California Air Resources Board

Proposed Identification of
CHLOROFORM

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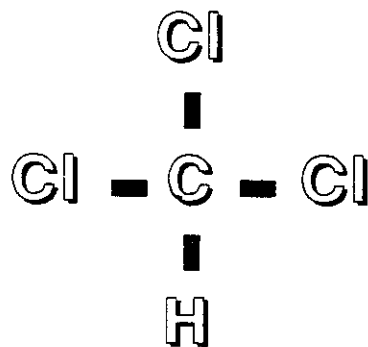
As a Toxic Air Contaminant

Part A
Exposure Assessment

State of California
Air Resources Board
Stationary Source Division

SEPTEMBER 1990

PROPOSED IDENTIFICATION OF CHLOROFORM
AS A TOXIC AIR CONTAMINANT

TECHNICAL SUPPORT DOCUMENT

REPORT TO THE AIR RESOURCES BOARD ON CHLOROFORM (CHCl$_3$)

PART A

PUBLIC EXPOSURE TO, SOURCES, AND EMISSIONS OF
CHLOROFORM IN CALIFORNIA

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REPORT TO THE AIR RESOURCES BOARD ON CHLOROFORM

Part A - Public Exposure to, Environmental Fate of, and Sources of
Atmospheric Chloroform in California

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I. INTRODUCTION

Chloroform is one of the family of chemicals known as chlorinated alkanes, chlorinated aliphatic hydrocarbon compounds containing single bonds. The formula for chloroform is $CHCl_3$ and the chemical structure is shown in Table II-1. It is known by a variety of synonyms, which include trichloromethane, methane trichloride, methyl trichloride, methenyl trichloride, trichloroform, and formyl trichloride.

Chloroform is directly produced for use as a solvent in laboratories for pharmaceutical manufacturing, government, industry and education, a grain fumigant, and a mold and fungus inhibitor. Direct sources of chloroform emissions include the manufacture of fluorocarbon 22 refrigerants and fluorocarbon 22 fluoropolymers. It is indirectly produced following chlorination of swimming pools and drinking water (for consumption and usage). Other known indirect sources are publicly owned treatment works (POTWs), cooling towers, the bleaching of pulp at paper and pulp mills with chlorine, bleach containing chlorine used for domestic cleaning and laundry, combustion of leaded gasoline, air stripping towers, perchloroethylene (PERC) production, and contamination of chlorinated products. Approximately 750 tons to 1100 tons per year are emitted into the California atmosphere. Chloroform persists in the atmosphere for 150 to 230 days.

This report is an evaluation of chloroform uses, emissions, ambient and indoor concentrations, statewide population exposure, ingestion, and atmospheric persistence and fate. The Air Resources Board (ARB) will consider the findings of this report together with the health effects finding of the Department of Health Services (DHS) to determine if chloroform should be identified as a Toxic Air Contaminant.

II. PHYSICAL AND CHEMICAL PROPERTIES OF CHLOROFORM

Chloroform, ($CHCl_3$), also known as trichloromethane, is a clear colorless volatile liquid with an ethereal scent that is nonflammable and does not form explosive mixtures at atmospheric temperatures and pressures. Chloroform is miscible with most organic solvents, is slightly soluble in water (8,000 mg per liter) and has a molecular weight of 119.38. Chloroform has a vapor pressure of 21.28 kPa (160 mmHg) at 20 °C which causes it to evaporate relatively quickly. Chloroform vapor has over four times the density of air and, in its concentrated gaseous form, will tend to settle to the ground before dispersing. The density of chloroform liquid is 3.27 pounds per gallon. Chloroform decomposes slowly with exposure to sunlight in the presence or absence of air, as well as in the dark in the presence of air. The major products of oxidation include phosgene, hydrogen chloride, chlorine, carbon dioxide and water.

Chloroform vapor does not react with oxygen at temperatures up to 290°C. However at 270°C, nitrogen dioxide oxidizes chloroform to form phosgene, hydrogen chloride, water, and carbon dioxide. Pyrolysis of chloroform vapor occurs at temperatures above 450°C, producing tetrachloroethylene, hydrogen chloride, and minor amounts of other chlorocarbons. Chloroform can be further chlorinated to carbon tetrachloride by elemental chlorine upon irradiation of the vapor. At 225°C to 275°C, bromination of chloroform vapor yields bromochloromethanes. Physical and chemical properties of chloroform are shown in Table II-1.

Table II-1

PHYSICAL PROPERTIES OF CHLOROFORM

Property	Value
Synonyms: trichloromethane, methane trichloride, methyl trichloride, methenyl trichloride, trichloroform, formyl trichloride	
CAS Registry No.	67-66-3
Molecular Weight	119.38
Structural Formula	$\begin{array}{c} Cl \\ | \\ Cl-C-Cl \\ | \\ H \end{array}$
Refractive index, $20^{\circ}C$	1.4467
Autoignition temperature, $^{\circ}C$	above 1,000
Flash point, $^{\circ}C$	None
Melting point, $^{\circ}C$	-63.2
Boiling point, $^{\circ}C$	61.3
Specific gravity, $25/4^{\circ}C$	1.48069
Vapor density, 101 kPa, $0^{\circ}C$, kg/m^3	4.36
Surface tension, mN/m	
Air, $20^{\circ}C$	27.14
Air, $60^{\circ}C$	21.73
Water, $20^{\circ}C$	45.0
Heat capacity, $20^{\circ}C$, $kJ/(kg*K)$	0.979
Critical temperature, $^{\circ}C$	263.4
Critical pressure, MPa	5.45
Critical density, kg/m^3	500
Critical volume, m^3/kg	0.002

Table II-1 (cont.)

PHYSICAL PROPERTIES OF CHLOROFORM

Property	Value
Heat of formation, 25°C, MJ/(kg*mol)	
Gas	-89.66
Liquid	-120.9
Latent heat of evaporation, at bP, kJ/kg	247
Solubility of chloroform in water,	
20°C, g/kg H_2O	8.22
Solubility of water in chloroform, 22°C,	
g/kg chloroform	0.806
Viscosity, liquid, 20°C, mPa*s	0.563
Vapor pressure, kPa	
0°C	8.13
10°C	13.40
20°C	21.28
30°C	32.80
40°C	48.85
50°C	70.13

III. PRODUCTION, USES AND EMISSIONS

Chloroform can be emitted to the air from direct and indirect sources. Direct sources include those where chloroform is used or commercially produced such as in the production of fluorocarbon 22. Indirect sources are those where chloroform is formed as a by-product. An example of the latter is the formation of chloroform from chlorinated water in swimming pools.

It is estimated that approximately 750 tons to 1100 tons per year of chloroform are emitted from known sources in California. Additional emissions may result from unidentified sources and from sources for which emissions can not be quantified at the present time.

A. PRODUCTION

Chloroform is commercially produced in the United States by several facilities, none of which are located in California (U.S. EPA, 1985). The United States had an estimated annual production of 462 million pounds of chloroform for 1987 (CEN, 1988). Figure 1 shows the U.S. production, imports, exports and use of chloroform from 1976 to 1986. During this ten year period, chloroform production increased in the United States at an average annual rate of 4% (CEN, 1987).

B. USES AND EMISSIONS

Direct sources of chloroform emissions include the manufacture of fluorocarbon 22 refrigerants and fluorocarbon 22 fluoropolymers. These two sources accounted for 60% and 30%, respectively, of the chloroform use in the United States in 1982. The Allied Corporation plant in El Segundo is the only producer of fluorocarbon 22 in California. Miscellaneous direct sources of chloroform accounted for 10% of the chloroform used in 1982 and include: pharmaceutical manufacturing, the production of oxybisphenoxarsine (OBPA) and 1,3-diisocyanate, laboratory use, and grain fumigation.

If the upper bound of the chloroform emission estimate from swimming pools is considered (to be conservative), the major indirect sources of chloroform emissions appear to be from the chlorination of swimming pools and drinking water (for consumption and usage). Chloroform is formed during the chlorination of water by a complex reaction mechanism between chlorine and organic precursors in the water, such as humic and fulvic acids. Major factors influencing this reaction are the amount and type of precursor present, temperature, pH, and chlorine dose. These factors will influence both the chloroform formation rate and the chloroform concentration (GCA, 1984). Table III-1 lists the sources and emissions of these categories.

Other known indirect sources are: publicly owned treatment works (POTWs), cooling towers, the bleaching of pulp at paper and pulp mills with chlorine, bleach containing chlorine used for domestic cleaning and laundry, combustion of leaded gasoline, air stripping towers, perchloroethylene (PERC) production, and contamination of chlorinated products. Dow Chemical, USA in Pittsburg is the only facility producing PERC in the State.

1. Direct Uses

Pharmaceutical Manufacturing

Synthetic pharmaceuticals are normally manufactured in a series of batch operations, many of which use solvents such as chloroform. Each step of the process may be a source of chloroform emissions. These steps include dryers, reactors, distillation units, storage and transfer, filters, extractors, centrifuges and crystallizers.

A survey by the Pharmaceutical Manufacturers Association indicates that in 1982 air emissions of chloroform nationwide were 1,600 tons (GCA, 1984). Based on the percentage of pharmaceutical facilities located in California relative to the country, statewide air emissions are estimated to be 190 tons of chloroform per year from pharmaceutical manufacturing facilities (see Appendix A-1).

Oxybisphenoxarsine and 1,3-Diisocyanate Production

Aerojet General Corp. in Sacramento has a permit to produce oxybisphenoxarsine (OBPA) and 1,3-diisocyanate. Both production processes use chloroform as a solvent. OBPA is a fungicide that is combined with rubber to prevent mold growth on gaskets and seals. 1,3-diisocyanate is an intermediate in the production of polyurethane resins and is an additive to fuels for the polaris missiles (U.S. EPA, 1985).

Although Aerojet still holds an active permit, they do not currently produce either OBPA or 1,3-diisocyanate (See Appendix A-2) (Skelton, 1989).

Laboratory Usage

Chloroform is used in hospital, industrial, government, university, and research laboratories as a general reagent and in high pressure liquid chromatography.

Science Applications International Corporation (SAIC) conducted a survey of laboratories in the South Coast Air Basin (SCAB). The survey consisted of questionnaires being sent to 431 out of 861 facilities in SIC codes 7391 (commercial research and development laboratories), 7397 (commercial testing laboratories), and 8071 (medical laboratories). Fifty-eight laboratories had gone out of business or had moved with no forwarding address. Thus, the effective survey size was 373, of which the response rate was 72.4 percent. The results showed that 8.5% of the responding laboratories used chloroform. Estimates of chloroform usage were scaled up to include all the laboratories in the SCAB. Total annual chloroform use (and, therefore, emissions) for all laboratories in the SCAB were estimated to be 4.4 tons (Rogozen, 1988). At this time there is not enough information to make a statewide estimate of chloroform emissions from laboratories.

U.S. PRODUCTION, IMPORTS, EXPORTS & USAGE OF CHLOROFORM
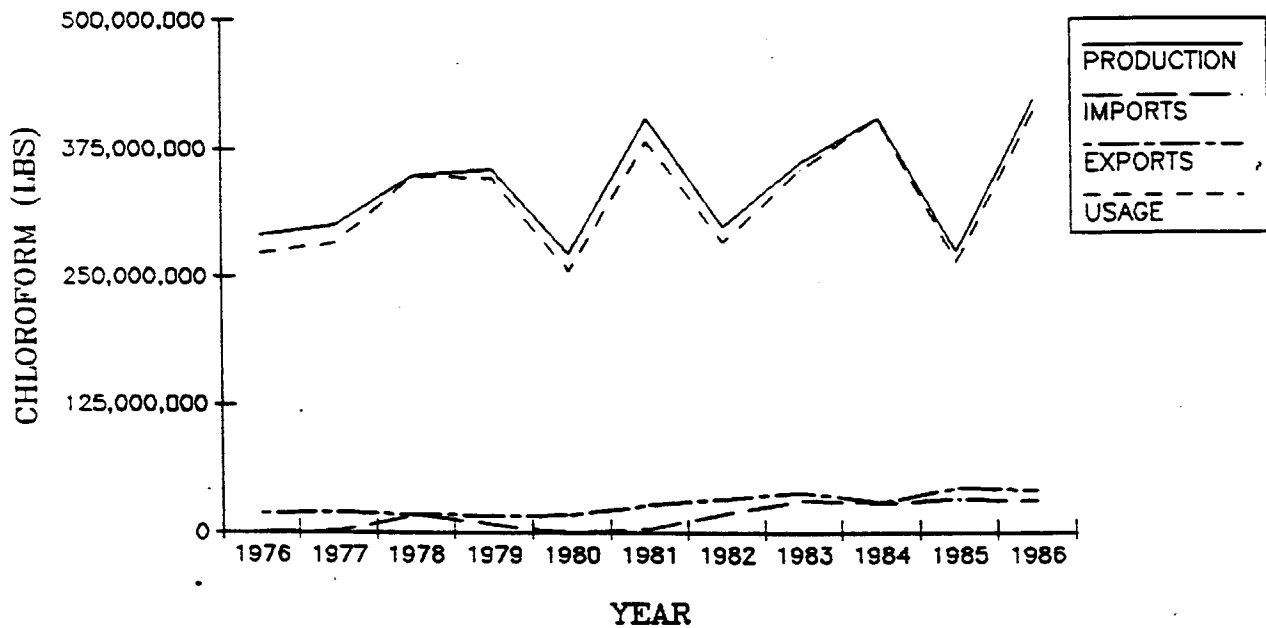
F I G U R E   III-1

Data on Production from: Chemical & Engineering News.

Data on Exports from:
   FT410 Annual (December), U.S. Exports, Schedule B Commodity Groupings,
   Schedule B Commodity by Country, U.S. Department of Commerce.
   FT446 Annual U.S. Imports, Schedule B Commodity by Country, U.S.
   Department of Commerce.

Data on Imports from:
   FT246 Annual, U.S. Imports for Consumption and General Imports, TSUSA
   Commodity by Country of Origin, U.S. Department of Commerce.

Data on Usage estimated from: the sum of the Production and the Exports
   minus the Imports for any given year.

Table III-1
California Chloroform Emission Inventory

Source Type	Emissions[1] (tons/year)	Inventory Year
Direct Uses		
Pharmaceutical Manufacturing	190	1984
OBPA/1,3-Diisocyanate	0	1989
Laboratory Usage	4[2]	1988
Grain Fumigation	0	1987
Fluorocarbon 22 Production	6	1986
Indirect Production		
Swimming Pools	3 - 340[3]	1985
Drinking Water (Consumption/Usage)	300	1987
Publicly Owned Treatment Works	3 - 50	1987
Cooling Towers	3[2]	1988
Pulp & Paper Mills	220[4]	1987
Laundry Bleach	14	1984
Combustion of Leaded Gasoline	Not Available	
Air Stripping Towers	2[5]	1989
Perchloroethylene Production	Not Available	
Contamination of Products	1	1981

Approximately: 750 - 1,100 tons/year

1. The figures in this table may not be the same as in the text due to rounding. Additional emissions may result from unidentified sources and from sources for which emissions have not been estimated.

2. Emission estimates are for the South Coast Air Basin only. Information on other parts of the state are not available at this time.

3. A range is reported to reflect the uncertainty in emission estimates due to minimal test results and wide variability among test data. Although the number of commercial pools statewide was taken into consideration, emissions may be underestimated for commercial pools because commercial pools generally have a larger surface area, more activity, and require more chlorination than residential pools.

4. Represents data from 12 out of 18 pulp & paper mills in California.

5. Emission estimate is for Aerojet General Corporation in Sacramento only. Information on other facilities in the state are not available.

Grain Fumigation

Chloroform has useful anesthetic and toxic properties which make it an effective fumigant or component in a mixture of fumigants. Chloroform is registered by the EPA as a pesticide and has been used as a carrier in grain fumigation, however, chloroform is no longer used or sold as a pesticide in California (DFA, 1987).

Fluorocarbon 22 Production

Chloroform is used as a feedstock in the production of some chlorofluorocarbons, including chlorodifluoromethane ($CHClF_2$) which is known as fluorocarbon 22. Fluorocarbon 22 goes under the trade names of Freon-22 (DuPont) and Genetron-22 (Allied) and is used as a refrigerant, as an intermediate in the production of fluorocarbon resins (fluoropolymers), and to a smaller extent as an aerosol propellant. The only producer of fluorocarbon 22 located in California is the Allied Corporation plant in El Segundo. The emissions are estimated to be 5.6 tons of chloroform per year from fluorocarbon 22 production (See Appendix A-3).

2. Indirect Production

Swimming Pools

The water in swimming pools is treated with chlorine in order to reduce the bacterial load on filters, oxidize organic matter, reduce odor, assist in color removal, and reduce bacteria and control plankton growth (Todd, 1970).

There is a wide range of chloroform emission estimates from swimming pools due to such variabilities as photodegradation of chloroform and its precursors, complexity of chemical reactions, differing chlorination practices, uncertain test protocal, limited test data, varying loading factors, and uncertain number of pools. The staff estimates that swimming pools in California emitted approximately 3 tons to 340 tons of chloroform in 1985 (See Appendix A-4). These emission

estimates do not include commercial pools such as in health clubs. The upper limit was estimated using the method developed by Science Applications International Corporation (SAIC) while the lower limit was estimated by adjusting the upper estimate based on preliminary data from an on-going study by the University of California at Davis (Chang, D., 1990).

In the SAIC study, chloroform emission flux of a residential swimming pool of approximately 15,880 gallons was studied. This pool had been covered and had not been chlorinated for approximatley three weeks prior to testing. Based on the measured flux rates of chloroform under still and agitated conditions, SAIC estimated that swimming pools emit approximately 12 to 320 ug/m^2- min (Rogozen et al., 1987). SAIC further assumed the fractions of time the pool spent under each condition within a year (i.e., still or agitated) to estimate a weighted average flux rate of 22.3 ug/m^2- min.

To estimate the number of swimming pools, the staff used the method developed by SAIC to categorize swimming pools into three types, inground pools, above ground pools, and spas and hot tubs. The total number of each type of pool was obtained from the National Spa and Pool Institute (NSPI) Survey 1985 (NSPI, 1985). An estimate of the surface area of swimming pools was then calculated by multiplying the number of pools by the assumed surface area for each type of pool. Using the emission factor developed by SAIC, along with the estimated surface area of swimming pools, the staff estimates that swimming pools could be responsible for an upper limit of approximately 340 tons of chloroform per year.

Although a number of commercial pools statewide was taken into consideration in the estimate, commercial pools are assumed to have the same surface area as residential pools due to insufficient data. The flux rate was developed for residential pools, but was also applied to commercial pools in the absence of other data. Emissions may be underestimated because commercial pools generally have a larger surface area, more activity, and require more chlorination than residential pools.

In a study being conducted by the University of California at Davis (UCD), researchers have made preliminary measurements of the concentrations of chlorine and chloroform from a residential "lap" pool and an outdoor recreational pool (Chang, D., 1990). The residential pool was similar in size (approximately 15,000 gallons) to the pool studied by SAIC. These preliminary data from the UCD study indicate a molar ratio of approximately 10 to 100 times lower than that calculated from the SAIC data (Rogozen et al., 1988 - Table 8.2-2 and pg. 8-38). A molar ratio is defined as the moles of chloroform formed per mole of chlorine consumed by chlorination (as discussed by SAIC).

Comparing the molar ratios from the UCD study and the SAIC study, chloroform emission estimates from swimming pools may be lower by a factor of 100. Thus the staff estimates the lower limit of emissions by adjusting the upper limit by dividing by a factor of 100. The resultant lower limit of emissions is therefore approximatley 3 tons per year.

Drinking Water (For Consumption and Usage)

Drinking water is also treated with chlorine. Similar to swimming pools, chlorination of drinking water reduces the bacterial load on filters, oxidizes organic matter, reduces odor, assists in color removal, reduces bacteria, and controls plankton growth in reservoirs (Todd, 1970). Although there is a higher organic content in untreated water during the winter months, the more extensive oxidation of certain chemicals that occurs during the summer months requires a higher chlorine feed. As a result, more chloroform is produced in drinking water during the summer than in the winter (GCA, 1984). Drinking water is often dispersed and aerated, speeding the evaporation of chloroform. Assuming all the chloroform will evaporate there is approximately 300 tons per year emitted to the air (See Appendix A-5).

Publicly Owned Treatment Works

Publicly Owned Treatment Works (POTWs) are wastewater treatment systems. Specifically, they include the wastewater collection system, wastewater and sludge treatment facilities, the facility's effluent systems, and the sludge disposal systems (UCD, 1987).

The University of California, Davis conducted a study on POTWs for the ARB in which 16 potentially toxic organic compounds, including chloroform were studied (UCD, 1987). The report included the development of a methodology to predict emissions from 29 major POTWs in California on a statewide, county-by-county, and plant-by-plant basis.

The study estimates air emissions of 36 tons of chloroform per year for California from POTWs. The study did determine that there were significantly larger concentrations of chloroform in the effluent streams than in the influent streams of facilities that post-chlorinated. Post-chlorination is chlorination of wastewater discharged from the facility. The authors of the study predicted that post-chlorination at the wastewater treatment facilities could increase chloroform emissions from 36 tons per year to approximately 50 tons per year (UCD, 1987). Subsequent to the 1987 study by UCD, the staff of the Los Angeles County Sanitation District conducted source testing on three POTWs under its jurisdiction and estimated that chloroform emissions from these POTWs ranged from 0.7 to 2.5 ug/L of wastewater treated at the facility. Using these emission factors and the estimated amount of wastewater treated statewide from the UCD study - 2,800 million gallons per day (UCD, 1987), the staff estimates that 3.4 tons per year are emitted from these facilities and will represent the lower limit estimated range of emissions.

For the purposes of this report, the annual statewide air emissions of chloroform from POTWs are therefore estimated to range from 3 tons to 50 tons.

Cooling Towers

Cooling towers are commonly used to eliminate waste heat from air conditioning systems, industrial processes, and power generation. In some of these towers chlorine is added to the cooling water to prevent fouling (formation of slime-forming organisms) of the heat exchange condenser tubes, which can inhibit the heat exchange process. Chloroform is formed by the aqueous reaction of chlorine with organic matter in the cooling water. Chloroform air emissions occur when the chloroform formed in the cooling water evaporates to the atmosphere.

SAIC conducted a survey of industrial cooling towers in the South Coast Air Basin. Based on this study, SAIC developed an emission factor of 0.0034 lb of chloroform formed for each pound of chlorine (Cl_2) used to chlorinate the cooling waters (Rogozen, 1988). Applying this factor, the SAIC (Rogozen et. al 1988) has estimated that 2.3 tons per year of chloroform are emitted into the atmosphere from industrial cooling towers.

SAIC also contacted the five utility power plants using cooling towers. In steam electric power generation, cooling water is used to absorb heat liberated when the steam used in the power cycle is condensed. The South Coast Air Basin has an estimated 0.4 tons of chloroform air emissions per year from utility power plants.

Chlorination of seawater will result in little or no chloroform formed. One reason why so little chloroform is produced is that when chlorine is added to seawater (which contains approximately 65 milligrams per liter of bromide ion) the bromide is quickly oxidized to HOBr while the hypochlorous acid is reduced to chloride ion. Consumption of 99% of the HOCl may occur within ten seconds and as a result little chloroform can form (Rogozen, 1988).

Air emissions of chloroform are estimated to be 2.7 tons per year in the South Coast Air Basin. There is not enough data to estimate chloroform emission from cooling towers on a statewide basis.

Pulp & Paper Manufacturing

Chloroform is produced when substances containing chlorine are added to the process water to bleach wood pulp. Chloroform is formed from the aqueous reaction of chlorine with organic substances in the wood pulp and then is released to the air during the bleaching process.

Chloroform is also formed while treating the effluent and continues to form after the effluent is released to receiving waters. Chlorine, calcium hypochlorite, sodium hypochlorite and chlorine dioxide are used commonly for bleaching the pulp. Emission factors were developed for different types of wood pulp operations based on chloroform mass balance

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calculations using measured chloroform concentrations in the wastewater treatment system influents and effluents at a number of mills (U.S. EPA, 1984). The categorization was used by the EPA in the development of effluent guidelines and based on a number of factors.

The staff estimates that 12 paper and pulp mill sources in California emitted approximately 220 tons of chloroform in 1987 (See Appendix A-6). Chloroform emissions from another six California facilities may be significant yet there is insufficient information to estimate their emissions at this time.

Laundry Bleach

Bleaching agents are widely used around the home for the laundry and for household cleaning of sinks and toilets. The largest category for domestic consumption of bleach is likely to be household laundry.

There are an estimated 13.5 tons of chloroform per year that are emitted indoors from the domestic consumption of bleach for household laundry (See Appendix A-7). There are no data at the present time to estimate emissions from household bleach used in other ways.

Combustion of Leaded Gasoline

Ethylene dichloride (EDC) is added to leaded gasoline as a scavenger. The lead reacts with EDC to produce lead chloride salts. These salts prevent the buildup of abrasive lead oxides on moving engine parts. The lead chloride salts tend to volatize and can be emitted with the exhaust to the air.

The exhaust gases from gasoline internal combustion engines operated on conventional leaded fuel and not equipped with catalytic converters contained parts-per-billion concentrations of chloroform which can, in congested urban areas, contribute significantly to the ambient concentration of chloroform. Exhaust gases from engines burning conventional leaded gasoline contain much higher levels of chloroform than do exhaust gases from engines equipped with catalytic converters and operating on non-leaded gasoline.

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According to SAIC, only one other report was found to have attempted to measure chloroform from automobile exhaust. The results of this report entitled "On the Occurrence of Aliphatic Chlorine and Bromine compounds in Automobile Exhaust" by E. Hasanen, et al., was inconclusive of the presence of chloroform.

Analysis of undiluted auto exhaust sampled by Washington State University confirmed the presence of parts per billion levels of chloroform in these emissions. Two types of cars were tested. They were 1) catalytic converter equipped cars operating on non-leaded gasoline and 2) conventional cars operated on leaded gasoline. The exhaust gases from catalytic converter equipped cars contained less than 100 parts per trillion of chloroform, while the exhaust gases from a conventional automobile contained 6 to 7 ppb of chloroform (Harsch, 1977). The study suggests that automobile exhaust is a significant source of chloroform in urban air (Harsch, 1977).

However, under well-ventilated conditions, the concentration of chloroform that will accumulate in the urban air is probably not excessively high because of its modest concentration in the exhaust gases. A considerable decrease in chloroform emissions will result from this source, as the lead concentration of gasoline decreases and as older non-catalytic equipped automobiles are replaced with newer automobiles burning unleaded gasoline and equipped with catalytic converters.

Air Stripping Towers

Air stripping towers are used to control contaminated water. Fresh air is introduced into the tower and is allowed to contact the contaminated water where most of the contaminants will be transferred to the fresh air. The fresh air becomes contaminated and is withdrawn at the other end of the tower.

Aerojet General Corporation in Sacramento County operates six air strippers, of which three emit chloroform (Skelton, 1989). The air strippers emissions are estimated to be 2.25 tons of chloroform per year (See Appendix A-8).

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Perchloroethylene Production

Chloroform is formed as a by-product during production of perchloroethylene (PERC) and trichloroethylene (TCE). PERC and TCE may be produced separately or as co-products by either chlorination or oxychlorination of ethylene dichloride (EDC) or other C_2 chlorinated hydrocarbons. There are no facilities in California producing EDC or TCE. Dow Chemical, U.S.A. in Pittsburg is the only California facility producing PERC (U.S. EPA, 1984). However, there is not enough data to estimate chloroform emissions from this facility.

Contamination of Chlorinated Products

Chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride in the methane chlorination process. Chlorination of methyl chloride also produces chloroform, methylene chloride and carbon tetrachloride. These products are separated by distillation, but still remain contaminated with low concentrations of chloroform. A previous study by SAIC estimated nationwide releases of chloroform from product contamination to be approximately 7 tons per year (Rogozen, 1988).

Assuming emissions from contaminated products are in proportion to the population, then there is an estimated 0.80 tons per year of chloroform emitted to the air on a statewide basis (See Appendix A-9).

C. EMISSION TRENDS

As discussed in Section B.2, there is a considerable uncertainty in the emission estimate for swimming pools and a range of emissions has been reported. If the upper bound of the range is considered, swimming pools may be the largest source of chloroform emissions in California. For 1985, inground pools accounted for approximately 87% of the estimated 340 tons of chloroform emitted from swimming pools, while above ground pools accounted for approximately 8% and spas and hot tubs accounted for 5%. Inground swimming pools have increased at an annual average rate of 2.7% between 1981 and 1985 in California. Spas and hot tubs have increased at an annual average rate of 26% between 1980 and

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1985 in the United States. Because there is no foreseen substitute for chlorine in swimming pools, chloroform emissions will continue to increase as more pools are built and chlorinated.

The emission estimates of drinking water (consumption/usage) and indoor emissions (bleach) are 300 tons/year from drinking water, and 14 tons/year from bleach. These estimates are based on the current population of 27,662,900 people in California (DOF, 1988). The population statewide for the year 2000 is estimated to be 32,853,000 and for the year 2010 is estimated to be 36,277,000 (DOF, 1986). The result is an anticipated increase of 19% and 31% for the year 2000 and 2010, respectively, in the statewide population from the current population. If emissions from drinking water and indoor emissions from bleach used in laundry are also increased accordingly, the chloroform emissions for the year 2000 are estimated to be 351 tons per year for drinking water and 16 tons per year from the use of bleach. For the year 2010, annual chloroform emissions are estimated to be 386 tons for drinking water and 18 tons from bleach.

No data is available to suggest a change in the current uses of commercially produced chloroform in the future. Data is unavailable to estimate changes in other sources, but no foreseen significant changes in these other sources of emissions is anticipated in the near future.

D. POTENTIAL SOURCES OF CHLOROFORM IN INDOOR AIR

Much of the chloroform emitted to ambient or indoor air is produced indirectly through the haloform reaction of chlorine with various organic precursors (Barcelona *et al*. 1979; Rogozen *et al*. 1988; U.S. EPA, 1984). Emissions of chloroform may also result from its direct use as a solvent in the production of items commonly found indoors; residues may vaporize into the indoor air from these products (Ozkaynak & Ryan, 1987).

1. Building Materials

The literature surveyed for this report does not indicate that chloroform is a significant component of commonly used building materials.

2. Consumer Products

Chloroform was not included in a nationwide survey of six chlorocarbons in 1,153 common household products (U.S. EPA, 1987). However, EPA researchers recently re-examined gas chromatography/mass spectra data from 1,043 of the original products (Sack and Steele, 1989). Investigators reported that chloroform was present in only three products: X-14 Mildew Spot Remover (1 percent by weight); Thoro Spot (1 percent by weight); and Carter's Ink Eradicator (0.1 percent by weight). The authors did not specify the number of chlorine-containing products examined.

In tests of approximately 5000 materials used in the U.S. space program (Ozkaynak & Ryan, 1987), chloroform was found in a variety of products commonly used indoors. Chloroform was generated at the highest level from pen and ink samples with a median of 10 ug/g of material tested and a maximum value of 89 ug/g reported. The categories of miscellaneous housewares and photo equipment were also reported to be sources of relatively high median levels of chloroform (4.85 and 2.50 ug/g respectively). Median chloroform levels of 0.04 to 0.90 ug/g were found in a variety of material categories including rubber, lubricant, adhesives, fabric, paper, photo film, tape and foam. In most cases, these tests produced elevated chloroform values due to the high temperature (120° F), low-pressure conditions of the experiments.

In a headspace screening experiment, researchers found chloroform emitted in varying amounts from household products used indoors (Sheldon, L., 1988; Wallace, L. 1987a). These products were: Old Dutch Cleanser, Brillo pads and Seventy-seven (liquid detergent). Chloroform was also generated from Talon G, a rodenticide and Ficam (bendiocarb), an insecticide. In the corresponding chamber study, these researchers tested the emission rates of three cleansers: Brillo, Seventy-seven and

BAB-O, a scouring powder. These products were applied in a sequence along with an insecticide, Baygon (propoxur) to surfaces placed inside the 34 m^3 chamber. The average chamber concentration of chloroform was 283 ± 5 ug/m^3 (58 ppb). Chloroform was emitted at a rate of 15ug/m^2-min. The scouring powder contained chlorine bleach and was believed to generate most of the chloroform. Since the scouring powder was applied last during this 4-hour test, the reported values may be underestimates.

Liquid bleach use in domestic laundering produces an estimated 13.5 tons of chloroform air emissions per year in California. This estimate is extrapolated from calculations by Rogozen et al. (1988). For a detailed explanation of this estimate, see Appendix A-7. This estimate does not account for potential emissions from other chlorine-containing household products.

3. Vaporization from Water Sources

Evidence indicates that vaporization from chlorinated drinking water is a major source of chloroform in the air environment (Andelman et al. 1986; McKone, 1987; Rogozen et al. 1988, Wallace et al. submitted for publication). Dissolved chloroform transfers rapidly and thoroughly from water to air; its half-life under experimental conditions appears to be about 20 minutes (Rogozen et al. 1988; U.S. EPA, 1985).

In a study of relationships between personal activities and indoor air exposure, Wallace et al. (1989) found indoor levels of chloroform to rise significantly in association with household use of hot water. During periods when hot water was used intensively, indoor air levels rose to an average of 31 ug/m^3 (6.35 ppb) but were negligible during periods of limited hot water use. Washing clothes or dishes was effective in elevating chloroform levels in all four of the homes studied. The single activities of taking hot showers, boiling water or using a humidifier were not associated with higher chloroform levels.

Rogozen et al. (1988) estimates that vaporization from chlorinated drinking water accounts for about half the ambient chloroform emissions in the South Coast Air Basin in southern California. In a simple one-compartment model of the indoor environment, Andelman et al. (1987)

estimates that indoor air concentrations are likely to be 1 to 50% that of the tap water concentrations. Studies of chloroform emissions by Andelman *et al.* (1986) indicated that about 50% of water-dissolved chloroform volatilized in an experimental shower system. Factors such as increased chloroform water concentration, drop height, water temperature and decreased shower drop size were each capable of increasing chloroform volatilization. There was strong evidence that volatilization from the small amount of water collecting at the shower bottom was substantial. Volatilization in the corresponding experimental bath system was less than in the shower system.

For example, a look at the data from Contra Costa County is helpful. Chloroform levels in overnight personal air samples are lower than those taken in Los Angeles. However, tap water samples in Contra Costa had higher levels of chloroform. Possible differences in ambient temperatures between Contra Costa and Los Angeles sites could affect the volatilization of chloroform into the air. However, it is possible that other sources besides tap water were responsible for the higher chloroform levels in personal air samples. Also, personal air monitors were not worn in the bath or shower, or carried into the bathroom. The highest personal air exposures would occur during bathroom activities.

Indoor swimming pools and spas may be a small proportion of the total number of swimming pools and spas statewide, but may provide relatively high exposures for the proportion of the population that owns or uses them. Most of the chloroform generated from chlorinated pools is formed *in situ*. Mean chloroform levels of 36 - 241 ug/m^3 (7.37 - 49.4 ppb) have been measured in the air directly above (0.1-2m above water surface) indoor swimming pools (Lahl *et al.*, 1981). A maximum of 384 ug/m^3 (78.7 ppb) was measured in one of these West Bremen, Germany pools. These levels are to be compared with an average chloroform concentration of about 0.1 ug/m^3 (0.02 ppb) measured in the ambient air during the same study. Emission flux rates were measured of 12 ug/m^2-min for still conditions and 320 ug/m^2-min for agitated water conditions in an outdoor residential pool in California (Rogozen *et al.*, 1988). Emission flux rates for indoor and outdoor pools are not likely to be similar. This is due to different concentration gradients between the actual chloroform concentration in the water and the aqueous chloroform

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concentration which would occur if chloroform in the overlying air and in the water were in equilibrium. In the case of an outdoor pool, the overlying air's chloroform content would not be much above ambient concentrations. Whereas, in the case of an indoor pool (Lahl et al. 1981), chloroform concentrations in the overlying air are much higher. Therefore, the concentration gradient would be lower for the indoor pool. Second, the flux rate also depends upon the mass transfer coefficient, which, in the case of chloroform, is dominated by the liquid phase mass transfer coefficient, which increases nonlinearly with increasing wind speed. For both reasons cited, emission flux rates from outdoor pools are likely to be higher than those from indoor pools.

Chloroform is formed *in situ* and then vaporizes following use of household products containing chlorine, along with water, for various bleaching or sterilization purposes (dish or clothes washing, toilet bowl sterilization, etc.). This source of chloroform may be significant in the indoor environment. For information on emissions data on such sources, see the section on consumer products (III-D-2) above.

IV. EXPOSURE TO CHLOROFORM

A. AMBIENT MONITORING FOR CHLOROFORM

This analysis is based on ambient data collected by the Air Resources Board (ARB) and maintained in the RAMIS TOXAQ database. Although these data have been reviewed and approved for use by the ARB's Monitoring and Laboratory Division (MLD) staff, the data are preliminary and subject to revision. All data used in the analysis were extracted from the data base on March 13, 1989, and do not reflect any changes that may have occurred since that time.

The toxics sampling network used for chloroform was comprised of 19 sites statewide. Nine of these sites are located in Southern California (south of Bakersfield), while the other 10 are located in the northern portion of the state. Data used in the following exposure analysis were collected during the period of January 1988 through December 1988 for the 10 northern sites and during the period of July 1988 through

Table IV-1

SUMMARY OF CHLOROFORM DATA[1]
January 1988 – December 1988

Site Location	J	F	M	A	M	J	J	A	S	O	N	D	Samples
SOUTHERN CALIFORNIA SITES													
<u>South Coast Air Basin</u>													
El Monte							o	o	o	o	o	o	13
Los Angeles							o	o	o	o	o	o	11
Long Beach							o	o	o	o	o	o	14
Rubidoux							o	o	o	o	o	o	13
Upland							o	o	o	o	o	o	13
<u>South Central Coast Air Basin</u>													
Santa Barbara							o	o	o	o	o	o	11
Simi Valley							o	o	o	o	o	o	15
<u>San Diego Air Basin</u>													
El Cajon							o	o	o	o	o	o	13
Chula Vista							o	o	o	o	o	o	12
NORTHERN CALIFORNIA SITES													
<u>San Francisco Bay Area Air Basin</u>													
Concord	o	o	o	o	o	o	o	o	o	o	o	o	24
Fremont	o	o	o	o	o	o	o	o	o	o	o	o	23
Richmond	o	o	o	o	o	o	o	o	o	o	o	o	24
San Francisco	o		o	o	o	o	o	o			o	o	16
San Jose	o	o	o	o	o	o	o	o	o	o	o	o	23
<u>San Joaquin Valley Air Basin</u>													
Bakersfield	o	o	o	o	o	o	o	o	o	o	o	o	21
Fresno	o	o	o	o	o	o	o	o	o	o	o	o	23
Modesto	o	o	o	o	o	o	o	o	o	o	o	o	24
Stockton	o	o	o	o	o	o	o	o	o	o	o	o	23
<u>Sacramento Valley Air Basin</u>													
Citrus Heights	o	o	o	o	o	o	o	o	o	o	o	o	20

[1] A "o" indicates at least one sample was collected during the month.

Table IV-2

SUMMARY OF ESTIMATED MEAN[1] ANNUAL CONCENTRATIONS
USING THREE METHODS FOR ESTIMATING VALUES BELOW THE LOD
(units are in part per billion)

AIR BASIN Site Location	LOD=0.0 Mean	LOD=0.01 Mean	LOD=0.02 Mean	<LOD Samples
SOUTHERN CALIFORNIA SITES				
South Coast Air Basin				
El Monte	0.04	0.04	0.04	2
Los Angeles	0.03	0.04	0.04	1
Long Beach	0.04	0.04	0.04	1
Rubidoux	0.02	0.02	0.03	4
Upland	0.03	0.03	0.03	2
Basin Summary	0.03	0.04	0.04	10
South Central Coast Air Basin				
Santa Barbara	0.04	0.04	0.04	0
Simi Valley	0.03	0.03	0.03	2
Basin Summary	0.03	0.03	0.04	2
San Diego Air Basin				
Chula Vista	0.01	0.02	0.02	7
El Cajon	0.03	0.03	0.03	1
Basin Summary	0.02	0.03	0.03	8
NORTHERN CALIFORNIA SITES				
San Francisco Bay Area Air Basin				
Concord	0.03	0.03	0.03	5
Fremont	0.01	0.02	0.02	12
Richmond	0.04	0.04	0.05	9
San Francisco	0.02	0.03	0.03	6
San Jose	0.02	0.02	0.03	9
Basin Summary	0.02	0.03	0.03	41
San Joaquin Valley Air Basin				
Bakersfield	0.02	0.03	0.03	5
Fresno	0.01	0.02	0.02	12
Modesto	0.01	0.02	0.02	12
Stockton	0.02	0.02	0.03	11
Basin Summary	0.02	0.02	0.03	40
Sacramento Valley Air Basin				
Citrus Heights	0.02	0.03	0.03	7

1. Means are computed as the sum of all observations divided by the total number of observations. This is for comparing the effects of the different LOD values. These data are based on 24 hour averages.

December 1988 for the 9 southern sites. The data for this period are hereafter referred to as "the study period". Individual 24-hour samples were collected in Tedlar bags and subsequently analyzed for chloroform using gas chromatography with an electron capture detector by the MLD's Northern Laboratory Branch (NLB) staff.

The available state-wide chloroform data for the study period are very limited, representing only 19 sites and a small percentage of all possible days during the sampling period. The months during which data are available for each site are summarized in Table IV-1. Although we recognize that 365 samples may not be necessary to characterize a representative mean statewide annual concentration, we do not know the minimum number of samples, nor the minimum number of sites required to estimate a mean annual concentration with satisfactory precision. Therefore, all analyses and estimates for exposure presented here are subject to an unknown level of uncertainty and should be used with appropriate caution.

The number of samples available per site during the study period range from 16 to 24 in Northern California and from 11 to 15 in Southern California. The Northern and Southern California averages are 1.8 and 2.1 observations per month, respectively. Overall, 31 percent of the observations are below the Limit of Detection (LOD), which is 0.02 parts per billion (ppb). The number of observations below the LOD for each site is given in Table IV-2.

Datasets with Limits of Detection (LOD)

Concentrations below the LOD were reported for each site except Santa Barbara. Even though no value is reported when a concentration is below the LOD, important information is still available from its existence. Obviously, the fewer the data points below the LOD, the less significant their impact on the analysis. Because removing these values from the dataset would bias the sample statistics and exposure estimates, four methods for dealing with values below the LOD were compared:

1. Replace the values below the LOD with zero;
2. Replace the values below the LOD with half the LOD;
3. Replace values below the LOD with the LOD; and
4. Replace values below the LOD with estimated order statistics (Gleit, 1985).

When there is a significant difference between the results using these four methods, the results for each method are reported.

Of the four methods given above, estimating order statistics is the ARB staff's preferred method for estimating values below the LOD. This method was discussed by Gleit who uses an iterative algorithm for estimating the order statistics for a finite sample (Gleit 1985). Gleit demonstrated the minimum variance attribute of the estimated order statistic. Our earlier work supports Gleit's conjecture that the estimated order statistic approach gave the least biased estimate when the true value was known when compared to the other three methods. After repeatedly generating random test sets of data from a known normal distribution, each method for estimating values below the LOD were compared and on the average the estimated order statistic achieved the best estimate.

However, we found with chloroform data that there were so many values less than or equal to the LOD that the Gleit method for estimating values below the LOD did not function properly, and produced unreliable results. Table IV-2 gives the site means for each of the remaining methods. Since it is possible to get different results with chloroform data by using a different method for estimating values below the LOD, results of the analysis that use each method will be given when informative. Otherwise, the method that gives the most conservative results will be used.

B. AMBIENT CONCENTRATIONS OF CHLOROFORM

Results of Analysis

The absolute range of concentrations sampled at each site during the study period is summarized in Table IV-3. Minimum and maximum concentrations, (values below the LOD are reported as <0.02), median and

Table IV-3

SUMMARY OF SAMPLE STATISTICS
January 1988 - December 1988
(units are in parts per billion)

AIR BASIN Site Location	Minimum Conc.	Maximum Conc.	Median Conc.	Mean[1] Conc.	Standard[2] Deviation
SOUTHERN CALIFORNIA SITES					
South Coast Air Basin					
El Monte	<0.02	0.09	0.04	0.04	0.017
Los Angeles	<0.02	0.08	0.03	0.04	0.012
Long Beach	<0.02	0.07	0.04	0.04	0.011
Rubidoux	<0.02	0.05	0.02	0.03	0.011
Upland	<0.02	0.06	0.03	0.03	0.008
Basin Summary	<0.02	0.09	0.03	0.04	0.012
South Central Coast Air Basin					
Santa Barbara	0.02	0.08	0.02	0.04	0.014
Simi Valley	<0.02	0.05	0.03	0.03	0.011
Basin Summary	<0.20	0.08	0.03	0.04	0.013
San Diego Air Basin					
Chula Vista	<0.02	0.04	<0.02	0.02	0.014
El Cajon	<0.02	0.05	0.03	0.03	0.007
Basin Summary	<0.20	0.05	0.02	0.03	0.011
NORTHERN CALIFORNIA SITES					
San Francisco Bay Area Air Basin					
Concord	<0.02	0.06	0.03	0.03	0.012
Fremont	<0.02	0.05	<0.02	0.02	0.012
Richmond	<0.02	0.20	0.02	0.05	0.040
San Francisco	<0.02	0.06	0.02	0.03	0.016
San Jose	<0.02	0.06	0.02	0.03	0.011
Basin Summary	<0.02	0.20	0.02	0.03	0.021

1. Basin Means are the mean of the site means. An LOD value of 0.02 ppb, when used to compute the mean, will provide a small positive proportional bias. An upper bound on the bias was calculated to be 33 percent. The mean is often called a measure of central tendency, but it is not the only measure of central tendency. The mean of a statistical sample is the value that would, on the average, be closest to any observation. The mean is often considered to be the number that is in the middle or the number that occurs most often. This is not always true. The number in the middle when the data are ordered may be the median and the number that occurs most often is called the mode. These data are based on 24 hour averages.

2. Basin Standard Deviations are pooled values of the standard deviations across sites within a basin. An LOD value of 0.00 ppb was used to calculate the standard deviation, an upper bound to the percent proportional bias was calculated to be 56 percent.

Table IV-3 (continued)

SUMMARY OF SAMPLE STATISTICS
January 1988 - December 1988
(units are in parts per billion)

AIR BASIN Site Location	Minimum Conc.	Maximum Conc.	Median Conc.	Mean Conc.	Standard Deviation
San Joaquin Valley Air Basin					
Bakersfield	<0.02	0.07	0.03	0.03	0.008
Fresno	<0.02	0.04	<0.02	0.02	0.012
Modesto	<0.02	0.03	<0.02	0.02	0.007
Stockton	<0.02	0.06	0.02	0.03	0.016
Basin Summary	<0.02	0.07	0.02	0.03	0.011
Sacramento Valley Air Basin					
Citrus Heights	<0.02	0.08	0.02	0.03	0.02

mean concentrations, as well as standard deviation are reported for each site. Mean chloroform concentrations were calculated as the mean of available monthly means because this approach provides equal weighting for each month when the number of samples per month varies. The standard deviations were also calculated from monthly means so they could be compared with the annual mean concentrations.

The site-specific ranges (i.e., the maximum and minimum concentrations) of the ambient chloroform concentrations listed in Table IV-3 are plotted in Figure IV-1, using an extended Box-plot format. Minimum concentrations range from below the LOD at 18 of the 19 sites to 0.02 ppb at Santa Barbara. Maximum concentrations range in value from 0.03 ppb at Modesto to 0.20 ppb at Richmond. After reviewing Figure IV-1, it appears that the distribution of ambient chloroform concentration are fairly uniform throughout the State. The highest concentrations reported in the state occurred at the Richmond site.

A median concentration that is significantly different from the mean indicates a non-normal distribution of the data. Since the mean annual concentration for chloroform is dependent on the choice of LOD value replacement methods, the staff is unable to determine if there is a significant difference between the median and the mean for each site. In the past, the distribution of the ambient air quality data has generally been assumed to be log-normal. The chloroform data were tested for normality and log-normality using the Shapiro-Wilk test statistic (Shapiro-Wilk 1965). The staff found that chloroform data have neither distribution, although chloroform data are skewed like a log-normal distribution.

Seasonal Distribution Tendencies

Seasonality is an important factor in understanding the distributional tendencies of ambient chloroform. The data for each site were categorized based on which calendar quarter of the year the samples were collected. The Kruskal-Wallis test was then used to determine if there was a significant difference between individual quarters for each site. The Kruskal-Wallis test is a non-parametric test based on ranks and is more powerful than the more well known Analysis of Variance tests when the data do not have a normal or log-normal distribution. As determined earlier, chloroform data have neither distribution. An advantage to using a rank-based analysis procedure is that every observation less than the LOD will be assigned the same rank value regardless of the choice of replacement value.

The Kruskal-Wallis test compares the median of the data for each quarter against the overall median for all data from a site. If the Kruskal-Wallis test statistic is significant, it means there is a quarter with data that are statistically different from those of another quarter. If the Kruskal-Wallis test statistic is not significant then we assume there is no seasonality in chloroform concentrations.

FIGURE IV-1

MEAN ANNUAL CHLOROFORM CONCENTRATION

PLOTTED USING EXTENDED BOX PLOTS

BASED ON JANUARY 1988–DECEMBER 1988 DATA

MONITORING SITES THROUGHOUT CALIFORNIA
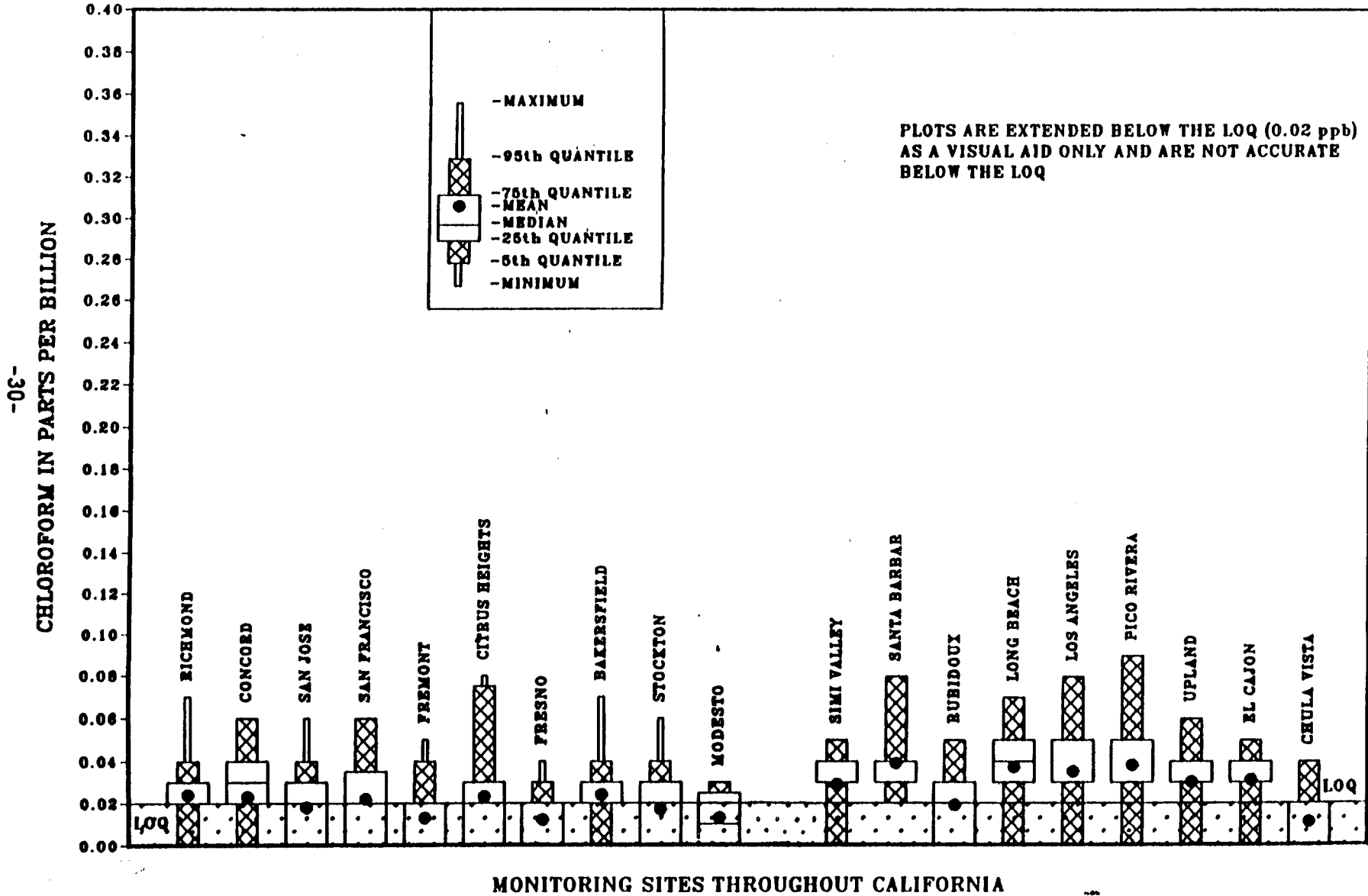
Chloroform data showed no consistent seasonal tendency as only three sites showed significant results. For each of the three sites with significant differences, the quarter with the highest means was different. This implies that there is no overall seasonality to the chloroform data. Results are given in Table IV-4.

When a set of data from a skewed distribution does not fit any of the standard, more commonly known distributions (e.g., Normal), interpretation of sample statistics such as the mean or the results from comparing several sets of such data using standard parametric tests such as the T-test and F-test can be misleading. While the mean is greatly influenced by skewed extreme values, the median is less so because it is computed on the basis of ranks. When the normality and log-normality assumptions are violated, it is useful to consider other statistics or methods to characterize and compare toxics data. Statistics such as the Peak-to-Mean ratio or the Coefficient of Variation, if interpreted properly, can be very useful when summarizing information regarding toxics data. Non-parametric tests such as Kendall's U-statistic or the Kruskal-Wallis Test can be more powerful in the absence of the necessary normality conditions when compared to parametric tests (Conover 1971). These statistical tools were used to evaluate seasonal and geographical distribution of chloroform and Peak-to-Mean ratios.

Geographical Distribution of Chloroform

To understand the geographic distribution of ambient chloroform concentrations, it is necessary to determine if there are relevant differences among the data reported for different sites. The Kruskal-Wallis test was used to determine if, within each basin, there are data for one site that are significantly different than data for another site. Air basins are chosen to reflect similar geographic and meteorological conditions; making comparisons across basins may lead to erroneous results.

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If the Kruskal-Wallis test statistic is significant, then Fisher's Least Significant Difference test is used to determine the sites considered to be different and those that are similar. The medians for all sites in a basin are not considered to be different if the Kruskal-Wallis test statistic is not significant. If two sites within a basin have no associated letters in common then the data for each of the two sites are considered to be significantly different. The most likely groupings for sites within each basin are given in Table IV-5. Because the Sacramento Valley Air Basin has only one toxic monitoring site, no results are given. It should be noted that test statistics based on rankings of the data will sometimes lead to other than intuitive results.

Peak-to-Mean Ratios

Peak-to-mean ratios were calculated to provide possible insights into the nature of chloroform emission release patterns. The technique is based on observations made for criteria pollutants. For example, carbon monoxide is a relatively inert criteria pollutant with generally widespread emissions. Over an annual period, peak-to-mean ratios for carbon monoxide tend to be fairly low, generally less than 5. Another criteria pollutant, sulfur dioxide, may be emitted from widespread sources but is also emitted from localized point sources. Peak-to-mean ratios for sulfur dioxide at sites influenced by localized sources tend to be much greater than 5. Ratios between 50 and 90 have been seen at some locations. Based on what we know about the characteristics of the criteria pollutants, we can divide peak-to-mean ratios into low and high ratios. Generally, a low peak-to-mean ratio, less than about 10, indicates either relatively constant and/or uniform emission sources or few emission sources but high, fairly constant background concentrations. A high peak-to-mean ratio, generally greater than about 10, usually indicates either intermittent and/or scattered emission sources or scattered emission sources with a highly variable background concentration.

Table IV-4

SUMMARY OF CHLOROFORM QUARTERLY MEANS[1]
AND RESULTS OF THE KRUSKAL-WALLIS TEST
FOR SIGNIFICANT DIFFERENCES BETWEEN QUARTERS
(units are in parts per billion)

AIR BASIN Site Location	First Mean	Second Mean	Third Mean	Fourth Mean	Significant[2] (P < 0.05)
SOUTHERN CALIFORNIA SITES					
South Coast Air Basin					
El Monte			0.043	0.036	NO
Los Angeles			0.037	0.034	NO
Long Beach			0.031	0.044	NO
Rubidoux			0.026	0.018	NO
Upland			0.036	0.027	NO
South Central Coast Air Basin					
Santa Barbara			0.045	0.032	NO
Simi Valley			0.038	0.023	YES
San Diego Air Basin					
Chula Vista			0.016	0.018	NO
El Cajon			0.030	0.033	NO
NORTHERN CALIFORNIA SITES					
San Francisco Bay Area Air Basin					
Concord	0.025	0.028	0.030	0.033	NO
Fremont	0.018	0.020	0.012	0.022	NO
Richmond	0.018	0.080	0.038	0.020	NO
San Francisco	0.033	0.025	0.013	0.030	NO
San Jose	0.016	0.020	0.018	0.030	NO
San Joaquin Valley Air Basin					
Bakersfield	0.027	0.018	0.030	0.032	NO
Fresno	0.014	0.015	0.017	0.032	NO
Modesto	0.020	0.017	0.017	0.023	NO
Stockton	0.013	0.020	0.016	0.035	YES
Sacramento Valley Air Basin					
Citrus Heights	0.018	0.022	0.036	0.030	NO

1. Means are computed as the average of all values reported for each quarter. These data are based on 24 hour averages.

2. Each quarterly means was calculated using 0.01 ppb as the replacement value for the observations that were below the LOD, this will provide the most conservative results when comparing sites within a basin.

Table IV-5

SUMMARY OF WITHIN BASIN SITE DIFFERENCES
BASED ON AVERAGE MONTHLY
RANKINGS AND MONTHLY MEANS

AIR BASIN Site Location	Grouping[1] Mean	Mean Rank	Mean[2] Conc.
SOUTHERN CALIFORNIA SITES			
South Coast Air Basin			
Long Beach	A	39.3	0.038
El Monte	A B	37.5	0.039
Los Angeles	A B	33.7	0.035
Upland	A B	32.1	0.032
Rubidoux	B	19.6	0.022
South Central Coast Air Basin			
Santa Barbara	A	15.8	0.039
Simi Valley	A	11.8	0.031
San Diego Air Basin			
Chula Vista	A	17.2	0.017
El Cajon	B	8.5	0.032
NORTHERN CALIFORNIA SITES			
San Francisco Bay Area Air Basin			
Concord	A	67.7	0.029
Richmond	A B	58.3	0.042
San Francisco	A B	57.2	0.026
San Jose	A B	51.6	0.022
Fremont	B	42.5	0.019
San Joaquin Valley Air Basin			
Bakersfield	B	62.9	0.027
Stockton	C B	49.6	0.021
Modesto	C	43.4	0.018
Fresno	C	42.7	0.017
Sacramento Valley Air Basin[3]			
Citrus Heights	--	--.-	0.027

1. Sites with the same letter are not considered to be significantly different.

2. Means are computed as the mean of all observations using 0.01 ppb as the replacement value for the concentrations reported to be below the LOD.

3. Since there is only one toxic monitoring site in the Sacramento Valley, no results are given for this basin other than the mean.

Peak-to-mean ratios for the study period are given in Table IV-6. Ratios for 18 of the 19 sites are relatively low. Only the Richmond site shows a ratio greater than 5. The mean used in the calculation of peak-to-mean ratios is the mean of all observations, with zero used to replace values less than the LOD. Using zero as the replacement value will introduce a positive bias (an overestimate) to the peak-to-mean ratios. Since the data from Santa Barbara has no values less than the LOD, there is no bias in the peak-to-mean ratio reported for that site. The peak-to-mean ratio for Santa Barbara compares well with the ratios for the other sites, which implies that any bias in the peak-to-mean ratios for the other sites is probably negligible for our purposes. The relatively low ratios at all sites suggest fairly consistent emission patterns across the state and throughout the year. Potential isolated large sources do not appear to impact the sampling network significantly. This is also apparent by comparing the Coefficient of Variation (C.V.) for each site. The C.V. is equal to the standard deviation divided by the mean, multiplied by 100, and is expressed as a percentage. The C.V. is similar to the peak-to-mean ratio in that it is a unitless number that is used to compare the dispersive tendencies of distributions. Without more refined information regarding the distributional characteristics of chloroform emissions, we cannot determine specifically the factors contributing to the observed distributional patterns.

C. POPULATION-WEIGHTED EXPOSURES ESTIMATES

Mean population exposure estimates were calculated using the study period chloroform data. Exposures for the South Coast Air Basin and San Francisco Bay Area Air Basin were estimated by interpolating station values to census tract centroids. For the other air basins, a basin-wide mean concentration was estimated from the means for all sites in the basin. It was then assumed that all people in those counties with a sampling site were exposed to this estimated basin-wide mean concentration. Population data used in the exposure analysis represent 1980 census data updated to 1985 levels.

From results presented earlier, chloroform shows no overall seasonal variation in the distribution of ambient concentrations. This implies that the six months of data available for the nine southern California sites can be considered representative of data for the entire year. Therefore, there should be no bias introduced to the exposure estimates due to the limited sampling period at the southern California sites.

Mean annual population weighted exposure estimates were calculated using each of the three replacement values for concentrations below the LOD. After rounding, each method yielded the same average concentration. The overall mean annual exposure estimate for chloroform weighted by population was calculated to be 0.03 ppb for each site. Results for the exposure analysis using each of the three LOD replacement values are given in Table IV-7. These values do not represent a range of values for the mean annual statewide population weighted exposure estimate, but only the range of values possible from using different replacement values for the observations reported to be below the LOD. The overall geographic mean was calculated to be 0.03 ppb. The difference is not significant between the population weighted exposure estimate and the overall geographic mean, which suggests that ambient chloroform concentrations are similar throughout the state.

Using 0.02 ppb as the replacement value for the observations below the LOD will generate a positive bias (an over estimate) in the statewide exposure estimate. At this time, we have no way of accurately estimating the percent bias in this estimate; although, it should be bounded above by the difference between the estimates using 0.02 and 0.00 as the replacement for observations reported to be below the LOD divided by the lower estimate. The percent bias ranges from zero at Santa Barbara to 89 at Fremont. Thirty-two percent is the overall average bias.

Table IV-6

SUMMARY OF CHLOROFORM PEAK-TO-MEAN RATIOS
AND COEFFICIENTS OF VARIATION
(concentrations are in parts per billion)

AIR BASIN Site Location	Peak Conc.	Mean[1] Conc.	Peak-to-Mean[2] Ratio	Number Samples	C.V.[3]
SOUTHERN CALIFORNIA SITES					
South Coast Air Basin					
El Monte	0.09	0.04	2.37	13	65.1
Los Angeles	0.08	0.03	2.29	11	68.4
Long Beach	0.07	0.04	1.89	14	44.1
Rubidoux	0.05	0.02	2.63	13	83.5
Upland	0.06	0.03	2.00	13	54.4
South Central Coast Air Basin					
Santa Barbara	0.08	0.04	2.05	11	42.0
Simi Valley	0.05	0.03	1.72	15	47.3
San Diego Air Basin					
Chula Vista	0.04	0.01	3.70	12	133.2
El Cajon	0.05	0.03	1.63	13	38.6
NORTHERN CALIFORNIA SITES					
San Francisco Bay Area Air Basin					
Concord	0.06	0.03	2.22	24	64.9
Fremont	0.05	0.01	4.17	23	120.1
Richmond	0.20	0.04	5.26	24	139.8
San Francisco	0.06	0.02	2.73	16	94.7
San Jose	0.06	0.02	3.53	23	95.6
San Joaquin Valley Air Basin					
Bakersfield	0.07	0.02	2.89	21	70.8
Fresno	0.04	0.01	3.33	23	113.4
Modesto	0.03	0.01	2.40	24	106.2
Stockton	0.06	0.02	3.64	23	110.4
Sacramento Valley Air Basin					
Citrus Heights	0.08	0.02	3.48	20	99.8

1. Means are calculated as the sum of all observations for each site divided by the total number of observations at each site.

2. Peak-to-Mean Ratios are calculated the max value divided by the average of all observations reported.

3. The Coefficients of Variation are calculated as the standard deviation of all observations divided by the average of all observations.

Table IV-7

SUMMARY OF AVAILABLE CHLOROFORM CONCENTRATIONS
AND POPULATION-WEIGHTED EXPOSURE ESTIMATES[1]
(units are in parts per billion)

Air Basin Site Location	LOD=0.00 Mean	LOD=0.01 Mean	LOD=0.02 Mean	Population
SOUTHERN CALIFORNIA SITES				
South Coast Air Basin (SoCAB)				
El Monte	0.04	0.04	0.04	
Los Angeles	0.03	0.04	0.04	
Long Beach	0.04	0.04	0.04	
Rubidoux	0.02	0.02	0.03	
Upland	0.03	0.03	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SoCAB				
	0.03	0.04	0.04	10,092,133
South Central Coast Air Basin (SCCAB)				
Santa Barbara	0.04	0.04	0.04	
Simi Valley	0.03	0.03	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SCCAB				
	0.04	0.04	0.04	925,822
San Diego Air Basin (SDAB)				
Chula Vista	0.01	0.02	0.02	
El Cajon	0.03	0.03	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SDAB				
	0.02	0.03	0.03	2,135,872
NORTHERN CALIFORNIA SITES				
San Francisco Bay Area Air Basin (SFBAAB)				
Concord	0.03	0.03	0.03	
Fremont	0.01	0.02	0.02	
Richmond	0.04	0.04	0.05	
San Francisco	0.02	0.03	0.03	
San Jose	0.02	0.02	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SFBAAB				
	0.02	0.02	0.03	4,394,374

1. Estimates are given using zero, 0.01 and 0.02 ppb as Upper, Middle and Lower estimates for concentrations reported to be below the LOD. These data are based on 24 hour averages.

Table IV-7 (continued)

SUMMARY OF AVAILABLE CHLOROFORM CONCENTRATIONS
AND POPULATION-WEIGHTED EXPOSURE ESTIMATES[1]
(units are in parts per billion)

Air Basin Site Location	LOD=0.00 Mean	LOD=0.01 Mean	LOD=0.02 Mean	Population
San Joaquin Valley Air Basin (SJVAB)				
Bakersfield	0.02	0.03	0.03	
Fresno	0.01	0.02	0.02	
Modesto	0.01	0.02	0.02	
Stockton	0.02	0.02	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SJVAB	0.02	0.02	0.03	1,740,700
Sacramento Valley Air Basin (SVAB)				
Citrus Heights	0.02	0.03	0.03	
POPULATION-WEIGHTED EXPOSURE FOR SVAB[2]	0.02	0.03	0.03	889,806

OVERALL POPULATION-WEIGHTED EXPOSURE[3]
FOR THE STATE OF CALIFORNIA

	0.03	0.03	0.03	20,178,400

1. Estimates are given using zero, 0.01 and 0.02 ppb as Upper, Middle and Lower estimates for concentrations reported to be below the LOD. A total of 20,178,400 people reside in the six basins comprising the study area, representing approximately 80 percent of the total State population. Basin-specific population-weighted mean concentrations using 0.02 ppb as replacement value for observations reported to be below the LOD vary from a minimum of 0.03 ppb in the San Francisco Bay Area, San Diego, and Sacramento Valley Air Basins to a maximum of 0.04 ppb in the South Central Coast, and South Coast Air Basins.

2. Exposure estimates are for Sacramento County residents only.

3. The population-weighted averages before rounding are 0.0278, 0.0306, and 0.0335 ppb, respectively.

D. INDOOR AIR EXPOSURE TO CHLOROFORM

This section reviews the available literature on human exposure to
chloroform in indoor air. Data from California-based studies are emphasized.
While the main purpose of this section is to define chloroform exposure
through the indoor air, we also present exposure data from food and water
ingestion. The final section examines exposure in the indoor air as a part
of total human exposure to chloroform.

1. Background

The Air Resources Board is directed, as part of its toxic air contaminants
identification process, to assess exposures to toxic substances found in
indoor air environments as well as in ambient conditions (Health and Safety
Code Section 39660.5). The estimation of indoor air pollutant levels has
increased in importance as a part of air exposure assessment because:

1. Californians spend most of their time (about 87 percent on average)
   indoors (Robinson *et al.*, 1989; preliminary data); and
2. personal and indoor air monitoring data on a spectrum of chemicals
   indicate that some pollutant concentrations are regularly higher
   indoors than outdoors.

By comparing indoor air measurements to those obtained in outdoor air, the
relative importance of indoor exposure can be established. Taken together,
indoor and outdoor monitoring data can provide a realistic estimate of total
personal exposure through the air environment.

Indoor air data can be obtained either by personal air sampling or by
fixed-site air sampling. Personal air samplers are adsorbent cartridges
attached to an individual's body and are carried along as the individual
participates in a variety of activities over numerous locations. In
contrast, fixed-site air samplers collect the air contaminants from a single
location. Individual exposure, in general is best estimated from personal

air sampling data. Since most people spend an estimated 80-90% of their time indoors, personal air sampling data are strongly weighted by indoor air data.

2. Indoor Air Exposure to Chloroform in California

The best data for estimating indoor air exposure for chloroform come from the Total Exposure Assessment Methodology (TEAM) studies conducted by the Environmental Protection Agency (EPA) during 1980-85 (referred to as TEAM 84 in this report; Wallace, 1987b; Wallace & Clayton, 1987; Pellizzari et al. 1987) and during 1987 (referred to as TEAM 87 in this report; Pellizzari et al. 1988). In the California portion of the TEAM 84 project, conducted in the metropolitan areas of Contra Costa county and Los Angeles, participants were selected and data accordingly weighted to represent target populations. Furthermore, participants were selected to overrepresent persons with high exposures, particularly with occupational exposures. While an attempt was made to select participants from the original TEAM 84 studies, data from the TEAM 87 studies were not weighted according to population estimates. EPA researchers did not perform statistical analysis of data for differences between seasons, geographical sites, or locations within homes for chloroform values. However, indoor and outdoor chloroform values from matched sites were statistically compared.

a. Personal Air Sampling Data

Each TEAM study participant carrying a personal air sampler was monitored for two consecutive 12-hour sampling periods. The daytime personal air sampling period reflects the individual's exposure at the workplace and other locations. The nighttime personal air sampling period (6 pm - 6 am) represents a greater percentage of time spent indoors in the home. The personal air data from the TEAM 84 and 87 studies are presented in Tables IV-8, IV-9. Overnight personal exposures were generally higher than the daytime exposures. This suggests that household sources or activities are more important in generating chloroform than occupational or outdoor sources or

Table IV-8

Summary of TEAM 84 Study of Exposure to Chloroform in Personal Air Samples:
25th, Median, 75th, 90th, 95th, and Maximum Percentile Concentrations

[Weighted Concentrations (ppb* by volume)][a]

Location	Date	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
Los Angeles	2/84	0.11	0.20	0.35	0.57	0.74	18.8	0.17	0.31	0.59	1.02	1.23	1.99
Los Angeles	5/84	0.01●	0.06	0.20	0.33	0.70	2.46	0.06	0.14	0.29	1.06	1.09	4.10
Contra Costa	6/84	0.01●	0.01●	0.09	0.34	0.53	0.85	0.01●	0.01●	0.20	0.49	0.55	1.29

● — Value is lower than the median quantification limit.

* — Original data reported in ug/m^3. (Conversion factor: .1 ppb = (4.88) ug/m^3)

a — Population-weighted concentrations based on the following estimated populations:

    Los Angeles   2/84 = 359,492
    Los Angeles   5/84 = 332,615
    Contra Costa 6/84 = 90,696

Source: Pellizzari et al., 1987

Table IV-9

Summary of TEAM 87 Study of Exposure to Chloroform in Personal Air Samples:
25th, Median, 75th, 90th, 95th, and Maximum Percentile Concentrations

[Un-Weighted Concentrations (ppb[*]by volume)]

Location	Date	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
Los Angeles	2/87	0.02@	0.09@	0.26	0.40	0.65	0.86	0.08@	0.20	0.41	0.71	1.99	8.54
Los Angeles	7/87	0.05	0.12	0.24	0.58	8.29	15.5	0.01@	0.08@	0.16	0.51	1.34	1.56

@ - Value is lower than the median quantification limit.

* - Original data reported in ug/m^3. (Conversion factor: 1 ppb = (4.88) ug/m^3)

Source: Pellizzari, et al., 1989

activities. However, this trend did not occur in Los Angeles in July of 1987; daytime chloroform levels were elevated above nighttime levels. It is unclear whether seasonal or other factors were responsible for this variation.

Chloroform personal air exposures were higher during the winter season than the spring/summer season for the Los Angeles area in 1984. Wintertime chloroform levels were also elevated over summertime levels in over-night samples in Los Angeles in 1987. However, this trend was not consistent for 1987 daytime chloroform levels. The factors responsible for this variation are not known.

We chose the median as the best statistic to represent the "average" exposure in the TEAM 84 and 87 studies. Median values were low for both daytime and overnight personal air samples (Tables IV-8 & IV-9) and were in the range of 0.03 to 1.50 ug/m^3 (0.01 to 0.31 ppb) for both TEAM studies. An examination of the 25th to 75th percentile values reveals that the central 50% of the population was exposed to from 0.03 to 2.90 ug/m^3 (0.01 to 0.59 ppb) in day or nighttime air. With the exclusion of the relatively high Los Angeles values of February, 1984, 75% of the personal air values were about or under 2.0 ug/m^3 (0.41 ppb).

The top 10 percent of the sampled population was exposed to substantially higher chloroform concentrations. This is indicated by the range between the 90th percentile and the maximum values. For personal air daytime exposures, the upper 10 percent of values ranged from 1.60 to 92.0 ug/m^3 (0.33 to 18.9 ppb). At night (from 6 a.m. to 6 p.m.), personal air exposures for the upper 10 percent ranged from 2.40 to 20.0 ug/m^3 (0.49 to 4.10 ppb).

b. Fixed-Site Sampling Data - Homes

The most recent information on indoor air from fixed site placement of the air sampling devices is from the TEAM 87 study conducted in Los Angeles, California (Pellizzari et al. 1989). Air sampling devices were placed in two

indoor locations (kitchen and living room) as well as an outdoor location. Twelve-hour day and night samples were collected during two seasons and the results of their analyses are presented in Table IV-11.

As was the case for the previously reported personal sampling data, the median values for the fixed site data were low for both living and kitchen areas; all medians were near or below 1.0 ug/m^3 (0.20 ppb). A look at the 25th to 75th percentile values shows that the central half of the living and kitchen area chloroform levels were in the range of 0.08 to 1.86 ug/m^3 (0.02 to 0.38 ppb) chloroform for 12-hour air samples. Reported 90th percentile and maximum chloroform concentrations indicate substantially higher values for the upper 10 percent of the kitchen and living area samples. These concentrations ranged from 2.68 to 13.0 ug/m^3 (0.55 to 2.66 ppb) for both in-home locations and both seasons. By comparison, the reported upper 10 percent of personal air exposures represented a wider range of values, from 1.96 to 75.6 ug/m^3 (0.40 to 15.5 ppb).

Chloroform concentrations obtained from fixed-site sampling during summer months appear to be lower than those obtained during winter months in TEAM 87 (Pellizzari *et al.*, 1989). A similar pattern was observed in the '84 TEAM study. However, statistical comparisons of these between-season differences were not conducted. Examination of reported data does not reveal substantial differences between daytime and nighttime concentrations or between kitchen and living room concentrations.

De Bortoli *et al.* (1986) studied the concentrations of volatile organic compounds in Italy and used low volume sampling pumps with flow rates similar to those used in the TEAM studies. The authors measured approximately 35 VOCs trapped on charcoal adsorbent. A total of 14 homes and a small office building were measured. The authors reported chloroform concentrations in the range of below 1 ug/m^3 (0.20 ppb) to 15 ug/m^3 (3.07 ppb) with a mean of 1.9 ug/m^3 (0.39 ppb). Most of the chloroform levels were below 1 ug/m^3.

c. Fixed-Site Sampling Data - Public Buildings

Sheldon *et al.* (1988) monitored chloroform levels in the indoor air of a
newly constructed office building. This building, located in rural North
Carolina, was monitored three times during the first 22 weeks after
construction was completed. Occupation began 6 weeks after construction.
Chloroform increased from a median three-day concentration of 0.81 ug/m^3
(0.17 ppb) to 13 ug/m^3 (2.66 ppb) over the 22 week period. Concentrations of
most other volatile organic compounds fell during the 22 week period. These
results indicate that sources other than construction materials were
responsible for the chloroform concentrations.

In the same study, Sheldon and associates (1988) conducted headspace and
chamber studies on building materials and products used in the office
building. Researchers observed significant chloroform emissions from a
number of products (see Section III. D.2 on Consumer Products), but not from
building materials. Volatilization of chloroform from tap water is also a
likely source.

Sheldon *et al.* (1988) also studied chloroform levels in older buildings.
In two homes for the elderly and one school the median values ranged from
0.03 to 1.8 ug/m^3 (0.01 to 0.37 ppb). Maximum values ranged from 0.54 to 4.9
ug/m^3 (0.11 to 1.0 ppb).

d. Comparison of Indoor to Outdoor Air Sampling Data

The 1984 TEAM researchers monitored outdoor air in a subsample of homes.
Outdoor air values were statistically compared with matched indoor values
(Table IV-10). Researchers used overnight personal air values in lieu of
fixed-site data. This .was justified as participants generally remained
inside their homes during the 6 p.m. to 6 a.m. period studied. In the TEAM
87 studies, fixed-site living area and kitchen samples were compared to
outdoor fixed-site data for all households (Table IV-10).

During both 1984 seasons in Los Angeles, researchers measured higher levels of chloroform in indoor air than in outdoor air. These differences were statistically significant when median values for matched-site samples were compared. Similarly, in the TEAM 87 study of the Los Angeles area, indoor air concentrations were typically higher than outdoor concentrations. These differences appear consistent, although not tested for statistical significance. TEAM 84 data from Contra Costa County provided the opposite result; median outdoor chloroform values were higher than indoor values.

Most pollutants analyzed were higher in the February sampling period than the May sampling period in Los Angeles (Wallace, 1988). This was true of both personal air and outdoor levels of chloroform. Outdoors, overnight levels exceeded daytime levels by 50 percent or more across the range of chemicals tested (Wallace, 1987b). Researchers attributed this pattern to a seasonal trend towards higher wintertime pollutant levels. This trend was confirmed by CARB monitoring data from nearby locations (Wallace, L., 1988).

E. OTHER ROUTES OF CHLOROFORM EXPOSURE

1. Water Ingestion

Chloroform is only one of several compounds formed as a by-product of the chlorination of water. Other compounds formed from the reaction of combinations of chlorine and/or bromine atoms and organic matter/ humic acid are referred to collectively as trihalomethanes (THM). The EPA has set the Maximum Contaminant Level (MCL) for total trihalomethanes (THM) in drinking water at 100 ug/L. No MCL exists for chloroform separately. Much of the available monitoring data for drinking water is therefore expressed in terms of total THM.

TABLE IV-10

Indoor and Outdoor Air Levels (ppb[*] by volume)
of Chloroform in California

	Number of Matched Samples	Twelve-Hour Overnight Samples			
		Indoor		Outdoor	
		Median	Maximum	Median	Maximum
Los Angeles (Feb., 1984)	24	0.33**	1.25	0.13	1.21
Los Angeles (May, 1984)	23	0.17**	4.10	0.01	0.49
Contra Costa (June, 1984)	10	0.08	1.29	0.12**	0.31

Source: Pellizzari *et al.* 1987

* - Original data reported in ug/m^3.
  (Conversion factor: 1 ppb = ug/m^3/4.883)
** - Wilcoxon signed rank test for difference in <u>medians</u> (indoor vs. outdoor air). Significant at 0.05 level.

The major source of drinking water for California is surface water; most of this is chlorinated. Approximately 40% of California's domestic water is supplied by groundwater. Much of the groundwater supply is blended with surface water and is also chlorinated.

In the 1976-77 National Organics Monitoring Survey, estimated total THM concentrations of 45, 49, 97 and 110 ug/L in drinking water were given for the communities of Oakland, Los Angeles, San Diego and Concord, California respectively (data cited in Hinman *et al.*, 1986). No estimates of chloroform concentrations were cited.

Table IV-11

Concentration of Chloroform from Fixed-Site Air Samplers:
TEAM 87 Study in Los Angeles
25th, Median, 75th, 90th, 95th, and Maximum Percentile Concentrations

[Un-Weighted Concentrations (ppb* by volume)]

Season	Site	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
Winter	Living Rm	0.09@	0.18	0.35	0.75	1.30	1.93	Not Done[a]					
Winter	Kitchen	0.08@	0.23	0.38	0.62	1.07	1.44	0.07@	0.19	0.35	0.80	1.06	2.38
Winter	Outdoors	0.01@	0.02@	0.12@	0.24	0.39	0.88	0.01@	0.06@	0.08@	0.17	0.22	1.54
Summer	Living Rm	0.02@	0.11@	0.28	0.55	0.75	0.84	Not Done[a]					
Summer	Kitchen	0.02@	0.13	0.28	0.61	1.00	1.25	0.02@	0.12@	0.28	0.62	2.13	2.66
Summer	Outdoors	0.01@	0.02@	0.12@	0.24	1.85	2.05	0.01@	0.03@	0.11@	0.88	1.27	2.68

@ - Value is lower than the median quantification limit.

* - Original data reported in ug/m^3. (Conversion factor: 1 ppb = (4.88) ug/m^3)

a - Time and locations not measured and not part of the experimental design.

Source: Pellizzari, et al., 1989

In a 1981-82 national survey of groundwater supplies, chloroform was reported at a median concentration of 1.4 ug/L for smaller water supply systems serving less than 10,000 people and 1.6 ug/L for the larger systems serving more than 10,000 people (Westrick, J. *et al.*, 1984). Maximum levels of 140 and 300 ug/L were reported for small and large systems, respectively. Water was sampled at the distribution system site.

An estimated range of 4 to 80 ug/L total THM was reported in five water supply systems in the Santa Clara Valley of California (Hinman *et al.*, 1986). Data on individual THM in two of these water supply systems (both surface water) indicate that chloroform comprised from 21 to 88% of the total THM.

' In a study of large public water systems, approximately 4 percent of the sampled wells were contaminated with chloroform at levels up to 54 ug/L (CDHS, 1986). The median concentration was 1.5 ug/L. Only 0.6 percent of sampled wells were chloroform contaminated in a study of small public water systems (CDHS, 1987). Chloroform was found in these wells at levels up to 84 ug/L. The median concentration was 2.2 ug/L.

Tap water samples were collected from each of the homes of the California 1984 TEAM study participants; the data are presented in Table IV-12. Chloroform was measured at median levels ranging from 14.5 to 48.9 ug/L (ppb) in Los Angeles and Contra Costa county. Maximum values ranged from 52.0 to 99.4 ug/L.

Water monitoring data prior to about 1980 generally reflects conditions before mitigation measures were commonly used by water suppliers to reduce total THM (Spath, 1988). Monitoring data for surface water supplies for the late 1980's may reflect the use of such mitigation measures. These data are not currently available in summarized form for California.

TABLE IV-12

Chloroform Concentrations (ug/l)
in Drinking Water Samples

	Sample Size	Median	Percentile 90th	95th	Max.
LA - 2/84	117	14.5	28.0	32.0	59.6
LA - 5/84	52	33.0	46.6	49.2	52.0
CC - 6/84	71	48.9	76.6	90.6	99.4

Source: Pellizzari et al., 1987

LA - refers to Los Angeles
CC - refers to Contra Costa

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2.   Food Ingestion

Chloroform is not routinely monitored in U.S. food and food products by the Federal Food & Drug Administration (personal communication, G. Diachenko, 6/10/88). As a consequence, no estimates for U.S. per capita daily intake exist.

Chloroform was found in process waters at levels of 4.6 to 57 ng/g (ppb) at five of fifteen food processing plants in five states by the headspace capillary gas chromatography method (Uhler & Diachenko, 1987).

Chloroform was detected in 13 of the 39 food products tested at these plants at levels of 2.3 to 31 ng/g in sodas and a variety of milk products. Chloroform was detected as a trace amount in process waters of only one of the two California plants tested, but no amounts were detected in the foods. Food processing plants which were judged likely to use contaminated water were chosen for this study.

Currently, the only solvent allowed in use for the production of decaffeinated coffee in the U.S. and Canada is methylene chloride. However, chloroform was found in 6 of 11 instant decaffeinated coffees at levels of 9.9 to 24 ppb and in 3 of 14 ground decaffeinated coffees at levels of 25 to 33 ppb by Heikes (1987) using a modified purge and trap procedure.

In a pilot project which monitored 39 foods purchased at retail markets in three geographical areas, chloroform was found in individual beverages and milk products at levels ranging from 9 to 178 ng/g (Entz et al., 1982). Chloroform was found at lower levels and incidences in composites (table-ready mixtures of foods) which combined beverages or milk products, indicating that significant losses through volatilization may occur during food preparation. No chloroform was found in prepared meat composites. Because of the limited sampling in this study, conclusions regarding the general magnitude of chloroform residues in foods could not be drawn.

In a sampling study of chlorinated halocarbons in butter, chloroform was detected in all 46 samples taken from 14 retail outlets in the Washington D.C. area (Miller and Uhler, 1988). An average of 92 ng/g and a range of 32 to 255 ng/g chloroform was found. In a similar study of margarine samples from 18 retail outlets also in the Washington D.C. area, no chloroform was detected in 13 of 18 samples taken (Entz & Diachenko, 1988). In 4 of the remaining 5 samples, less than 10 ppb chloroform was found. Chloroform was detected at less than 50 ng/g in all five samples. Somewhat higher levels were detected at a margarine manufacturing plant sampled in the same study. Chloroform was detected in the 100-150 ng/g range for 2 of 19 samples. The remaining samples contained non-detectable amounts or less than 50 ng/g chloroform.

Fish from polluted marine waters of Norway were sampled and found to have levels of chloroform ranging from 120 to 220 ug per kg (ppb) of fat weight in five species of fish (Ofstad et al., 1981). Chloroform was found in half the samples tested. In another study, five species of fish from relatively unpolluted waters in the Irish Sea were found to have 72 to 649 ng chloroform per gram of muscle tissue (Dickson & Riley, 1976). Chloroform was also detected at 56 to 129 ng per gram muscle weight in three species of mollusks.

Chloroform levels in adhesives used for margarine packaging ranged from only trace amounts detected to 5 ug/g (ppm) for 3 of 11 samples analyzed (Entz & Diachenko, 1988). However, the amount of chloroform that might migrate from packaging to margarine under various conditions is unknown. FDA has approved chloroform as an indirect food additive in its use as a component of adhesives and as an adjuvant substance required in the production of polycarbonate resins (U.S. EPA, 1985)

Chloroform has been exempted from tolerance when used as a solvent in pesticide formulations (CFR, 1982d) or when used as a fumigant after harvest for various cereal crops (CFR, 1982e). No data was found on chloroform residues from these uses. Chloroform is not currently registered for use as a fumigant in California (T. Formoli, 1988).

F. ESTIMATES OF TOTAL EXPOSURE FROM INDOOR AIR COMPARED TO EXPOSURE FROM INGESTION OF WATER AND FOOD

Exposure to chloroform in the indoor air environment provides a significant proportion of the total daily exposure to this toxic air contaminant.

We estimated daily doses for "average" and "high" exposures to chloroform in indoor air or water from median and 90th percentile values, respectively. These estimates are derived from the five 1984 and 1987 California TEAM data sets representing different seasons, geographical areas and times. The data are presented in Table IV-13. Note that the total exposure estimates for indoor air are based on data expressed in ug/m^3.

These data are converted to ppb by volume in Tables IV-8, IV-9, IV-10 and IV-11. Total exposure estimates for drinking water are expressed in ppb by weight. Values expressed in ppb by volume are not directly equivalent to values expressed in ppb by weight.

1. Indoor Air Pollution

Daily exposures to chloroform in the indoor air are estimated from overnight personal air concentrations. Overnight personal air concentrations are the most representative measure available in the TEAM data sets of human exposures to a toxicant present in the household air environment. The 12-hour daytime personal air sample concentrations represent greater amounts of time spent in the outdoors and in the workplace, and are not used in this total exposure analysis.

By assuming that about 10 m^3 of air are breathed over a 12-hour period, it is estimated that the "average" human is exposed to from 0.3 to 15 ug chloroform during that time. A simple doubling of these values estimates daily exposure to be 0.6 to 30 ug.

With the exclusion of the exceptionally low Contra Costa values, it is likewise estimated that the "high" daily exposures are in the range from 25.1 to 52.0 ug for 12-hour exposure and 50.2 to 104 ug for daily exposure.

Exposure to chloroform from inhalation of indoor air appears to be of a lesser magnitude than that from drinking water. However, this source of exposure is a significant component of the total daily exposure. Risk assessments based on drinking water exposure alone will significantly underestimate health risk from chloroform.

2. Drinking Water

Tap water samples from the 1984 TEAM study provide the basis for daily estimates of chloroform exposure. Assuming that about two liters of water are drunk per day, the "average" human consumption is estimated to be from 29.0 to 97.8 ug of chloroform per day. Similarly, it is estimated that the

"high" daily exposures are in the range of 56.0 to 153.2 ug per day. In a worst case scenario where the chloroform concentration is assumed equivalent to the MCL for total trihalomethanes (100 ug/L), the estimate for daily exposure is 200 ug.

3. Food

Chloroform exists as a contaminant in food products. Data exists for a variety of beverages, fishes, butters and margarines. However, the FDA has not monitored chloroform in a sufficient variety of food and food products to estimate a per capita daily chloroform intake.

4. Indoor Swimming Pool Visits

Lahl et al., (1981) estimate that a single swimming pool visit in Bremen, West Germany may yield an average exposure of 50 micrograms per person per visit. This estimate assumes a one-hour visit, a 30-minute swim and about one cubic meter of air breathed. Under the maximum exposure conditions, these researchers estimate an exposure of 500 ug per person per visit. This estimate assumes an hour of vigorous swimming and maximum chloroform outgassing and absorption.

G. INDOOR AIR EXPOSURE RELATIVE TO TOTAL EXPOSURE

Exposure to chloroform in indoor air provides a significant proportion of the total daily exposure to this toxic air contaminant. This exposure is a significant addition to exposure through drinking chlorinated tap water and breathing ambient air. Risk assessments based on human exposure to chloroform only through drinking water and ambient air greatly underestimate total chloroform exposure.

Most chloroform is produced from the haloform reaction of chlorine with various organic precursors. This chloroform is released into indoor air by vaporization from a number of sources: chlorinated tap water, chlorinated pools and spas and household bleach product use for disinfection. Chloroform is also used as a solvent in the manufacture of products commonly

found in homes or offices. Products as varied as rubber, photo equipment or stain remover may contain and off-gas chloroform. The best sources of exposure data in the indoor household environment come from the Total Exposure Assessment Methodology (TEAM) studies conducted by EPA in 1984 and 1987. Chloroform was found at higher levels in indoor air than outdoor air in both TEAM studies. The range of medians for chloroform in the outside air was 0.03 to 0.65 ug/m^3 (0.01 to 0.13 ppb). The range of medians for chloroform measured from fixed-site samplers in the inside air was higher: 0.56 to 1.11 ug/m^3 (0.11 to 0.23 ppb). In overnight personal air samples the median range was 0.03 to 1.50 ug/m^3 (0.01 to 0.31 ppb), also higher than outdoor air.

Chloroform levels were higher in the winter than in the summer for both TEAM studies. The factors responsible for this are unknown; however a possible cause might be reduced ventilation of houses during the colder winter months. For personal air samples, nighttime levels were higher than daytime levels. This suggests that household sources or activities are more important than occupational or outdoor sources or activities in personal exposure to chloroform. Nighttime levels were not substantially higher than daytime levels for fixed-site kitchen and living area samples.

The average chloroform levels in personal air samples were low. These ranged from 0.03 to 1.5 ug/m^3 (0.01 to 0.31 ppb) for both TEAM studies. The upper 10% of the sample population received substantially higher exposures. These were in the range of 1.6 to 92.0 ug/m^3 (0.33 to 18.8 ppb) of chloroform. All average values for fixed-air kitchen and living area samples were below or near 1.0 ug/m^3 (near 0.20 ppb). The upper 10% of the fixed air sample values ranged from 2.68 to 13.0 ug/m^3 (0.55 to 2.66 ppb). Maximum and 95th percentile values for kitchen and living areas were generally lower than personal sample values. This suggests that personal activities play an important role in determining peak exposures to chloroform.

The median chloroform level in a new office building rose to 13 ug/m^3 (2.66 ppb) during the 22 weeks following construction (Sheldon *et al.*, 1988). This finding indicates that sources other than construction materials were responsible for the chloroform concentrations. These sources might include vaporization from water sources or from products brought in and/or used in buildings after construction. Sheldon *et al.*, (1988) also monitored chloroform in older buildings. Median concentrations of chloroform were much lower, in the range of 0.03 to 2.0 ug/m^3 (0.01 to 0.41 ppb). These lower concentrations could reflect the relative lower energy efficiency of older buildings.

We estimate the indoor inhalation exposure to chloroform, based on median personal air exposure, to range from 0.6 to 30 ug per day. It is clear that some portion of the population is exposed to higher levels; we chose the 90th percentile statistic to represent those higher exposures. Excluding the exceptionally low Contra Costa values, we estimate the upper exposures to range from about 50 to 104 ug per day. These upper and lower indoor air exposure ranges are comparable to the "average" chloroform exposure range through drinking chlorinated tap water.

We estimate a daily "average" drinking water exposure of 29 to about 98 ug per day. We estimate the upper drinking water exposures, to be 56 to about 153 ug per day, based on the 90th percentile values from the TEAM 84 data.

Chloroform exists as a contaminant in food products. Data exists for a variety of beverages, fishes, butters and margarines. However, the FDA has not monitored chloroform in a sufficient variety of food and food products to estimate a per capita daily chloroform intake.

Individuals who use indoor swimming pools or spas significantly increase their personal exposures. Lahl *et al.* (1981), estimate that swimming pool visits can increase one's total exposure by from 50 to 500 ug per visit.

TABLE IV-13

Estimated Doses of Chloroform Exposure
Through Different Media

INDOOR AIR

Location-Date	Estimated inhaled dose based on median conc., personal air at home 12-hr. (ug/12 hours)	Estimated inhaled dose based on 90th percentile, personal air at home 12-hr. (ug/12 hours)	Ref.
LA - 2/84	15.0	50.0	a
LA - 5/84	6.7	52.0	a
CC - 6/84	0.3	0.3	a
LA - 2/87	9.8	34.7	b
LA - 7/87	3.7	25.1	b

DRINKING WATER

Location-Date	Estimated ingested dose based on median conc., tap water (ug/day)	Estimated ingested dose based on 90th percentile, tap water (ug/day)	Ref.
LA - 2/84	29.0	56.0	a
LA - 5/84	66.0	93.2	a
CC - 6/84	97.8	153.2	a
Estimated dose based on assumption that 100% of the MCL consists of chloroform (MCL = 100 ug/L):		200	c

FOOD

No national or statewide estimates for per capita daily intake of chloroform are available.   d

(continued)

Table IV-13 (cont.)

INDOOR SWIMMING POOL VISITS

Location-Date	---Estimated Inhaled Dose ---		
	Average exposure	Maximum exposure	
Bremen - West Germany	50 ug/visit	500 ug/visit	e

References:
- a: Pellizzari, E. *et al*., 1987
- b: Pellizzari, E. *et al*., 1989
- c: U.S. E.P.A., Health Assessment Document for Chloroform, 1985
- d: Diachenko, G, 1988
- e: Lahl, U. *et al*., 1981

Calculations:

Air: 10 m^3 of air is assumed breathed per 12 hour period
Example: If the 12-hour overnight personal air median is 1.50 ug/m^3, the 12-hour estimate is 15.0 ug.

Water: 2 liters of water is assumed drunk per day
Example: If the tap water sample median is 14.5 ug/L, the 24-hour estimate is 29 ug.

V. PERSISTENCE IN THE ATMOSPHERE

Atmospheric Fate of Chloroform

A. INTRODUCTION

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, the number of potentially important, gas-phase, chemical reaction pathways in the atmosphere include:

o   Photosynthesis during daylight hours

o   Reaction with the hydroxyl (OH) radical, mainly during daylight hours

o   Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours

o   Reaction with the nitrate (NO_3) radical during the nighttime hours

o   Reaction with dinitrogen pentoxide (N_2O_5) during the nighttime hours

o   Reaction with nitrogen dioxide (NO_2)

o   Reaction with ozone (O_3)

o   Reaction with gaseous nitric acid (HNO_3)

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3).

In this section, we describe the available literature data concerning the chemical and physical removal processes for chloroform and estimate its resulting atmospheric lifetime. We will also briefly summarize some of the available literature concerning typical ambient atmospheric concentrations of chloroform. Chloroform is gaseous under

atmospheric conditions, and hence only the gas-phase processes need be considered.

B. CHEMICAL LOSS PROCESSES

1. Ozone

No experimental data are available concerning the rate constant for the gas-phase reaction of chloroform with ozone. However, the fact that any elementary reaction between O_3 and the alkanes has a room temperature rate constant of $\leq 10^{-23}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Carter 1984), combined with the lower reactivity of haloalkanes compared to the alkanes towards the H-atom abstraction processes (Atkinson 1986, 1987), allows us to place an upper limit on the room temperature rate constant for the reaction of O_3 with CHCl$_3$ of k(O_3+ CHCl$_3$) $\leq 10^{-23}$ cm^3 molecule^{-1} s^{-1}.

2. OH Radicals

Kinetic data for the reaction of OH radicals with chloroform have been obtained by Howard and Evenson (1976), Cox et al. (1976), Davis et al. (1976), Jeong and Kaufman (1982) and Klopffer et al. (1986). These data are given in Table V-1, and those of Howard and Evenson (1976), Cox et al. (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are plotted in Arrhenius form in Figure V-1 [both adapted from Atkinson (1988)].

The room temperature rate constant obtained from the relative rate study of Cox et al. (1976) is uncertain by a factor of ~2, because of uncertainties in the number of NO to NO$_2$ conversions occurring after the initial OH radical reaction. The rate constant derived from the study of Klopffer et al. (1986) is not used in the evaluation of the rate constant for this reaction because of the lack of details concerning their experimental conditions.

It can be seen that the absolute rate constants of Howard and Evenson (1976), Davis *et al.* (1976) and Jeong and Kaufman (1982) are in excellent agreement. Thus, a unit-weighted, least-squares analysis of the data of Howard and Evenson (1976), Davis *et al.* (1976) and Jeong and Kaufman (1982), using the equation $k=AT^2e^{-B/T}$, yields the recommended expression of

$$k(CHCl_3) = (6.30 \, {}^{+1.18}_{-1.00}) \times 10^{-18} \, T^2 \, e^{-(504 \pm 56)/T} \, cm^3 \, molecule^{-1} \, s^{-1}$$

over the temperature range 245-487 K, where the error limits are two least-squares standard deviations (Atkinson 1988). From this expression, values of the rate constant for the reaction of OH radicals with $CHCl_3$ at 298 K (room temperature) and 265 K (the average tropospheric temperature) are

$$k(CHCl_3) = 1.03 \times 10^{-13} \, cm^3 \, molecule^{-1} \, s^{-1} \text{ at 298 K}$$

and

$$k(CHCl_3) = 6.6 \times 10^{-14} \, cm^3 \, molecule^{-1} \, s^{-1} \text{ at 265 K}$$

with an estimated overall uncertainty of $\pm$ 20% at 298 K and $\pm$ 35-40% at 265 K. The rate constant at 298 K is identical to those recommended by Atkinson (1986) and the recent NASA evaluation panel (DeMore *et al.* 1987).

3.   NO_3 Radicals

No experimental data are available concerning the rate constant for gas-phase reaction of NO_3 radicals with chloroform. However, by analogy with the experimental data for the C_4-C_9 alkanes (Atkinson *et al.* 1988) and the observation that the rate constant for H-atom abstraction from $CHCl_3$ by OH radicals is lower than those for the $\geq C_2$ alkanes (Atkinson 1986, 1988), the room temperature rate constant for the reaction of NO_3 with $CHCl_3$ is expected to be $k(NO_3 + CHCl_3) < 10^{-17} \, cm^3 \, molecule^{-1} \, s^{-1}$.

Table V-1

Rate Constants k and Arrhenius Parameters ($k = AT^n e^{-B/T}$) for the Gas-Phase Reaction of the OH Radical with $CHCL_3$

| $10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature Range Covered (K)
			10.1 ± 1.5	296 ± 2	DF-LMR	Howard and Evenson (1976)	
			20.2	298	RR [relative to k(OH + methane) = 8.45 × 10^{-15}]^a	Cox et al. (1976)	
			4.39 ± 0.28	245	FP-RF	Davis et al. (1976)	245-375
			11.4 ± 0.7	298			
.69 ± 0.71		1134 ± 106	21.8 ± 1.4	375			
			5.51 ± 0.41	249	DF-RF	Jeong and Kaufman (1982), Jeong et al. (1984)	249-487
			10.1 ± 0.65	298			
			16.0 ± 1.0	339			
			23.2 ± 1.6	370			
			30.8 ± 2.0	411			
			44.8 ± 2.7	466			
.91 × 10^{-8} .63 ± 0.68	2.65 ± 1.13	262 ± 398 1183 ± 45	55.0 ± 3.9	487			
			29	300	RR [Relative to k(OH + toluene) = 5.91 × 10^{-12}]^a	Klopffer et al. (1986)	

[a] As evaluated by Atkinson (1988).
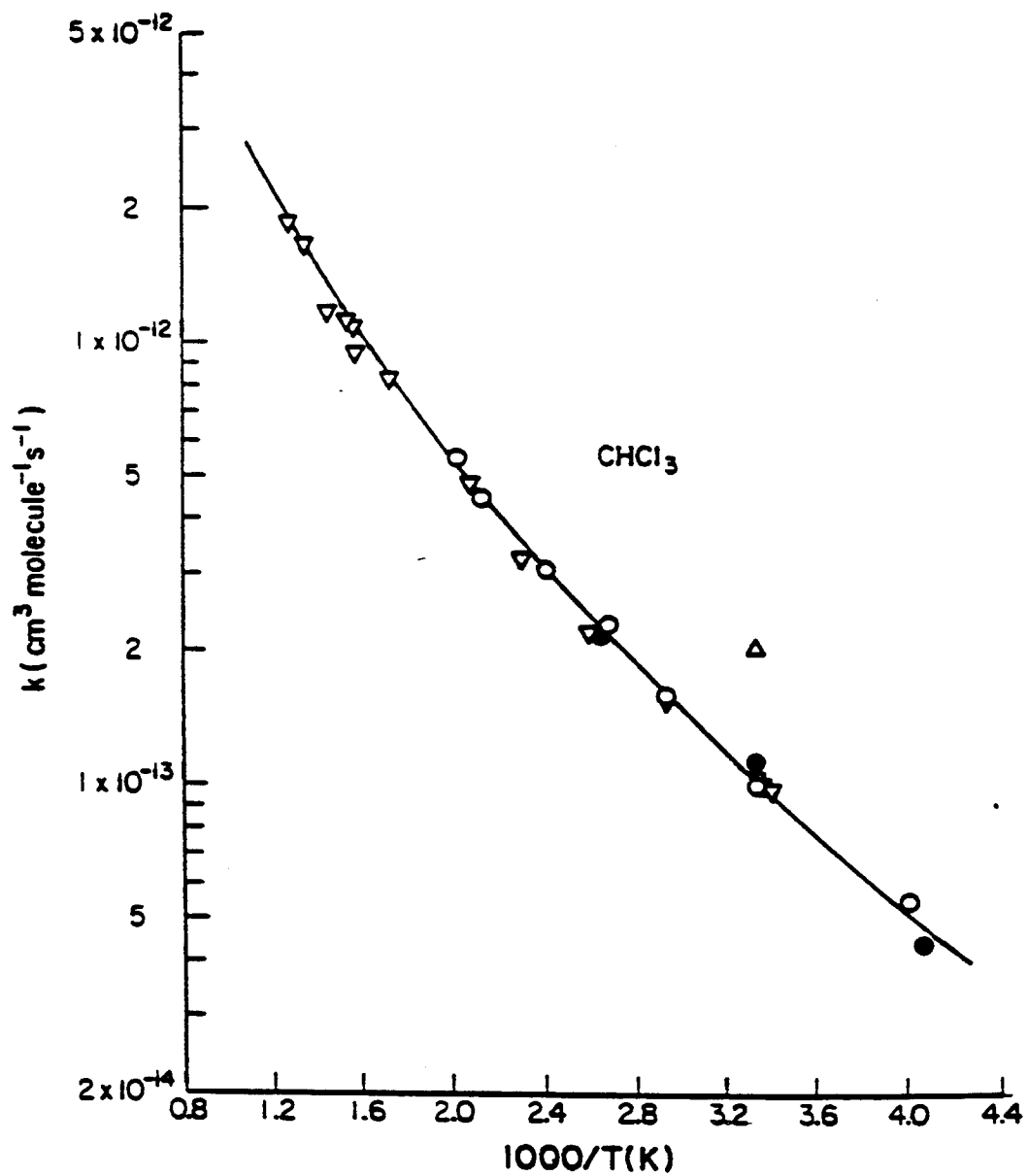
FIGURE V-1.

Available kinetic data for chloroform. Data from: ◯ Jeong and Kaufman (1982), ● Davis et al. (1976), △ Cox et al. (1976), ☐ Howard and Evenson (1976).

4. Other Chemical Species

Based on chemical considerations, none of the other reactive species present in the troposphere (Section V-A) are expected to react with chloroform, certainly not at rates which are significant relative to its rate of reaction with OH radicals.

5. Photolysis

Several determinations of the absorption cross section of chloroform have been reported in the literature (Robbins 1977, Hubrich and Stuhl 1980, Simon *et al.* 1988). The long wavelength cutoff in the UV absorption spectrum of chloroform (the wavelength for which the absorption cross-section σ falls below a value which corresponds to photolysis being of negligible importance [i.e., $\sigma < 10^{-23} cm^2$]) is reported to be at 260 nm (Hubrich and Stuhl, 1980). Based on these data, chloroform will not undergo photolysis in the troposphere at any measurable rate (WMO 1985, DeMore *et al.* 1987), since only radiation of wavelength ≤ 290 nm penetrates into the troposphere.

Thus, the only significant chemical removal process for $CHCl_3$ in the troposphere is by reaction with the OH radical.

C. ATMOSPHERIC REACTIONS

Since the OH radical reaction is the only significant loss process, only this reaction need be considered in evaluating the products formed from the atmospheric degradation of $CHCl_3$.
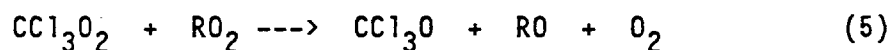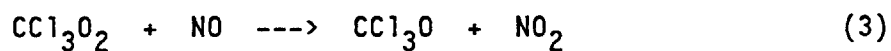
Chloroform is expected to undergo H-atom abstraction by OH radicals to form water and the CCl_3 radical

$$OH \; + \; CHCl_3 \; ---> \; \overset{\cdot}{C}Cl_3 \; + \; H_2O \qquad (1)$$

The CCl₃ radical will then react rapidly with molecular oxygen to form
the peroxy radical (Cooper *et al.* 1980)

$$CCl_3 + O_2 \longrightarrow CCl_3O_2 \qquad\qquad (2)$$
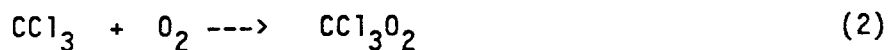
with a room temperature rate constant of 5.1×10^{-12} cm^3 molecule^{-1} s^{-1},
follwed by reaction with NO (if present), HO₂ radicals or other peroxy
radicals (RO₂) [Reactions (3-5)]

$$CCl_3O_2 + NO \longrightarrow CCl_3O + NO_2 \qquad\qquad (3)$$

$$CCl_3O_2 + HO_2 \longrightarrow CCl_3OOH + O_2 \qquad\qquad (4)$$

$$CCl_3O_2 + RO_2 \longrightarrow CCl_3O + RO + O_2 \qquad\qquad (5)$$

Only for the NO reaction is a rate constant available, of 1.7×10^{-11}
cm^3 molecule^{-1} s^{-1} at 298 K (Dognon *et al.* 1985).

Although the reactions with H₂O or RO₂ given above have not been
experimently studied, the products are those expected based upon other
alkyl peroxy radical reactions.

The CCl₃O radical then undergoes rapid unimolecular decomposition
to produce COCl₂ (phosgene) and a Cl atom (Rayez *et al.* 1987), with a
rate constant $>1 \times 10^5$ sec^{-1} at 298 K (Atkinson 1988). The Cl atoms
will react with other organics (mainly CH₄) present in the atmosphere to
yield HCl which is then rained out of the troposphere.

D. PHYSICAL LOSS PROCESSES

The physical removal process can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles, at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our current understanding of these processes, which are dynamic in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Biddleman 1988).

Information concerning physical removal processes for chloroform is very limited. No data appear to have been reported for dry deposition. A calculated washout ratio of 8.35 at 293 K has been reported (Terry-Dana *et al*. 1985). This washout ratio can be compared to ratios of 10^5 to 10^6 for compounds which are efficiently removed by precipitation events (such as phenol and particles). Since the washout ratio for $CHCl_3$ is some four to five orders of magnitude less than that corresponding to efficient wet deposition, it is clear that wet deposition of chloroform will be negligible compared with chemical reaction with OH radicals.

E. ATMOSPHERIC FORMATION PROCESSES

No chemical formation processes for $CHCl_3$ in the atmosphere have been identified.

F. ATMOSPHERIC LIFETIMES

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of $1/e$ (= 0.368) of the initially present concentration of that chemical (Pitts *et al. 1986*). *Also,*

$$\frac{1}{\tau} = \frac{1}{\tau_{chemical}} + \frac{1}{\tau_{physical}}$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemicals with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{chemical}} = \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}}$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3 respectively. In turn, these reactive loss processes are determined by the rate of constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example:

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ) and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda \phi_\lambda J_\lambda d_\lambda$$

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The presently accepted 12-hr daytime average tropospheric OH radical concentration in the northern and southern hemispheres is 1.5 x 10^6 radicals cm^{-3} (Prinn *et al.* 1987), which is derived from a knowledge of the total worldwide emissions of CH_3CCl_3 and the present atmospheric burden of CH_3CCl_3. Using this value and the rate constants given above for 265 K (the "average" temperature of the troposphere) and 298 K, a range of atmospheric lifetime for chloroform of 150 to 230 days (assuming a temperature of 265 K) is obtained. This is in reasonable agreement with calculated atmospheric lifetime of 120 and 180 days reported by Rasmussen *et al.* (1982) and Khalil *et al.* (1983), respectively, based upon measurements of the atmospheric concentrations of $CHCl_3$ and the estimated anthropogenic $CHCl_3$ emissions into the troposphere.

Clearly, chloroform is a persistent compound in the troposphere, and it will be dispersed from its anthropogenic emission sources not only regionally and over continental distances, but also globally (in agreement with atmospheric measurements).

G. AMBIENT CONCENTRATIONS

The average observed concentrations of chloroform in seven U.S. cities in 1980 and 1981 have been reported by Singh *et al.* (1982) to range from 73 parts per trillion (ppt) in St. Louis to 703 ppt in Riverside, CA. The minimum and maximum concentrations observed in Riverside between July 2-12, 1980 was 109 and 4,750 ppt, respectively. In a separate study, Singh *et al.* (1981) reported the diurnal variation of chloroform in Phoenix, AZ to range between ~50 and 330 ppt.

With respect to tropospheric background levels of chloroform, average values of 30 and 19 ppt were reported for 1981 for the northern and southern hemispheres, respectively, leading to a global tropospheric average of 25 ppt (Khalil *et al.* 1983). No data were given for the rate of increase in the tropospheric background levels of chloroform.

H. CONCLUSIONS

The only significant loss process for chloroform in the troposphere is reaction with hydroxyl radicals, leading to a tropospheric lifetime in the range of 150 to 230 days.

APPENDIX A

APPENDIX A-1: Pharmaceutical Manufacturing

EMISSION ESTIMATE

A survey conducted by the Pharmaceutical Manufacturers Association (PMA, 1984) resulted in the following disposal statistics on a national level. (Mg = megagram)

Annual chloroform purchase	1,150 Mg
Direct air emissions	575 Mg
Sewer	150 Mg
Incineration	100 Mg
Contract haul	50 Mg
Other disposal or loss	250 Mg

Approximately half of the pharmaceutical industry responded to the survey. The above numbers are therefore doubled and are used to estimate chloroform emissions. From the above categories, direct air emissions (575 Mg) and sewer emissions (150 Mg) will result in air pollution, assuming the chloroform in the sewer will eventually evaporate to the air. If we double the sum from these two categories, there is an estimated 1,450 Mg of chloroform released to the air in the United States from the pharmaceutical industry.

California has approximately 12% of the 800 pharmaceutical facilities in the the U.S. (GCA, 1984). If we assume that California is responsible for 12% of the chloroform emissions caused by pharmaceutical production in the United States then:

$$\frac{1450 \text{ Mg } CHCl_3}{year} \times 12\% \times \frac{1.1023 \text{ tons}}{1 \text{ Mg}} = \frac{190 \text{ tons } CHCl_3}{year}$$

There is an estimated 190 tons of chloroform emissions per year from pharmaceutical manufacturing sources in California.

APPENDIX A-2: OBPA & 1,3-Diisocyanate & Deaeration

EMISSION ESTIMATE

The Sacramento County Air Pollution Control District reported in 1984 that Aerojet has chloroform emissions equal to 7 tons per year (Skelton, 1984).

The Sacramento County Air Pollution Control District contacted Aerojet by telephone in March 1989, and the district reports that both the OBPA and 1,3-diisocyanate process are presently idle but the permits are still active (Skelton, 1989). The 1,3-diisocyanate process has been inactive for a few years. The OBPA process has been inactive for over a year. The future of the OBPA process will depend on whether there are anymore contracts requiring the process. The 1,3-diisocyanate process permit will probably be canceled.

APPENDIX A-3: Fluorocarbon 22 Production

<u>EMISSION ESTIMATE</u>

Emissions of chloroform occur in the following sources in the production of fluorocarbon 22: equipment leaks, storage tanks, process vents, handling operations, equipment openings, secondary waste streams, and liquid spills. The Allied Corp. plant in El Segundo has 5.1 megagrams per year chloroform emissions for equipment leaks and 0.01 megagrams per year emissions for equipment openings while the other sources have no reported emissions. The total is then 5.11 megagrams chloroform per year as stated in the <u>Technical Report:</u> <u>Chlorofluorocarbon Production</u> (TRCP, 1986).

$$\frac{5.11 \text{ Mg}}{\text{year}} = \frac{5.6 \text{ tons of CHCl3}}{\text{year}}$$

A common practice in the industry is to produce more than one type of chlorofluorocarbons in the same production equipment by switching feedstocks periodically. This practice is referred to as campaigning. At facilities that campaign, emissions of the feedstock materials occur only during that portion of the year that the feedstock is used. The equipment leaks and process vents emissions were estimated assuming that the chloroform is used 100% of the time. This assumption over estimates total emission from equipment leaks and process vents, such that 5.6 tons per year may be a high estimate of chloroform emissions.

Annual statewide air emissions of chloroform from Fluorocarbon 22 production are estimated to be 5.6 tons.

APPENDIX A-4: Swimming Pools

Chloroform emissions from swimming pools are very complex due to such factors as sunlight, meteorological conditions, chlorination practices, activities, and the number of pools. The lower and upper limits of chloroform emissions from swimming pools reported in the text reflect this complexity.

The upper limit of chloroform emissions was estimated using the method developed by SAIC while the lower limit was estimated by adjusting the upper limit to reflect differences in the data from an on-going study at the University of California, Davis (UCD). According to the UCD study, the molar ratios (defined as the moles of chloroform produced per mole of chlorine consumed in the swimming pools) as measured in their tests may be lower by a factor of 100 compared to those of the SAIC study (Chang, D., 1990).

The following paragraphs summarize the methods discussed in the SAIC study. The upper limit of the emission estimate will be discussed subsequently. Note that this estimate does not include commercial pools.

SAIC categorized swimming pools into three types, inground pools, above ground pools, and spas and hot tubs. The number of pools in California for each group are estimated separately because sales data are kept separate.

SAIC conducted swimming pool emission tests under two conditions, which resulted in two emission flux estimates for chloroform. The first condition is when the water is undisturbed, and the second condition for when the water is agitated. When the surface water is undisturbed by the pool activity, the average flux was 12 micrograms of chloroform per square meter per minute. When the surface water was agitated, the average flux was 320 micrograms of chloroform per square meter per minute. A weighted flux rate of 22.3 micrograms (22.3×10^{-9} kg) of chloroform per square meter per minute is obtained by using the two flux rates and the hours/days spent in each condition per month and year (Rogozen, 1988).

This flux estimate takes into account the amount of chlorination and the season of the year when it is added. Enough chlorine is added to allow the formation of chloroform and so the flux estimate will not use time as a variable. Temperature is also not directly accounted for in the flux rate. Temperature is related to the time of the year and also the amount of chlorination. The warmer seasons of the year require more chlorination and this is accounted for in the flux estimate.

An estimate of swimming pool emissions is obtained by multiplying the total water surface area by the weighted flux rate.

EMISSION ESTIMATE

Surface Area for Inground Pools

There are an estimated 570,000 inground swimming pools in
California (Rogozen, 1988). The area of the pool at which the flux
tests were conducted was approximately 40 square meters. SAIC
qualitative judgement is that this is the typical size of an
inground swimming pool in the South Coast Air Basin (SCAB) and that
the actual average size would not differ by more than a factor of
1.5. Assuming that 40 m^2 is representative of the average inground
pool in California then the total water surface area for inground
pools is estimated to be:

$$\frac{40 \ m^2}{pool} \times 570,000 \ pools = 2.28 \times 10^7 m^2 \ surface \ area$$

Surface Area For Above Ground Pools

Approximately 115,900 above ground pools are in use in California.
The above ground pools are divided according to their size into
three groups as shown below. An assumption is made that the 1985
sales of each relative size pool is representative of all sales in
the past (Rogozen, 1988).

The average diameter is assumed to be 10 feet (3.048 meters), 20
feet (6.096 meters), 24 feet (7.315 meters) for the small, medium,
and large pools respectively. Using the equation for area
(pi)(dia/2)^2, the surface areas are 78.5 square ft.(7.3 m^2), 314.2
square ft.(29.2 m^2), 452.4 square ft.(42.0 m^2). for each small,
medium, and large pool, respectively.

%*	Relative Size	Dia(ft.)	Number of Pools	Surface Area(m^2)	Total Surface Area(m^2)
52.5	small 12' or less	3.048	60,800	7.3	444,000
41.3	medium 15' to 24'	6.096	47,900	29.2	1,398,000
6.2	large 24' or more	7.315	7,200	42.0	302,000
----			-------		---------
100			115,900		2,144,000

*Expressed as a percentage of total estimated above ground pools in
California.

The three sizes of above ground pool in California have an
estimated 2,144,000 square meters of surface area.

Surface Area of Spas and Hot Tubs

California has an estimated 20% or 223,800 spas and hot tubs of the total 1,119,000 (NSPI, 1985) spas and hot tubs in the United States (Rogozen, 1988).

The average capacity of a spa or hot tub is 1000 gallons (133.68 cubic ft.). Assuming a water depth of 2 ft.(0.61 m) the corresponding surface area would be 66.84 square ft.(6.21 m^2). The total surface area for spas and pools is then:

$$\frac{6.21 \ m^2}{pool} \times 223,800 \ spas \ \& \ hot \ tubs = 1,390,000 \ m^2 \ surface \ area$$

Estimate of Emissions by Surface Area

The total surface area of all the swimming pool sources in California is then :

22,800,000 m^2 total surface area of inground pools

 2,144,000 m^2 total surface area of above ground pools

 1,390,000 m^2 total surface area of spas and hot tubs

26,334,000 square meters of total surface area

The annual estimated emissions are:

$$\frac{22.3 \times 10^{-9} \ kg}{m^2 \ min} \times 26,334,000 \ m^2 \times \frac{525,600 \ min}{yr} = \frac{308,700 \ kg}{yr}$$

$$\frac{308,700 \ kg \ CHCl3}{year} \times \frac{2.2046 \ lb}{1 \ kg} \times \frac{1 \ ton}{2,000 \ lb} = \frac{340 \ tons \ CHCl3}{year}$$

There is an estimated 340 tons of chloroform emissions per year from swimming pool sources in California.

APPENDIX A-5: Drinking Water (For Consumption and Usage)

The emission estimate is based on data collected from two EPA surveys: National Organics Reconnaissance Survey (NORS), (Symons, 1975) and the National Organics Monitoring Survey (NOMS), (U.S. EPA, 1977). The surveys estimate the average amount of chloroform generated in finished drinking water. Drinking water samples were analyzed from a total of 137 cities nationwide, including 8 cities in California (GCA, 1984).

EMISSION ESTIMATE

The United States has an estimated water consumption/use rate of 587 liters (155 gallons) per capita per day (GCA 1984). Only 2 liters per capita per day are actually consumed or digested. Most of the chloroform evaporates to the air as a result of its use or disposal. The amount of chloroform generated in each of the 137 cities sampled was divided by the total amount of water treated to give a weighted national average of 41 micrograms of chloroform per liter of water (GCA, 1984).

Instead of using the national emission factor, one for California may be estimated by using only the data from the NOMS and NORS surveys which correspond to cities in California. Eight cities were surveyed and the data is presented below.

CITY	Emission Factors* NOMS	NORS	AVG	POPULATION 1980	CITY/CA RATIO	WEIGHTED AVG
1 Coalinga	--	16	16	166,593	.1229	.02
2 Dos Palos	--	61	61	13,123	.0582	.04
3 Fresno	ND	--	ND	218,202	4.0676	0.0
4 Los Angeles	32	32	32	2,966,850	55.3067	17.70
5 Oakland	200	--	200	339,337	6.3258	12.65
6 Sacramento	5.6	--	5.6	275,741	5.1402	.29
7 San Diego	35	52	43.5	875,538	16.3214	7.10
8 San Francisco	76	41	58.5	678,974	12.6571	7.40
				5,364,358	100%	45.20

ND: Not Detectable

*Emission factors are expressed as micrograms of chloroform per liter of water.

The weighted California emission factor of 45.20 micrograms of chloroform per liter of water will be used instead of the national weighted emission factor. This emission factor multiplied by the water annually consumed/used statewide, results in the annual emissions of chloroform for California from drinking water.

To estimate the water consumed/used in California per year the estimated 587 liters of water per person is multiplied by the population of California, 27,662,900 (DOF, 1988).

$$\frac{587 \text{ liters}}{\text{person day}} \times 27,662,900 \text{ people} \times \frac{365 \text{ days}}{\text{year}} = \frac{5.927 \times 10^{12} \text{ liters}}{\text{year}}$$

California consumed/used an estimated 5.927×10^{12} liters of water per year.

Chloroform Emissions are:

$$\frac{5.927 \times 10^{12} \text{ liters}}{\text{year}} \times \frac{45.2 \times 10^{-6} \text{ grams}}{\text{liter}} \times \frac{\text{kg}}{1000 \text{ grams}} = \frac{267,900 \text{ kg}}{\text{year}}$$

$$\frac{267,900 \text{ kg CHCl3}}{\text{year}} \times \frac{2.2046 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{295 \text{ tons CHCl3}}{\text{year}}$$

There is approximately 300 tons of chloroform emissions per year from drinking water sources in California.

APPENDIX A-6: Pulp & Paper Mills

Below is a summary of the chloroform emission estimates for pulp and paper mills. The calculations are detailed in the following pages.

CITY	FACILITY	PULP TYPE	CHC13 EMISSIONS (Tons/yr)	SOURCE
Anderson	Simpson Paper Co	kraft	18.07	1
Antioch	Gaylord Corp	kraft	16.06	1
FairHaven	Simpson Paper Co.	kraft	51.39	1
Fullerton	Kimberly-Clark	de-ink	12.32	3
Los Angeles	Pacific Coast Packaging	de-ink	1.97	1
Ponoma	Garden State Paper Co.	de-ink	55.19	1
	Potlatch Corp	NA	NA	
	Simpson Paper Co	de-ink	7.73	3
Red Bluff	Diamond International	NA	NA	
	Packaging Corp of America	NA	NA	
Richmond	CertainTeed Corp	-----	0.0	1
Rocklin	Bohemia Lumber,Inc.	NA	NA	
Santa Ana	B.J.Fibres, Inc	de-ink	4.42	3
Somoa	Louisiana-Pacific Corp	kraft	48.18	1
Stockton	National Gypsum Co	de-ink	1.97	1
Vernon	Genstar Building	NA	NA	
	Flintkote, Co.	NA	NA	
		TOTAL	217.30 tons	

NA: Not Available

1 Emission estimates are based on information from the Lockwood Directory 1987.

2 Emission estimates are based on information from the U.S. EPA report Survey of Chloroform Emission Sources.

3 Emission estimates are based on information from the SAIC's report Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin.

The following table contains emission factors used in the chloroform emission estimates.

TYPE OF PULP & PAPER MILLS	EF[*]
Integrated Mills	
Market bleached kraft pulp	0.22
Bleached kraft paperboard,	0.23
-coarse paper, & tissue paper	
Secondary Fiber Mills	
Deink: fine paper	0.36
Deink: tissue paper	0.16

[*]Emission factors were originally expressed in kilograms of chloroform emitted per thousand kilograms of pulp produced. These emission factors can also be expressed as tons of chloroform emitted per thousand tons of pulp produced (U.S. EPA, 1984).

EMISSION ESTIMATES

Simpson Paper Co. in Anderson
   The Lockwood Directory 1987 reports the average daily production of 225 tons (82,125 tons per year) of kraft, some of which is market pulp. The kraft pulp has an emission factor of 0.22 tons of chloroform per thousand tons of pulp produced, such that:

$$\frac{82.125 \text{ tons pulp}}{\text{year}} \times \frac{0.22 \text{ tons CHCl3}}{1,000 \text{ tons pulp}} = \frac{18.07 \text{ tons CHCl3}}{\text{year}}$$

Gaylord Corp. in Antioch
   The Lockwood Directory 1987 lists the average daily production of 600 tons unbleached kraft and 200 tons of kraft (73,000 tons of pulp per year) by chemical pulping. The kraft pulp has an emission factor of 0.22 tons of chloroform per thousand tons of pulp produced, such that:

$$\frac{73.000 \text{ tons pulp}}{\text{year}} \times \frac{0.22 \text{ tons CHCl3}}{1,000 \text{ tons pulp}} = \frac{16.06 \text{ tons CHCl3}}{\text{year}}$$

Simpson Paper Co. in Fairhaven
   The Lockwood Directory 1987 lists the average daily production of 640 tons (233,600 tons per year) of which 400 tons is market kraft pulp. Since the other 240 are not specified, the assumption is made that all 640 tons are market kraft. This is a worst case estimate. The emission factor is 0.22 tons of chloroform per thousand tons of pulp produced, such that:

$$\frac{233.600 \text{ tons pulp}}{\text{year}} \times \frac{0.22 \text{ tons CHCl3}}{1,000 \text{ tons pulp}} = \frac{51.39 \text{ tons CHCl3}}{\text{year}}$$

Kimberly-Clark in Fullerton
    This pulp mill is not listed in the Lockwood Directory 1987, but is
    listed in the SAIC report (Rogozen,1988). The pulp mill produces
    secondary tissue paper pulp as well as market bleached kraft.

    The secondary tissue paper pulp produced is reported as 29,419
    thousand kilograms per year and has an emission factor of 0.16
    kilograms of chloroform per thousand kilograms of pulp produced,
    such that:

$$\frac{29,419 \text{ kkg pulp}}{\text{year}} \times \frac{0.16 \text{ kg CHCl3}}{\text{kkg pulp}} = \frac{4,707 \text{ kg CHCl3}}{\text{year}}$$

$$\frac{4,707 \text{ kg CHCl3}}{\text{year}} \times \frac{2.2046 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{5.19 \text{ tons CHCl3}}{\text{year}}$$

    The market bleached kraft pulp is also reported as 29,419 thousand
    kilograms per year and has an emission factor of 0.22 kilograms of
    chloroform per thousand kilograms of pulp produced, such that:

$$\frac{29,419 \text{ kkg pulp}}{\text{year}} \times \frac{0.22 \text{ kg CHCl3}}{\text{kkg pulp}} = \frac{6,472 \text{ kg CHCl3}}{\text{year}}$$

$$\frac{6,472 \text{ kg CHCl3}}{\text{year}} \times \frac{2.2046 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{7.13 \text{ tons CHCl3}}{\text{year}}$$

Pacific Coast Packaging Corp. in Los Angeles
    The Lockwood Directory 1987 reports the average daily production of
    15 tons (5,475 tons per year) of deinked pulp. The emission factor
    is 0.36 tons of chloroform per thousand tons of pulp processed,
    such that:

$$\frac{5,475 \text{ tons pulp}}{\text{year}} \times \frac{0.36 \text{ tons CHCl3}}{1,000 \text{ tons pulp}} = \frac{1.97 \text{ tons CHCl3}}{\text{year}}$$

Garden State Paper Co. Inc. in Ponoma
    The Lockwood Directory 1987 reports average daily production of 420
    tons (153,300 tons per year) of deinked pulp. The emission factor
    for deinked pulp is 0.36 tons of chloroform per thousand tons of
    pulp produced, such that:

$$\frac{153,300 \text{ tons pulp}}{\text{year}} \times \frac{0.36 \text{ tons CHCl3}}{1,000 \text{ tons pulp}} = \frac{55.19 \text{ tons CHCl3}}{\text{year}}$$

Potlatch Corp. in Ponoma
    The pulp mill is not listed in the Lockwood Directory 1987, but is
    listed in the Locating and Estimating Air Emissions From Sources of
    Chloroform (U.S. EPA, 1984). There is not enough information to
    estimate emissions.

Simpson Paper Co. in Ponoma
    The SAIC report lists the pulp mill as a secondary fiber mill which
    produces fine papers (Rogozen, 1988). There is 19,477 thousand
    kilograms of deinked pulp produced per year with an emission factor
    of 0.36 kilograms of chloroform per thousand kilograms of pulp
    produced, such that:

$$\frac{19.477 \text{ kkg pulp}}{\text{year}} \times \frac{0.36 \text{ kg CHC13}}{\text{kkg pulp}} = \frac{7.012 \text{ kg CHC13}}{\text{year}}$$

$$\frac{7.012 \text{ kg CHC13}}{\text{year}} \times \frac{2.2046 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{7.73 \text{ tons CHC13}}{\text{year}}$$

Diamond International Corp. in Red Bluff
    The pulp mill is not listed in the Lockwood Directory 1987, but is
    listed in the Locating and Estimating Emissions From Sources of
    Chloroform (U.S. EPA, 1984) report as a miscellaneous integrated
    pulp mill. There is not enough information to estimate emissions.

Packaging Corp. of America in Red Bluff
    The Lockwood Directory 1987 reports the chemi-mechanical average
    daily production of 70 tons. The result is molded pulp products.
    An Emission factor is not available at this time.

CertainTeed Corp. in Richmond
    The Lockwood Directory 1987 reports the pulp mill idle. Assuming
    the plant is still idle, there are no chloroform emissions.

Bohemia Lumber Inc. in Rocklin
    The Lockwood Directory 1987 reports the average daily production of
    400 tons of defibrated wood pulp and the resulting product is
    medium density fibreboard. An emission factor is not available at
    this time.

B.J. Fibres Inc. in Santa Ana
    The SAIC report lists the pulp mill as using bleached kraft process
    to manufacture paperboard, coarse paper and tissue paper (Rogozen,
    1988). There is 17,433 thousand kilograms per year of pulp
    produced with an emission factor of 0.23 kilograms of chloroform
    per thousand kilograms of pulp produced, such that:

$$\frac{17.433 \text{ kkg pulp}}{\text{year}} \times \frac{0.23 \text{ kg CHC13}}{\text{kkg pulp}} = \frac{4.010 \text{ kg CHC13}}{\text{year}}$$

$$\frac{4.010 \text{ kg CHC13}}{\text{year}} \times \frac{2.2046 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{4.42 \text{ tons CHC13}}{\text{year}}$$

Lousiana-Pacific Corp. in Somoa
   The Lockwood Directory 1987 reports the average daily production
   rate of 600 tons (219,000 tons per year) of market kraft pulp. The
   emission factor is 0.22 tons of chloroform per thousand tons of
   pulp produced, such that:

$$\frac{219,000 \text{ tons pulp}}{\text{year}} \times \frac{0.22 \text{ tons CHCl}_3}{1,000 \text{ tons pulp}} = \frac{48.18 \text{ tons CHCl}_3}{\text{year}}$$

National Gypsum Co. in Stockton
   The Lockwood Directory 1987 reports the average daily production of
   15 tons (5,475 tons per year) of deinked fine paper pulp. The
   emission factor is 0.36 tons of chloroform per thousand tons of
   pulp processed, such that:

$$\frac{5,475 \text{ tons pulp}}{\text{year}} \times \frac{0.36 \text{ tons CHCl}_3}{1,000 \text{ tons pulp}} = \frac{1.97 \text{ tons CHCl}_3}{\text{year}}$$

Genstar Building Materials Company in Vernon
   The Lockwood Directory 1987 reports the average daily production
   rate of 35 tons of unbleached defibrated wood pulp. An emission
   factor is not available at this time.

Flintkote Co. in Vernon
   The pulp mill is not listed in the Lockwood Directory 1987, but is
   listed in the Locating and Estimating Air Emissions From Sources of
   Chloroform (U.S. EPA, 1984). There is not enough information to
   estimate emissions.

APPENDIX A-7: Indoor Emissions (Bleach)

EMISSION ESTIMATE

The SAIC report (Rogozen, 1988), using data collected from the Simmons 1984 Study of Media and Market, states that 6,516,250,000 cups of bleach are annually used in the United States. This number is based on a wash load using one cup of bleach. Liquid bleach typically contains 5.25% by weight sodium hypochlorite (NaOCl) and powder bleaches contain no chlorine (Cl_2). SAIC reports that 76.4% of the bleach used is in the liquid form. The density of bleach is given as 9.11 pounds per gallon.

$$\frac{6,516,250,000 \text{ cups bleach}}{year} \times \frac{gallon}{16 \text{ cups}} \times \frac{9.11 \text{ lb}}{gallon} = \frac{3.7 \times 10^9 \text{ lb}}{year}$$

$$\frac{3.7 \times 10^9 \text{ lb bleach}}{year} \times \frac{0.0525 \text{ lb NaOCl}}{\text{lb bleach}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} \times 76.4\%$$

$$= \frac{74,400 \text{ tons NaOCl}}{year}$$

An emission factor for bleach use is given as 0.00168 lb of chloroform formed per lb of chlorine used (Rogozen, 1988). This factor can also be expressed as 3.36 lb of chloroform per ton of chlorine used. The tonnage of chlorine (Cl_2) contained in each ton of NaOCl used must be calculated so the emission factor can be used.

$$\text{ton of NaOCl} \times \frac{70.906 \text{ tons of Cl2 per mole}}{74.442 \text{ tons of NaOCl per mole}} = 0.9525 \text{ ton of } Cl_2$$

$$\frac{74,400 \text{ tons NaOCl}}{year} \times \frac{0.9525 \text{ tons Cl2}}{\text{ton of NaOCl}} \times \frac{3.36 \text{ lb CHCl3}}{\text{ton Cl2}}$$

$$= \frac{238,135 \text{ lb CHCl3}}{year}$$

This is the chloroform emissions in the United States from domestic bleach use.

There are approximately 27,662,900 people living in California (DOF, 1988). There are approximately 243,400,000 people living in the U.S. (Census, 1987). This means that California has an estimated 11.37% of the country's population. Assuming California is responsible for 11.37% of the U.S. chloroform emissions from laundry use, then:

$$\frac{238,135 \text{ lb CHCl3}}{\text{year}} \times 11.37\% \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{13.5 \text{ tons CHCl3}}{\text{year}}$$

Annual statewide air emissions of chloroform from domestic bleach use (excluding bleach used in cleaning) are estimated to be 13.5 tons.

APPENDIX A-8: AIR STRIPPING TOWERS

Aerojet General Corporation in Sacramento County operates six air strippers of which three have chloroform emissions in the following amounts (Skelton, 1989):

<u>CHC13 Emissions</u>

1. Air stripper	1.8	lb/day
2. Air stripper	8.0	lb/day
3. Air stripper	2.5	lb/day
	12.3	lb/day

$$\frac{12.3 \text{ lb CHC13}}{\text{day}} \times \frac{365 \text{ days}}{\text{year}} \times \frac{1 \text{ ton}}{2,000 \text{ lb}} = \frac{2.25 \text{ tons CHC13}}{\text{year}}$$

Annual statewide air emissions of chloroform from these sources are 2.25 tons per year. This estimate does not include other air strippers that have chloroform emissions in California, due to insufficient data.

APPENDIX A-9: CONTAMINATION OF CHLORINATED PRODUCTS

There are approximately 27,662,900 people living in California (DOF, 1988). There are approximately 243,400,000 people living in the U.S. (Census, 1987). This means that California has an estimated 11.37% of the country's population. Assuming that the nation estimate of chloroform emissions from contaminated chlorinated products are in proportion to the population then California is responsible for 11.37% of the U.S. chloroform emissions from contaminated products.

$$\frac{7 \text{ tons of CHC13}}{\text{year}} \times 11.37\% = \frac{0.80 \text{ tons of CHC13}}{\text{year}}$$

Annual statewide air emissions of chloroform from contaminated chlorinated products are estimated to be 0.80 tons.

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