products   (under FDA jurisdiction)

5%
39 kg   Pesticide products   (under EPA jurisdiction)

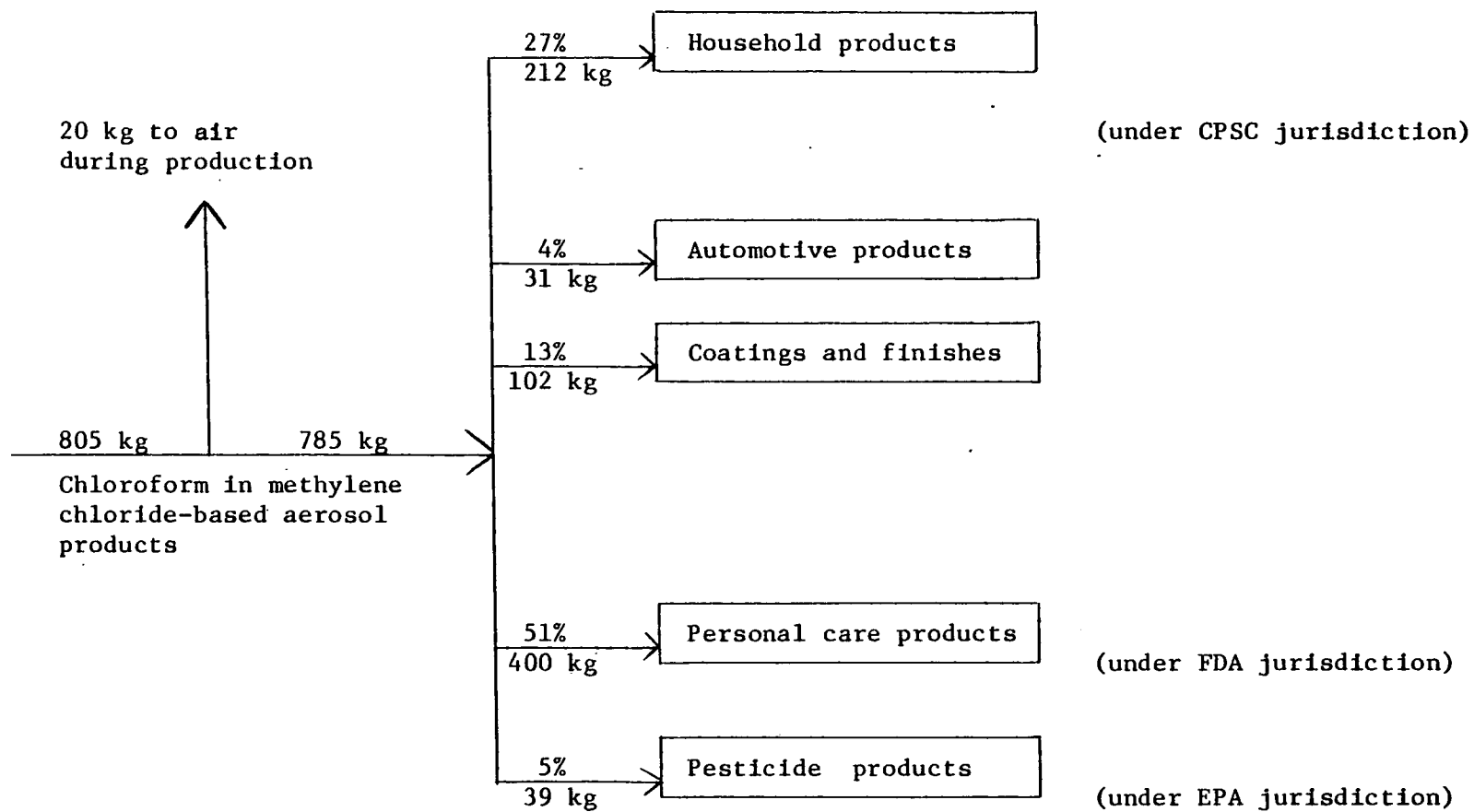Figure 3.8 Flow Diagram of Chloroform in Methylene Chloride-Based Aerosols

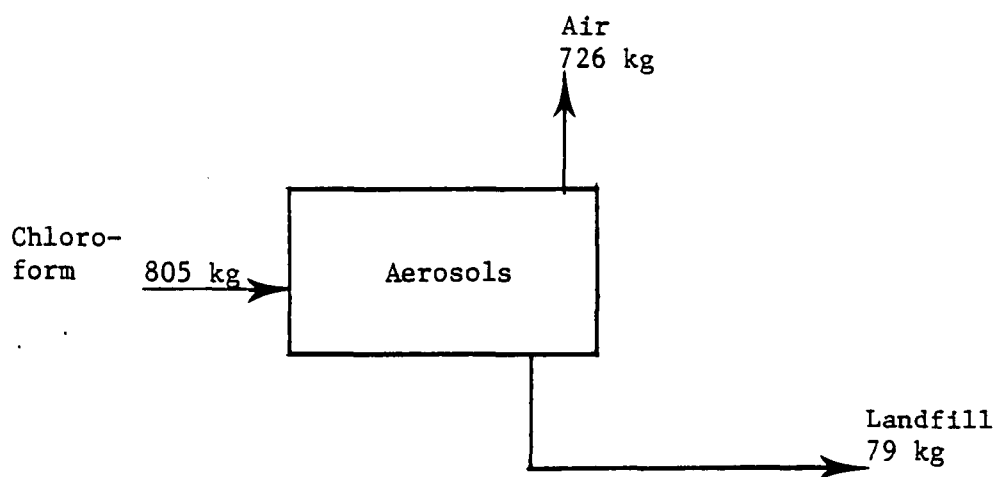Figure 3.9   Multimedia Releases of Chloroform from Use of Aerosol
Products Containing Methylene Chloride
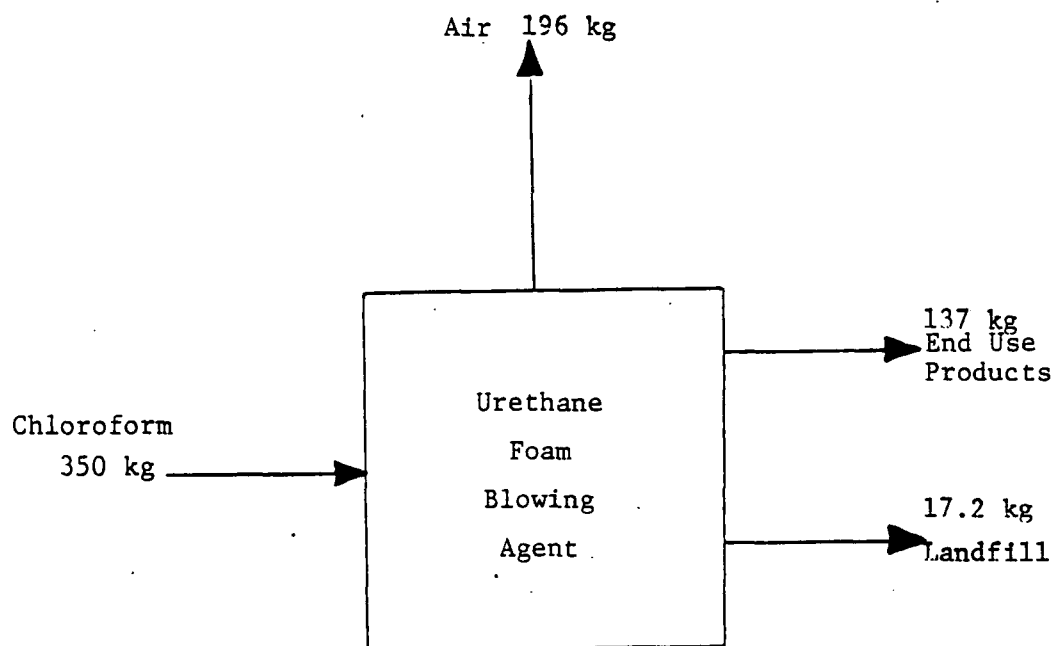
Air 196 kg

Chloroform
350 kg ──→ │ Urethane Foam Blowing Agent │ ──→ 137 kg End Use Products

──→ 17.2 kg Landfill

Figure 3.10 Multimedia Releases of Chloroform from Use of Methylene
Chloride as a Blowing Agent in Urethane Foam

3.3.2.6 Releases of Chloroform from Miscellaneous Use of Methylene Chloride

Approximately 210 kg of chloroform ($\pm$20%) were released from miscellaneous uses of methylene chloride in 1978. These uses included traffic paints, cesspool cleaners, adhesives, extraction of spices, beer hops, and coffee, plastics processing, and others. No estimate could be made on the chloroform releases from specific end uses. It can be assumed, however, that approximately 70-80 percent is emitted directly to air (147-168 kg), 10-15 percent is landfilled (21-32 kg), and 10-15 percent is discharged to water or groundwater (21-32 kg). Since the miscellaneous uses have not been differentiated, our estimates for multimedia releases are not considered more accurate than $\pm$85%.

3.3.3 Releases of Chloroform Contaminant of Carbon Tetrachloride

3.3.3.1 Handling, Storage, and Transportation Emissions

Technical grade carbon tetrachloride can contain up to 150 ppm chloroform (Kirk-Othmer 1978). To account for possible analytic error associated with this value, we assigned a confidence limit of $\pm$10%. Carbon tetrachloride is produced by 13 plants owned by eight chemical corporations (see Table 3.7). These plants produced 334,000 kkg ($\pm$10%) of carbon tetrachloride in 1978 (USITC 1979). Assuming that all of this carbon tetrachloride contained 150 ppm chloroform, the amount of chloroform contained in the carbon tetrachloride is estimated as 50 kkg (+10%, -20%).

Atmospheric emissions of carbon tetrachloride during storage, loading, ballasting, and transit are summarized in Table 3.8 (Rams et al. 1979). These emissions total 191 kkg. These calculations are based on information in AP-42 (USEPA 1977). The total has an estimated uncertainty of $\pm$25%. The emissions of chloroform associated with this carbon tetrachloride are estimated as 0.029 kkg (+41%, -34%).

3.3.3.2 Production of CFC-11 and CFC-12 from Carbon Tetrachloride

Production of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) accounts for over 87 percent of the industrial utilization of carbon tetrachloride (CCl_4). There are currently five producers of chlorofluorocarbons in the United States. Their production capacities and plant locations are shown in Figure 3.11 and Table 3.9, respectively. In 1978, 148,000 kkg ($\pm$10%) of CFC-12 and 88,000 kkg ($\pm$10%) of CFC-11 were produced in the United States (USITC 1979). This represents a 9 percent reduction in chlorofluorocarbon production from 1977. This trend is believed to have continued, resulting in a 25 percent recuction in CFC-11 production and a 14 percent decrease in CFC-12 production for 1979 (see Table 3.2). This decrease in production is a result of EPA regulations which banned the use of chlorofluorocarbons as aerosol propellants as of December 15, 1978 (Federal Register 1978). Use of chlorofluorocarbons as aerosol propellants previously accounted for about 50 percent of the CFC-11 and CFC-12 marketed (Kirk-Othmer 1978, Mannsville Chemical Products 1978a). Currently, CFC-11 and CFC-12 are used as refrigerants, foam blowing agents, and solvents. Unless there is a ban on all chlorofluorocarbon

Table 3.7 Carbon Tetrachloride Plant Production Estimates

Plant	1978 capacity millions of pounds	Fraction of total industrial output (%)	Estimated 1978 production (kkg/yr)	Process type
Allied, WV	8	0.47	1,555	Hydrocarbon chloronolysis carbon disulfide
Diamond, WV	11	0.65	2,151	Methane chlorination
Dow Chemical, TX	135	8.0	26,473	Hydrocarbon chloronolysis methane chlorination
Dow Chemical, CA	80	4.7	15,553	Hydrocarbon chloronolysis methane chlorination
Diamond, WV	125	7.4	24,488	Hydrocarbon chloronolysis
du Pont, TX	500	30	99,273	Hydrocarbon chloronolysis
FMC, WV	300	18	59,563	Carbon disulfide
Inland, PR	N/A	–	–	–
Stauffer, AL	200	12	39,709	Carbon disulfide
Stauffer, KY	35	2.1	6,949	Hydrocarbon chloronolysis methane chlorination
Stauffer, NY	150	9.9	29,451	Carbon disulfide
Vulcan, LA	90	5.3	17,538	Hydrocarbon chloronolysis
Vulcan, KS	60	3.5	11,582	Hydrocarbon chloronolysis methane chlorination
TOTAL	1,694	101	334,285	

Due to rounding, percents did not total 100, nor did estimated 1979 production match the reported 334,319 kkg (USITC 1979).

Source: Rams et al. 1979

Table 3.8 Method I Storage, Loading, Ballasting, and Transit Emissions

Plant	Production Capacity	Storage		Loading				Ballasting			Transit			
		Breathing	Working	Tank cars/ Trucks	Tankers	Ocean Barges	Barges	Tankers	Ocean Barges	Barges	Tank Cars/ Trucks	Tankers	Ocean Barges	Barges
Allied WV	1,708	.026	.67	.22	—	—	.059	—	—	—	.0037	—	—	.044
Diamond WV	4,818	.072	1.9	.63	—	—	.17	—	—	—	.010	—	—	.13
Dow TX	26,486	.40	10	.69	.41	.91	—	.32	.34	—	.011	.55	.69	—
Dow CA	15,942	.24	6.2	3.3	.062	.11	—	.048	.041	—	.055	.083	. 083	—
Dow LA	24,509	.37	9.6	3.2	—	—	β5	—	—	—	.053	—	—	.64
Du Pont TX	95,681	1.4	37	2.5	1.5	3.3	—	1.1	1.2	—	.041	2.0	2.5	—
FMC WV	59,436	.89	23	12	—	—	.82	—	—	—	.20	—	—	.62
Inland PR	—			—	—	—	—	—	—	—	—	—	—	—
Stauffer AL	39,666	.59	15	2.1	—	—	2.2	—	—	—	.034	—	—	1.7
Stauffer KY	7,045	.11	2.7	.55	—	—	.34	—	—	—	.0091	—	—	.26
Stauffer NY	29,451	.44	11	.77	.52	.91	—	.40	.34	—	.013	.69	.69	—
Vulcan LA	17,589	.26	6.9	2.3	—	—	.61	—	—	—	.038	—	—	.46
Vulcan KS	11,988	.18	4.7	3.1	—	—	—	—	—	—	.052	—	—	—
TOTALS	334,319	5.0	129	31	2.5	2.5	5.0	1.9	1.9	—	.52	3.3	4.0	3.9
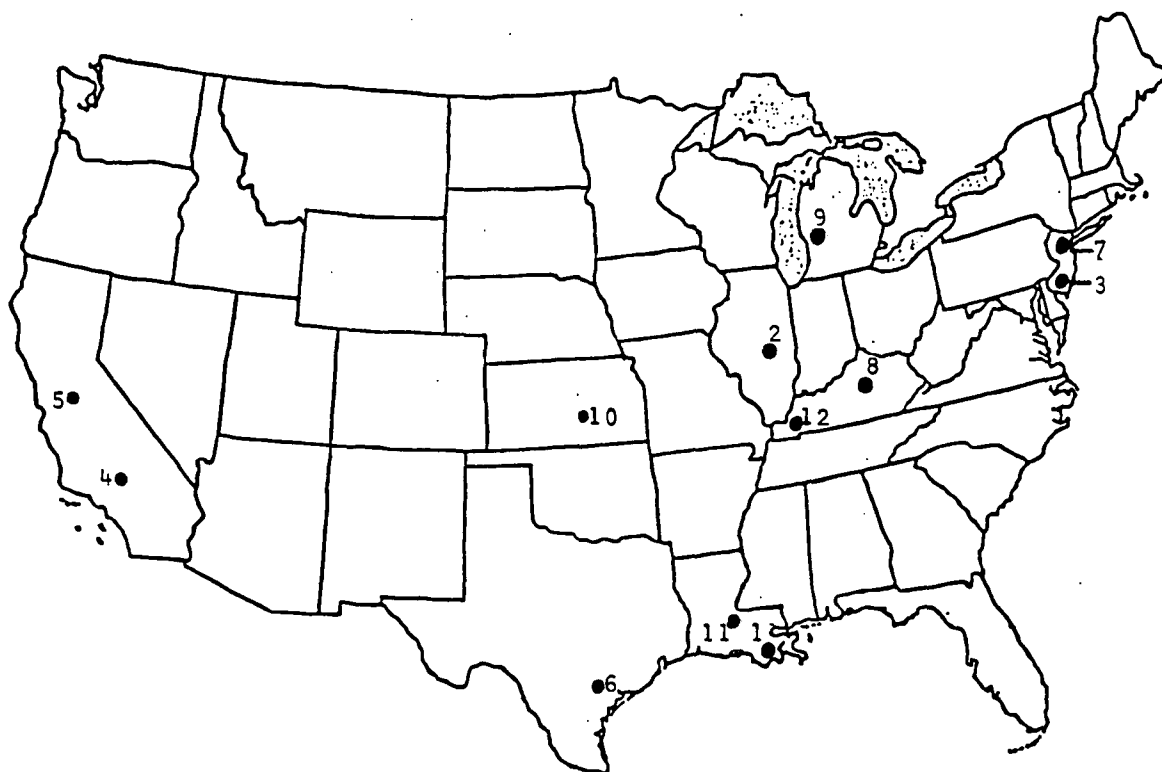
COMPANY		LOCATION
Allied Chemical Corporation Specialty Chemicals Division	1. 2. 3. 4.	Baton Rouge, Louisiana Danville, Illinois Elyabech, New Jersey El Segundo, California
E.I. du Pont de Nemour and Company, Inc. Freon Products Division	5. 6. 7. 8. 9.	Antioch, California Corpus Christi, Texas Deepwater, New Jersey Louisville, Kentucky Montague, Michigan
Essex Chemical Corporation Racon Inc.	10.	Wichita, Kansas
Kaiser Aluminum and Chemical Corporation Kaiser Chemicals Division	11.	Gramercy, Louisianna
Pennwalt Corporation Inorganic Chemicals Division	12.	Calvert City, Kentucky

Figure 3.11 Locations of Chlorofluorcarbon Production Plants

Table 3.9 Locations and Capacities of Chlorofluorocarbon Production Plants

Company	Location	Annual Capacity (kkg)	% of Annual Capacity
Allied Chemical Corporation Specialty Chemicals Division	Baton Rouge, Louisiana Danville, Illinois Elyabech, New Jersey El Segundo, California	1.8144×10^5	36.7%
E.I. du Pont de Nemours and Company, Inc. Freon® Products Division	Antioch, California Corpus Christi, Texas Deepwater, New Jersey Louisville, Kentucky Montague, Michigan	2.268×10^5	45.9%
Essex Chemical Corporation Racon Inc.	Wichita, Kansas	$.20412 \times 10^5$	4.1%
Kaiser Aluminum and Chemical Corporation Kaiser Chemicals Division	Gramercy, Louisiana	$.29484 \times 10^5$	6.0%
Penwalt Corporation Inorganic Chemicals Division	Calvert City, Kentucky	$.36288 \times 10^5$	7.3%
	TOTAL	4.944×10^5	

usage, production of CFC-11 and CFC-12 should stabilize at the 1979 production level and thereafter increase at a 5 percent annual rate (Mannsville Chemical Products 1978a, SRI 1979, Wolf 1979).

The production of CFC-11 and CFC-12 accounted for 293,000 kkg (+10%) of carbon tetrachloride in 1978 (Rams et al. 1979). Assuming that the carbon tetrachloride contained the maximum reported concentration of chloroform, 150 ppm (+10%), 44 kkg (+20%, -18%) of chloroform were present.

CFC-11 and CFC-12 are produced in an integrated facility using a liquid phase catalytic reaction of anhydrous hydrogen fluoride, carbon tetrachloride, and chlorine. A typical process diagram, based on processes utilized by Allied Chemical Corporation and E. I. du Pont de Nemours and Company, is shown in Figure 3.12. Possible primary sources of emissions from this process include storage of raw materials, the vent on the hydrogen chloride recovery column, and vents on the distillation column. Secondary emissions can result from the disposal of waste hydrogen chloride, spent alumina, waste sulfuric acid, waste sodium chloride, spent catalyst and from releases occuring during usage of the contaminated finished product.

During the production process, chloroform can react with hydrogen fluoride, producing CFC-22. The amount of chloroform consumed during the production process is unknown, but we assume that all the chloroform not emitted during production was consumed.

A. Air Emissions

The amount of carbon tetrachloride released during storage depends on the type of storage tanks used, the storage conditions, and the type of emission control system. Allied Chemical estimated breathing and working losses from the fixed roof tank at their production facility, with no emission control devices, at 0.00035 kkg/kkg of product (Pitts 1978). E. I. du Pont (Smith 1978b) calculated storage tank losses for carbon tetrachloride to be 0.002 kkg/kkg of product. These estimates were made using procedures outlined in the Compilation of Air Pollutant Emission Factors, AP-42 (EPA 1977, Pitts 1979a). To account for assumptions utilized in AP-42, the uncertainty associated with these emission factors is +25%.

Assuming that emissions from the Allied Chemical plant are typical of the industry and that the chloroform level in the feedstock is 150 ppm, releases of chloroform to the atmosphere from manufacture of 236,000 kkg of CFC-11/12 can be calculated as 0.012 kkg (+58%, -38%).

B. Process Emissions

Emissions of carbon tetrachloride during chlorofluorocarbon production and from waste streams originating from the production process can occur from various point and nonpoint sources. These sources include landfilling of spent antimony chloride catalyst, which contains 10 percent carbon tetrachloride; byproduct hydrogen chloride, anhydrous
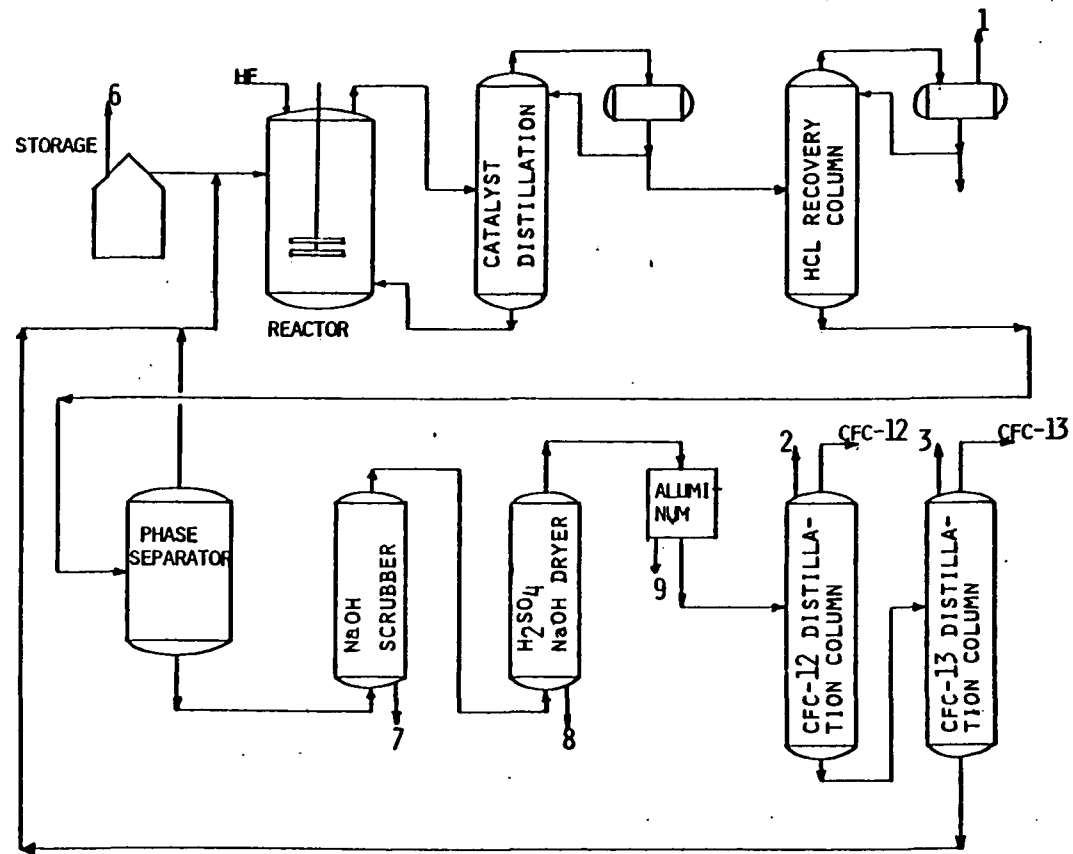
Figure 3.12   Chlorofluorocarbon Production Process
Source: Pitts 1979b

hydrogen chloride recovery column vent; distillation column vents, the caustic scrubber, sulfuric acid and alumina dryers; and fugitive emissions. A study of emissions of carbon tetrachloride from the chlorofluorocarbon production process estimated atmospheric emissions of 367 kkg ($\pm$30%) (Rams et al. 1979). Assuming 150 ppm chloroform in the carbon tetrachloride, emissions contain an estimated 0.055 kkg (+44%, -64%).

C. Emissions from Contaminated Finished Products

Levels of carbon tetrachloride in fluorocarbons were estimated by industry to be below 2 ppm (NAS 1978a,b). From this value, the amount of carbon tetrachloride in products has been estimated as 0.47 kkg ($\pm$30%), and the amount of chloroform as 7.1×10^{-5} kkg (+41%, -63%). We assume that all of this chloroform would be released to the atmosphere.

Total emissions of chloroform to the atmosphere from the production of CFC-11 and CFC-12 are 0.067 kkg (+46%, -40%).

D. Water Emissions

Carbon tetrachloride is contained in the aqueous waste streams from the caustic scrubber and the H_2SO_4 dryer (streams 7 and 8 in Figure 3-12). We assume that due to limited solubility of carbon tetrachloride in water only residual traces would be left after biological treatment of these waste streams.

Another source of carbon tetrachloride in wastewater is through leakage or disposal into the plant sewage system. The amount of emissions from these sources is unknown, but we assume them to be small. Thus, the total amount of chloroform emitted in waste streams from these production sources is believed to be small.

E. Land Emissions

It has been estimated that 3.9 kkg ($\pm$75%) of carbon tetrachloride are in spent catalyst from fluorocarbon production, which is landfilled (Rams et al. 1979). The amount of chloroform in the landfilled catalyst is estimated as 0.0006 kkg (+89%, -22%).

3.3.3.3 Use of Carbon Tetrachloride in Fumigants

Carbon tetrachloride is used in the formulation of pesticides applied as fumigants for nonagricultural purposes. These uses include application of fumigants to protect harvested crops and products in storage, and prevention of insect, rodent, and other vermin infestation in mills, warehouses, grain elevators, railcars, ship holds, and other storage areas (SRI 1976).

Carbon tetrachloride is effective in grain disinfestation when long exposure is possible. Due to its excellent penetration and diffusion capabilities, it is a preferred fumigant for use under a wide range of conditions. In liquid form, it is poured or pumped into storage areas. It vaporizes upon contact within the first few feet of grain, and penetrates through the bulk of the stored grain. Applications are generally performed a short time after the grain is harvested and stored, and may be repeated as the grain is packaged and transported for use.

Grain fumigants, including carbon tetrachloride, constitute the major type of pesticide used for nonagricultural applications. There are currently 119 pesticide products registered for manufacture in the United States which contain carbon tetrachloride. These products, primarily grain and spot fumigants, are manufactured by a total of 55 companies, listed in Table 3.10. These production sites are clustered in several centers: the New York-New Jersey area, the Baltimore-Washington area, West Virginia, the Cleveland-Detroit area, the Chicago area, St. Louis-Kansas City area, New Orleans-Alabama area, the Houston area, Los Angeles area, and the San Francisco Bay area.

In 1978, 13,300 kkg (+40%) of carbon tetrachloride were used in the production of fumigants. Of this amount, 1,200 kkg (+35%) were stockpiled (Rams et al. 1979). Because of the nature of the fumigation process, all of the carbon tetrachloride used in fumigants, or a total of 12,100 kkg (+40%), was emitted to the atmosphere during application. The amount of chloroform emitted to the atmosphere from the use of carbon tetrachloride in fumigants is estimated as 1.8 kkg (+40%, -40%); the amount of chloroform in the stockpiled fumigants is estimated as 0.18 kkg (+50%, -39%).

3.3.3.4 Minor Uses of Carbon Tetrachloride

Carbon tetrachloride has many nonconsumptive industrial uses (Rams et al. 1979). These include laboratory uses, metal cleaning, use in the production of paints, adhesives, textiles, embalming supplies, pharmaceuticals, plastics, rubber, chlorinated paraffins, and various other miscellaneous uses. Emissions of carbon tetrachloride to the atmosphere from these uses amounted to 11,800 kkg (+95%) in 1978 (Rams et al. 1979). The amount of chloroform in these emissions is estimated as 1.8 kkg (+111%, -96%).

Of the amount of carbon tetrachloride used in embalming supplies, 831 kkg (+95%) are contained in caskets. The amount of chloroform in this embalming fluid, which is assumed to be in temporary storage, is estimated as 0.12 kkg (+125%, -95%).

3.3.3.5 Stockpiled Carbon Tetrachloride

It has been reported that 17,100 kkg (+95%) of carbon tetrachloride were stockpiled in 1979 (Rams et al. 1979). The amount of chloroform in the stockpiled carbon tetrachloride is estimated as 2.6 kkg (+111%, -96%). We assume that none of the stockpiled carbon tetrachloride is emitted to the atmopshere because it is stored in sealed drums and tanks.

3.3.4 Releases from Perchloroethylene/Carbon Tetrachloride Production

Perchloroethylene is formed by the chlorination of hydrocarbons at or near pyrolytic conditions. Production of perchloroethylene and carbon tetrachloride from the chlorination of hydrocarbons has been estimated at 318,800 kkg (Farmer et al. 1980, Rams et al. 1979). The hydrocarbon feed to the process can be any of several hydrocarbons or a mixture of hydrocarbons. One source of the mixed hydrocarbon feedstock is distillate residue from chloromethane processes. This

Table 3.10   United States Producers of Registered Pesticide Products
             which Contain Carbon Tetrachloride

Agway, Inc.	Syracuse, New York
Atomic Chemical Co.	Spokane, Washington
Bartels & Shores Chemical Co.	Greenwood, Mississippi
Big F Insecticides, Inc.	Memphis, Tennessee
Brayton Chems, Inc.	W. Burlington, Iowa
Cardinal Chemical Co.	San Francisco, California
Chemi Sol Chemical & Sales Co.	Hutchinson, Kansas
Colorado International Corp.	Lakewood, Colorado
Coyne Chemical Co.	Los Angeles, California
Dettelbach Chemicals Co.	Atlanta, Georgia
Diamond Shamrock Agricultural Chemicals	Newark, New Jersey Des Moines, Iowa Green Bayou, Texas Baltimore, Maryland
Douglas Chemical Co.	Liberty, Missouri
Dow Chemicals, U.S.A.	Midland, Mississippi Freeport, Texas Pittsburg, California
Farmland Industries, Inc.	Kansas City, Missouri
Ferguson Fumigants	Hazlewood, Missouri
FMC	Middleport, New York Baltimore, Maryland
Grain Conditioners, Inc.	New Orleans, Louisiana
Hill Manufacturing Co.	Atlanta, Georgia
Hockwald Chem. (Division of Oxford Chem.)	Brisbane, California
Huge Company, Inc.	St. Louis, Missouri

Table 3.10 United States Producers of Registered Pesticide Products
Which Contain Carbon Tetrachloride (Continued)

Industrial Fumigant Co.	Olathe, Kansas
J-Chem	Houston, Texas
Knox Chemicals Co.	St. Louis, Missouri
Leitte, E.H. Co.	Lake Elmo St. Paul, Minnesota
Lester Labs, Inc.	Atlanta, Georgia
Levensons, Inc.	Omaha, Nebraska
Lystad, Inc.	Grand Forks, North Dakota
MFA Oil Co.	Shenandoah, Iowa
Momar, Inc.	Atlanta, Georgia
Morgro Chemical & Energy Corp.	Salt Lake City, Utah
Oxford Chemicals	Atlanta, Georgia
Parsons Chemicals	Grand Lodge, Mississippi
Patterson Chemical Company, Inc.	Kansas City, Missouri
PBI-Gordon Corp.	Kansas City, Kansas
Quinn Drug & Chemicals	Kansas City, Missouri
Research Products Co.	Salinas, Kansas
Riverdale Chemicals Co.	Chicago Heights, Illinois
Selig Chemical Industries	Atlanta, Georgia
Southland Pearson & Co.	Mobile, Alabama
Southwestern Grain Supply Co.	Amarillo, Texas
Staffel Company	San Antonio, Texas
Stephenson Chemicals Co., Inc.	College Park, Georgia

Table 3.10 United States Producers of Registered Pesticide Products
Which Contain Carbon Tetrachloride (Continued)

Stauffer Chemicals Co.	Perry, Ohio Mt. Pleasant, Tennessee Henderson, Nevada Ardsley, New York
Techne Corp.	Kansas City, Missouri
Thompson-Hayward Chemicals	Kansas City, Kansas
Universal Corporaters, Inc.	Minneapolis, Minnesota
Vulcan Materials Co.	Wichita, Kansas
Warren-Douglas Chemical Co., Inc.	Omaha, Nebraska
Weevil-Cide Co.	Salina, Kansas
Weil Chemical Co.	Memphis, Tennessee
West Chemicals Products, Inc.	Long Island, New York
Wood Folk Chem Works, Inc.	Ft. Valley, Georgia
Zep Manufacturing Corp.	Atlanta, Georgia

particular feedstock contains chloroform, which may be released to the air with vented emissions from the hydrocarbon storage tanks. Chloroform was found at 0.037 mole percent (less than 0.1 percent by weight) in the combined emissions from hydrocarbon storage and hex wastes from perchloroethylene distillation. An emission factor of 5.6×10^{-3} kkg/kkg of capacity was estimated (Hobbs and Stuewe 1979b). This emission factor represents an upper limit, since many producers do not store hydrocarbon wastes for feed.

An upper limit estimate of chloroform releases was determined by multiplying the emissions factor by the percent of chloroform in the emission stream to obtain an emission factor for chloroform alone, and then multiplying this product by the quantity of perchloroethylene and carbon tetrachloride produced by this production process.

$$\left(\begin{array}{c} \text{Emission rate} \\ \text{from hydrocarbon} \\ \text{storage} \end{array} \right) \left(\begin{array}{c} \text{Chloroform} \\ \text{level} \end{array} \right) \left(\begin{array}{c} \text{Production of} \\ \text{perchloroethylene} + \\ \text{CCl4} \end{array} \right) = \begin{array}{c} \text{Total} \\ \text{chloroform} \\ \text{released} \end{array}$$

$$(5.6 \times 10^{-3} \text{ kkg/kkg}) \quad (0.001) \quad (318,800 \text{ kkg}) \quad = \quad 1.8 \text{ kg/yr}$$

This estimate is not considered more accurate than +60%, -80% because of uncertainty related to the frequency with which hydrocarbon waste contaminated with chloroform is used as feedstock.

3.4 SUMMARY OF ENVIRONMENTAL RELEASES FROM CHLOROFORM USES

The major environmental release of chloroform resulting from its industrial use is that associated with pharmaceutical extraction. This source accounted for 1,000 kkg or 73 percent of chloroform released to the environment in 1978. Most of this, 570 kkg, was released to the atmosphere. The amount of chloroform used in laboratories is unknown but we estimate it to be large because of chloroform's excellent solvent properties. The releases from laboratory uses could also be large because of the uncontrolled conditions under which chloroform is used. The remaining releases of chloroform associated with its industrial use are small and account for about 23% of the total releases.

Table 3.11 summarizes the releases of chloroform associated with its use.

Table 3.11 Summary of Environmental Releases from Chloroform End-Uses (kkg)

Use	Quantity released (kkg)	Quantity released to		
		Air	Land	Water
CFC-22 production	190	190	0	0
CFC-22 refrigerant	0.005	0.005		
Pharmaceutical extractions	1,000	570	384	46
Fumigants	37.8	37.8	0	0
Laboratory Uses	Potentially large	?	?	?
Contamination of methyl chloride		?	?	?
Contamination of methylene chloride				
- storage	0.0014	0.0014		
- paint remover	1.28	0.96	0.128	0.192
- metal cleaning	0.843	0.65	0.088	0.105
- aerosols	0.805	0.726	0.079	0
- urethane foam	0.213	0.196	0.017	0
- other	0.21	0.157	0.026	0.027
Contamination of perchloroethylene	?	0.0018		
Contamination of carbon tetrachloride				
- storage	0.029	0.029		
- CFC-11/CFC-12	0.0676	0.067	0.00058	
- fumigants	1.8	1.8		
- other	1.8	1.8		

4.0 RELEASE SOURCE EVALUATION

The objective of this chapter is to pinpoint specific geographic areas and specific processes or operations where significant environmental releases of chloroform may occur.

4.1 DIRECT PRODUCTION

There are five domestic producers of chloroform with plants at seven sites. Chloroform emissions are low, amounting to only about 0.2 percent of the total chloroform produced. Nevertheless, releases to air and water may be locally significant, particularly from fugitive emissions and storage and handling losses. Table 4.1 summarizes air emissions and water emissions for the seven plants producing chloroform. It is important to note that, in the absence of other information, emissions were estimated using the same emission rate for all plants and with the assumption that production was 71 percent of capacity at each plant. Consequently, actual emissions may vary significantly from those shown in Table 4.1. Based on these emission estimates, the Gulf Coast, with producers located in Freeport, Texas; Plaquemine, Texas; and Geismer, Louisiana; is the most significant area for environmental releases from chloroform production.

Table 4.1 Summary of Chloroform Releases to Air and Water from Production of Chloroform (assuming controlled conditions)

Producer	Production site	Percent of total	Releases to air (kkg)	Releases to water (10^3 kkg)
Allied Chemical	Moundsville, WV	6.3	13.6	0.6
Diamond Shamrock	Belle, WV	8.1	17.5	0.8
Dow Chemical	Freeport, TX	20.3	43.9	1.9
Dow Chemical	Plaquemine, TX	20.3	43.9	1.9
Stauffer	Louisville, KY	15.3	33.1	1.9
Vulcan	Geismer, LA	9.4	20.3	0.9
Vulcan	Wichita, KS	20.3	43.9	1.9

4.2 INDIRECT PRODUCTION

Environmental releases of chloroform will occur as water is distributed and used in municipalities which directly chlorinate their water supplies (especially surface water sources) without treating to remove trihalomethanes before distribution. Public water utilities

which draw their supplies from source waters contaminated with chlorinated organics run an even greater risk of subsequent chloroform formation.

The 1975 NORS study (Symons et al. 1975) identified 37 cities of various population sizes whose treated water contained chloroform at concentrations greater than 30 µg/ℓ. Table 4.2 lists these cities in the survey whose drinking water contains high levels of chlorofrom and major population centers whose drinking water contains at least 30 µg/ℓ of chloroform. In a more recent study, treated water drawn from the Occoquan Reservoir in Northern Virginia contained levels of chloroform ranging from 24 to 409 µg/ℓ (Hoehn et al. 1977). These monitoring data, however, are not up to date, and do not reflect changes in treatment strategies that municipalities may have adopted in order to lower trihalomethane levels in their drinking waters. For example, Cincinnati stopped the practice of prechlorinating source water (from the heavily industrialized Ohio River) in late 1975. Chloroform levels in finished water subsequently fell from 300 ppb to 20-50 ppb (Dallaire 1977). It is not known to what extent other municipalities with high levels of chloroform in finished waters have altered their treatment strategies, or how effective these changes have been. The use of ozone as an alternative disinfectant in water treatment may, in fact, enhance trihalomethane formation when practiced in conjunction with postchlorination (Riley et al. 1978).

Steam electric power plants (nuclear and fossil fuel) are potential "hot spots" for chloroform releases when large quantities of once-through cooling waters and cooling tower waters are chlorinated to control biofouling. The quantities of chloroform produced and released from this source depend on the organic content of cooling waters, the doses of chlorine applied, the length of contact time, and the quantities of spent cooling water discharged annually.

Paper mills are a key source of chloroform releases; pulp bleaching effluents contain high concentrations (up to ∿2.0 ppm) of chloroform (NAS 1978a,b). Aerated lagoons may act to protect surface waters from substantial chloroform contamination, but significant quantities of chloroform may be released to air due to pulp bleaching operations. Information regarding specific locations of paper mills, the extent of pulp bleaching at these mills, the types of pulp bleached and bleaching processes employed, the quantities of effluents discharged annually, and the use of aerated lagoons to treat these effluents is necessary in order to identify the mills that are sources of major chloroform releases.

Gasoline combustion is reported to be a source of atmospheric chloroform releases. In a study of exhaust gases from two cars (Harsch et al. 1977), much higher chloroform concentrations were found in exhaust from a car running on unleaded gasoline (6-7 ppb) than leaded gasoline (< 100 ppt). Since only two cars were tested, more research is necessary to assess the significance of this source of indirect chloroform production, particularly in urban areas with high concentrations of gasoline-powered vehicles.

Table 4.2 Chloroform Concentration in Finished
Drinking Water of Various U.S. Cities

City	Chloroform concentration (μg/ℓ)
San Juan, PR	47
Philadelphia, PA	86
Washington, DC	41
Baltimore, MD	32
Annandale, VA	67
Wheeling, WV	72
Miami, FL	311
Atlanta, GA	36
Charleston, SC	195
Cincinnati, OH	45
St. Paul, MN	44
Columbus, OH	134
Piqua, OH	131
Youngstown, OH	80
Houma, LA	134
Davenport, IA	88
Topeka, KS	88
Cape Girardeau, MO	116
St. Louis, MO	55
Huron, SD	309
Dos Palos, CA	61
Los Angeles, CA	32
San Diego, CA	52
San Francisco, CA	41
Ilwaco, WA	167

Source: Symons et al. 1975

4.3 CHLOROFORM USES

4.3.1 CFC-22 Production

Chloroform releases from storage at the five CFC-22 production sites comprise the major source of potential environmental problems associated with the use of chloroform. As calculated in Section 3.1.1, total air emissions amount to 190 kkg (+20%), and would be distributed according to each producer's market share. This apportionment is detailed in Table 4.3, and the five release sites were shown on the map in Figure 3.1.

Table 4.3 Air Emissions of Chloroform from the Production of CFC-22

Location	Producer	Quantity (kkg)	% of total
El Segundo, CA	Allied Chemical	81.7	43
Louisville, KY	E. I. duPont	38	20
Gramercy, LA	Kaiser Aluminum & Chemical	30.4	16
Calvert City, KY	Pennwalt Corporation	22.8	12
Witchita, KS	Racon, Inc.	17.1	9
		190.0	100

4.3.2 Other Chloroform Uses

Although approximately 14,640 kkg of chloroform were available for miscellaneous uses, only 7 percent of this total could be accounted for. Most of the 13,600 kkg unaccounted for is probably used in laboratories or is stockpiled. There are no known areas of concentrated emissions from miscellaneous uses.

Releases of chloroform as a contaminant in other chloromethanes (methyl chloride, methylene chloride, and carbon tetrachloride) are also not significant for any geographic areas. These products are contaminated with chloroform at low levels, and their uses are geographically dispersed.

5.0 SUMMARY OF DISPOSAL AND DESTRUCTION OF SOLID AND LIQUID CHLOROFORM WASTES

This chapter summarizes the information on the quantities of chloroform-containing solid and liquid wastes destroyed and disposed of during the production and uses of chloroform. Table 5.1 summarizes this information.

The amount of chloroform present in the heavy-end waste stream of the methanol hydrochlorination followed by methyl chloride chlorination process is 23.1 kkg. Assuming that the incinerator used in the destruction of heavy-end waste achieves a 95 percent efficiency, the quantity of chloroform released to air from incineration of this heavy-end waste is 0.87 kkg. Of the heavy-end waste stream, 5.8 kkg is landfilled. Because of the lack of information on the types of containment procedures used, the amount of chloroform released from the landfills is unknown and assumed to be minimal.

The quantity of chloroform present in the solid wastes from the CFC-22 production process, pharmaceutical extractions, and contaminants in methylene chloride and carbon tetrachloride amounted to only about 34 kkg. The majority of this solid waste is from use of chloroform in pharmaceutical extractions. Most of this quantity is disposed of in landfills.

Table 5.1 Solid and Liquid Chloroform-Containing Waste: Quantities, Disposal, and Environmental Releases

Type of waste produced	Solid waste (kkg)	Destroyed by incineration (kkg)	Released to air from incineration (kkg)	Landfilled (kkg)
Methanol hydrochlorination followed by methyl chloride chlorination	23.1	16.4	0.86	5.8
CFC-22 catalyst disposal	0.9	--	--	--
Pharmaceutical extractions	34	?	?	34
Contaminant of methylene chloride				
- Paint removers	0.128	--	--	0.128
- Metal cleaning	0.105	0.017	0.00085	0.088
- Aerosol products	0.079	--	--	0.079
- Foam blowing agent	0.017	--	--	0.017
- Miscellaneous uses	0.026	--	--	0.026
Contaminant of carbon tetrachloride				
- Spent catalyst from CFC-11 and CFC-21 production	0.00058	--	--	0.00058
- Embalming supplies	0.12	--	--	0.12

6.0 SUMMARY OF UNCERTAINTIES

Table 6.1 lists the estimates for environmental releases of methyl chloroform by process and media of release along with the corresponding uncertainty estimate for each value. The rationale for assigning a specific uncertainty to each number is discussed in detail in Chapters 2 and 3. Our recommendations for "fine tuning" the materials balance to reduce the uncertainty of these estimates are discussed in Chapter 7.

Table 6.1 Summary of Uncertainties

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Production: Methanol hydro-chlorination followed by methyl chloride chlorination	● Total chloroform produced	122,400	–	+10
	● Total chloroform released from methylene chloride and chloroform distillation column vent	0.26	+30	+38
	● Total controlled fugitive losses of chloroform	3.6	+20	+53
	● Breathing losses of chloroform (controlled conditions)	72.4	+40/-20	+54/-39
	● Working losses of chloroform (controlled conditions)	34.7	+70/-20	+80/-30
	● Chloroform in carbon tetrachloride residue	23.0	–	+25
	● Chloroform landfilled in still bottoms	5.8	+50	+72
	● Chloroform incinerated with still bottoms	16.4	+15	+39
	● Secondary emissions to air from incineration of carbon tetrachloride residue	0.86	+15	+39
	● Releases of chloroform to cooling water	70	+75/-50	+90/-56
	● Releases of chloroform to water in spent caustic and acid wastes	1.6	+75	–
	● Chloroform evaporated from spent caustic and acid wastes	1.3	–	+110/-100
	● Chloroform remaining in water from spent caustic and acid wastes	0.3	–	+125/-100

*kkg unless otherwise noted

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Production: Methane chlorination process	• Total chloroform produced	36,100	–	+30
	• Releases of chloroform from recycled methane inert gas purge vent	0.03	+50/-25	+80/-55
	• Releases of chloroform from distillation area emergency gas vent	0.19	+50/-25	+80/-55
	• Total controlled fugitive losses of chloroform	0.6	+20	+50
	• Breathing losses of chloroform (controlled conditions)	11.2	–	+75/-25
	• Working losses of chloroform (controlled conditions)	9.2	–	+75/-25
	• Release of chloroform to cooling water	21	+75/-50	+110/-76
	• Release of chloroform to spent acid and spent caustic wastes	0.4	+75	
	• Chloroform evaporated from spent caustic and spent acid	0.3	+10	+152/-100
	• Chloroform remaining in water	0.1	+30	+150/-100
Transportation Losses	• Total chloroform released from transportation	177	–	+50

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Chlorination of Municipal Water Supply	● Total chloroform produced	912	–	+10/−50
	● Evaporation of chloroform to air from use of potable water	820	±5	+15/−55
	● Release of chloroform to natural waterways	92	±50	+60/−100
Chlorination of Municipal Sewage	● Total chloroform produced	91	–	±50
	● Chloroform released to air	82	±6	±56
	● Chloroform released to water	9	±50	±100
Chlorination of Cooling Water at Power Plants	● Total chloroform produced	2,460	–	+20/−50
	● Chloroform released to air	2,340	±5	+25/−55
	● Chloroform discharged to surface water	120	±100	+120/−100
Bleaching of Paper Pulp	● Total chloroform produced	6,700	–	±50
Combustion of EDC in Leaded Gasoline	● Total chloroform produced and released to air	965	–	+5/−90
Tropospheric Photodecomposition of Trichloroethylene	● Total chloroform produced	450	–	+700/−90

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Du Pont Process for CFC-22 Manufacture	• Condenser vent emission rate (kkg/kkg)	0.165	± 10	
	• Chloroform concentration in vent stream (volume %)	6.26	± 10	
	• Fugitive emissions (kg)	0.83	± 50	
	• Production rate of CFC-23 (kkg/kkg)	9.6×10^{-3}	± 20	
	• CFC-23 condenser vent emissions	1.4×10^{-6}	-	
	• CFC-22 condenser vent emissions	75×10^{-6}	-	
	• Emissions due to catalyst regeneration	1.14	ND	
Allied Chemical Process for CFC-22 Manufacture	• Chloroform emissions from storage	120	± 25	
	• Fugitive emissions	0.67	± 50	
	• Production rate of CFC-23 (kkg/kkg)	9.6×10^{-3}	± 20	
	• Catalyst disposal	0.9	ND	
	• Total air emissions from CFC-22 manufacture	190		± 20
CFC-22 Usage	• Chloroform content of CFC-22	1 ppm	+25/-50	
	• Air emissions	0.005		+150/-100
Pharmaceutical Extractions	• Total chloroform used in extractions	1,000		± 20
	• Chloroform released to air	570		± 35
	• Chloroform landfilled	384		± 35
	• Chloroform released to water	46		± 35

ND – not determined

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Fumigants	● Amount of chloroform used in fumigants	42		+12/-11
	● Amount of chloroform in stockpiled fumigants	4.2		+24/-21
	● Amount of chloroform emitted to the atmosphere	37.8		±11
Laboratory Use/ Stockpiles	● Total quantity of chloroform used in laboratories and stockpiled	13,600	may be large	may be large
Contaminant of Methyl Chloride	● Total chloroform in methyl chloride	0.17	±75	
Contaminant of Methylene Chloride	● Total chloroform in methylene chloride	4.27	±30	
	● Releases of chloroform from storage of methylene chloride	2.5		
	● Releases of chloroform from handling of methylene chloride			
	● Releases of chloroform from use of methylene chloride-based paint removers	1.280	±20	
	- emissions to air	0.960	±15	
	- emissions to water	0.192	±15	±33
	- emissions to land	0.128	±15	±34

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
Chloroform Contained in Carbon Tetrachloride - CFC-12 and CFC-11 Production	• Production of CFC-12	148,000		$\pm$10
	• Production of CFC-11	8,000		$\pm$10
	• Amount of CCl_4 used in the production of CFC-11 and CFC-12	293,000		$\pm$10
	• Amount of $CHCl_3$ in CCl_4	150 ppm		$\pm$10
	• Amount of $CHCl_3$ in the CCl_4 utilized in the production of CFC-11 and CFC-12	44		+20/-18
	• Allied Chemical Corporation estimated breathing and working losses	0.00035		$\pm$25
	• E. I. DuPont de Nemours and Company storage losses	0.0002		$\pm$25
	• Estimated emissions of $CHCl_3$ from the storage of CCl_4	0.012		+58/-38
	• Estimated amount of $CHCl_3$ emitted to the atmosphere during the production process	0.055		+44/-64
	• CCl_4 in finished product	0.47		$\pm$30
	• $CHCl_3$ in finished product	7.1×10^{-5}		+41/-63
	• Total atmosphere emissions	0.067		+46/-40
	• CCl_4 in spent catalyst	3.9		$\pm$75
	• $CHCl_3$ in catalyst landfilled	0.00058		+89/-22

Table 6.1 Summary of Uncertainties (continued)

Source	Description	Quantity (kkg)*	Individual uncertainty (percent)	Overall uncertainty (percent)
CCl_4 in Fumigants	• CCl_4 used in fumigants	13,300		±40
	• CCl_4 in fumigants stockpiled	1,200		±35
	• CCl_4 emitted to atmosphere during fumigant use	12,100		±40
	• $CHCl_3$ emitted to atmosphere during CCl_4 fumigant use	1.8		±40
	• $CHCl_3$ in stockpiled CCl_4 fumigants	0.18		+39/−50
Minor Uses of CCl_4	• Emission of CCl_4 to the atmosphere	11,800		±95
	• $CHCl_3$ emitted from minor uses	1.8		+111/−96
	• CCl_4 used in embalming supplies	831		±95
	• $CHCl_3$ in embalming supplies	0.12		+125/−95
Stockpiled CCl_4	• CCl_4 stockpiled	17,100		±95
	• $CHCl_3$ in CCl_4 stockpiled	2.6		+111/−96
Perchloro-ethylene	• Total chloroform emitted from hydrocarbon feed	1.8		+60/−80

7.0 DATA GAPS

In preparing the Level I materials balance for chloroform, JRB found numerous data gaps which prevented an accurate assessment of chloroform release patterns and quantities. Some of this information is available in the literature, but could not be obtained within the time frame or scope of the study. Other data gaps require detailed monitoring data, input from industrial sources, and/or plant visits.

7.1 DIRECT PRODUCTION

Our estimates for chloroform releases to air from direct production processes were based largely on emission factors derived from information supplied by one plant for each production process. It was necessary to assume that all five plants producing chloroform by chlorination of methanol had the same operating conditions and controls. Furthermore, the emission factors were taken from a secondary source since the primary plant data were not available; the method used to determine these emission factors is not known. The primary sources for the plant data are available at the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards. These sources could not be obtained within the time frame of the study. Ideally, air emission factors should be determined from actual monitoring data. In the absence of monitoring data, estimates should be obtained from more than one plant.

No reliable information was available on the releases of chloroform to water (cooling water, spent caustic, and spent acid). Estimates were made using the available information, but the reliability of these estimates is low. Again, monitoring data or, at a minimum, estimates from producers should be obtained.

Finally, no information was available on the quantity of carbon tetrachloride still bottoms produced in the methane chlorination process. Carbon tetrachloride is produced by the methane chlorination process and the still bottoms contain small quantities of chloroform. It is claimed these wastes are incinerated, but it would be useful to determine secondary air emissions from the incineration of still bottoms.

7.2 INDIRECT PRODUCTION

In order to derive more accurate estimates for the quantities of chloroform produced annually through chlorination of municipal drinking water supplies and sewage effluents, it is necessary to have plant-specific data for representative municipal waterworks throughout the nation. Information on specific treatment schemes employed by these public utilities, such as chlorine doses applied daily (if, in fact, chlorination is practiced), any pretreatment methods which may be used to reduce the concentration of trihalomethane precursors in water, the nature of source waters (i.e., surface versus ground), pH and temperature of treated waters, and the amount of water or wastewater handled

daily would enable a much more accurate quantification of nationwide chloroform production from these sources. Also, regular monitoring of trihalomethane concentrations in treated water and sewage would reveal "hot spots" of chloroform production and subsequent environmental releases. Chloroform production will vary based on the amounts of organic precursors in source waters, seasonal variations in the chlorine demand of treated waters, and the specifics of the treatment process employed. A national survey of public water utilities and a nationwide monitoring effort of the type performed by EPA in 1975 (i.e., NORS) are two possible means of obtaining data required in order to derive valid and accurate estimates of indirect chloroform production via municipal chlorination practices. The same suggestions would apply for deriving information on the industrial sources (bleaching of paper pulp, cooling water chlorination) of indirect chloroform formation, and estimates of the amounts produced by these sources.

The chlorination of other industrial effluents which contain high concentrations of THM precursors may be a significant source of indirect chlorform releases. Sources of such releases include the textile industry and food processing operations; there may be many other industries which chlorinate wastewaters and, therefore, contribute to chloroform formation. However, none of these are identified in the available literature. Monitoring for chloroform in untreated waste streams and chlorinated effluents from such industries will identify those plants which are indirectly producing and subsequently releasing major quantities of chloroform.

The combustion of leaded gasoline has also been cited as a potentially significant source of chloroform in the environment, based mainly on a single monitoring study performed in 1977 in which exhaust from only two automobiles was analyzed. Using such limited data for a nationwide estimate of chloroform by combustion of leaded gasoline leads to a high uncertainty. Additional monitoring data and research into the sources of chlorine in gasoline and the mechanism of chloroform formation are needed before the extent of chloroform production through gasoline combustion can be accurately assessed.

7.3 USES OF CHLOROFORM

Information provided on the use patterns of chloroform was sketchy, and several estimates were made in order to quantify these uses.

7.3.1 Manufacture of CFC-22 from Chloroform

A major data gap identified in this study was the discrepancy in the percentage of chloroform produced which is used as feedstock for CFC-22 manufacture. According to Dow (Farber 1980) and estimates supplied by Wolf (1979), Radian Corp. (1979), and Boberg (1980), 90 percent of the 1978 chloroform production was used for CFC-22 manufacture. The production figures supplied by USITC (1979) and an estimate by Mannsville (1978a) suggest that only about 81 percent of the chloroform is used for CFC-22 production. This is a point which needs to be clarified, since it is not clear what fraction of the

chloroform produced is used for miscellaneous end uses or exported. For this balance we used Dow's estimate that 90 percent of the chloroform is used for CFC-22.

In the production of CFC-22 from chloroform, the product gases are cleaned by alkali scrubbing. No data detailing chloroform content of the waste streams from this process were available. Specific details of du Pont's catalyst regeneration, ratio of CFC-23 to CFC-22 production, and an estimate of fugitive emissions were not available. Similar details were also not available for the process used by Allied Chemical, and no information about the processes used by Pennwalt, Kaiser, or Racon was obtained.

One of the more important pieces of data lacking for this report is the level of chloroform impurity in CFC-22 product. One industry source indicated that the level was low, but that CFC-22 was not analyzed for traces of chloroform (Boberg 1980).

7.3.2 Minor Uses

As discussed in Section 3.2, numerous companies, government agencies, and chemical distributors were contacted in an effort to quantify chloroform used as a fumigant, a solvent, a laboratory chemical, and in the pharmaceutical, textile, and dye industries. The consensus among contacts was that the use of chloroform in textile and dyes and as an industrial solvent is extremely limited. The total production figure for chloroform, minus the fraction used for CFC-22, is the upper bound for the estimate of chloroform going to minor uses (13,600 kkg). If further research indicates that the fraction going to these uses is greater than the 10 percent estimated in this report, closer examination of the minor use of chloroform may be warranted.

7.3.3 Secondary Product Contaminants

Industry estimates were available for chloroform contaminant levels in methyl chloride, methylene chloride, and carbon tetrachloride. Environmental releases of chloroform from use of these chloromethanes are believed to be comparatively small. Better estimates of these releases are not warranted.

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APPENDIX   A

PHYSICAL AND CHEMICAL PROPERTIES OF CHLOROFORM

I. PHYSICAL AND CHEMICAL PROPERTIES

Chemical Abstracts serial number   000067663

Synonyms   Trichloromethane
Trichloroform
Methenyl trichloride
Formyl trichloride
Methyl trichloride

Molecular formula $CHCl_3$

Molecular weight   119.38

Boiling point   61.3°C, 142.3°F (760 mm Hg)

Melting point   -63.2°C, -81.7°F

Vapor pressure   100 mm Hg (10.4°C)
200 mm Hg (25°C)

Optical rotation $n_D^{20} = 1.4476$

Specific gravity   1.48069 (25°C),
(water = 1.000 at 4°C)

Solubility   1.0 g/100 ml H_2O at 15°C
1 ml in 200 ml H_2O (25°C);
soluble in ethanol, ethyl ether,
benzene, acetone, and carbon di-
sulfide

Explosive limit   None

Flash point   None

Vapor density   4.0 g/liter (25°C; 760 mm Hg)

Conversion factors (25°C; 760 mm Hg)   1 mg/liter = 205 ppm
1 mg/cu m = 0.205 ppm
1 ppm   = 4.89 mg/cu m

Source: NCI 1977

APPENDIX B

PRODUCTION PROCESS DESCRIPTION

AND

RELATED EMISSION CALCULATION

PROCESS DESCRIPTIONS

In the United States the main processes of producing chloromethanes consist of methanol hydrochlorination followed by further chlorination of the methyl chloride produced. As of May 1977 about 90% of methyl chloride, 75% of methylene chloride, and 77% of chloroform capacities in the United States were based on these processes. Some carbon tetrachloride is formed as a by-product in the chlorination of methyl chloride but is not generally directly purified into product by domestic producers. The unpurified carbon tetrachloride is either sold as is or is used in-house as feed to carbon tetrachloride--perchloroethylene producing facilities.

METHANOL HYDROCHLORINATION AND METHYL CHLORIDE CHLORINATION PROCESSES

Basic Process

Although some domestic producers manufacture methyl chloride exclusively by hydrochlorination of methanol, it is common practice to combine this reaction with the continuous chlorination of methyl chloride to produce methylene chloride and chloroform, along with carbon tetrachloride in small amounts as a by-product. These two processes are discussed as an integral process for the purpose of this report.
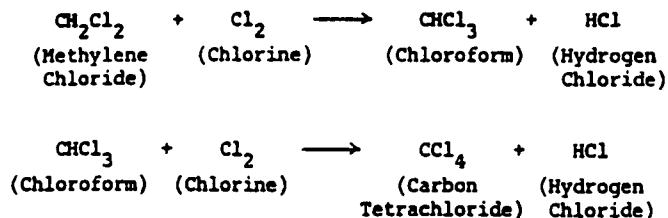
Methyl chloride is produced by the reaction

$$CH_3OH \ + \ HCl \ \longrightarrow \ CH_3Cl \ + \ H_2O$$
(Methanol) (Hydrogen   (Methyl   (Water)
             Chloride)   Chloride)
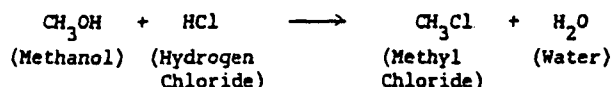
Methylene chloride, chloroform, and by-product carbon tetrachloride are then produced from methyl chloride by the reactions

$$CH_3Cl \ + \ Cl_2 \ \longrightarrow \ CH_2Cl_2 \ + \ HCl$$
(Methyl   (Chlorine)   (Methylene   (Hydrogen
Chloride)   Chloride)   Chloride)
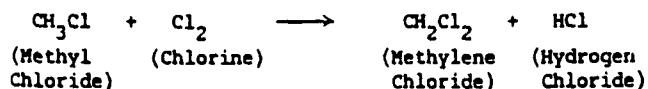
Source: Reprinted from Hobbs and Stuewe 1978,
          Hobbs and Stuewe 1979a

$$CH_2Cl_2 \quad + \quad Cl_2 \quad \longrightarrow \quad CHCl_3 \quad + \quad HCl$$
(Methylene   (Chlorine)   (Chloroform) (Hydrogen
 Chloride)   Chloride)

$$CHCl_3 \quad + \quad Cl_2 \quad \longrightarrow \quad CCl_4 \quad + \quad HCl$$
(Chloroform) (Chlorine)   (Carbon   (Hydrogen
                             Tetrachloride) Chloride)

A typical continuous-process flow diagram for the basic process is shown in Fig. B-1

Methanol is hydrochlorinated by feeding equimolar proportions of vaporized methanol (Stream 1) and hydrogen chloride (Stream 2) at 180--200°C to the hydrochlorination reactor. The reactor is packed with any one of a number of catalysts, including alumina gel, cuprous or zinc chloride on activated carbon or pumice, or phosphoric acid on activated carbon. The reactor is maintaned at a temperature of about 350°C. The reaction is exothermic. Methanol conversion of 95% is typical.

The reactor exit gases (Stream 3) enter the quench tower, where unreacted hydrogen chloride and methanol are removed by water scrubbing. The discharge from the quench tower (Stream 4) is stripped of virtually all dissolved methyl chloride and most of the methanol, both of which are recycled to the hydrochlorination reactor (Stream 5). The remaining aqueous solution from the stripper (Stream 6) consists of dilute hydrochloric acid, which is used in-house or is sent to waste-water treatment.

Methyl chloride from the quench tower (Stream 7) is fed to the drying tower, where concentrated sulfuric acid removes residual water. The dilute sulfuric acid effluent (Stream 8) is sold or is reprocessed on-site.

A portion of the dried methyl chloride (Stream 9) is compressed, cooled, and liquefied as product. The rest of the dried methyl chloride (Stream 10) is fed to the chlorination reactor. The methyl chloride and chlorine (Stream 11) are mixed in the reaction chamber to form methylene chloride and chloroform, along with hydrogen chloride and a small amount of carbon tetrachloride. The reactions are exothermic.
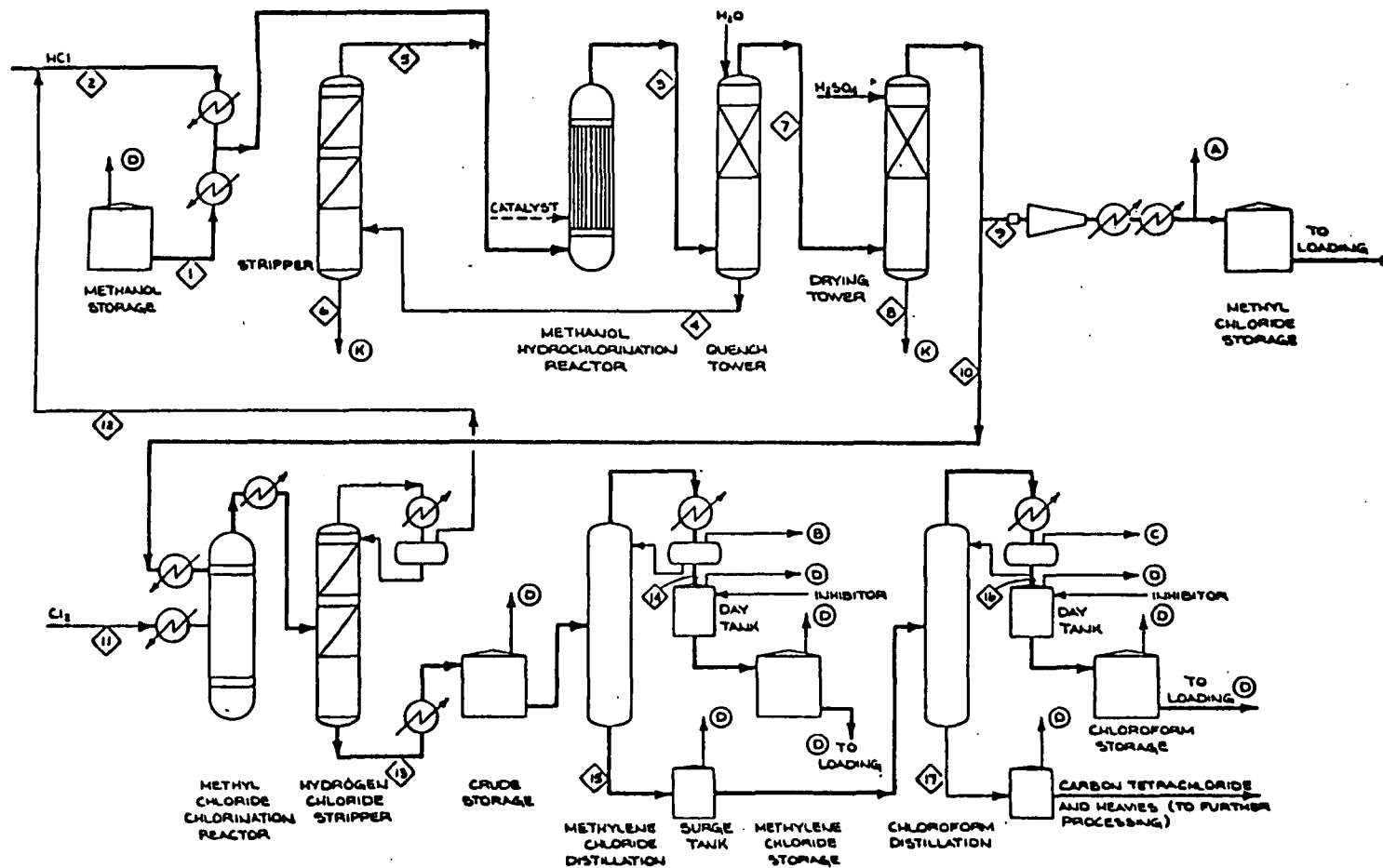
Figure B.1 Process Diagram for Production of Chloroform by Methanol Hydrochlorination
Followed by Methyl Chloride Chlorination

Source: Hobbs and Stuewe 1978

Hydrogen chloride is stripped from the condensed crude product and is recycled to the methanol hydrochlorination reactor (Stream 12). The amounts of individual products (methyl chloride, methylene chloride, chloroform, and by-product carbon tetrachloride) determine whether sufficient hydrogen chloride by-product will be available for operation of the reactor. The crude methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 13) are transferred to a storage tank, which feeds to the methylene chloride distillation column. The methylene chloride product from this distillation (Stream 14) is fed to a day tank, where inhibitors are added as stabilizers, and is then sent to methylene chloride storage and loading. Bottoms from methylene chloride distillation (Stream 15) go to the chloroform distillation column. The chloroform product (Stream 16) is also taken to a day tank where inhibitors are added for control of hydrochloric acid, and then sent on to storage and loading. Bottoms from chloroform distillation (Stream 17) consist of crude carbon tetrachloride, which is stored for subsequent transfer to a separate carbon tetrachloride--perchloroethylene process or is sold.

Process emissions originate at the vents used for purging inert gases from the condensers associated with methyl chloride product recovery (Vent A), with distillation of methylene chloride (Vent B), and with distillation of chloroform (Vent C), as shown in Fig. B-1. Fugitive emissions occur when leaks develop in valves, pumps, seals, or other equipment. Corrosion caused by the hydrogen chloride and chlorine in the process can result in leaks, which hinder control of fugitive emissions.

Emissions result from the storage of feed material, intermediates, products, and by-products and from handling of the products.

Two potential sources of secondary emissions (K on Fig. B-1) are aqueous wastes from the methyl chloride stripper and waste sulfuric acid from the methyl chloride drying tower.

Methane Chlorination Process

Methane can be chlorinated thermally, photochemically, or catalytically, with thermal chlorination being the most important method.[1] Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are produced in this process by the following reactions:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
(methane)   (chlorine)   (methyl chloride)   (hydrogen chloride)

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
(methyl chloride)   (chlorine)   (methylene chloride)   (hydrogen chloride)

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
(methylene chloride)   (chlorine)   (chloroform)   (hydrogen chloride)

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$
(chloroform)   (chlorine)   (carbon tetrachloride)   (hydrogen chloride)
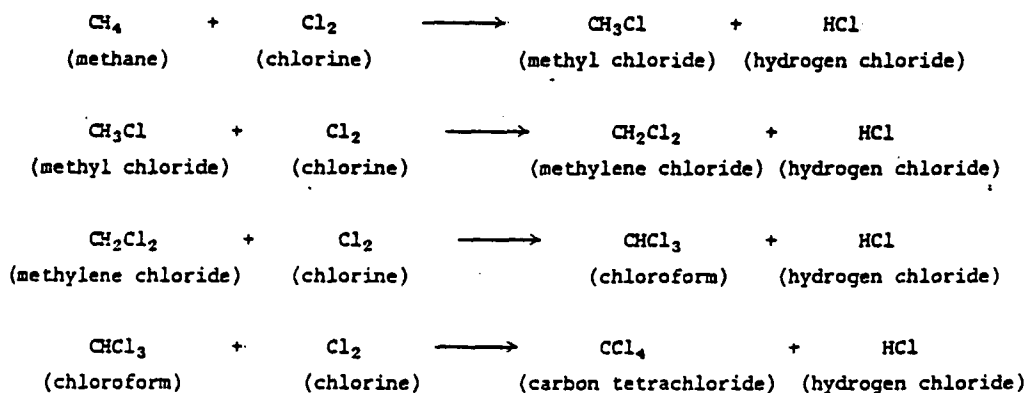
A typical continuous process flow diagram for the basic process is shown in Fig. B-2.

Methane (Stream 1) is mixed with chlorine (Stream 2); then the mixture is pre-heated before it is fed to the chlorination reactor, which is operated at a temperature of about 400°C[1] and a pressure of about 200,000 Pa.[2] Nearly 100% chlorine conversion and 65% methane conversion are typical with product yields of about 58.5% methyl chloride, 29.3% methylene chloride, 9.7% chloroform and 2.3% carbon tetrachloride.[3] (Methyl chloride can be recycled to the reactor after separation to enhance yields of the other chloromethanes.) Gases exiting the reactor (Stream 3) are partly condensed and then scrubbed with chilled chloro-methanes from the process to absorb most of the chloromethanes from unreacted methane and by-product hydrogen chloride. The unreacted methane and by-product hyrogen chloride from the absorber (Stream 4) are fed serially to a hydrogen chloride absorber, caustic scrubber, and drying column, with the purified methane (Stream 5) being recycled to the chlorination reactor.

Source: Reprinted from Hobbs and Stuewe 1979a

Figure B-2   Process Flow Diagram for Production of Chloromethanes by Methane Chlorination

Source: Hobbs and Stuewe 1979a

Condensed material from the separator and liquid effluent from the absorber are combined (Stream 6) and fed to a stripper. Overheads from the stripper, which include hydrogen chloride, methyl chloride, and some of the higher boiling chloromethanes (Stream 7), are fed to a water scrubber, where most of the hydrogen chloride is removed as weak hydrochloric acid (Stream 8). The overheads are then scrubbed with dilute sodium hydroxide solution to remove residual hydrogen chloride. Water is then removed from the crude chloromethanes in a drying column.

The crude chloromethanes from the drying column (Stream 9) are compressed, condensed, and fed to a methyl chloride distillation column. Methyl chloride from the distillation column can be recycled back to the chlorination reactor (Stream 10) or be condensed and then transferred to storage and loading as product (Stream 11).

Crude methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 12) are neutralized, dried, and combined with bottoms from the methyl chloride distillation column (Stream 13) in a crude storage tank. The crude chloromethanes (Stream 14) pass to a methylene chloride distillation column. Methylene chloride from the overheads (Stream 15) is condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product methylene chloride is transferred to product storage and loading. Bottoms from the methylene chloride distillation column (Stream 16) are fed to a chloroform distillation column, with chloroform overheads (Stream 17) being condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product chloroform is transferred to storage and loading. Bottoms from the chloroform distillation column (Stream 18) are fed to a carbon tetrachloride distillation column, with carbon tetrachloride overheads (Stream 19) being condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product carbon tetrachloride is transferred to storage and loading. Bottoms from the carbon tetrachloride distillation column are incinerated.

Vented gases from the four distillation columns could be recycled to the absorber, as is indicated in Fig. B-2.

Process emissions from the model plant result from venting of the inert gases from the recycle methane stream (Vent A, Fig. B-2, from regeneration of the methane recycle stream drying bed (Vent B, Fig. B-2 · , and from emergency venting of the distillation-area inert gases (Vent C.)

Fugitive emissions can occur when leaks develop in valves, pump seals, and other
equipment. Corrosion caused by the hydrogen chloride and chlorine in the process
can result in leaks that hinder control of fugitive emissions.

Emissions result from the storage of intermediates and products and from the
handling of products.

Potential sources of secondary emissions (K on Fig. B-2 .) are aqueous discharges
from the three caustic scrubbers, the sulfuric acid drying column, and the dryer.
Another potential source is the incineration of heavies from carbon tetrachloride
distillation.

APPENDIX B

Breathing Losses of Chloroform from the Methyl Chloride Chlorination Process

Calculations for estimation of breathing losses from fixed storage tanks are detailed below based on an empirical formula developed by API which relates losses to several variables related to storage (USEPA 1977). Table 2.4 shows assumptions which were made regarding storage. Section 2.1.2.1 further discusses the assumptions used in making these estimates.

$$LB = 2.21 \times 10^{-4} m \left[\frac{P}{14.7-P} \right]^{0.68} \times D^{1.73} \times H^{0.51} \times T^{0.5} \, T_p c K_c$$

where LB = fixed roof breathing losses (lb/day)

m = molecular weight = 119

P = true vapor pressure at bulk liquid conditions (psia) = 3.259

D = tank diameter; variable (Table 2.4)

H = average vapor space height; variable (Table 2.4)

T = average ambient temperature change from day to night

Tp = paint factor; assume 1

c = adjustment factor for small diameter tanks; variable

Kc = crude oil factor = 1

7,000 gallon (26,250 ℓ) (12 tanks)

$$LB = 2.21 \times 10^{-4}(119) \left[\frac{3.259}{14.7-3.259} \right]^{0.68} \times 10^{1.73} \times 6.5^{.51} \times 20^{.5} \times 1 \times 0.51 \times 1$$

$$= 0.0263 \times 0.0263 \times 0.28^{0.68} \times 10^{1.73} \times 6.5^{0.51} \times 20^{0.5} \times 1 \times 0.51 \times 1$$

$$= 0.0263 \times 0.42 \times 53.7 \times 2.5 \times 4.47 \times 0.51 \times 1$$

$$= 3.4 \text{ lb/day}$$

3.4 lb/day x 0.454 kg/lb x 12 tanks x 365 days = 6.8 kkg

16,000 gallon (60,000 ℓ) (2 tanks)

$$LB = 2.21 \times 10^{-4}(119) (0.28)^{0.68} \times 15^{1.73} \times 6.5^{0.51} \times 20^{0.5} \times 1 \times .75 \times 1$$

$$= 0.0263 \times 0.42 \times 108 \times 216 \times 4.5 \times 1 \times .75 \times 1 = 10.5 \text{ lb/day}$$

0.5 lb/day x 0.454 kg/lb x 2 tanks x 365 days = 3.5 kkg

<u>50,000 gallon (185,000 ℓ) (6 tanks)</u>

LB = $2.21 \times 10^{-4}(119)\ (0.28)^{0.68} \times 22^{1.73} \times 10^{0.51} \times 20^{0.5} \times 1 \times .83 \times 1$

   = $0.0263 \times 0.42 \times 210 \times 3.2 \times 4.5 \times 1 \times .83 \times 1 = 27.7$ lb/day

27.7 lb/day x 0.454 kg/lb x 6 tanks x 365 days = 27.5 kkg

<u>100,000 gallons (375,000 ℓ)</u>

LB = $2.21 \times 10^{-4}(119)\ (0.28)^{0.68} \times 33^{1.73} \times 17^{.51} \times 20^{.5} \times 1 \times 1 \times 1$

   = $0.0263 \times .42 \times 423.7 \times 4.2 \times 4.5 \times 1 \times 1 \times 1$

   = 88.4 lb/day

88.4 lb/day x 0.454 kg/lb x 2 tanks x 365 days = 29.3 kkg

Assuming refrigerated vapor recovery of 75 percent efficiency, then actual chloroform emissions from these tanks are:

    0.293 kkg x 0.25 = 7.3 kkg

<u>461,000 gallons (1,720,000 ℓ) (2 tanks)</u>

LB = $2.21 \times 10^{-4}(119)\ (0.28)^{0.68} \times 70^{1.73} \times 17.5^{.51} \times 20^{.5} \times 1 \times 1 \times 1$

   = $0.0263 \times 0.42 \times 1,556 \times 4.3 \times 4.47 \times 1 \times 1 \times 1$

   = 330 lb/day

330 lb/day x 0.454 kg/lb x 2 tanks x 365 days = 109 kkg

Again, assuming 75 percent recovery by refrigerated vapor condensation, then:

(Total emissions) = (Total uncontrolled emissions) x (percent unrecovered)

    109 kkg x 0.25 = 27.3 kkg

<u>Working Losses of Chloroform from Methyl Chloride Chlorination Process</u>

    Calculations for working losses from fixed roof storage are detailed below, using the assumptions shown in Table 2.5 and the following empirical formula (USEPA 1977):

$LW = 2.4 \times 10^{-2}\ MPKnKc$

where LW = fixed roof working losses (lb/10^3 gal)

M = molecular weight = 119

P = true vapor pressure (psia) = 3.259

Kn = turnover factor - variable

Kc = crude oil factor = 1

7,000 gallon tanks (26,250 ℓ) (12 tanks)

$LW = 2.4 \times 10^{-2} \times MPKnKc$

$.024 \times 119 \times 3.259 \times 0.44 \times 1 = 4.1$ lb/10^3 gal

Storage requires eight 7,000 gallon (26,250 ℓ) tanks of which all are 50 percent full. Turnover in these tanks occurs 125 times/yr. Therefore, annual throughput is estimated as follows:

(No. of tanks) x (Tank volume) x (percent capacity) x (No. of turnovers) = volume throughput

8 tanks x 7,000 gallons x 50 percent capacity x 125 turnovers = 3,500 x 10^3 gallons

4.1 lb/10^3 gallons x 3,500 x 10^3 gallons = 14.4 x 10^3 lb

14.4 x 10^3 lb x 454 x 10^{-6} kkg/lb = 6.5 kkg

16,000 gallons (60,000 ℓ) (2 tanks)

$LW = 2.4 \times 10^{-2}\ MPKnKc$

$.024$ lb/10^3 gal x 110 lb/lb mole x 3.259 x .44 x 1 = 4.1 lb/10^3 gal

2 tanks x 16,000 gallons x 50 percent x 125 turnovers = 2,000 x 10^3 gal throughput

4.1 lb/10^3 gallon x 2,000 x 10^3 gallons = 8.2 x 10^3 lb

8.2 x 10^3 lb x 454 x 10^{-6} kkg/lb = 3.7 kkg

50,000 gallons (187,500 ℓ) (6 tanks)

LW = 2.4 x 10^{-2} MPKnKc

.024 lb/10^3 gal x 119 lb/lb mole x 3.259 x 1 x 1 = 9.3 lb/10^3 gal

6 tanks x 50,000 gallons x 50 percent x 20 turnovers = 3,000 x 10^3 gàl throughput

9.3 lb/10^3 gal x 3,000 x 10^3 gal = 27.9 x 10^3 lb

27.9 x 10^3 lb x 454 x 10^{-6} kkg/lb = 12.7 kkg

100,000 gallons (375,000 ℓ) (2 tanks)

LW = 2.4 x 10^{-2} MPKnKc

.024 lb/10^3 gal x 110 lb/mole x 3.259 x 1 x 1 = 9.3 lb/10^3 gal

2 tanks x 100,000 gallons x 50 percent x 20 turnovers = 2,000 x 10^3 gal throughput

9.3 lb/10^3 gal x 2,000 x 10^3 gal = 18.6 x 10^3 lb

18.6 x 10^3 lb x 454 x 10^{-6} kkg/lb = 8.4 kkg

Assuming refrigerated vapor recovery at 75 percent efficiency, emissions are:

    8.4 kkg x 0.25 = 2.1 kkg

461,000 gallons (1,728,750 ℓ) (2 tanks)

LW = 2.4 x 10^{-2} MPKnKc

.024 x 110 x 3.259 x 1 x 1 = 9.3 lb x 10^3 gal

2 tanks x 460,000 gallons x 50 percent capacity x 20 turnovers = 9,220 x 10^3 gal thoughput

9.3 lb/10^3 gallon x 9,220 x 10^3 gal = 85.7 x 10^3 lb

85.7 x 10^3 lb x 454 x 10^{-6} kkg/lb = 38.9 kkg

Assuming refrigerated vapor recovery at 75 percent efficiency, then actual emissions are:

$$38.9 \text{ kkg} \times 0.25 = 9.7 \text{ kkg}$$

Breathing Losses of Chloroform from the Methane Chlorination Process

Breathing losses from the storage of chloroform are calculated below using the assumptions shown in Table 2.7 and the following empirical formula:

$$LB = 2.21 \times 10^{-4} \text{ m} \left[\frac{P}{14.7-P} \right]^{0.68} \times D^{1.73} \times H^{0.51} \times T^{0.5} \text{ TpCKc}$$

where LB = fixed roof working losses (lb/day)

    m = molecular weight = 119

    P = true vapor pressure at bulk conditions (psia) = 3.259

    D = tank diameter

    H = average vapor space height

    T = ambient temperature change from day to night - assume 20°

    Tp = paint factor; assume 1

    C = adjustment factor for small diameter tanks - variable

    Kc = crude oil factor = 1

$$LB = 2.21 \times 10^{-4} \text{ (119)} \left[\frac{3.259}{14.7-3.259} \right]^{0.68} \times D^{1.73} \times H^{0.51} \times T^{0.5} \times \text{TpCKc}$$

7,000 gallons (26,250 ℓ) (5 tanks)

$$0.0263 \times 0.28^{0.68} \times 10^{1.73} \times 0.65^{0.51} \times 20^{0.5} \times 1 \times .51 \times 1$$

$$0.0263 \times .42 \times 53.7 \times 2.5 \times 4.47 \times 1 \times 0.51 \times 1 = 3.4 \text{ lb/day}$$

$$3.4 \text{ lb/day} \times 454 \times 10^{-6} \text{ kkg/lb} \times 5 \text{ tanks} \times 365 \text{ days} = 2.8 \text{ kkg}$$

16,000 gallons (60,000 ℓ) (1 tank)

$$0.0263 \times 0.28^{0.68} \times 15^{1.73} \times 6.5^{0.51} \times 20^{0.5} \times 1 \times .75 \times 1$$

$$0.0263 \times 0.42 \times 108 \times 2.6 \times 4.5 \times 1 \times .75 \times 1 = 10.5 \text{ lb/day}$$

$$10.5 \text{ lb/day} \times 454 \times 10^{-6} \text{ kkg/lb} \times 1 \text{ tank} \times 365 \text{ days} = 1.7 \text{ kkg}$$

<u>300,000 gallons (1,125,000 ℓ) (1 tank)</u>

$0.0253 \times 28^{0.68} \times 51^{1.73} \times 12^{0.51} \times 20^{0.5} \times 1 \times 1 \times 1$

$0.0253 \times .42 \times 900 \times 3.6 \times 4.5 \times 1 \times 1 \times 1 = 161$ lb/day

161 lb/day $\times 454 \times 10^{-6}$ kkg/lb $\times 365$ days = 26.7 kkg

Assuming refrigerated vapor recovery at 75 percent efficiency, then (chloroform releases from the $1.1 \times 10^6 \ \ell$ tank) = (total emission) $\times$ (percent not recovered)

26.7 kkg $\times$ 0.25 = 6.7 kkg

Total breathing emissions from storage = 2.8 kkg + 1.7 kkg + 6.7 kkg = 11.2 kkg

<u>Working Losses of Chloroform from Methane Chlorination Process</u>

Working losses are estimated using the following empirical formula:

$LW = 2.4 \times 10^{-2} \, MPK_nK_c$

where LW = fixed roof working losses (lb/10^3 gal)

M = molecular weight = 119

P = true vapor pressure at bulk liquid conditions = 3.259

Kn = turnover factor - variable

Kc = crude oil factor

<u>7,000 gallon tanks (26,250 ℓ) (5 tanks)</u>

$LW = 2.4 \times 10^{-2} \times 119 \times 3.259 \times 0.44 \times 1 = 4.1$ lb/10^3 gal

Storage requires five 7,000 gallon tanks which are 50 percent full. Turnover in these tanks is 125 times/yr. Therefore, annual throughput is estimated as follows:

(Number of tanks) x (tank volume) x (percent capacity) x (number of turnovers) = volume throughput

5 tanks x 7,000 gallons x 50 percent capacity x 1.25 turnovers = 2,220 x 10^3 gallons

4.1 lb/10^3 gallons x 2,200 x 10^3 gallons = 9 x 10^3 lb

9 x 10^3 lb x 454 x 10^{-6} kkg/lb = 4.1 kkg

16,000 gallon tanks (60,000 ℓ) (1 tank)

0.024 lb/10^3 gal x 110 lb/lb mole x 3.259 x .44 x 1 = 4.1 lb/10^3 gal

16,000 gallons x 1 tank x 50 percent capacity x 125 turnovers = 1,000 x 10^3 gal throughput

4.1 lb/10^3 gallons x 1,000 x 10^3 gallons = 4.1 x 10^3 lb

4.1 x 10^3 lb x 454 x 10^{-6} kkg/lb = 1.9 kkg

300,000 gallon tanks (1,125,000 ℓ) (1 tank)

.024 lb/10^3 gal x 110 lb/lb mole x 3.259 x 1 x 1 = 9.3 lb/10^3 gal

300,000 gallons x 1 x 50 percent capacity x 20 turnovers = 3,000 x 10^3 gal throughput

9.3 lb/10^3 gal x 3,000 x 10^3 gal = 27.9 x 10^3 lb

27.9 x 10^3 lb x 454 x 10^{-6} kkg/lb = 12.7 kkg

Again, assuming 75 percent vapor recovery, then, chloroform emissions from the 300,000 gallon tank:

12.7 kkg x .25 = 3.2 kkg

Total working losses:

(4.1 kkg) + (1.9 kkg) + (3.2 kkg) = 9.2 kkg

APPENDIX C
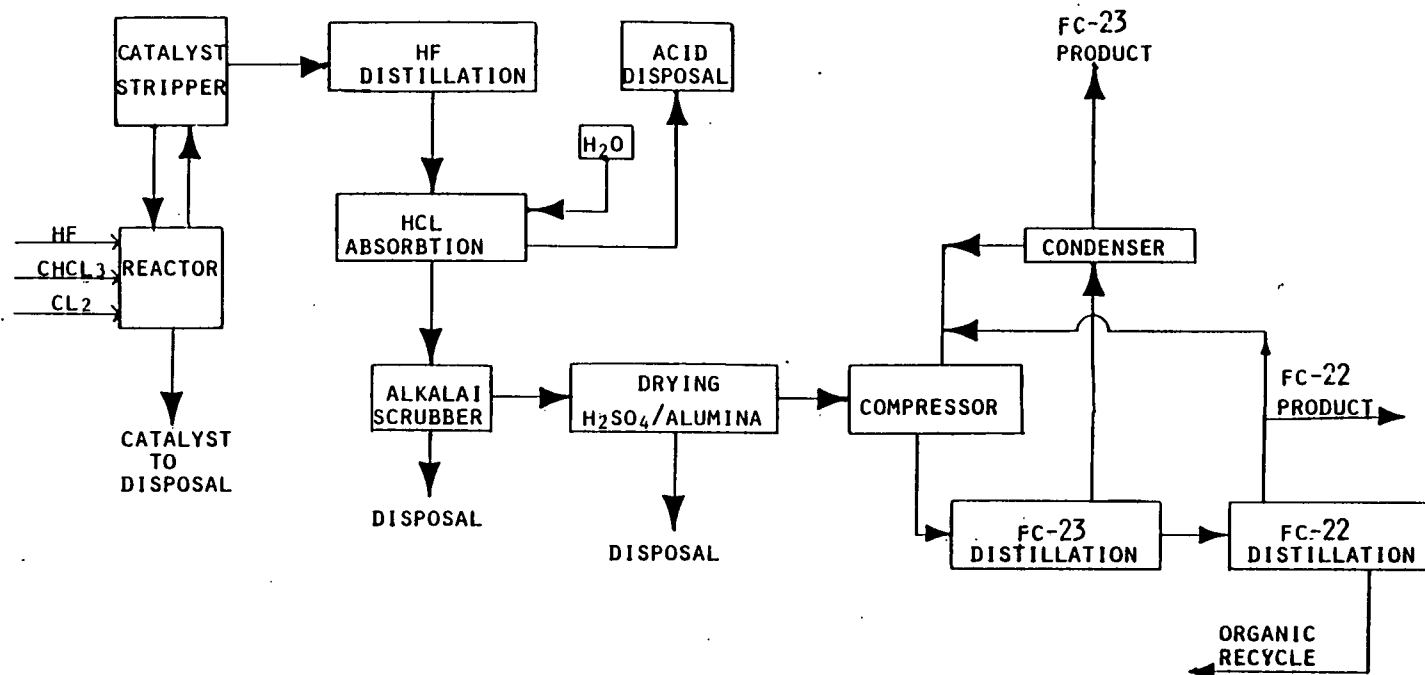
PROCESS DIAGRAMS FOR

CFC-22 PRODUCTION

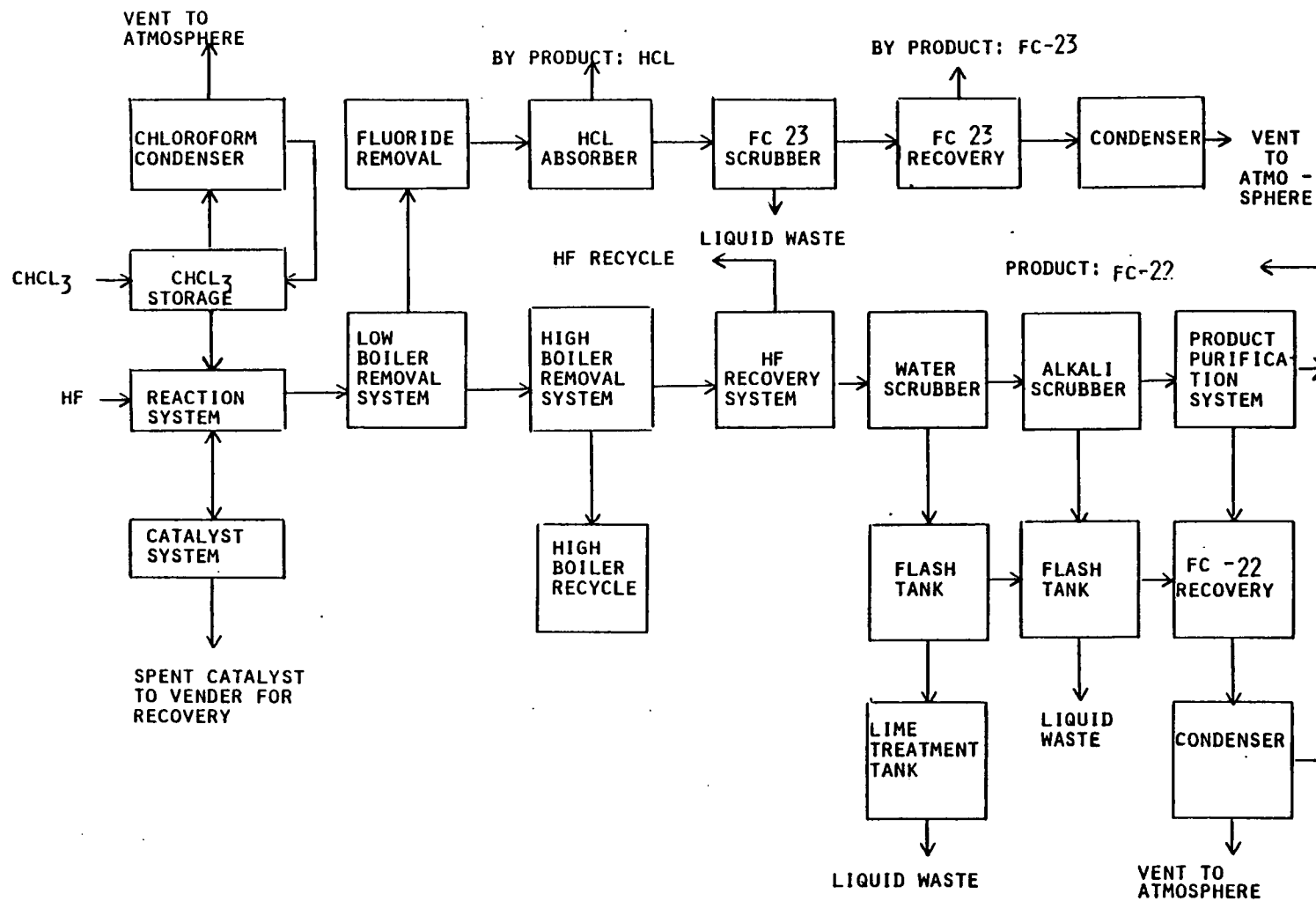Figure C-1 Allied Chemical Process for CFC-22 Production
Source: Pitts 1978

Figure C-2 Du Pont Process for CFC-22 Production
         Source: Smith 1978b