California Air Resources Board

Technical Support Document

Proposed Identification of

TRICHLOROETHYLENE

as a Toxic Air Contaminant

Part A
Exposure Assessment

State of California
Air Resources Board
Stationary Source Division

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REPORT TO THE AIR RESOURCES BOARD ON TRICHLOROETHYLENE (TCE)

Part A - Public Exposure To, Sources and Emissions of Atmospheric Trichloroethylene in California

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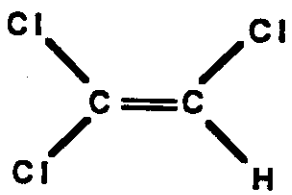
I.

INTRODUCTION

Trichloroethylene (TCE) is one of the family of chemicals known as chlorinated alkenes -- chlorinated aliphatic hydrocarbon compounds containing a double bond. TCE has the chemical formula C_2HCl_3 and the chemical structure is shown in Figure I-1.

FIGURE I-1
Structure of TCE



Trichloroethylene

TCE has a wide number of uses in the industrial, governmental, and consumer sectors of the economy. It is used in California in a variety of operations and products, including degreasing operations, polyvinyl chloride (PVC) production, adhesive formulations, and paints and coatings. TCE is also used in California in miscellaneous chemical synthesis and solvent applications, and as a refrigerant and heat exchange liquid. The major use of TCE in California, and nationwide, is as a degreasing solvent.

Part A of this report is an evaluation of TCE uses, emissions, ambient and indoor concentrations, population exposure, and atmospheric persistence and fate. The Air Resources Board will consider the findings of this report together with the health related effects findings of the Department of Health Services and determine if TCE should be identified as a toxic air contaminant.

II.

PHYSICAL PROPERTIES OF TRICHLOROETHYLENE

Trichloroethylene is a dense, volatile, colorless liquid. It is only slightly soluble in water but miscible with organic solvents and other halogenated compounds. It is photochemically reactive (see Chapter V), lipophilic, and is not known to contribute to either global warming or to the depletion of the stratospheric ozone layer. Some physical properties of trichloroethylene are shown on Table II-1.

TABLE II-1

Physical Properties of TCE

Property	Value	Reference
Boiling Point	189°F	2
Conversion - $\mu g/m^3$: ppb	5.37 $\mu g/m^3$ per ppb	
ppb : $\mu g/m^3$	0.19 ppb per $\mu g/m^3$	
Density, liquid (68°F)	1.46 gm/cm^3	2
Dielectric constant (60°F)	3.47	4
Diffusivity, air (68°F)	.081 cm^2/sec	7
Flammability limits, air	12 & 86 vol%	5
Heat capacity, liq. (68°F)	.23 BTU/lb-°F	5
Heat of combustion	3,150 BTU/lb	6
Heat of vaporization	103 BTU/lb	5

Property	Value	Reference
Henry's Law constant, water	8.2 atm-m^3/mole	3
Index of refraction (68°F)	1.48	4
Melting point	-73°C	2
Molecular weight	131	
Partition coefficient		
1-octanol:water (77°, 99°F)	318:1, 960:1	1, 8
undecane:water (77°F)	354:1	1
blood:water (99°F)	7:1	8
Solubility, water (68°F)	.0011 gm/gm	5
Thermal conductivity (122°F)	.08 BTU/[hr-ft^2-(°F/ft)]	2
Vapor pressure (20°C)	60 torr	2
Viscosity, liquid (60°F)	.65 cp	2

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III.

PRODUCTION, USES, AND EMISSIONS OF TRICHLOROETHYLENE

A. PRODUCTION OF TRICHLOROETHYLENE

Trichloroethylene (TCE) is not produced in California. Trichloroethylene is only produced in the U.S. by Dow Chemical in Freeport, Texas and PPG Industry in Lake Charles, Louisiana (U.S. EPA, 1985a).

As shown in Figure III-1, national production of TCE between 1974 and 1984 dropped considerably, while imports and exports increased slightly (U.S. International Trade Commission (U.S. ITC); and U.S. Department of Commerce). In 1985, TCE production decreased 15 percent from the 1984 level and is 50 percent less than that in 1979 (United States International Trade Commission, 1985). In 1985, the U.S. production of TCE was 80,300 tons (U.S. ITC).

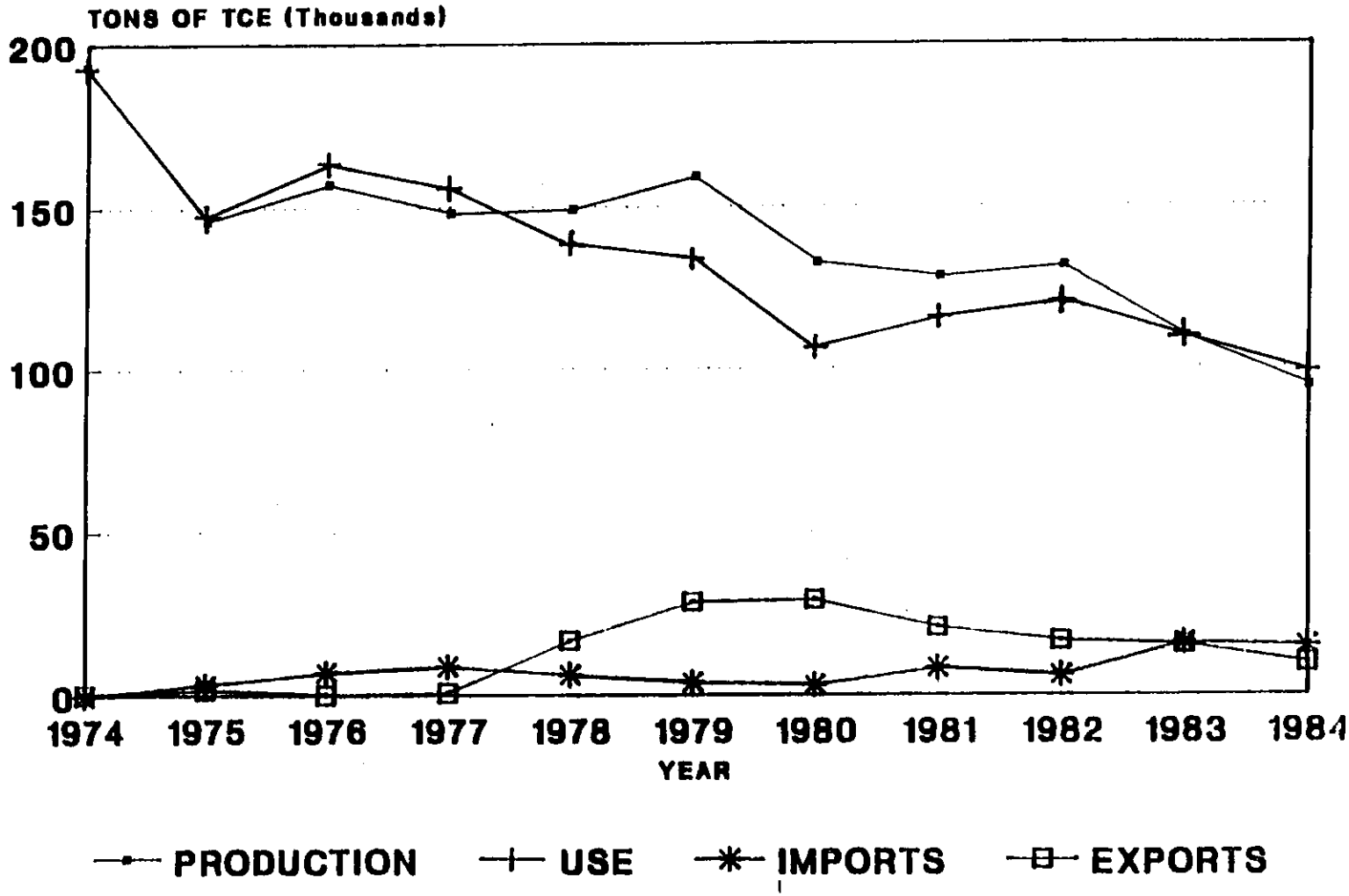
The U.S. demand for trichloroethylene is forecasted to decline steadily through 1990. This a result of improved emission control and recycling features in new metal cleaning equipment. The decline in demand may not affect the U.S. production of TCE since production is also dependent on imports and exports (Chemical Marketing Reporter, 1986). Presently, we do not have information on future trends for imports and exports of TCE.

B. USES AND EMISSIONS OF TRICHLOROETHYLENE

Trichloroethylene has a wide number of uses in the industrial, governmental, and consumer sectors of the economy. Trichloroethylene is used in California in the following products and processes: degreasing

FIGURE III-1

U.S. PRODUCTION, IMPORTS, EXPORTS AND USE OF TCE FROM 1974 TO 1984



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operations; polyvinyl chloride (PVC) production; adhesive formulations; and painting and coating operations. Trichloroethylene is also used in California in miscellaneous chemical synthesis and solvent applications, and as a refrigerant and heat exchange liquid. The largest source category of facilities in California with TCE emissions greater than 100 tons per year is degreasing.

Other sources that emit TCE include: publicly owned treatment works (POTWs); groundwater aeration and air strippers; sanitary sewers; surface impoundments; and municipal landfills. Trichloroethylene is also present in trace concentrations in waste oil (U.S. EPA, 1985a). On-site solvent recovery, industrial wastewater treatment, and collection lines (or sewage lines) before the wastewater enters the POTWs are also potential emission sources, however due to lack of information these sources could not be evaluated.

As Figure III-1 indicates, national use of TCE dropped almost 50 percent between 1974 and 1984, from an estimated 195,000 to 102,000 tons per year (TPY) (U.S. ITC, U.S. Dept. of Commerce).

National usage of TCE in 1983 and the amounts for different use types are shown in Table III-1. The total trichloroethylene use in 1983 was 110,500 tons (U.S. Inter. Trade Comm., 1974-85; U.S. Dept. of Commerce, Imports, 1974-84; U.S. Dept. of Commerce, Exports, 1974-1984). Over 50 percent of the national usage was from degreasing operations, which accounted for 61,710 tons.

California use has also declined over the last decade. According to the Halogenated Solvents Industry Alliance (HSIA), 4,880 tons of TCE were shipped into California in 1983. Of this initial value, 2,580 tons of TCE were shipped directly to Chevron Chemical Company in Richmond for use as a chemical intermediate in the production of the fungicide difolatan (Cleary et al., 1986). The remaining TCE (2,300 tons) was available for distribution. HSIA estimated that 10 percent of the remaining 2,300 tons of

TABLE III-1

Estimated National Use of TC[illegible] 1983[a]
(TPY)

Source Type	U.S. Usage
Degreasing Operations	61,710
Paints and Coatings	570
Adhesive Formulations	460
PVC Production	7,160
Fungicide Production	ND[b]
Other Chemical Production	ND
Miscellaneous	2,580
Total Determined Usage[c]	110,500

a. All data are for 1983 except for PVC production which was 1984 data (EPA, 1985a).

b. ND: Not determined.

c. This total usage is not the sum of the numbers shown in the table. Instead, the total usage was calculated from data obtained from U.S. Inter. Trade Comm., 1974-85; U.S. Dept. of Commerce, Imports, 1974-84; and U.S. Dept. of Commerce, Exports, 1974-1984.

TCE were distributed out of state, leaving 2,070 tons for use in California. Estimated use and emissions of TCE in California for 1983 are given in Table III-2.

In 1988, the California Air Resources Board (ARB) conducted a survey of California halogenated solvent distributors. The survey was designed to estimate the usage of TCE in degreasing, adhesive formulation, paints and coatings, and other miscellaneous activities. This estimate is based on the assumption that all TCE distributed in 1987, was used in 1987. Fifty-seven of the 67 distributors surveyed responded (approximately 85 percent response rate). Because all major distributors responded to the survey, the ARB staff believes that the data received accounted for most of the TCE distributed in California.

As shown in Table III-3, data from this survey shows that approximately 1023 tons of TCE were used in California in 1987 (ARB, 1989). This major decrease from the 4,650 tons of TCE used in 1983 was due largely to the shutdown of the fungicide production facility in Richmond, California (Chevron Chemical Co., 1987) and a decrease of 1,242 tons of TCE used in degreasing operations. According to the survey, the California halogenated distributors in 1987 sold an estimated 268 tons of TCE to degreasing facilities, 55 tons to adhesive formulation facilities, 68 tons to paints and coatings facilities, and 457 tons to facilities for miscellaneous applications. Respondents to the survey reported distributing an additional 129 tons of TCE although they did not indicate its intended use. For the purpose of this report, the tonnage is added to the miscellaneous category (457 + 129 = 586 tons) and is assumed to be emitted to the atmosphere. Methods used for estimating usage and emissions of TCE in California are presented in Appendix A.

1. Degreasing

Degreasing is an integral part of many industrial activities such as automobile manufacturing, electronics, furniture manufacturing, appliance

TABLE III-2

Estimated California Use and Emissions of TCE: 1983[a]
(TPY)

Source Type	California Usage	California Emissions
Degreasing Operations	1,510	1,400
Paints and Coatings	60	60
Adhesive Formulations	50	50
PVC Production	170	3
Fungicide Production	2,580	1
POTWs[b]	NA[c]	160
Distribution Facilities	NA	1
Solvent Reclamation	NA	<1
Other Chemical Production	ND[e]	ND
Miscellaneous	280	0-280
Total Determined Usage/ Total Emissions	4,650	1,700-2,000 [d]

a. All data are for 1983 except for PVC production (1984 data), fungicide production (1986 emissions data), and solvent reclamation (1985 data). Data on total emissions were not available for municipal landfills, surface impoundments, hazardous waste landfills, sanitary sewers, groundwater aeration, waste oil combustion, and motor vehicles.

b. POTWs: Publicly owned treatment works, also known as municipal sewage treatment facilities.

c. NA: Not applicable.

d. Total emission estimates are rounded to the nearest hundred tons.

e. ND: Not determined

TABLE III-3

TCE Use and Emissions In California: 1987

Source Type	Use (tons)	Emissions (tons/year)	Inventory Year
Direct Uses			
Degreasing	268	250	1987
Adhesive Formulation	55	55	1987
Paints & Coating	68	68	1987
Distribution	NA	<1	
PVC Production	175	<1	1987
Miscellaneous	586	586[1]	1987
Total Distributed	1,023	959	
Waste Treatment and Disposal Activities			
Recycling		<1	
POTWs [2]	NA	23	1986
Groundwater Aeration and Air Strippers	NA NA	20 - 30[3]	1986/1987
Landfills	NA	ND	

NA: Not applicable

ND: Not determined

1. This estimate represents emissions from both the identified and unidentified miscellaneous sources. Some amounts of TCE in this category may actually be used in degreasing operations, in adhesive formulation, and in paints and coatings.
2. POTWs are wastewater treatment plants that are owned by a public entity.
3. Emissions estimates are for the San Francisco Bay Area, Sacramento County, and South Coast Air Basin only. Information on other parts of the State is not available at this time. These numbers also include emission estimates for one facility that was listed in an Environmental Protection Agency report because this facility is also in the San Francisco Bay Area (U.S. EPA, 1987a).

manufacturing, and textile, paper, plastic, and glass manufacturing. PEI Associates estimates that there are several thousand cold cleaning, vapor, and conveyor type degreasing units in operation in California. The number of degreasing units using TCE in California is unknown (PEI, Associates, 1985).

Solvent degreasers function by immersing the part to be cleaned in liquid or vaporized solvent contained in the degreasing tank. In a typical cold cleaning operation, dirty parts are cleaned manually by spraying and then soaking in the tank. Open top vapor degreasers clean with the condensation of hot solvent vapor on colder metal parts. Conveyorized degreasers may operate with either cold or vaporized solvent. They are continuously loaded and are usually hooded or enclosed. After cleaning, the parts are either suspended over the tank to drain or are placed on an external rack that directs solvents back into the tank (U.S. EPA 1985b, U.S. EPA, 1977).

Solvent evaporation occurs with all types of degreasing equipment. The major sources of evaporation are the degreasing tank, the carry-out of solvent on cleaned parts, and the disposal of waste solvent. The amount of these emissions varies with the type of equipment used and the operating parameters (PEI Assoc., Inc., 1985).

Degreasing is the largest source of TCE emissions in California. The United States Environmental Protection Agency (EPA) has estimated that approximately 0.94 ton of TCE is emitted per ton of fresh solvent used in degreasing operations (U.S. EPA, 1985b). Thus, emissions from degreasing operations were estimated to be approximately 1,400 tons in 1983 and 250 tons in 1987 (see Tables III-2 and III-3).

As a result of increased recycling of TCE and tighter specifications for metal cleaning equipment, the use of TCE as a degreaser is projected to steadily decline through 1990 (Chemical Marketing Reporter, 1986).

2. Adhesive Formulation

All trichloroethylene used in adhesive formulation is assumed to be emitted into the atmosphere (U.S. EPA, 1985a). In 1983, estimated usage for adhesives was 50 tons (Table III-2). In 1987, emissions were estimated to be 55 tons (ARB, 1989). The miscellaneous category may also include emissions from the uses of TCE in adhesive formulation; however, the uses of TCE in the miscellaneous category are expected to be much smaller as compared to the uses in degreasing operations.

3. Paints and Coatings

Trichloroethylene is used in paint and coating formulations. In this report, the staff assumed that all the TCE in paints and coatings is emitted to the atmosphere. In 1983, emissions were estimated at 60 tons for paints and coatings (Table III-2). In 1987, TCE emissions from this category were estimated to increase slightly to 68 tons (ARB, 1989). Again, the miscellaneous category may also include some TCE emissions associated with paints and coatings.

4. Polyvinyl Chloride Production

Keysor-Century Corp. is the only facility in California that uses TCE in polyvinyl chloride (PVC) production. In addition to vinyl chloride and vinyl acetate, TCE is used as a secondary raw material and as a reaction chain terminator in the PVC production process. In 1987, the South Coast Air Quality Management District (SCAQMD) estimated that this plant used approximately 175 tons of TCE. Most of the TCE used is reacted in the PVC production processes. The unreacted portion, along with vinyl chloride and vinyl acetate, is incinerated. Based on information in the South Coast permit files, Keysor-Century Corp. emitted 269 lbs or 0.13 tons of TCE (Yuhas, L., 1989). More than 40 percent of the emissions is from TCE storage, and the rest is from fugitive losses and incinerator exhaust.

5. Fungicide Production

In 1983, approximately 2,580 tons of TCE were used in fungicide production by the Chevron Company in Richmond, California. However, in March 1987, Chevron stated that it no longer handled, used, or stored TCE at this facility because its fungicide (difolatan) production was discontinued in September 1986 (Chevron Chemical Company, 1987) (Ward, G., 1989). According to Chevron, the fungicide plant in Richmond is permanently shut down, and the difolatan is no longer produced anywhere in California (Ward, G., 1989). Therefore, TCE emissions from fungicide production in California were zero in 1987.

6. Miscellaneous

Trichloroethylene emissions from this category in 1987 are estimated to be approximately 586 tons (457 tons identified for miscellaneous purposes in the survey and 129 tons that were not identified by the distributors, but are assumed for miscellaneous applications) (ARB, 1989). As mentioned in the previous section, this estimate may be lower if TCE in the miscellaneous category is used for degreasing or for other purposes.

There is not enough data to identify the sources and applications of TCE in the miscellaneous category. However, it is believed that TCE has several uses such as a component of correction fluid in the printing industry, a solvent for flushing liquid oxygen in the aerospace industry, and a refrigerant and heat exchanger liquid. All TCE used in the miscellaneous category is assumed to be emitted to the atmosphere.

C. OTHER SOURCES OF EMISSIONS

In addition to the direct uses discussed above, TCE is handled and emitted by distribution facilities, solvent reclaimers, groundwater aeration treatment facilities, publicly owned treatment works (POTWs), municipal

landfills, surface impoundments, and hazardous waste landfills. The TCE emitted from POTWs and Groundwater Aeration and Air Stripping Towers is approximately 53 tons per year (Table III-3).

1. Distributors

The ARB staff assumes that all of the TCE used in the state is sold by chemical distributors. Distribution operations include transport, storage, and repackaging of TCE. An estimated 2,300 tons of TCE were sold through distribution facilities in California in 1983 with an estimated 1 ton of emissions. In 1987, the estimated amount of TCE distributed was 1,023 tons. The emission estimates from these facilities was less than one ton. Emissions from these facilities come from the storage tanks. The data were calculated using AP-42 equations and assumptions about the throughput of trichloroethylene and the number and size of storage tanks (U.S. EPA, 1985a; U.S. EPA, 1985b).

2. Recycling

There are approximately 20 commercial solvent reclaimers in California (DHS, 1984). The three largest reclaimers process an estimated 80 percent of the solvents sent for recycling in California (Kozumplit, 1986). An estimated 100 tons of trichloroethylene were sent for recycling in California in 1985 and TCE emissions from these facilities were estimated to be less than one ton. Emissions primarily result from the storage and handling of waste and reclaimed solvents, although some emissions come from distillation condensers at reclamation facilities.

3. Publicly Owned Treatment Works

Publicly owned treatment works (POTWs) are identified as sources of TCE emissions because wastewater from the commercial or industrial discharges containing TCE is being treated at these facilities. Based on a 1987 study

by the University of California at Davis (UCD), there were 29 major POTWs in California which emitted approximately 23 tons of TCE in 1986 (UCD, 1987) (Table III-3). In the UCD study, emissions were determined by subtracting the amount of TCE in the effluent from that in the influent and only the volatilization process was taken into account in calculating the emissions.

On-site wastewater treatment plants may also be sources of TCE emissions. If TCE is used at a facility and if its wastewater is either treated or simply discharged into the sewers, TCE is emitted. However, there is not sufficient information to estimate TCE emissions from these facilities.

4. Groundwater Aeration and Air Stripping Towers

Groundwater in several regions of the state has been contaminated with toxic or potentially toxic substances. Specifically, where spent solvents such as trichloroethylene or methylene chloride were dumped into ponds or lagoons or simply released into sewers, these solvents slowly leaked into the soil, contaminating groundwater. Due to the environmental concerns about contaminated groundwater, some industries are now extracting this groundwater for treatment. If the concentrations of the toxic substances or compounds in groundwater are relatively low, the groundwater is simply aerated and then released into sewers or rivers. As the result of aeration, the groundwater becomes relatively clean because most of the toxic substances have been emitted into the atmosphere by volatilization.

If the concentrations of toxic substances are high, groundwater is treated in air stripping towers before it is released into the sewers or rivers. In an air stripping tower, the contaminated groundwater is fed into a packed-bed column. Fresh air is introduced counter currently and is allowed to contact the contaminated water where a concentration gradient drives the contaminants from the water to the fresh air. The fresh air

becomes contaminated and is withdrawn at the other end of the tower. Incinerators, carbon adsorbers, and flares have been used to reduce air emissions from air stripping towers.

Data from the Bay Area Air Quality Management District (BAAQMD) showed 10 facilities with air strippers with TCE-contaminated groundwater. Based on the groundwater pumping rates, the maximum TCE concentrations in the groundwater at each stripper, and the assumption that these strippers operated continuously during the year, it is estimated that 12.5 tons of TCE were emitted from these facilities in 1987 (Holmes, 1989). Because the TCE concentrations in contaminated groundwater will decrease over time and because the strippers may not operate continuously, the emissions may have been overestimated.

Preliminary data from the South Coast Air Quality Management District (SCAQMD) showed approximately 1.9 to 3.2 tons of TCE emissions from seven groundwater aeration facilities for 1986 (SCAQMD, 1987).

An EPA contractor identified 21 facilities with air strippers in California in 1986. It is not known whether contaminated groundwater treated at these facilities contains TCE; emission estimates were available for only two of these facilities. For one facility, TCE emission was estimated as 1.4 tons; for the other, only 0.7 ton of volatile organic compound (VOC) emissions were estimated (U.S. EPA, 1987a). Information regarding TCE emissions from this second facility is not available.

5. Landfills

Landfills are potential sources of TCE emissions. There are about 1,000 active landfills and 1,200 closed landfills in California (Barnickol, 1986).

The quantity of TCE disposed at municipal landfills in California is undetermined. Trichloroethylene might be disposed at municipal landfills as

residues in discarded paint cans, as well as by other means. There is no statewide estimate of TCE emissions from municipal landfills. An EPA report includes an estimate of 0.3 TPY of TCE emissions from municipal landfills in Santa Clara Valley (U.S. EPA, 1986b). This estimate is described as a conservative one designed for screening purposes. Emissions are being controlled from some of the largest municipal landfills in the state by gas recovery well systems.

To comply with the Calderon bill passed in 1986 (Health and Safety Code Section 41805.5) operators of landfills are required to test landfill gases for several toxic and potentially toxic substances. Tests performed in 1987 and 1988 at several municipal landfills in California showed TCE concentrations in the landfill gases (Harding Lawson Associates, 1987; Environmental System & Service, 1988; The Mark Group, 1988; and NUS Corporation, 1988). However, there is not sufficient information to estimate TCE emissions from landfills.

Total emissions of TCE from hazardous waste landfills and surface impoundments in California have not been determined. The EPA has modeled trichloroethylene emissions from hazardous waste landfills as: 436 TPY for a large landfill (3,339,520 sq.ft.), 55 TPY for a medium landfill (417,740 sq.ft.), and 5.4 TPY for a small landfill (41,380 sq.ft.) (U.S. International Trade Commission, 1985; U.S. EPA 1986a). The EPA modeling is based on the quantities of trichloroethylene disposed and on assumptions about the movement of trichloroethylene upward through the landfill cover. Based on this information, hazardous waste landfills in California may be a source of trichloroethylene as well as other volatile organic compounds.

Both commercial and private surface impoundments exist in California but TCE emissions from surface impoundments throughout California have not been determined.

D. EMISSION TRENDS

The staff of the Chemical Marketing Reporter expects a continued steady decline in U.S. consumption of TCE through the year 1990 (Chemical Marketing Reporter, 1986). This decline in usage is expected as a result of 1) improved emission control and recycling features in new metal cleaning equipment, 2) the use of substitute compounds such as 1,1,1-trichloroethane, and 3) the possibility of further air quality rules regulating the use of trichloroethylene (Chemical Marketing Reporter, 1986). Shipments of TCE to California for uses other than as a fungicide intermediate declined from 2,300 tons in 1983 to 1,060 tons in 1985 (Morgan et al., 1986). Emissions of TCE in California are expected to decline at the same time that emissions in U.S. decline.

E. POTENTIAL SOURCES OF INDOOR TRICHLOROETHYLENE

Trichloroethylene is also emitted to the indoor environment. Several studies of indoor exposure in residences have found higher concentrations of TCE indoors than outdoors (see Chapter IV, Indoor Exposure to TCE). Furthermore, TCE concentrations in a new office building were much greater one month after completion than immediately upon completion, and greater indoors than outdoors. From this information, study researchers stated that indoor sources related to occupant activities probably had a greater impact on the high TCE concentrations than the building materials (Pellizzari et al., 1984). Results of another study indicate that higher ambient concentrations of TCE are found in apartments than in houses, although no specific sources were identified (Pleil, et al., 1985).

A number of investigators have studied potential indoor emissions of TCE arising from the use of consumer products and volatilization from TCE-contaminated water. The EPA has conducted a major study on the human exposure to volatile organic compounds in indoor as well as outdoor environments. This study was called the Total Exposure Assessment Methodology (TEAM) study (see Chapter IV, Indoor Exposure to TCE).

1. Consumer Products

TCE is used in a variety of consumer products including household cleaners, typewriter correction fluids, adhesives and cosmetics. Moseley and Pellizzari (1986) characterized the types of consumer products which contain and emit TCE (as well as 18 other VOCs). A summary of their results can be found in Table III-4.

One investigator reported that females sometimes showed higher exposure to TCE than males, and the authors hypothesized that this may be due to the chemical's use as a solvent in cosmetics and in opaquing fluids used in offices (Wallace et al., 1986b).

Wallace et al. (1986a) reported on consumer products applied onto building materials (e.g., a wood surface). The consumer products were allowed to age one week (except for cleaning products), and were then placed in an environmental chamber. The airborne concentrations of 17 target VOCs were measured for 4 hours using Tenax GC as the adsorbent. The investigators reported a slight elevation of TCE in the test chamber compared to the empty chamber, 7.0 compared to 5.7 $\mu g/m^3$ (1.3 to 1.1 ppb) respectively, as a result of using cleaning agents. The investigators also measured an emission rate of approximately 0.4 $\mu g/min/m^2$ surface area for TCE from these cleaning products.

The EPA has recently published a survey of five chlorinated hydrocarbon concentrations (including TCE) in a variety of consumer items (U.S. EPA, 1987b). The samples were randomly selected brand-name items selected off-the-shelf from stores in six U.S. cites. Trichloroethylene was reported in a number of products including paint removers and cleaners, but was most consistently found in liquid paper or typewriter correction fluids. The correction fluids represented 67 percent of all products and brands which tested positive. The range of TCE concentrations in these fluids was 16 to 97 percent by weight.

TABLE III-4

Occurence of TCE in Consumer and Industrial Products[a]

	Occurrence[b]	Comments
Household Cleaners	4 out of 8	44% TCE in one product, 40% in another
Industrial Cleaners	5 out of 12	1-10% TCE in one product
Paints/Coatings	3 out of 14	
Adhesives	13 out of 41	
Building Materials	2 out of 12	
Pesticides, Consumer & Industrial	3 out of 84	
Cosmetics	3 out of 18	
Ink Pens	4 out of 8	
Tapes	7 out of 25	
Consumer Electronics	7 out of 13	
Molding/Casting Compounds	3 out of 10	
Cameras & Film	2 out of 4	
Fabrics	7 out of 15	
Misc. Household Items	3 out of 7	

a. As reported in the California TEAM Study (M.A. Moseley & E.D. Pellizzari, 1986), based on information from headspace analyses conducted by NASA.

b. The occurrence is the number of products that tested positive for trichloroethylene (TCE), out of the number of products tested.

2. Volatilization from Water

Potable water that is used indoors and that is contaminated by TCE and other VOCs may release these compounds into the indoor environment by volatilization. Andelman (1985) reported measurement of TCE in the air near a shower using water containing TCE. The author used a continuous real-time sampling device equipped with an infra-red detector which had a detection limit of 0.5 mg/m^3 (90 ppb). The airborne concentrations near the shower increased with time. For example, in a bathroom located upstairs in one of the homes which used well water containing approximately 40 mg TCE per liter (mg/L), no TCE could be detected before the shower was turned on. The TCE concentrations progressively increased to a concentration of 81 mg/m^3 (1.5×10^4 ppb) after the shower ran for 17 minutes. These results were further investigated using a model shower system (Andelman et al., 1986, not peer reviewed). The shower chamber volume was 0.4 m^3 and the concentration of TCE in the water of 3 or 6 mg/L. He reported that approximately 80 percent of the TCE volatilized after 60 minutes of the water running and this depended on experimental conditions such as water temperature.

McKone (1987) estimated exposure factors for seven VOCs by developing a mathematical model for a typical home with a shower and bathroom. Average concentrations for TCE based on a water concentration of 1 mg/L were calculated. Trichloroethylene concentrations in air were based on one hour of showering time (from 7 to 8 a.m.) and a bathroom use period from 7 a.m. to 9 a.m. The exposure for the rest of the household was based on a period of 24 hours. The average calculated airborne TCE concentrations were: for the shower - 18 mg/m^3 (3.4×10^3ppb); for the bathroom - 3.5 mg/m^3 (6.5×10^2 ppb); and for the rest of the house - 0.1 mg/m^3 (19 ppb).

In 1986, the California Department of Health Services measured a number of wells and ground water systems in California for organic chemical contamination (DHS, 1986). Trichloroethylene was detected in 188 out of 2,947 wells at a median concentration of 3.2 μg/liter (μg/L) of water.

The DHS reported that the maximum concentration of TCE was 538 μg/L and that the highest concentrations were generally found in wells which served heavily urbanized areas.

3. Other Factors Influencing Indoor Concentrations of TCE

The potential for TCE to infiltrate indoor air from outdoor air exists when homes and offices are located near point or area sources of TCE. For example, degreasing operations are thought to be the primary source of TCE in the Santa Clara Valley (U.S. EPA, 1986b) where the EPA estimated that approximately 34 metric tons per year would be released into the air. Further, the electronics industries located in the Santa Clara Valley pump and discharge potentially contaminated water and as a result, air emissions could be generated by aeration of the water.

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IV.

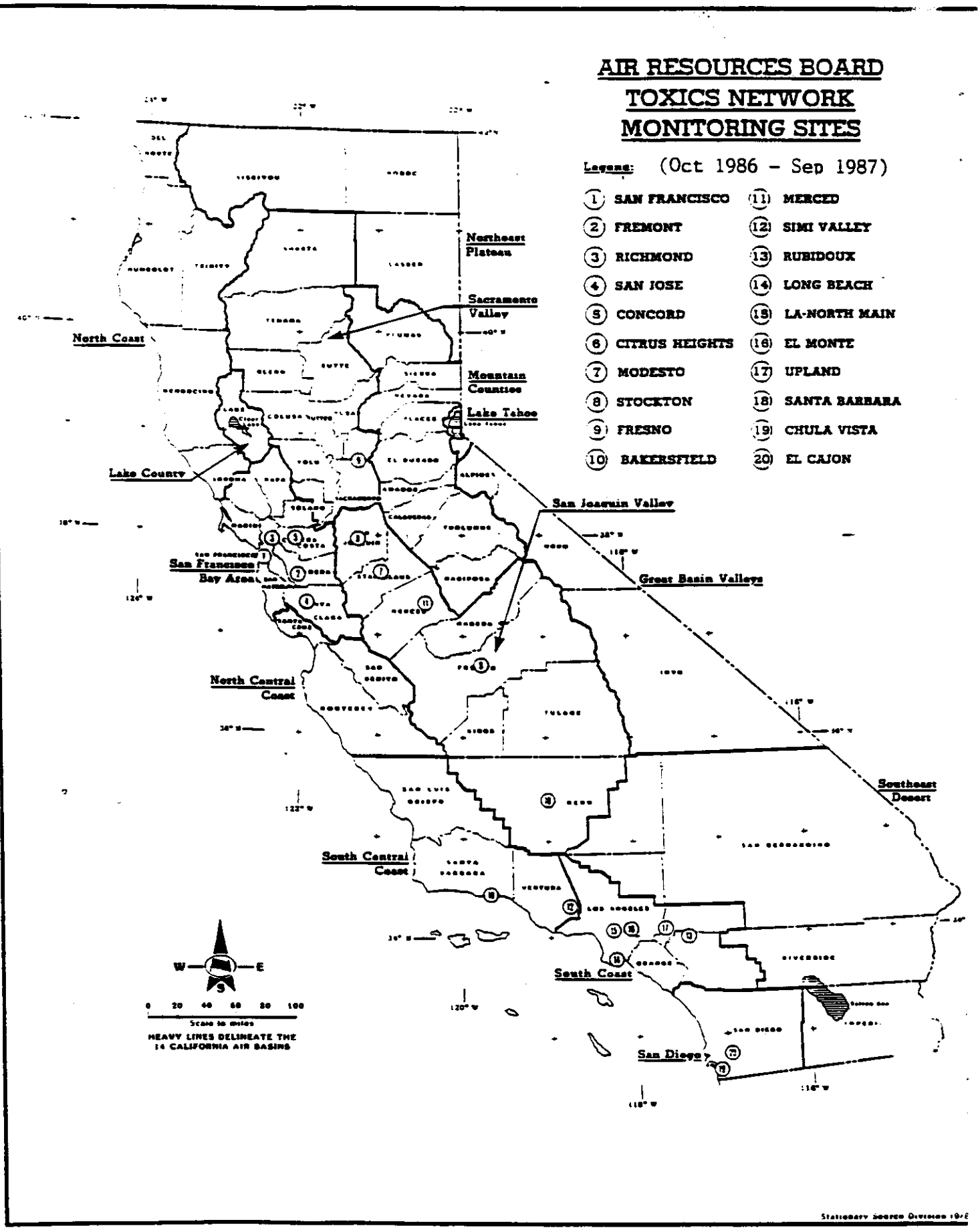
EXPOSURE TO TRICHLOROETHYLENE

A. AMBIENT MONITORING FOR TRICHLOROETHYLENE

The ARB monitors for TCE at 20 sites in California. Nine of these sites are in Southern California (south of Bakersfield), while the other 11 are in the northern portion of the State. The statewide monitoring sites are indicated on Figure IV-1. Samples are collected in 30 liter Tedlar bags over a 24-hour period using low volume samplers. Samples were taken approximately every 12 days at each site. For the samples collected during the study period discussed below, ARB Monitoring and Laboratory Division's Southern Laboratory Branch was responsible for analyzing samples taken at the nine Southern California sites while the Northern Laboratory Branch was responsible for analyzing samples from the eleven Northern California sites. The analysis of the samples for TCE consists of a pre-concentration step (absorbent trapping using Tenax), followed by gas chromatographic analysis employing an electron capture detector. Standard operating procedures for sampling and analysis are provided in Appendix B.

Data used in the following exposure analysis were collected during the study period of October 1986 through September 1987. In February 1987, the San Francisco site was relocated to a new site approximately 1.8 miles southeast of the old site. Although no overlapping data are available for the two sites, we have assumed for purposes of this analysis that concentrations measured at the old and new sites are comparable and that both locations can be treated as a single site. In addition, a recent investigation revealed potentially significant problems with some of the

FIGURE IV-1


AIR RESOURCES BOARD
TOXICS NETWORK
MONITORING SITES
Legend: (Oct 1986 - Sep 1987)
1 SAN FRANCISCO
2 FREMONT
3 RICHMOND
4 SAN JOSE
5 CONCORD
6 CITRUS HEIGHTS
7 MODESTO
8 STOCKTON
9 FRESNO
10 BAKERSFIELD
11 MERCED
12 SIMI VALLEY
13 RUBIDOUX
14 LONG BEACH
15 LA-NORTH MAIN
16 EL MONTE
17 UPLAND
18 SANTA BARBARA
19 CHULA VISTA
20 EL CAJON
Northeast Plateau
Sacramento Valley
North Coast
Mountain Counties
Lake Tahoe
Lake County
San Joaquin Valley
San Francisco Bay Area
Great Basin Valleys
North Central Coast
Southeast Desert
South Central Coast
South Coast
San Diego
W
E
S
0 20 40 60 80 100
Scale in miles
HEAVY LINES DELINEATE THE 14 CALIFORNIA AIR BASINS

data for the Upland monitoring site. The monitoring device had a leak and it was unsure how this would affect the monitoring data. Therefore, the data from the Upland site were not used in this analysis.

B. AMBIENT CONCENTRATIONS OF TRICHLOROETHYLENE

The statewide TCE data for the October 1986 through September 1987 study period represent 19 sites and a small percentage of all possible days during this period.

1. Study Period Data Collected

A total of 403 samples were collected and analyzed during the study period. Table IV-1 summarizes the months for which data are available from each monitoring site. Although the data are fairly complete for Southern California, several Northern California sites show missing data for one or more months. Three sites, Merced, San Francisco and Bakersfield, have two or three consecutive months with no observations. The number of samples available from each site during the study period ranges from 8 to 22 in Northern California and from 26 to 32 in Southern California. The Northern and Southern sites average 1.45 and 2.35 observations per month, respectively. The average for all sites in the state is 1.77 observations per month.

Only 7 of the 403 samples analyzed had concentrations below the limit of quantification (LOQ) for TCE, equal to less than 2 percent of the total observations. The ARB's LOQ for TCE analysis is 0.02 parts per billion (ppb). Three of the below-LOQ samples were collected at the Citrus Heights site (Sacramento); the other four below-LOQ samples were collected at the Concord, Long Beach, Simi Valley, and Stockton monitoring sites. The concentrations of the below-LOQ samples were estimated using Gleit's method (Gleit, 1985) described below.

TABLE IV-1

Summary of Available TCE Data:
October 1986 Through September 1987*

Site Location	O	N	D	J	F	M	A	M	J	J	A	S	Number of Samples
SOUTHERN CALIFORNIA SITES													
South Coast Air Basin													
El Monte	o	o	o	o	o	o	o	o	o	o	o	o	29
Los Angeles	o	o	o	o	o	o	o	o	o	o	o	o	27
Long Beach	o	o	o	o	o	o	o	o	o	o	o	o	32
Riverside	o	o	o	o	o	o	o	o	o	o	o	o	27
South Central Coast Air Basin													
Santa Barbara	o	o	o	o	o	o	o	o	o	o	o	o	21
Simi Valley	o	o	o	o	o	o	o	o	o	o	o	o	32
San Diego Air Basin													
Chula Vista	o	o	o	o	o	o	o	o	o	o	o	o	32
El Cajon	o	o	o		o	o	o	o	o	o	o	o	26
NORTHERN CALIFORNIA SITES													
San Francisco Bay Area Air Basin													
Concord	o	o		o		o		o	o	o		o	9
Fremont	o	o		o	o	o	o	o	o	o	o	o	18
Richmond	o	o	o	o	o	o	o	o	o	o	o		18
San Francisco	o	o	o		o	o	o	o			o	o	14
San Jose	o	o	o	o	o	o	o	o	o	o	o	o	22
San Joaquin Valley Air Basin													
Bakersfield	o		o	o				o	o		o	o	8
Fresno	o	o	o	o	o	o		o	o	o	o	o	17
Merced	o	o	o	o	o	o	o	o	o	o			18
Modesto	o	o	o	o	o	o	o	o	o	o	o		18
Stockton	o	o	o	o	o	o	o	o	o	o	o	o	21
Sacramento Valley Air Basin													
Citrus Heights		o	o	o	o	o	o		o	o	o	o	14

TOTAL SAMPLES 403

* A "o" indicates at least one sample was collected during the month.

2. Site-Specific TCE Concentrations

Table IV-2 summarizes various sample statistics of the concentrations measured at each monitoring site during the study period. In addition to the minimum and maximum concentrations, the median and mean concentrations and the standard deviation are listed for each site. Mean TCE concentrations were calculated as the mean of individual monthly means. This approach provides equal weighting for each month when the number of samples per month varies. In calculating the mean TCE concentration at each site, the concentration of below-LOQ samples was estimated using a method developed by Gleit (Gleit, 1985). Gleit's method assumes that the sample of concentrations is a random sample from a normal distribution. Data that are judged not to be normally distributed may be transformed to approximate normality. Gleit's method accounts for the concentrations below the LOQ by setting them equal to the "below-LOQ mean", the mean of the portion of the normal distribution below the LOQ. Setting the unknown concentrations to their average value seems intuitively reasonable, and the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations. A detailed description of the method used to estimate the concentration of data below the LOQ is provided in Appendix C.

The site-specific ranges of the minimum and maximum ambient TCE concentrations listed in Table IV-2 are plotted in Figure IV-2. Minimum concentrations at the 19 sites range from below the LOQ (<0.02 ppb) at five of the sites to 0.18 ppb at Bakersfield. More than half of the sites have minimum concentrations of 0.05 ppb TCE or less. Maximum concentrations range in value from 0.04 ppb at Citrus Heights to 1.8 ppb at Simi Valley. The maximum concentrations for the Southern California sites are not statistically different from those for the Northern sites.

Maximum TCE concentrations were reported most often during the period of August through October, accounting for 55 percent of the reported maximum values. Other maxima were measured in November and December. These five months (August through December) account for 80 percent of the maxima and

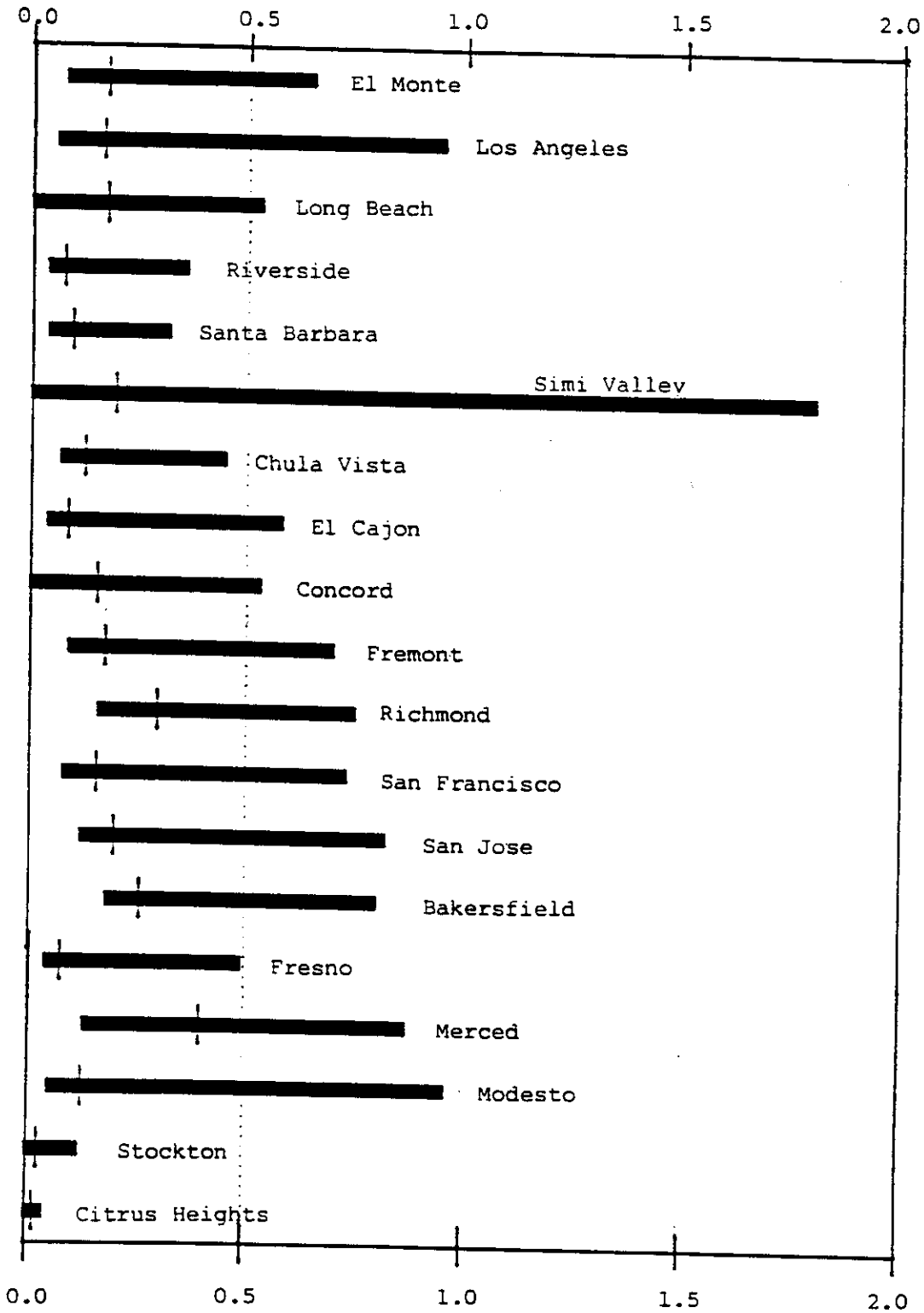
TABLE IV-2

Summary of TCE Data Collected
During October 1986 Through September 1987
(ppb)

AIR BASIN Site Location	Minimum Conc.	Maximum Conc.	Median Conc.	Mean* Conc.	Standard# Deviation
SOUTHERN CALIFORNIA SITES					
South Coast Air Basin					
El Monte	0.08	0.65	0.18	0.23	0.12
Los Angeles	0.06	0.95	0.17	0.29	0.12
Long Beach	<0.02	0.53	0.18	0.19	0.08
Riverside	0.04	0.36	0.08	0.11	0.05
Basin Summary	<0.02	0.95	0.16	0.19	0.10
South Central Coast Air Basin					
Santa Barbara	0.04	0.32	0.10	0.14	0.07
Simi Valley	<0.02	1.80	0.20	0.14	0.16
Basin Summary	<0.02	1.80	0.14	0.14	0.12
San Diego Air Basin					
Chula Vista	0.07	0.45	0.13	0.23	0.07
El Cajon	0.04	0.58	0.09	0.18	0.11
Basin Summary	0.04	0.58	0.11	0.21	0.09
NORTHERN CALIFORNIA SITES					
San Francisco Bay Area Air Basin					
Concord	<0.02	0.53	0.16	0.19	0.16
Fremont	0.09	0.70	0.18	0.27	0.19
Richmond	0.16	0.75	0.30	0.34	0.16
San Francisco	0.08	0.73	0.16	0.21	0.16
San Jose	0.12	0.82	0.20	0.30	0.20
Basin Summary	<0.02	0.82	0.20	0.26	0.17
San Joaquin Valley Air Basin					
Bakersfield	0.18	0.80	0.26	0.36	0.21
Fresno	0.04	0.49	0.08	0.13	0.12
Merced	0.13	0.87	0.40	0.42	0.19
Modesto	0.05	0.96	0.13	0.22	0.23
Stockton	<0.02	0.12	0.03	0.04	0.03
Basin Summary	<0.02	0.96	0.18	0.23	0.17
Sacramento Valley Air Basin					
Citrus Heights	<0.02	0.04	0.02	0.02	0.01

* - Means are the mean of the monthly means.
\# - Standard Deviations were derived from monthly means. Basin Standard Deviations are pooled values of the standard deviations across sites within a basin.

FIGURE IV-2
MEDIAN ANNUAL TCE CONCENTRATIONS WITH MINIMUM AND MAXIMUM OBSERVATIONS
(Based on October 1986 - September 1987 Data)
(ppb)



70 percent of the second highest values. Sixty percent of the minima occurred during the months of May through July. These data suggest that higher TCE concentrations might be expected during months other than May through July. This would be generally consistent with seasonal dispersion tendencies for primary pollutants, assuming that emissions are uniform throughout the year. Seasonal dispersion tendencies result in higher ambient concentrations during winter months due to stagnant air patterns. However, more complete data and a longer period of record are needed before we can be certain that a seasonal dispersion pattern exists.

Median TCE concentrations are also summarized in Table IV-2. At 18 of the 19 sites, the median concentration is lower than the calculated mean; the exception is Simi Valley whose median concentration is slightly higher than the mean. The relationship of the median concentration to the mean of all samples can indicate several things, including how the data are distributed. For example, a median concentration that is significantly different from the mean may be indicative of a non-normal distribution of the data. In the past, the distribution of the ambient air quality data has generally been assumed to be log-normal. To test the TCE monitoring data for normality and log-normality we used the Shapero-Wilk test statistic (see Appendix D for a description of the test). We found that TCE data have neither normal nor log-normal distribution.

Even though the TCE monitoring data have been shown to have neither a normal nor log-normal distribution, Gleit's expected order statistic approach was used on a site-by-site basis for each of the four sites for which data below the LOQ was reported. This was done because the distribution is unknown. If the distribution could have been identified, then an optimal estimation procedure could have been applied.

The Kruskal-Wallis Test is a nonparametric test for detecting significant differences between subsample medians. The Kruskal-Wallis test was used to determine whether significant differences between the site-specific distribution of the TCE data exist. The Kruskal-Wallis test was

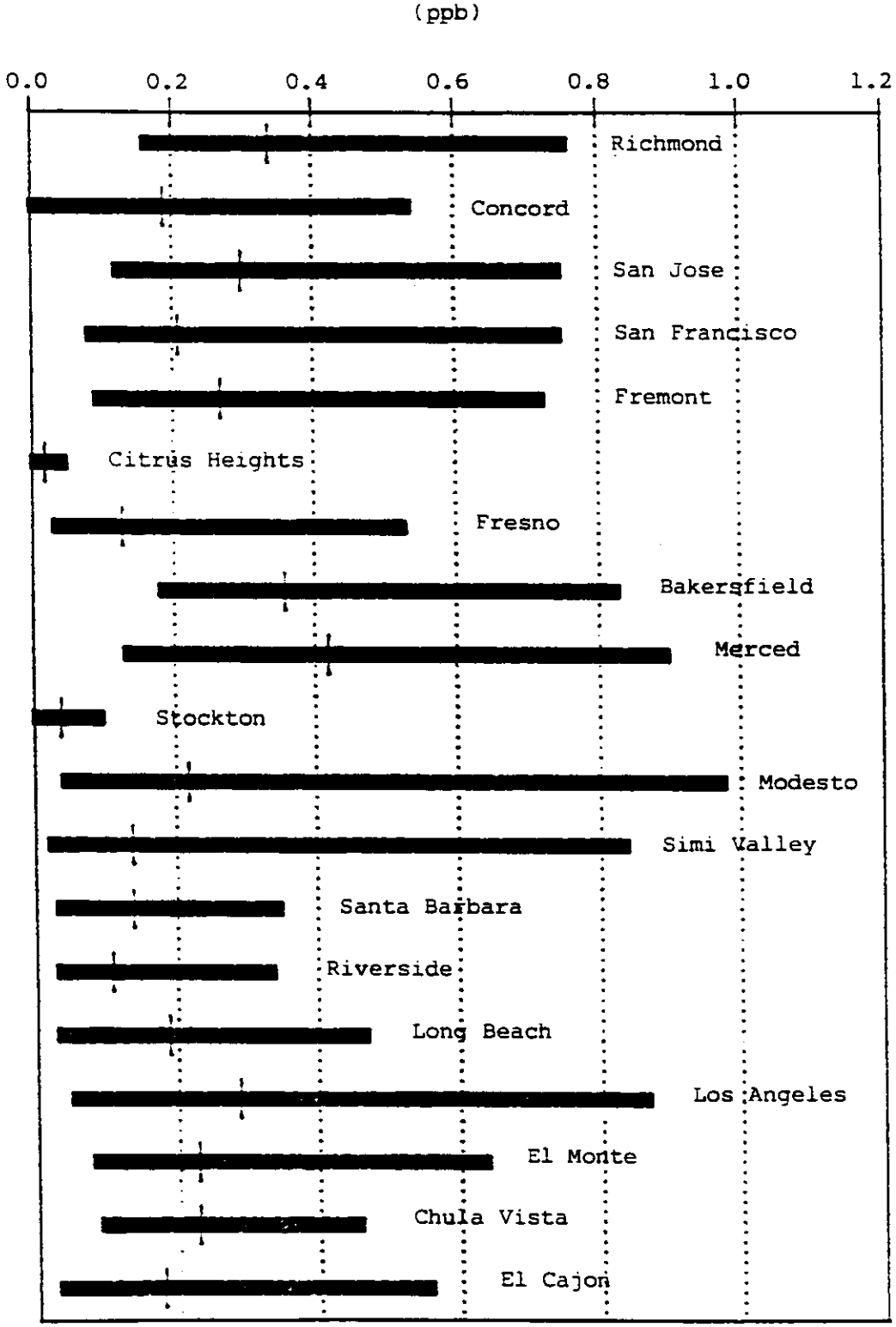
used rather than the more well known F-test, because the statistical distribution of TCE concentrations is unknown (see Appendix D for a description of the Kruskal-Wallis test). Taken on a Northern California versus Southern California basis, the means for the Southern California sites are not distributed differently from the means for the Northern California sites. The mean of the individual site means for Northern California is 0.22 ppb and the value for Southern California is 0.19 ppb, a difference that is not statistically significant. Although this similarity may be a characteristic of ambient TCE concentrations, it could also be the result of the limited sample size or sampling error.

On a site-by-site basis, estimated mean TCE concentrations range in value from 0.02 ppb for Citrus Heights to 0.42 ppb for Merced. Mean concentrations for each site are given in Table IV-2 and are plotted in Figure IV-3. In addition to the estimated mean, the upper and lower empirical confidence interval bounds defined by the 5th and 95th quantiles for the data from each sites are also plotted.

The Kruskal-Wallis test shows a statistically significant difference among the data from the sites in Northern California. Data from Northern California separate into two groups, a group of lower values consisting of data from Citrus Heights and Stockton and a group of higher values which represents the rest of Northern California. When the data for Citrus Heights and Stockton are removed from the Northern California dataset, the Kruskal-Wallis test shows no significant difference in the data from the remaining Northern California sites.

Data for the Southern California sites all overlap, which suggests that the distribution of the ambient TCE concentration data are similar and may be the same for each of the Southern California sites. However, without a longer period of record and possibly more sampling sites, we cannot determine if this characteristic is true for the entire state or whether uncertainties in the data are masking less significant differences.

FIGURE IV-3
MEAN ANNUAL TCE CONCENTRATIONS WITH
5 AND 95 PERCENT QUANTILES BOUNDS
(Based on October 1986-September 1987 Data)



3. Basin-Wide Mean Concentrations

The highest basin-wide mean concentration (shown on Table IV-2) occurred in the San Francisco Bay Area (0.26 ppb), followed by the San Joaquin Valley (0.23 ppb), San Diego (0.21 ppb), the South Coast (0.19 ppb), and the South Central Coast (0.14). A basin-by-basin evaluation of the TCE data indicates that the San Francisco Bay Area Air Basin has no site that is significantly different from any other. In the San Joaquin Valley Air Basin, data for all sites are similar except Stockton.

This consistency also holds true for the data from sites in the Southern California air basins. Simi Valley is the only site with data that appear different. This difference is directly attributable to a single extreme value (1.8 ppb). Data for sites in the South Central Coast Air Basin and San Diego Air Basin are consistent with the data for the South Coast sites, implying that a single distribution representing all sites in Southern California is plausible.

4. Peak-to-Mean Ratios

Peak-to-mean ratios were calculated to provide possible insights into the nature of TCE 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 greater than 10. 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.

Peak-to-mean ratios for the study period are given in Table IV-3. Ratios for 18 of the 19 sites are low. Only the Simi Valley site shows a ratio greater than 5. The ratio for Simi Valley, 12.0, is 2.72 times the next highest ratio of 4.4, calculated for Modesto. The relatively high peak-to-mean ratio at Simi Valley is due to a single isolated value of 1.80 ppb, 6.67 times the next highest value of 0.27 ppb. 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 (Table IV-3). The C.V. is equal to the standard deviation divided by the mean. 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. Even though it is less sensitive to isolated extreme values, the C.V. reflects the same singular high value for Simi Valley. However, we cannot determine specifically the factors contributing to the distributional patterns of TCE without more detailed information on the spatial emission of TCE.

C. POPULATION-WEIGHTED EXPOSURE ESTIMATES

We have estimated the mean population-weighted exposure to TCE in California using the October 1986 to September 1987 data. This was done by first calculating three estimates of exposure, the site-specific mean annual TCE concentrations, and the upper and lower Bootstrap confidence interval bounds about the exposure means (see Appendix D for description of technique). These parameters are given in Table IV-4 and are plotted in Figure IV-4.

TABLE IV-3

Summary of TCE Peak-to-Mean Ratios:
October 1986 Through September 1987
(ppb)

AIR BASIN Site Location	Peak Conc.	Mean Conc.	Peak-to-Mean Ratio	Number of Samples	C.V.*
SOUTHERN CALIFORNIA SITES					
South Coast Air Basin					
El Monte	0.65	0.23	2.80	29	52.2
Los Angeles	0.95	0.29	3.30	27	52.2
Long Beach	0.53	0.19	2.80	32	42.1
Riverside	0.36	0.11	3.30	27	45.5
South Central Coast Air Basin					
Santa Barbara	0.32	0.14	2.30	21	50.0
Simi Valley	1.80	0.14	12.90	32	114.3
San Diego Air Basin					
Chula Vista	0.45	0.23	2.00	32	30.4
El Cajon	0.58	0.18	3.21	26	61.1
NORTHERN CALIFORNIA SITES					
San Francisco Bay Area Air Basin					
Concord	0.53	0.19	2.50	9	84.2
Fremont	0.70	0.27	2.60	18	70.4
Richmond	0.75	0.34	2.30	19	47.1
San Francisco	0.73	0.21	3.48	14	76.2
San Jose	0.82	0.30	2.90	22	66.7
San Joaquin Valley Air Basin					
Bakersfield	0.80	0.36	2.20	8	58.3
Fresno	0.49	0.13	3.80	17	92.3
Merced	0.87	0.42	2.10	18	45.2
Modesto	0.96	0.22	4.40	18	104.5
Stockton	0.12	0.04	3.00	21	75.0
Sacramento Valley Air basin					
Citrus Heights	0.04	0.02	2.00	14	50.0

* Coefficient of Variation

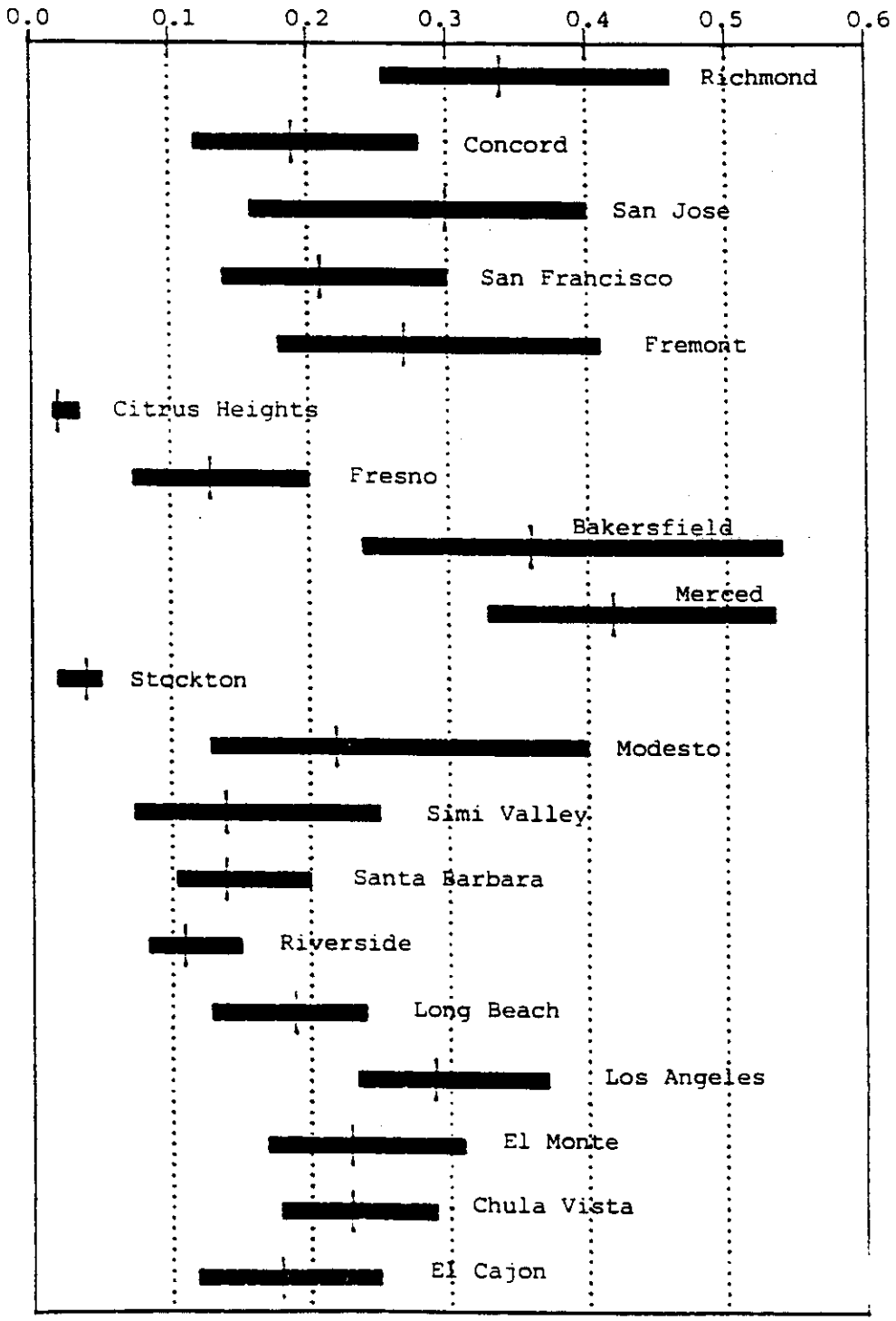
TABLE IV-4

Summary of Mean TCE Concentrations and
Upper and Lower Bound Intervals:
October 1986 Through September 1987
(ppb)

Air Basin Site Location	Lower Bound Interval	Mean Conc.	Upper Bound Interval
SOUTHERN CALIFORNIA SITES			
South Coast Air Basin			
El Monte	0.17	0.23	0.30
Los Angeles	0.23	0.29	0.36
Long Beach	0.13	0.19	0.23
Riverside	0.08	0.11	0.14
South Central Coast Air Basin			
Santa Barbara	0.11	0.14	0.19
Simi Valley	0.08	0.14	0.24
San Diego Air Basin			
Chula Vista	0.20	0.23	0.28
El Cajon	0.12	0.18	0.24
NORTHERN CALIFORNIA SITES			
San Francisco Bay Area Air Basin			
Concord	0.13	0.19	0.27
Fremont	0.19	0.27	0.40
Richmond	0.26	0.34	0.45
San Francisco	0.14	0.21	0.29
San Jose	0.16	0.30	0.40
San Joaquin Valley Air Basin			
Bakersfield	0.24	0.36	0.53
Fresno	0.08	0.13	0.19
Merced	0.33	0.42	0.53
Modesto	0.13	0.22	0.31
Stockton	0.03	0.04	0.05
SACRAMENTO VALLEY AIR BASIN			
Citrus Heights	0.01	0.02	0.04

FIGURE IV-4
MEAN ANNUAL TCE CONCENTRATIONS WITH
95 PERCENT CONFIDENCE BOUNDS FOR THE MEAN
(Based on October 1986-September 1987 Data)

(ppb)



The site-specific data were used to determine the overall population-weighted exposure estimates for each air basin and for an overall statewide exposure estimate. Exposures for the South Coast and San Francisco Bay Area Air Basins 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. The results of the exposure analysis, which are discussed below, are summarized in Table IV-5. As mentioned previously, the data used for these exposure estimates represent less than 2 samples per month at only 19 sites throughout California. Therefore, the exposure estimates and bounds presented here should be used with caution.

The overall statewide mean TCE exposure, weighted by population, is estimated at 0.22 ppb. A total of 20,339,250 people reside in the study areas, representing approximately 80 percent of the State's population. Basin-specific, population-weighted mean concentrations vary from a minimum of 0.02 ppb in Sacramento Valley Air Basin to a maximum of 0.26 ppb in the San Francisco Bay Area Air Basin. With the exception of the Sacramento Valley Air Basin, air basins in Southern California generally show no lower exposure values than those in Northern California.

Figure IV-5 shows the total number of people exposed to various mean annual TCE concentrations (rounded off to the nearest 0.05 ppb). The distribution of the plotted data is fairly concentrated. This is due to the overall uniformity in mean concentrations estimated for the various exposure study areas. Half of all people in the study areas are estimated to be exposed to an estimated mean concentration of at least 0.21 ppb TCE.

Figure IV-6 shows the same data as in Figure IV-5, but plotted as the cumulative population exposed to an estimated mean TCE concentration. The

TABLE IV-5

Summary of TCE Population-Weighted Exposure
Estimates: October 1986 Through September 1987
(ppb)

Air Basin Site Location	Mean Estimate	Population Represented
SOUTHERN CALIFORNIA SITES		
Population-Weighted Exposure for South Coast Air Basin	0.23	10,092,133
Population-Weighted Exposure for South Central Coast Air Basin	0.14	925,822
Population-Weighted Exposure for San Diego Air Basin	0.21	2,135,872
NORTHERN CALIFORNIA SITES		
Population-Weighted Exposure for San Francisco Bay Area Air Basin	0.26	4,394,374
Population-Weighted Exposure for San Joaquin Valley Air Basin	0.23	1,901,243
Population-Weighted Exposure for Sacramento Valley Air Basin*	0.02	889,806
OVERALL POPULATION-WEIGHTED EXPOSURE	0.22	20,339,250

* Exposure estimates are for Sacramento County residents only.

FIGURE IV-5

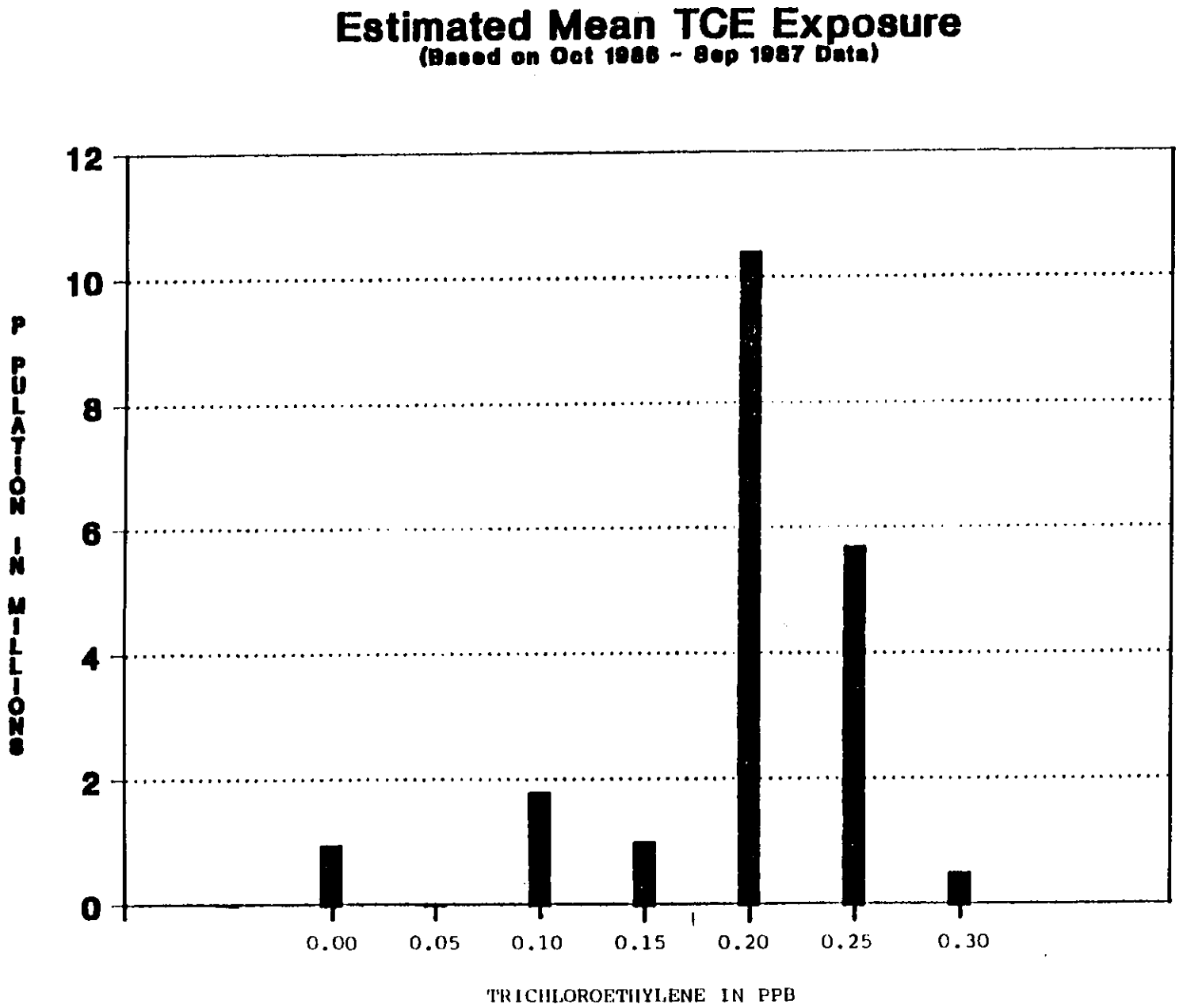
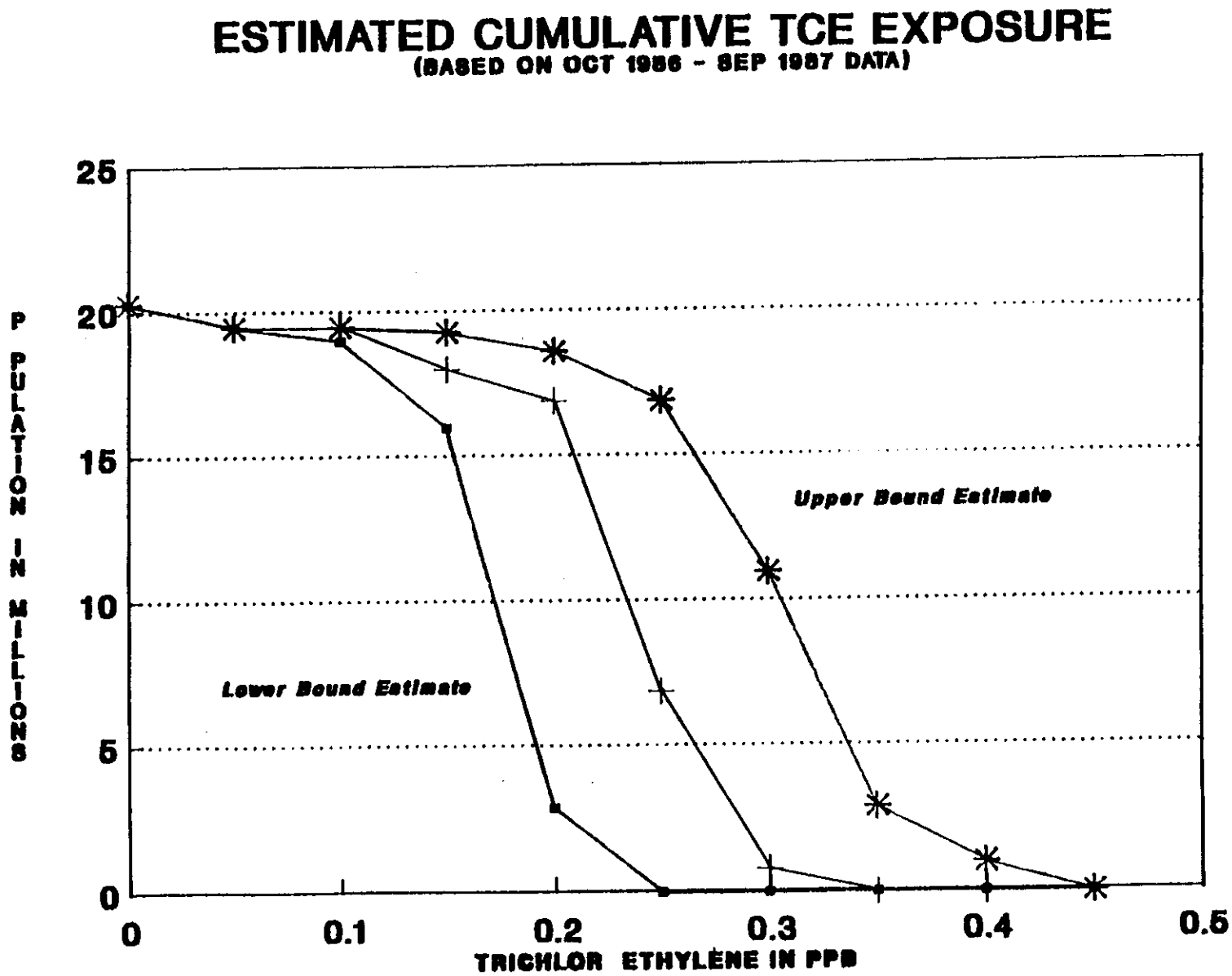

Estimated Mean TCE Exposure
(Based on Oct 1986 - Sep 1987 Data)
POPULATION IN MILLIONS
12
10
8
6
4
2
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
TRICHLOROETHYLENE IN PPB

FIGURE IV-6


ESTIMATED CUMULATIVE TCE EXPOSURE
(BASED ON OCT 1986 - SEP 1987 DATA)
POPULATION IN MILLIONS
25
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
TRICHLOR ETHYLENE IN PPB
Upper Bound Estimate
Lower Bound Estimate

approximate lower and upper bounds about the estimated mean are also shown in Figure IV-6. In the study areas 95 percent of all people were exposed to an estimated mean concentration of at least 0.08 ppb.

The overall geographic mean TCE concentration was 0.18 ppb. This value is roughly 18 percent lower than the population-weighted exposure estimate of 0.22 ppb, indicating that the highest concentrations of TCE tended to be in the areas of higher population density. However, this value is highly influenced by the low annual mean TCE concentration for the Sacramento Valley Air Basin (measured at the Citrus Heights monitoring site). When the data from Sacramento are removed, the geographic mean TCE concentration is 0.21 ppb, only slightly lower than the population-weighted mean concentration, indicative of fairly consistent exposures statewide.

D. EXPOSURE TO TRICHLOROETHYLENE NEAR EMISSION SOURCES

To assess the impact of TCE emission sources in nearby population, the ARB used annual emissions data in conjunction with meteorological data to estimate population exposure in census tracts surrounding three facilities that emit TCE. These facilities (located in Manhattan Beach, San Leandro and Oakland) were chosen because they represent three of the largest emitters of TCE in California.

The concentrations presented in this section do not represent the total ambient air exposure of the people living in the vicinity of the modeled sources. The concentrations reported are those which would exist if the modeled facility was the only TCE emission source affecting the nearby population. In reality, there are other emission sources, large and small, located in the basin which contribute to the total TCE concentration to which the modeled population is exposed.

A 40 kilometer by 40 kilometer grid with 500 meter receptor spacing was utilized to model emissions from the Manhattan Beach facility. A 50

kilometer by 40 kilometer grid with 500 meter receptor spacing was used to model emissions from the Oakland and San Leandro facilities. The rectangular grid was chosen for the Bay Area facilities so that the same population grid would apply to both facilities. The three facilities were centered on their respective grids.

For each grid, the ISCST air quality model was used to predict above ambient annual average TCE concentrations. Meteorological data input into the model were obtained from the nearest available meteorological station to each facility. Meteorological data for the Manhattan Beach facility was obtained from Lennox Airport records for 1981. Meteorological data for the Oakland and San Leandro facilities were obtained from Oakland Airport records for 1962. These years of meteorological data (1981, 1962) were selected because they were the most recent years available and they represent poor years in terms of pollutant dispersion.

The modeling results were used to calculate the maximum annual average exposure. For the Manhattan Beach facility, 1,750 people are estimated to be exposed to maximum annual average concentrations from 1.0 to 7.0 $\mu g/m^3$ (0.19 to 1.30 ppb) of TCE. For the Oakland and San Leandro facilities, 2,400 people are estimated to be exposed to maximum annual average concentrations from 0.30 to 1.40 $\mu g/m^3$ (0.06 to 0.26 ppb) of TCE. The estimated exposures from the Oakland and San Leandro facilities are from their combined emissions.

Using the DHS' best estimate for unit risk for TCE (2×10^{-6} $(\mu g/m^3)^{-1}$) and a maximum (worst case) concentration of 7 $\mu g/m^3$, 14 excess cancer cases could occur for every 1 million persons exposed.

E. INDOOR AIR EXPOSURE TO TRICHLOROETHYLENE

Indoor air exposure assessment has become increasingly important to evaluate total daily exposure to toxic substances. Certain pollutants are

at higher concentrations indoors than outdoors and people spend about 80 to 90 percent of their time indoors (Robinson, 1977).

The most extensive information on the measurement of trichloroethylene indoors, as well as other volatile organic compounds (VOCs), is from the Total Exposure Assessment Methodology (TEAM) studies sponsored by the Environmental Protection Agency (EPA) and conducted from 1980 to 1985 and in 1987.

The 1980 to 1985 studies (TEAM 84 -- Wallace, 1987a; Wallace, 1986; Pellizzari et al., 1986; U.S. EPA, 1987a,b) measured VOCs in samples collected from personal air samplers, breath samples, fixed outdoor samplers, and from water. Approximately 800 volunteers in five U.S. cities participated in the TEAM 84 studies. Two of the areas studied by the TEAM 84 project were in major metropolitan areas in California and were studied during different seasons. These areas were Los Angeles in February 1984 and May 1984, and Contra Costa (located in Northern California) in June 1984. Approximately 240 volunteers in California participated in the study.

A new TEAM study was conducted in 1987 (TEAM 87 -- Pellizzari et al., 1989) and the investigators collected VOCs using personal air samplers, fixed-site outdoor air samplers, and fixed-site indoor air samplers. As in the TEAM 84 studies, the TEAM 87 study investigators also collected VOC samples during two seasons (February and July, 1987), but collected samples in the Los Angeles area only. Breath and water samples were not collected, but the indoor samples now included fixed-site air samples (Pellizzari, et al. 1989).

In addition to the TEAM studies, several other investigators have studied indoor air exposure to TCE, however, few have been conducted in California and most were conducted outside the U.S.

1. Data from Personal Air Sampling in California

Both the TEAM 84 and TEAM 87 volunteers wore personal air samplers which consisted of an adsorbent-filled cartridge connected to a portable low volume sampling pump. The adsorbent-filled cartridges were worn near a volunteer's breathing zone and the VOCs adsorbed and measured represented exposure to these compounds during the 24-hour sampling period. An identical cartridge and pump were used outdoors at selected volunteers' homes, except that the apparatus was placed in a single fixed location and was not carried by the individual. For the TEAM 84 studies, two 12-hour samples (for a total exposure period of 24 hours) were obtained from each volunteer as well as from the fixed outdoor sampling site. There was no fixed indoor sample, therefore for the data analysis, the investigators substituted the personal sample for the 12 hours representing the night hours from 6 p.m. to 6 a.m.

Direct comparisons of TCE concentrations indoors and outdoors based on the TEAM 84 data are summarized in Table IV-6 (from Pellizzari et al., 1986). All samples for the comparisons were matched, i.e., the samples of indoor VOCs were collected at the same time as the samples of outdoor VOCs. For L.A in February 1984, the median concentration of TCE indoors was 0.22 ppb (maximum of 9.30 ppb) and outdoors was 0.13 ppb (maximum of 0.56 ppb). During the May 1984 sampling period, the reported median indoor concentrations were 0.09 ppb with a maximum of 2.05 ppb. The matched concentrations of TCE outdoors was 0.02 ppb (maximum of 0.45 ppb). The matched median concentrations for Contra Costa were 0.07 ppb (0.73 ppb maximum) for indoors and 0.02 ppb (0.06 ppb maximum) for outdoors.

The matched indoor to outdoor TCE comparisons for L.A. as well as for Contra Costa indicate that the median levels of TCE indoors were approximately 2 to 5 times greater than the median levels measured outdoors. Also, the reported concentrations in Contra Costa for all VOCs measured either indoors or outdoors, were consistently lower than the concentrations measured in Los Angeles.

TABLE IV-6

Weighted Median Overnight Indoor and Outdoor Concentrations of TCE Based on Matched Personal Samples from the TEAM 84 Study

		parts per billion (ppb)[1]		
Location	Date	Indoor	Outdoor	Ratio
Los Angeles (n=24)	2/84	0.22	0.13	1.7
Los Angeles (n=23)	5/84	0.09	0.02	4.5
Contra Costa (n=10)	6/84	0.07	0.02	3.5

1 -- Source: U.S. EPA, 1987a. Data originally reported in $\mu g/m^3$.

PROPOSED IDENTIFICATION OF TRICHLOROETHYLENE AS A TOXIC AIR CONTAMINANT

TECHNICAL SUPPORT DOCUMENT

REPORT TO THE AIR RESOURCES BOARD ON TRICHLOROETHYLENE (TCE)

PART A

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

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August, 1990

Population-weighted concentrations for exposure based on the personal sampling pumps are summarized in Table IV-7. The 25th, median, and 75th percentile values are presented in this table to characterize the distribution of concentrations around the median value. The 90th and 95th percentiles as well as maximum values are presented to illustrate the distribution of the higher concentrations measured.

The TEAM 87 study was, conducted in February and July, 1987 in Los Angeles only (Pellizzari et al., 1989). The 25th, median, 75th, 90th, and 95th percentiles as well as maximum values of TCE concentrations representing personal air samples are presented in Table IV-8. These data are not population-weighted. The median day and night TCE concentrations for personal air (in ppb) measured during February were approximately double the concentrations measured in July (0.13 and 0.12 ppb for day and night samples, respectively measured in February; to 0.06 and 0.06 ppb for day and night samples measured respectively in July).

Although both TEAM 84 and TEAM 87 studies measured homes in Los Angeles (some of the same homes measured in TEAM 84 were measured in TEAM 87), the data cannot be compared. The data for TEAM 84 was population-weighted, whereas, due to the smaller number of homes, the TEAM 87 data was not (E. Pellizzari, personal communication to D. Westerdahl).

2. Data from Fixed-Site Sampling

Investigators place air sampling devices at fixed-sites indoors and outdoors to measure concurrent pollutant concentrations at specific locations. The devices can be placed indoors in a number of rooms to investigate "hot spots" and room-to-room differences in pollutant concentrations.

Table IV-7

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

[Weighted Concentrations (ppb*)][a]

Location	Date	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
.os Angeles	2/84	.12	.41	1.86	6.89	14.14	18.61	.08	.20	.64	1.28	2.61	12.28
os Angeles	5/84	.01	.22	1.02	4.65	10.05	65.13	.01	.06	.16	.47	1.19	31.63
'ontra osta	6/84	.02	.09	.20	1.86	4.84	39.08	.02	.05	.18	.39	.52	1.19

- Original data reported in ug/m^3; 1 ppb = 5.37 ug/m^3
  (See Appendix E for original data)
- 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 = 98,696

ource: EPA 1987b

Table IV-8

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

[Un-Weighted Concentrations (ppb*)]

Location	Date	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
.os Angeles	2/87	.05	.13	.26	.64	.79	1.11	.03	.12	.47	1.41	3.00	5.79
.os Angeles	7/87	.03	.06	.24	.64	2.44	41.87	.03	.06	.21	.66	2.36	3.76

* - Original data reported in ug/m^3; 1 ppb = 5.37 ug/m^3
(See Appendix E for original data)

Source: Pellizzari, et al., 1989

a. TEAM 87 Studies

The most recent information based on fixed-site placement of indoor air sampling devices is from the TEAM 87 study conducted in California (Pellizzari et al., 1989). Fixed-site sampling was not performed during the TEAM 84 study. Air sampling devices were placed in two indoor locations (kitchen and living room) as well as in an outdoor location. Twelve-hour day and 12-hour night samples were collected during two seasons in Los Angeles. The 25th, median, 75th, 90th, and 95th percentiles as well as maximum concentrations are presented in Table IV-9. Again, these values are not weighted according to population, but are actual values of the samples taken. The median concentrations measured in the living room in winter appear to be higher than the concentrations measured in the kitchen (0.12 and 0.06 ppb, respectively; daytime values). The concentrations measured during the summer in the kitchen and living room are identical (0.05 and 0.05 ppb, respectively; daytime values) and are not much different from the median concentrations measured in the kitchen during winter. A seasonal comparison of night-time levels is possible only for the kitchen where the median concentration during the winter is twice that of the summer (0.13 vs 0.06 ppb).

Only the winter fixed-site samples (Table IV-9) permit comparison of indoor/outdoor concurrent data. Over the distribution of concentrations from the 25th percentile to the maximum concentrations, the indoor TCE levels are high (based on the kitchen samples) compared to the outdoor levels.

b. Other Studies in Homes

De Bortoli et al. (1986) studied the concentrations of volatile organic compounds in homes in Italy and used low-volume sampling pumps with flow-rates similar to those used in the TEAM studies. He measured approximately 35 VOCs trapped on charcoal adsorbent. Fourteen homes and one small office building were measured. The mean value represented 4-7 days of sampling,

Table IV-9

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

[Un-Weighted Concentrations (ppb*)]

eason	Site	Day Percentiles						Night Percentiles					
		25	Median	75	90	95	Max	25	Median	75	90	95	Max
nter	Kitchen	.03	.06	.25	.63	.85	1.09	.05	.13	.26	.75	1.20	2.83
nter	Living Rm	.04	.12	.27	.49	1.04	1.40	Not Done[a]					
nter	Outdoors	.01	.01	.04	.06	.09	.14	.01	.05	.06	.13	.15	.30
ummer	Kitchen	.03	.05	.14	.34	.68	1.32	.03	.06	.19	.86	1.79	2.34
ummer	Living Rm	.03	.05	.13	.35	.76	.92	Not Done[a]					
ummer	Outdoors	Not Listed[b]						Not Listed[b]					

- Original data reported in ug/m^3; 1 ppb = 5.37 ug/m^3
  (See Appendix E for orignal data)
- Time and locations not measured and not part of the experimental design.
- No TCE listed with other compounds measured.

and, to reduce the sampling volume, the investigators sampled for 10 minutes per hour. The total volume of air drawn through the adsorption tubes were from 3 to 15 liters. The authors reported a range of TCE concentrations indoors of 0.19 to 16.00 ppb, with a mean concentration of 3.35 ppb.

Lebret et al. (1986) reported weekly average concentrations of 45 VOCs in more than 300 homes in the Netherlands. Samples of VOCs were collected on charcoal tubes with a sampling flow rate of 100 ml/min for a period of five to seven days. Only two percent of the homes had TCE levels above the detection limit of 0.37 ppb. The median concentration of TCE in the homes measured were generally less than 0.37 ppb. However, maximum values of between 2.05 and 29.77 ppb TCE were detected in 3 homes representative of different ages.

c. Offices

Wallace et al. (1987b) reported on the concentrations of VOCs in 10 public-access buildings. These buildings were monitored for three-day periods during which six consecutive 12-hour air samples were taken. Volatile organic compounds, including TCE were collected on Tenax and analyzed by GC/MS. One of the most significant findings occurred at three new buildings measured before and after occupancy. Mean three-day TCE concentrations ranged from 0.19 to 0.56 ppb before occupancy. However, mean three-day concentrations after occupancy ranged from 1.49 to 7.07 ppb which the authors indicated could have been attributed to use of commercial cleaning products. Trichloroethylene was one of the VOCs which increased in concentration after the building was occupied.

3. Contribution to Total Exposure

Section 39660.5(d) of the Health and Safety Code states "the state board shall identify the relative contribution to total exposure to the contaminant from indoor concentrations, taking into account both ambient and indoor air environments." Based upon available data and assuming

Californians spend 80 to 90 percent of their time indoors (Robinson, 1977), indoor inhalation may be the major route of exposure to TCE. A comparison of matched (simultaneous) indoor and outdoor TCE concentrations was conducted as part of the TEAM 84 study. The results of this comparison (Table IV-6) indicate that median indoor concentrations of TCE are two to five times greater than ambient concentrations. However, this may not always be the case since indoor concentrations of TCE appear to be very dependent upon the use of consumer products containing TCE (see Chapter III., Section E. Potential Sources of Indoor Trichloroethylene).

F. OTHER ROUTES OF TRICHLOROETHYLENE EXPOSURE

Other routes of exposure to TCE include the ingestion of TCE-contaminated water and the consumption of TCE-tainted food. Water appears to present the major source of exposure through ingestion.

1. Water Ingestion

According to the World Health Organization (WHO, 1985) in its review of TCE, the compound is widely distributed in surface water, rain water, and well water. For example, McConnel et al. (1975) reported that rain water contained TCE in the range of a few micrograms per liter.

Cothern et al. (1986) estimated, based on EPA surveys, that of the approximately 23 million persons exposed to levels of TCE ranging from 0.5 to 5.0 μg/L, 76 percent of the people obtained their water from surface water supplies. The higher concentrations in this range, however, are thought to come from groundwater systems.

The California Department of Health Services (CDHS, 1986) measured a number of toxic compounds including TCE in large public water systems in California (January 1984 to December 1985). Approximately 3,000 wells were sampled. Trichloroethylene was found in 188 of the wells with a median

concentration of 3.2 μg/L. A maximum concentration of 538 μg/L was also reported. The CDHS noted that those wells supplying heavily urbanized areas generally had the higher concentrations of TCE. The Department of Health Services developed an action level for TCE of 5 μg/L. This is based on a cancer risk estimate by the National Academy of Science of a 10^{-6} excess risk of cancer due to lifetime exposure to drinking water containing 5 μg/L TCE.

Concentrations of TCE were also measured in tap water during the TEAM 84 studies (U.S. EPA, 1987a). The levels in water measured in Los Angeles and Contra Costa are presented in Table IV-10 as weighted median and upper percentile concentrations. For the February and May sampling times in Los Angeles, the weighted median (and range) of TCE concentrations in water were 0.04 (0.03-0.24) μg/L and 0.03 (0.03-0.56) μg/L, respectively. For the Contra Costa samples, the weighted median (and range) of TCE concentrations was 0.05 (0.03-0.09) μg/L. The median levels of TCE in Los Angeles and Contra Costa were very similar, but the maximum concentrations were higher in Los Angeles.

2. Food

There is limited information on the concentrations of TCE found in food, especially in food purchased in California. There are reports of TCE in food measured in European countries. McConnel et al. (1975) reviewed the levels of TCE in foods in Great Britain and Europe and reported a range of 0.02 μg/kg measured in Yugoslavian wine to 60 μg/kg measured in tea.

Ofstad et al. (1981) reported on TCE concentrations in fish in Norway. The concentrations of TCE ranged from 5 μg/kg in a commercial salmon fillet to approximately 400 μg/kg in the cod liver oil.

Recently, Uhler and Diachenko (1987) reported the concentrations of volatile halocarbons in process water as well as in processed foods. Out of

TABLE IV-10

TCE in Drinking Water:
Median, Maximum and 90th, 95th Percentile Concentrations
(μg/l)

Location	(n)	Percentile Median	90th	95th	Max.
Los Angeles 2/84	117	0.04	0.19	0.19	0.24
Los Angeles 5/84	52	0.03	0.26	0.42	0.56
Contra Costa 6/84	71	0.05	0.08	0.09	0.09

15 processing plants, two had detectable amounts of TCE in the process water. None of the food items measured in the 15 plants had detectable levels of TCE (limit of less than 1 nanogram [ng] per gram of food).

Entz and Diachenko (in press) reported the concentrations of TCE in 50 margarine samples purchased in 1980-1982 and 18 samples purchased in 1984, all from the Washington, D.C. area. Out of the 50 samples, 1 sample had TCE concentrations in the 100-500 ppb range, 9 samples were in the 10-50 ppb range, 7 samples were in the 3-10 ppb range, and 35 samples had undetectable amounts of TCE. Of the 18 samples measured in 1984, three samples were in the 10-50 ppb range, one was in the 3-10 ppb range and 14 samples had undetectable amounts of TCE.

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

A summary of estimated exposure from indoor air as well as from water and food is presented in Tables IV-11 and IV-12. On a daily basis, the most consistent source of exposure to TCE appears to be from indoor air pollution.

1. Indoor Air Pollution

Based on the TEAM studies conducted in California in 1984 and in 1987, the amount of inhaled TCE as determined from personal sampling measurements are estimated for the day and nighttime samples. The amounts inhaled are estimated based on assuming a person breathes 10 cubic meters of the air in a 12-hour period. The range of median inhaled doses is from 2.5 μg/ 12-hour nighttime exposure (Contra Costa, June, 1984) to 22 μg/ 12 hour daytime exposure (Los Angeles, February, 1984). However, a few individuals are exposed to higher amounts of TCE. For example, at the 90th percentile concentrations of TCE (Daytime, Los Angeles; TEAM 84), the individuals inhaled approximately 370 μg per 12-hour period.

TABLE IV-11

Estimated Inhaled Doses of TCE from Air Based on 12 Hour Personal Sampling: Based on Day and Nighttime Median or 90th Percentile Concentrations

Location-Date	Concentrations Used to Estimate 12 hr Inhaled Dose[a]			
	Median Day	Median Night	90th %ile Day	90th %ile Night
	Estimated 12-Hour Inhaled Dose (μg) [b]			
Los Angeles-2/84	22	11	370	69
Los Angeles-5/84	12	3.4	250	25
Contra Costa 6/84	5	2.5	100	21
Los Angeles-2/87	7.1	6.7	34.6	75.8
Los Angeles-7/87	3.1	3.1	34.5	35.6

a. Median and 90th Percentile concentrations based on TEAM 84 (U.S. EPA, 1987b) and TEAM 87 (Pellizzari et al., 1989) studies.
b. Assumption is that 10 cubic meters of air breathed per 12 hr period.

TABLE IV-12

Estimated Ingested Doses of TCE from Drinking Water

Location-Date	Estimated Daily Ingested Dose (μg/day) [a] Based on Median Conc[b]	Based on 90th %ile[a]
Los Angeles-2/84	0.08	0.38
Los Angeles-5/84	0.06	0.52
Contra Costa-6/84	0.06	0.16

a. Assumption is that 2 liters of drinking water are drunk per day.

b. Median and 90th percentile concentrations from TEAM 84 data (Pellizarri, et al. 1987).

FOOD

There are no state or national estimates of ingested dose of TCE based on consumption of food. However, based on the available studies, the following estimated doses were made:

Norwegian Study[a] — Consumption 1 lb salmon with 5 μg/kg TCE = 2.3 μg.

US Study[b] — Consumption of .125 lb margarine with 10-50 μg/kg TCE contamination = 0.6 to 2.8 μg.

a -- Ofstad et al., 1981
b -- Entz and Diachenko, in press

2. Drinking Water

The estimates for ingested dose of TCE from drinking water are from the TEAM 84 study conducted in California during February and May, 1984 (U.S. EPA, 1987a). These are based on the assumption that 2 liters of water are ingested per day. Based on the median measured concentrations of TCE, the estimated daily ingested dose was less than 1 microgram per day (Table IV-12).

3. Food

The amount of TCE from food is extremely difficult to calculate, since there are no surveys in California. From the limited analysis of food in the U.S. and internationally, there appears to be only certain food products contaminated with TCE (for example, certain margarines). The specific amounts of these products consumed were not known, but if a person consumed the amount of product provided as examples in Table IV-12, the total amount of TCE ingested could be several micrograms.

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V.

ATMOSPHERIC PERSISTENCE AND FATE OF TRICHLOROETHYLENE

A. PERSISTENCE OF TRICHLOROETHYLENE

The atmospheric persistence of a pollutant is its tendency to remain in the atmosphere (troposphere) in its original form. Persistence can be measured as the time required to remove the pollutant from the ambient air by chemical or physical means. There are several chemical and physical mechanisms that operate to remove pollutants from the atmosphere. These mechanisms include: photolysis (degradation by solar radiation), photo-oxidation (reaction with reactive species found in polluted atmospheres), adsorption on particles that fall out of the air (dry deposition), wet deposition from interaction with fog or rain (wash-out). Chemical mechanisms appear to be the dominant force responsible for removing TCE from the atmosphere.

Two commonly used measures of persistence are half-life ($t_{1/2}$) and lifetime (τ). Half-life is defined as the time required for the concentration of TCE to fall to one-half of its initial value, whereas lifetime is defined as the time it takes for the pollutant concentration to fall to 1/e of its initial value (e = 2.718).

In analyzing human exposure to TCE, a knowledge of its persistence is important for two reasons: 1) if the removal time is long compared to the time needed to advect (disperse by wind) the pollutant across an air basin, the concentration throughout the basin can be inferred from measurements at specific locations; 2) If attenuation of the pollutant concentration in the plume from a source occurs mostly by dispersion of the plume rather than by

chemical or physical removal (that is, if the pollutant is persistent), routine modeling procedures like Gaussian modeling can estimate the local effect of the source. If removal is fast (that is, if the pollutant is not persistent), much more complicated modeling may be needed to estimate local effects.

1. Physical Removal Mechanisms

We have not found estimates of the rates for the physical removal of TCE from the atmosphere. However, Cupitt (1980), has estimated the lifetime of ethylene dichloride under conditions of removal by rain washout, dry deposition, and adsorption on aerosols (that fall out) as 390 years, 13 years, and 25 years, respectively. The physical properties of a substance that control these removal mechanisms are its polarity (dipole moment), solubility in water, adsorptivity on particles (e.g., on carbon), and its vapor pressure. Since TCE is comparable to ethylene dichloride in all these properties, we have assumed that TCE has similarly long removal times for these removal mechanisms. Therefore, chemical removal mechanisms will be the predominant factors influencing the persistence and fate of TCE.

2. Chemical Removal Mechanisms

The atmospheric lifetime of a substance (a measure of its persistence) is directly related to the rate constant for the chemical removal reactions that take place and the concentration of any reactants involved. For a second order reaction of TCE with atmospheric oxidants (e.g. OH radical, O_3, or NO_3 radical), the following relationship holds:

$$\text{TCE} + \text{B} \xrightarrow{k_2} \text{products}, \qquad \tau = 1/(k_2\,[\text{B}]), \qquad t_{1/2} = \frac{0.693}{k_2\,[\text{B}]}$$

(where k_2 is the 2nd order reaction rate constant, [B] is the concentration of the atmospheric oxidant)

Atmospheric persistence of TCE is affected by three chemical reactions. These are: 1) attack during daylight hours by hydroxyl radicals (OH radicals or $OH^{\cdot}$); 2) attack by ozone (O_3); and 3) attack at night by NO_3 radicals (Finlayson-Pitts and Pitts, 1986).

a. Reaction with OH Radical

Attack by OH radicals appears to be the dominant chemical reaction affecting the persistence of TCE (U.S. EPA, 1985; Pitts, 1984). The atmospheric lifetime of TCE as a consequence of its reaction with OH radical (τ_{OH}) is dependent on the concentration of OH radical in the atmosphere ([OH]) and the OH radical reaction rate constant for TCE (k^{OH}). The τ_{OH} can be determined by the following:

$$\tau_{OH} = 1/\ k^{OH}\ [OH] \quad \text{or} \quad (k^{OH}\ [OH])^{-1}$$

Atkinson (1986) has reviewed the work of several investigators who have studied the kinetics and mechanics of OH radical reactions. From the results of those studies, he has produced a model for calculating the OH radical reaction rate constant (k^{OH}) for the reaction with TCE:

$$k^{OH} = 5.63 \times 10^{-13}\ e^{(427/T)}$$

(where T is the absolute temperature in ^{o}K).

Note the unusual decrease in the reaction rate constant, k^{OH}, as temperature increases. From this Atkinson calculated the k^{OH} at 298 K^{o} to be 2.36×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}.

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The atmospheric concentration of OH radical exhibits seasonal, altitudinal, diurnal and geographical variations (Atkinson, 1986). Also, because temperature decreases with increasing altitude in the troposphere, k^{OH} will vary with altitude. Therefore the lifetime (τ_{OH}) for TCE will vary with the atmospheric conditions under study.

Several investigators have estimated the [OH] in the troposphere. Calvert (1976) estimated [OH] in the morning in Los Angeles at 2.6×10^6 molecules/cm^3. This corresponds to a diurnal average of about 1×10^6 mol./cm^3. For less polluted atmospheres (i.e. lower criteria pollutant levels that are involved in OH radical formation), a commonly used value is 0.5×10^6 molecules/cm^3 (Atkinson, 1986). For the SCAB, the annual mean temperature at the base of the inversion has been estimated as 288 K^o (59^{o}F). With this value, and the range of [OH] (0.5 to 1×10^6mol. /cm^3), the lifetime of TCE was calculated to be 4.6 days (SCAB) to 9.3 days (less polluted areas).

EPA (1985) summarized several authors' estimates of the chemical lifetime of TCE in the air. These authors also recognize attack of TCE by OH radicals to be the dominant removal mechanism for TCE. Their estimates for the lifetime of TCE range from 4 to 15 days.

b. Reactions with Ozone and Nitrate Radicals

The lifetime of TCE as a result of its reaction with ozone or nitrate radical can be determined in the same manner as was done above with OH radical, $\tau = 1/ (k_2 [B])$. Based on an ozone reaction rate constant for TCE of $<3 \times 10^{-20}$ cm^3 molecule^{-1} sec^{-1} (Atkinson and Carter, 1984) and a tropospheric ozone concentration 1×10^{12} molecules/cm^3 (Cupitt, 1980), the lifetime of TCE as a consequence of its reaction with ozone is at least 386 days.

Based on a nitrate radical reaction rate with TCE of 2.9×10^{-16} cm^3 $molecules^{-1}$ sec^{-1} and a 12 hour nighttime nitrate radical concentration of 10 ppt (2.4×10^8 molecule/cm^3), the lifetime of TCE with respect to reaction with nitrate radical is approximately 330 days (Atkinson, 1989). Both nitrate radical and ozone chemical reaction removal processes are too long to compete with the OH radical reaction.

With a lifetime as short as 4.6 days, TCE is only moderately persistent in the air in comparison to other pollutants. However, the ARB staff (Allen, 1987) estimated the time to disperse (advect) pollutants across the South Coast Air Basin to be less than three days in virtually all situations. Therefore, it is reasonable to treat TCE as persistent; that is, Gaussian modeling can estimate near-source concentrations, and air monitoring data can be applied to areas away from the monitoring sites.

3. Other Possible Reactions

Several investigators, who have irradiated TCE in smog chambers, have found much shorter lifetimes for TCE, on the order of a few hours (U.S. EPA, 1982; Dimitriades et al., 1983). This discrepancy between smog chamber observations and calculations based on OH radical attack exists for perchloroethylene (PCE) as well. Dimitriades (1983) argues, with empirical support, that the reactions of PCE in smog chambers is dominated by attack by chlorine atoms and this occurs very quickly. He further argues that chlorine atoms are too scarce in the real atmosphere to be effective in removing PCE. Any chlorine atoms available are effectively scavenged by hydrocarbon pollutants present in the atmosphere. In a personal communication with ARB staff, Atkinson (1987) agreed with this conclusion and stated his belief that the same argument applies to TCE. Therefore, in the absence of chlorine atom attack, attack by the OH radical controls the removal of TCE from the troposphere (U.S. EPA, 1985; Pitts, 1984).

B. FATE OF TRICHLOROETHYLENE

The atmospheric fate of TCE following its reaction with OH radical has been studied by several investigators. The products of these reactions of TCE are illustrated in Figure V-1. The first reaction is the addition of OH radical to the double bond of TCE, resulting in an OH-chloroalkene adduct (structure 1 on Figure V-1). This adduct will quickly add O_2 and then react with NO to produce a hydroxychloroalkoxy radical (2). The hydroxychloroalkoxy radical is expected to decompose to yield phosgene (COCl2) (3). The addition of OH radical at the hydrogen-substituted carbon would be as follows:

$$OH + CCl_2{=}CHCl \longrightarrow CCl_2CHClOH \quad (1)$$

$$CCl_2CHClOH + O_2 \longrightarrow OOCCl_2CHClOH$$

$$OOCCl_2CHClOH + NO \longrightarrow NO_2 + OCCl_2CHClOH \quad (2)$$

$$OCCl_2CHClOH \longrightarrow HOCHCl + COCl_2 \quad (3)$$

Initial addition of OH at the other carbon would lead, through a similar reaction sequence, to the alkoxy radical $HOCCl_2C(O)HCl$ (4) which, upon decomposition, would yield formyl chloride (HCOCl) (5).

$$HOCCl_2\overset{O}{\overset{\|}{C}}HCl \ (4) \longrightarrow HOCCl_2 + HCOCl \quad (5)$$

Both formyl chloride and phosgene have been observed as products in laboratory studies (Pitts et al., 1984). Because yields are less than unity, however, other reactions of the chlorinated alkoxy radicals must occur.

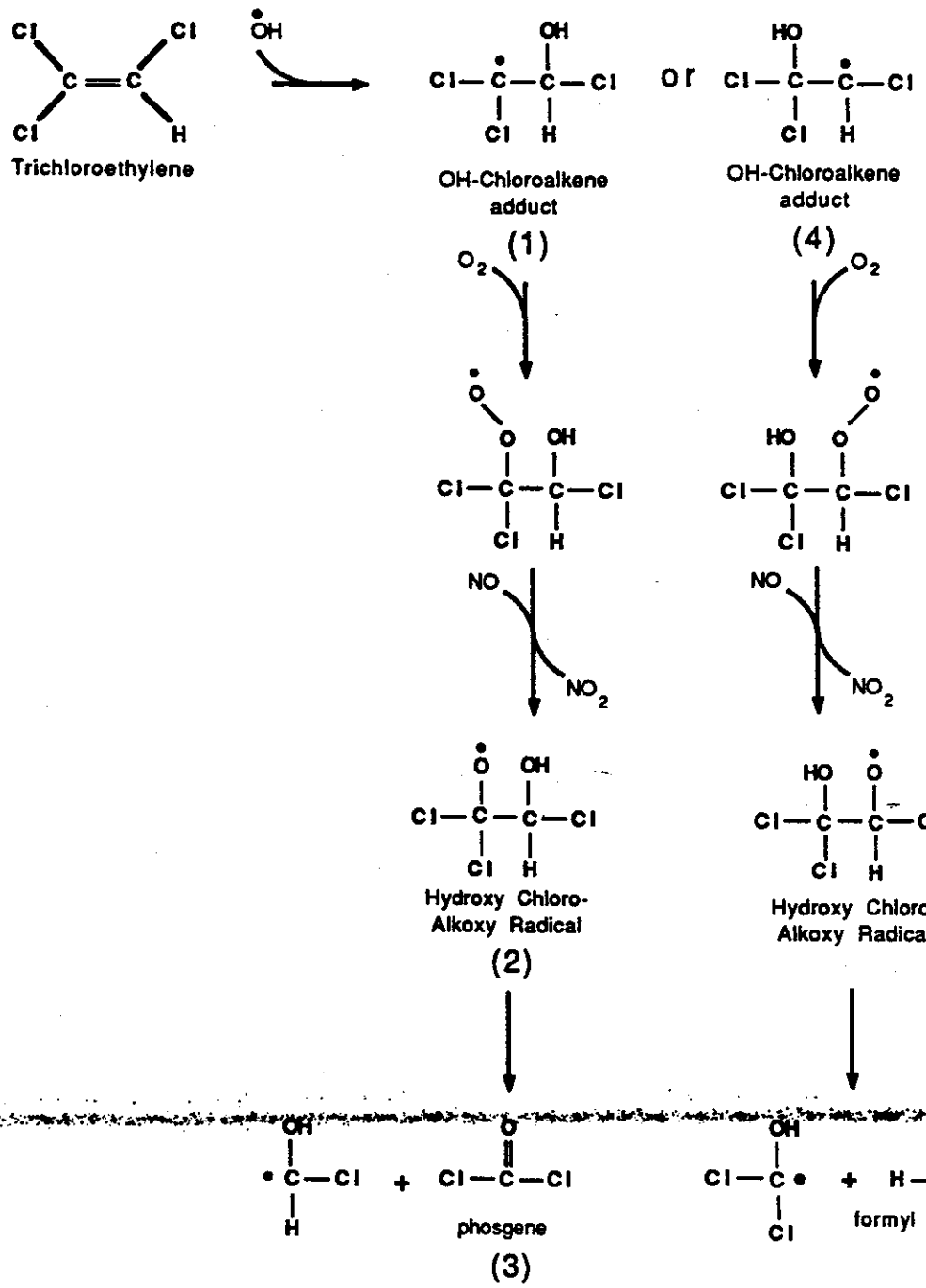
The reaction products of TCE in smog chambers are formyl chloride (CHOCl), phosgene ($COCl_2$), and dichloroacetyl chloride ($Cl_2CHCOCl$)

(Atkinson, 1986; and Finlayson-Pitts and Pitts, 1986). However, the dichloroacetyl chloride is probably the product of chlorine atom attack on TCE (Dimitriades et al., 198 ; U.S. EPA, 1982) and is probably a minor product, if even that, in the atmosphere. This chlorine atom attack is shown on Figure V-2. Where attack by the OH radical dominates (as in the atmosphere) the major products are phosgene and formyl chloride in roughly equal yields of 20 to 25 percent (Pitts, 1984).

Formyl chloride is unstable, being subject to photolysis and OH radical attack. Phosgene is not susceptible to the OH radical and may be fairly persistent. Singh (1978) estimated the lifetime of phosgene to be greater than 10 days. In 1979 and 1980, he measured phosgene in the air in Oakland and Riverside at about 90 ppt during short-term sampling (Singh, 1983). However, Finlayson-Pitts and Pitts (1986) suggest that phosgene photolyzes rapidly.

FIGURE V-1

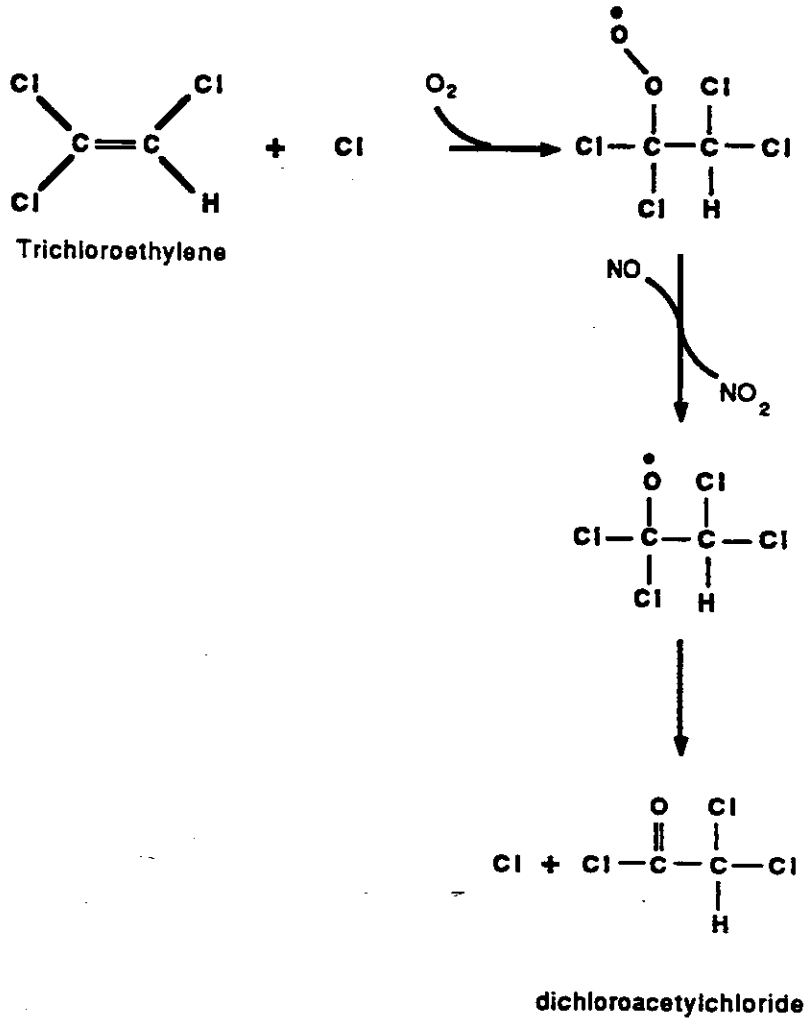
FATE OF TRICHLOROETHYLENE



RDB/11/89

FIGURE V-2

Reaction Products via Chlorine Substitution



RDB/11/89

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APPENDICES

Appendix A

Methods for Estimating Usage and Emissions of Trichloroethylene in California

Appendix A

Methods for Estimating Usage and Emissions of Trichloroethylene in California

Degreasing:

The staff of the ARB estimated the usage of trichloroethylene from degreasers in California as the difference between the total usage in California and the usage by specific source types other than degreasing. No direct estimate of the usage of trichloroethylene in degreasers was available. The Halogenated Solvents Industry Alliance (HSIA) provided the ARB staff with 1) the quantities of trichloroethylene sold in California from U.S. producers, and 2) an estimate of the quantities of trichloroethylene transhipped out of the State. The HSIA reported that 4,880 tons of trichloroethylene were shipped into California in 1983 (Cleary et al, 1986). Of this total, 2,580 tons were shipped to Chevron Chemical Company in Richmond, California, for use as a chemical intermediate in fungicide productions (Cleary et al, 1986). Of the remaining trichloroethylene, HSIA members estimated that ten percent was shipped out of California (Cleary et al, 1986). Thus, the quantity of trichloroethylene estimated to be available for uses other than in fungicide production was:

$$(4{,}880 \text{ tons} - 2{,}580 \text{ tons})(1.00 - 0.10) = 2{,}070 \text{ tons}$$

Subtracting the quantities of trichloroethylene used in other identified uses in 1983 yields an estimate of the quantity available for use in degreasing:

(Qty. avail) - (Qty used in adhesives, paints & coatings, PVC prod., & miscellaneous) = (Qty used in degreasing)

$$(2{,}070 \text{ tons})-(50 \text{ tons})-(60 \text{ tons})-(170 \text{ tons})-(280 \text{ tons}) = 1{,}510 \text{ tons}$$

The ARB staff used an EPA emission factor of 0.94 tons of trichloroethylene evaporated per ton of fresh trichloroethylene used (U.S. EPA, 1985). The weighted emission factor used by the EPA included factors for the different degreaser types, the degree of control on the degreasers, and the amount of trichloroethylene sent to and returned from solvent reclaimers. Emissions of trichloroethylene from degreasing were then estimated as:

$$(1{,}510 \text{ tons})(0.94 \text{ tons emitted/ton fresh solvent used}) = 1{,}420 \text{ tons}$$

ARB staff rounded this estimate to 1,400 tons of trichloroethylene emissions to account for the uncertainties involved in the estimation procedure.

Other Uses:

The EPA (1985) reported U.S. usage of trichloroethylene for adhesives, paints and coatings, and miscellaneous. Population fractions were used to estimate California usage from U.S. usage for these categories. California's population was 11 percent of the U.S. population in 1980 (U.S. Department of Commerce, Bureau of the Census, 1982). Thus, California usage was estimated as 11 percent of U.S. usage for these categories. All of the trichloroethylene used in adhesives, paints, and coatings was assumed to evaporate (U.S. EPA, 1985). Miscellaneous emissions were estimated as less than or equal to usage.

The usage and emissions estimate for the use of trichloroethylene in PVC production is based on information supplied by Keysor-Century Corporation in Saugus, California, to an EPA contractor (Pandullo, 1986). The Keysor facility is the only known facility using trichloroethylene in PVC production in California.

Distribution:

An estimated 2,300 tons of trichloroethylene were sold through distribution facilities in California in 1983. The basis of this estimate is described in the body of the report. EPA data on national distribution were used in estimating the California emissions (U.S. EPA, 1985). Emissions were calculated as:

$$(2{,}300 \text{ TPY distributed in CA}) \left(\frac{43 \text{ TPY emitted in U.S.}}{72{,}400 \text{ TPY distributed in U.S.}}\right) = 1 \text{ TPY}$$

Solvent Reclamation:

An estimated 100 tons of trichloroethylene were sent for recycling in California in 1985. The quantity of trichloroethylene sent for recycling in California was estimated by using: 1) the quantity of halogenated solvent reported on hazardous waste manifests, and 2) the estimated percent of trichloroethylene contained in the halogenated solvents.

The California Department of Health Services (1986) reported that 9,685 tons of halogenated solvents were sent for solvent reclamation in California in 1985. Four solvent reclamation facilities in California were surveyed on the percent of trichloroethylene in the halogenated solvents received by the facilities (Schneider, 1987; Nagpal, 1987; Gustufson 1987; O'Morrow, 1987). These four facilities handle 64 percent of the solvents sent for reclamation in California (Kozumplit, 1986). A weighted average was calculated using 1) the percent of trichloroethylene in the halogenated solvents received and 2) the percent of solvents handled by the facility. For these facilities, a weighted average of 1.0 percent of the halogenated solvents received are trichloroethylene. Based on this information, it is assumed that 1.0 percent of all halogenated solvents sent for solvent reclamation in California are trichloroethylene. Thus, the quantity of trichloroethylene sent for solvent reclamation was estimated as:

$$(9{,}685 \text{ TPY}) (.01) = 100 \text{ TPY}.$$

In a similar manner, a weighted average was calculated of the emission losses of trichloroethylene during handling and processing by the solvent reclaimers. A weighted average of 0.6 percent of emissions losses was calculated based on information from two facilities handling 35 percent of the solvents sent for reclamation in California (Schneider, 1987; Nagpal, 1987; Kozumplit, 1986). Thus, trichloroethylene emissions are estimated as:

$$(100 \text{ TPY}) (.006) = 0.6 \text{ TPY}.$$

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APPENDIX B

Standard Methods of Analysis for Trichloroethylene

METHOD NO. ADDL002

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF VOLATILE ORGANICS IN AMBIENT AIR USING TENAX TRAP PRECONCENTRATION GAS CHROMATOGRAPHY AND TANDEM PHOTOIONIZATION/ELECTRON CAPTURE DETECTORS

1.0 SCOPE

This document describes a procedure for the determination of volatile halogenated hydrocarbons and aromatics having a boiling point of less than 120°C. This procedure is based on documents received from the ARB Haagen-Smit Laboratory, El Monte, as well as EPA Method TO1.

2.0 SUMMARY OF PROCEDURE

Ambient air is continuously sampled and collected in a Tedlar bag over a 24 hour period and immediately sent to the laboratory for analysis. A sample from the bag is drawn through a sampling valve attached to a Tekmar LSC-2 Tenax Sample Concentrator (see Figure I) with a vacuum pump at 50 cc/min for four minutes (total sample volume: 200 cc). The organic constituents are trapped on Tenax and when the collection is complete, the Tenax is purged with 40 cc of helium to remove any trapped moisture. The sample is then thermally desorbed onto the head of the GC column. The GC column is temperature programmed and component peaks

eluting from the column are sequentially detected and quantified, first by a photoionization detector (PID) and then by an electron capture detector (ECD). The components are identified based on retention times. Positive identification or confirmation requires the use of an appropriately configured GC/MS.

3.0 INTERFERENCES/LIMITATIONS

a. Components having similar GC retention times will interfere, causing misidentification and/or faulty quantitation.

b. Because of the very low sample concentrations, extreme care must be taken to insure that the sample is not degraded or contaminated by the Tedlar sampling bag, sampling apparatus, or delayed delivery to the laboratory. Exposure of the Tedlar sampling bag to temperatures greater than 25°C should be minimized.

c. Only components of the sample which can be detected by PID/ECD detectors will be quantified.

4.0 APPARATUS

a. Varian Model 6000 Gas Chromatograph/PID/ECD system equipped with a Varian Vista 402 dual channel data system.

b. Tekmar LSC-2 Sample Concentrator equipped with Tenax trap and sampling valves as shown in Figure 1.

c. Matheson Model 8240 Mass Flow Controller accurately calibrated in the 5-100 cc/min range.

d. Laboratory timer, accurate to within 0.1 minutes.

e. Gas tight microliter syringe, 50 ul.

f. GC column - 10' x 2 mm i.d. glass column packed with 1 percent SP-1000 on Carbopack B, 60/80 mesh.

5.0 REAGENTS

a. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 1)

Compound	Concentration (ppb)
Chloroform	107
Carbon tetrachloride	105
Perchloroethene	106
Vinyl chloride	104
Benzene	107

b. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 2)

Compound	Concentration (ppb)
1,2-Dichloroethane	101
1,1,1-Trichloroethane	98
Trichloroethene	100
1,2-Dibromoethane	102

c. Stock Gas Standard - Scott-Marrin Blend (assayed against primary cylinders)

Compound	Concentration (ppb)
Dichloromethane	4272
Chloroform	528
1,2-Dichloroethane	3104
1,1,1-Trichloroethane	424
Carbon tetrachloride	46
Trichloroethene	336
1,2-Dibromoethane	5
Perchloroethene	43
Vinyl chloride	4736
Benzene	1888

d. Control Gas Standard - Scott-Marrin Blend (assayed against primary cylinder)

Compound	Concentration (ppb)
Dichloromethane	6
Chloroform	0.2
1,2-Dichloroethane	0.2
1,1,1-Trichloroethane	3.6
Carbon tetrachloride	0.3
Trichloroethene	1.8
1,2-Dibromoethane	2.5
Perchloroethene	1.2
Vinyl chloride	3.3
Benzene	4.8

e. Surrogate Gas Standard (Scott-Marrin Blend)

Compound	Concentration (ppm)
Bromochloromethane	10
1,3-Bromochloropropane	33

6.0 PROCEDURES

a. Sample Trapping

1. The preconcentration system is shown in Figure 1.

2. The high concentration inlet is used for high concentration calibration standards and for other samples with concentrations higher than ambient levels. The sample is introduced through the high concentration inlet and 6 port valve into an appropriate size loop of known volume. The sample then passes through a 10 port valve, mass flow meter, and vacuum pump. Before an analysis, the system is leak checked by blocking the sample inlet port and observing that the mass flow meter reading drops to zero. The high concentration inlet then is connected to a Tedlar sample bag valve and the gas bag valve is opened. The loop is then flushed with sample gas for three minutes. After three minutes of flushing, the 6 port valve is reset so that the sample contained in the loop is carried into the trap by the helium purge gas. This continues for three minutes to ensure that all of the contents of the loop are trapped.

3. Ambient samples are introduced from Tedlar bags as described above, except that the sample loop is bypassed and the sample goes directly to the 10 port valve. After flushing the system with sample for three minutes, the 10 port valve is reset so that 200 cc's of sample is trapped (50 cc/min. for four minutes). After sample trapping is complete, the Tenax trap is flushed with 40 cc of helium to remove water vapor and any nonadsorbed reactive gases.

4. In both ambient and high concentration cases, after the sample has been trapped, the Tekmar LSC-2 heats the Tenax trap to 180°C while the trap is swept with the G.C.'s internal carrier gas for four minutes. The contents of the trap are thus desorbed and collected on the head of the G.C. column. The trap is baked out after the end of the desorption cycle. In the bakeout cycle, the trap is flushed with helium purge gas for eight minutes while being held at 225°C in order to prepare the trap for the next cycle. After bakeout the trap is isolated from the system and ready for the next sample.

b. Analysis

1. The concentrated sample is separated under the chromatographic condition detailed below. The resulting chromatogram (see Figure II) is then integrated and quantified by reference to calibration standard gases.

2. Instrument Conditions:

GC: Column: 10' x 2 mm i.c. glass column, packed with 1 percent SP-1000 on Carbopack B 60/80 mesh

Temperatures: Injection: 200°C

Detector: 350°C

Oven: 45°C, hold for four minutes, 5°C/min ramp, to 210°C, hold for eight minutes

Flow Rates: Carrier: He, 20 cc/min

ECD make up: N_2, 40 cc/min

Detectors: ECD: Range X 10, Attenuation X 32

PID: Range X 1, Attenuation X 32, 10.2 ev lamp

Conc: Tekmar LSC-2: Purge: 4 minutes

Desorb: 4 minutes at 180°C

Bake: 8 minutes at 225°C

3. All blanks, standards, control samples, and ambient samples are spiked with surrogate compounds by injecting 50 microliters of the surrogate gas standard (5.e.) during sample trapping. The surrogate compounds, chosen such that they simulate the characteristics of the analytes of interest and are unlikely to occur in the environment, are added to insure that systematic errors or equipment failures will be noted and corrected promptly.

4. The first step in a calibration is to analyze a system blank. This is done by trapping and analyzing a 200 cc sample of auxiliary carrier gas. The system blank must be free of interfering peaks. A system blank must also be run after a high concentration sample is analyzed in order to detect any carry-over within the system.

5. A calibration is performed using a 1.25 cc loop of stock standard gas (5.c.). Two hundred cubic centimeters of helium gas is passed through the loop to carry the standard onto the trap. The calibration analysis is made as a normal analysis. The calculated concentration value for each component should be inspected to insure consistency with previous analyses. The stored chromatographic information may then be used to recalculate the response factors for the subsequent analyses. The G.C. data system will not accept updated response factors which are in excess of plus or minus 15 percent of historic data.

6. Following calibration, 200 cc of the control sample (5.d.) is concentrated on the trap and analyzed. The control sample data are plotted on control charts of the normal Shewhart type. Upper and lower warning limits are plus or minus two times the standard deviation. Any analysis which falls outside the upper and lower warning limits is repeated and the laboratory quality control officer is advised. Upper and lower control limits are plus or minus three times the standard deviation. If any analysis falls outside the upper or lower control limit, the method is discontinued until the out of control situation is remedied. The laboratory quality control officer is advised and provided with written documentation of the out of control condition and how it was remedied. All data generated prior to the out of control situation must be reviewed for possible decertification by laboratory management.

7. Multipoint calibrations are conducted monthly. Each multipoint calibration includes a trap blank and three standard concentration levels to bracket the concentration ranges expected in ambient air. If subsequent data indicate that the resulting least squares analyses are consistently acceptable, less frequent multipoint calibrations may be made.

7.0 PERFORMANCE

a. All ambient field samples are analyzed in duplicate. The relative error between analyses must be less than 20 percent. Duplicate analyses having greater than 20 percent relative error must be decertified.

b. The percent recovery of the surrogate is recorded in the instrument laboratory workbook for each analysis. If this value is outside the 80% to 120% range, the sample analysis must be repeated.

8.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

The method sensitivity, precision and accuracy are outlined in Table I. These data were produced with gaseous calibration standards, and using carrier gas as the sample matrix. The relative accuracy of the method, with the exception of dichloromethane, is based on reference to the Research Triangle Institute Certified Gas Standards (NBS traceable). Authoritative reference calibration standards for dichloromethane are under development at NBS but are not yet available. The concentration value of the present standard was assigned by the commercial manufacturer and found to be in good agreement with diluted pure dichloromethane prepared in our laboratory. The absolute accuracy of the method has not been determined by interlaboratory testing.

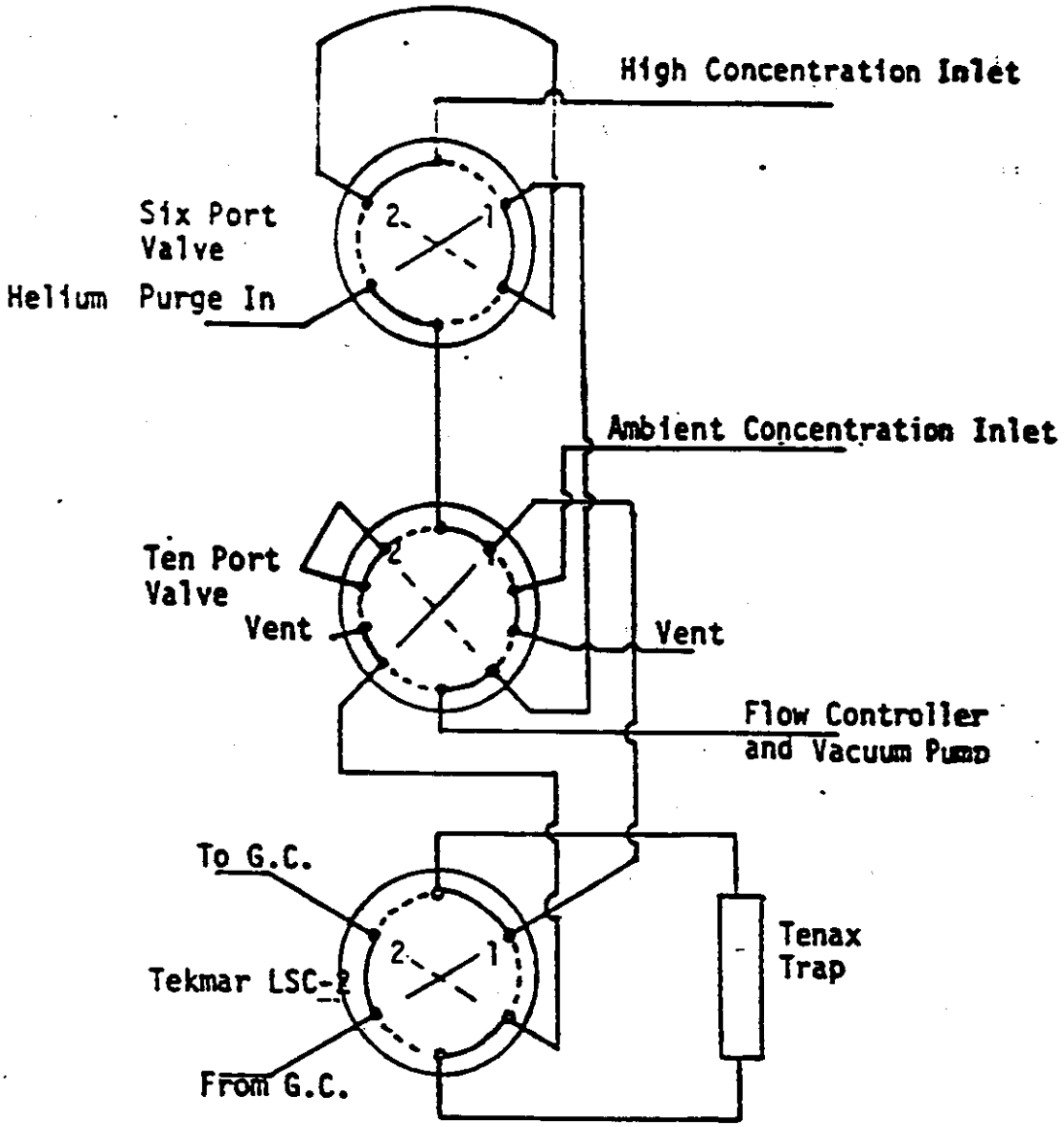
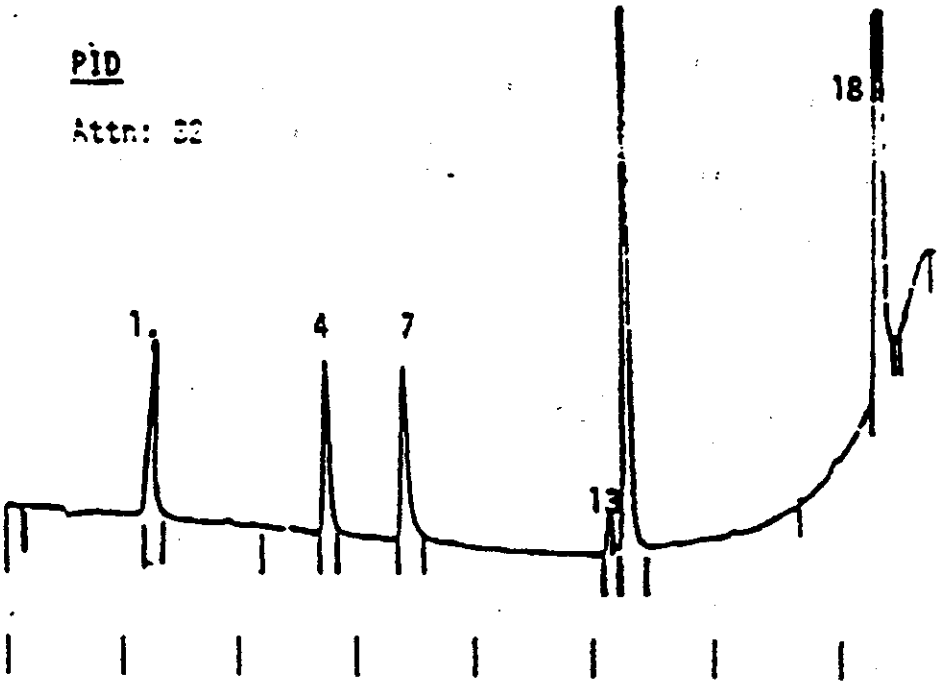
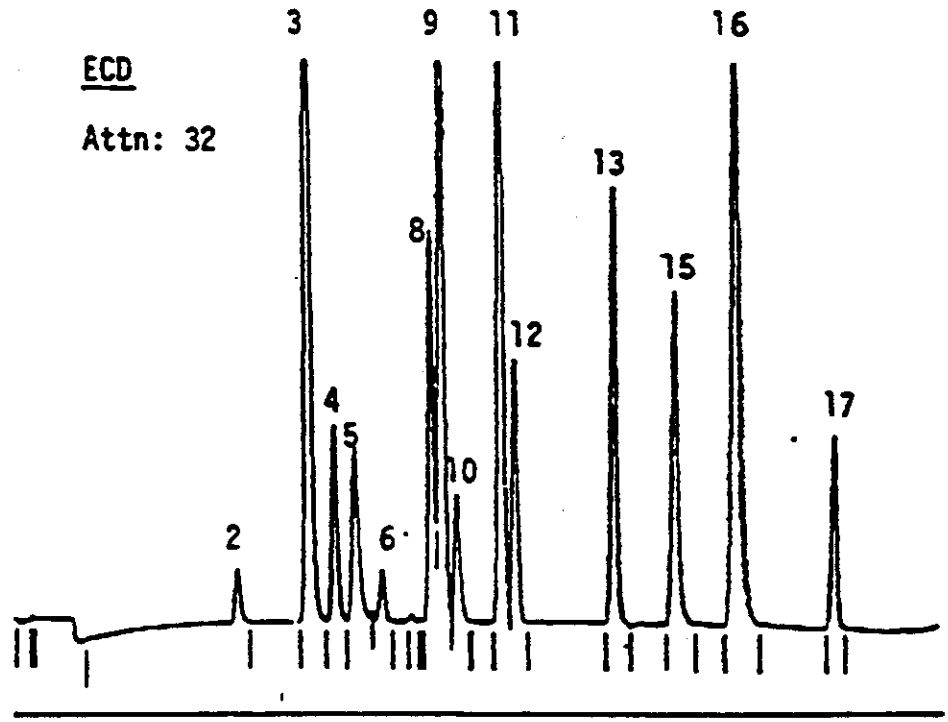


Figure 1. Schematic of concentrator system. Sampling Conditions are: 200 cc volume, purge at 40cc/min, 1 min., desorb at 180 C for 4 min., bake for 8 min. at 225 C.

SYSTEM GUIDE

Operational Step	Valve Position			
	6-Port	10-Port	LSC-2	Purge Gas
Loop Fill	1	1	1	Off
Loop Trap	2	1	1	On
Ambient Trap	1	2	1	Off
Trap Desorb	1	1	2	Off
Trap Bake Out	1	1	1	On





1. Vinyl Chloride
2. Dichloromethane
3. Trichlorofluoromethane
4. 1,1-Dichloroethylene
5. Bromochloromethane
6. 1,1-Dichloroethane
7. t-1,2-Dichloroethylene
8. Chloroform
9. Freon 113
10. 1,2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Carbon Tetrachloride
13. Trichloroethylene
14. Benzene
15. 1,2-Dibromoethane
16. Bromochloropropane
17. Tetrachloroethylene
18. Toluene

Table I

Method Sensitivity and Precision

Compound	Correlation Coefficient	Slope	R.S.D* (Percent)	Detector	LOD ppbv
Vinyl Chloride	0.997	0.946	16	PID	0.8
Dichloromethane	0.999	0.975	5	ECD	0.6
1,1-Dichloroethylene	0.991	0.966	6	ECD	0.05
Chloroform	0.999	0.901	3	ECD	0.02
1,2-Dichloroethane	0.999	1.054	7	ECD	0.1
1,1,1-Trichloroethane	0.999	0.989	9	ECD	0.01
Carbon Tetrachloride	0.999	0.980	6	ECD	0.005
Trichloroethylene	0.999	0.992	6	ECD	0.02
Benzene	0.998	0.950	10	PID	0.5
1,2-Dibromoethane	0.974	1.067	9	ECD	0.005
Tetrachloroethylene	0.994	1.080	10	ECD	0.01

* R.S.D. - Relative Standard Deviation at 5 x LOD, n = 5

APPENDIX C

DESCRIPTION OF GLEIT'S METHOD

APPENDIX C

DESCRIPTION OF GLEIT'S METHOD

Gleit's method accounts for the concentrations below the LOD by setting them equal to the 'below-LOD mean" μ_{BLOD}, the mean of the portion of the normal distribution below the LOD. Setting the unknown concentrations to their average value seems intuitively reasonable, and the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations.

The below-LOD mean of a normal distribution of a variable with a limit of detection L is given, in terms of L and the mean μ and the standard deviation σ of the distribution, by equation 1:

$$\mu_{BLOD} = \mu - \sigma^{*}[f((L-\mu)/\sigma)/F((L-\mu)/\sigma)] \qquad (1)$$

In equation (1), f and F are, respectively, the probability density function and cumulative distribution function of the standard normal distribution. The "Estimated Concentrations for Samples Below the LOD" reported in Table II-2 are the below-LOD means of the assumed lognormal distributions of the concentrations. These below-LOD means are computed from equation (2) in terms of parameters of the associated normal distribution: the LOD L, the mean concentration from Table II-2, and the estimated standard deviation (which is not tabulated).

$$\exp(\mu+0.5^{*}\sigma^{2})^{*}F((L-\mu-\sigma^{2})/\sigma)/F(L-\mu/\sigma) \qquad (2)$$

We now describe how Gleit's method estimates the mean and variance of the assumed normal distribution. The mean and variance cannot be estimated by merely substituting into standard formulas, if below-LOD concentrations are to be set to the below-LOD mean. On the one hand, the mean and variance must be known in order to calculate the below-LOD mean from (1); on the other hand, the below-LOD mean must be known if it is to be used in the calculation of the mean and variance. Statistical theory, by

asserting that a "best-fitting" mean and variance for the distribution exist, provides a way out of this dilemma. Gleit uses a simple iterative procedure to compute these best-fitting parameters. Since his procedure can be simply described in words, a written description is given, supplemented where necessary by equations written in a notation more convenient than Gleit's.

Starting with initial guesses $\mu(0)$ and $\sigma^2(0)$ for the mean and variance, the procedure repeatedly generates new estimates of the mean and variance by the two-step computation described below until successive estimates of the mean and variance converge sufficiently (The K-th pair of estimates are denoted by $\mu(K)$ and $\sigma^2(K)$.). The two steps are:

(a) the K+1-st below-LOD mean $\mu_{BLOD}(K+1)$ is computed by substituting $\mu(K)$ and $\sigma(K)$ (the square root of $\sigma^2(K)$) into equation (1).

(b) The K+1-st estimate of the mean, $\mu(K+1)$, is computed in the usual way with $\mu_{BLOD}(K+1)$ substituted for the sample values below the LOD. The K+1-st estimate of the variance, $\sigma^2(K+1)$, is also computed in the usual way, with an analogous substitution for sample values below the LOD: the squared deviations from the mean of concentrations below the LOD are set equal to the average squared deviation from the mean of the below-LOD portion of the distribution.

Let the N sample items be X(1),....,X(N), and let p be the number of sample items below the LOD. $\mu(K+1)$ is computed by:

$$\mu(K+1) = (1/N)\ \Sigma\ Y(J), \text{ where } Y(J)=X(J) \text{ if } X(J)\ R\ L$$
$$\text{and } Y(J)= \mu_{BLOD}(K+1) \text{ otherwise}$$

$\sigma^2(K+1)$ is computed by:

$$\sigma^2(K+1)=(1/N)\ \Sigma\ D^2(J), \text{ where } D^2(J)=(X(J) - \mu(K+1))^2$$
$$\text{if } X(J)\ \ L, \text{ and } D^2(J)= \sigma^2_{BLOD}(K+1) \text{ otherwise.}$$

The quantitiy $^2\sigma_{BLOD}(K+1)$, the average squared deviation of the below-LOD portion of the distribution, is computed from the following equation:

$$^2\sigma_{BLOD}(K+1) = \sigma^2(K)^*[1-Z(K)^*(f(Z(K))/F(Z(K)))],$$
$$\text{where } Z(K)=((L-\mu(K))/\sigma(K)).$$

Gleit's method nearly always converges in a few steps unless there are only a few distinct values above the detection limit, in which case it may converge very slowly. Gleit's method and closely related methods appear to be the best available estimators of the mean when the sample includes values below the LOD, as is demonstrated by the simulations reported in Gleit's paper.

APPENDIX D

Descriptions of Statistical Tests for Interpretating Exposure Data

Kruskal-Wallis Test, Shapiro-Wilk Test, and Bootstrap Confidence Intervals

APPENDIX D

KRUSKAL-WALLIS TEST

The Kruskal-Wallis Test is a rank statistic defined by the equation:

$$T = 12/(N(N+1)) \quad (R_i - 1/2n_i(N+1))^2/n_i$$

Where N is the total number of data to be ranked, n_i is the number of data in any one group to be ranked and R_i is the sum of the ranks in a group.

The exact distribution of T is found under the assumption that all observations were obtained from the same or identical population. The method is that of randomization which was used also in finding the distribution of the Mann-Witney Test. Under the above assumptions, each arrangement of the ranks 1 to N into groups is equally likely and occur with equal probability which is the reciprocal of the number of ways the N ranks maybe divided into groups being tested. The value of T is computed for each arrangement. The probabilities associated with equal values of T are then added to give the probability distribution of T.

SHAPIRO-WILK TEST

The Shapiro-Wilk test is an analysis of variance test for normality. The test statistic is obtained by dividing the square of an appropriate linear combination of the sample order statistics by the symmetric estimate of variance. This ratio is both scale and origin invariant and hence the statistic is appropriate for a test of the composite hypothesis of normality.

BOOTSTRAP CONFIDENCE INTERVALS

The Bootstrap Methodology is a way of generating confidence bounds for the sample mean from the empirical distribution using minimal assumptions. The primary assumption made in the Bootstrap is that the sample is representative of the underlying distribution. The fundamental theory behind the Bootstrap is beyond the scope of this memo, so the interested reader may pursue the topic by investigating the following references:

B. Efron, The Two Sample Problem with Censored Data, PROCEEDINGS OF THE FIFTH BERKELEY SYMPOSIUM ON MATHEMATICAL STATISTICS AND PROBABILITY(1967), no. 4, pp. 831-853.

--------, Bootstrap Methods: Another look at the Jackknife,ANNUALS OF STATISTICS,7(1979),NO.1.

--------, Controversies in the Foundations of Statistics, AMERICAN MATHEMATICAL MONTHLY 85(1979),no.4, pp.231-246.