State of California
AIR RESOURCES BOARD

Staff Report: Initial Statement of Reasons for Proposed Rulemaking

Public Hearing to Consider the Adoption of a Regulatory Amendment Identifying Ethylene Dichloride as a Toxic Air Contaminant

Agenda Item No.: 85- -
Scheduled for Consideration: September 19, 1985
Release Date: August 5, 1985

OVERVIEW AND RECOMMENDATION

I. INTRODUCTION

The Air Resources Board ("ARB" or "Board") identifies toxic air contaminants and develops regulations for the control of their emissions according to the requirements of state law. A toxic air contaminant (TAC) is an air pollutant that the Board or the Department of Food and Agriculture* finds "may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."** This report recommends that the Board find ethylene dichloride ("EDC," $ClH_2C - CH_2Cl$) to be a toxic air contaminant.

Section II of this Overview to the report presents the regulatory background and reviews the procedures by which the Board considers substances for the TAC designation. The Overview also summarizes the technical and toxicological information that supports the staff's recommendation. Section IIIA is a summary of Part A, which presents data on the uses of EDC, its emissions, and the public's exposure to EDC via the ambient air. Section IIIB summarizes the Department of Health Services' (DHS) analysis in Part B of the health effects of EDC. Section IV of this Overview discusses potential environmental effects of the recommended action, and Section V contains the staff's recommendation to the Board.

II. REGULATORY BACKGROUND AND PROCEDURES

Division 26, Chapter 3.5 of the Health and Safety Code* and Food and Agriculture Section 14021 et seq. set forth the procedure for identifying and

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* See Section II.

** Health and Safety Code Section 39655.

controlling toxic air contaminants in California. (These provisions were enacted in September 1983 as Assembly Bill 1807, Stats. 1983, ch. 1047; see Part C to this report.) The Department of Food and Agriculture is responsible for identifying and controlling TACs in their pesticial uses. The ARB has authority over TACs in all their other uses.

HSC Section 39650 sets forth the Legislature's findings about substances which may be TACs. The Legislature has declared:

> "That public health, safety, and welfare may be endangered by the emission into the ambient air of substances which are determined to be carcinogenic, teratogenic, mutagenic, or otherwise toxic or injurious to humans."

The findings also include directives on the consideration of scientific evidence and the basis for regulatory action. With respect to the control of TACs, the Legislature has declared:

> "That it is the public policy of this state that emissions of toxic air contaminants should be controlled to levels which prevent harm to the public health."

The Legislature has further declared that, "while absolute and undisputed scientific evidence may not be available to determine the exact nature and extent of risk from toxic air contaminants, it is necessary to take action to protect public health."

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*HSC; all statutory references are to the Health and Safety Code, except as otherwise stated.

In the evaluation of substances, the Legislature has declared that the best available scientific evidence, gathered from both public agencies and private sources including industry, should be used. The Legislature has also determined that this information should be reviewed by a scientific review panel and by the public.

The Board's determination of whether or not a substance is a toxic air contaminant includes several steps specified by HSC. First, we request the DHS to evaluate the health effects of a substance (Section 39660). The evaluation includes a comprehensive review of all available scientific data. Upon receipt of a report on health effects from DHS and in consideration of their recommendations, we prepare and submit a report to the Scientific Review Panel (SRP) for its review (Section 39661). The report consists of the DHS report (Part B), material prepared by the ARB staff on the use, emissions and ambient concentrations of the substance (Part A), and various supporting documents in Part C. It serves as the basis for future regulatory action by the Board. The report is also made available to the public, which may submit comments on the report to the SRP.

After receiving the SRP's written findings on the report, the Board issues a public hearing notice and a proposed regulation stating whether or not the substance is a toxic air contaminant. If, after a public hearing and other procedures to comply with Government Code Section 11340 et seq., the Board determines that a substance is a toxic air contaminant, its findings must be set forth in a regulation (Section 39662). The HSC also sets forth procedures for developing and adopting control measures for substances identified as TACs (Sections 39665-39667).

III. EVALUATION OF ETHYLENE DICHLORIDE

The ARB and the DHS prioritize candidate substances for evaluation and regulation as toxic air contaminants pursuant to HSC Section 39660(f). That section states that the selection of a substance for consideration as a TAC is to be based on the risk to the public posed by the substance, the amount or potential amount of emissions from use of the substance, its manner of usage in California, its atmospheric persistence, and its concentration in the ambient air.

Under these guidelines, we selected EDC for the Board's consideration as a TAC because it is a known animal carcinogen, it is ubiquitously emitted from the evaporation and burning of leaded gasoline and other activities, it is persistent in the atmosphere, and its presence in the atmosphere has been documented.

A. EMISSIONS, PERSISTENCE AND AMBIENT CONCENTRATIONS OF EDC.

Data in Part A are summarized in Table I.

In 1983, the use of gasoline and pesticides accounted for most EDC emissions in California. However, actions taken by the U.S. Environmental Protection Agency have largely eliminated EDC's use (and emissions) as a pesticide and, by 1986, should reduce gasoline-related emissions of EDC by about 88 percent. By then, solvents and minor industrial uses of EDC will be the dominant sources of emission. We expect these uses to increase.

EDC is a persistent pollutant that has been documented in the air of the South Coast Air Basin. No point source is known to cause local concentrations greatly exceeding the range of average ambient concentrations in the table.

The draft of Part A was released for public review and comment. Comments and our responses are presented in Part C.

TABLE I

Summary of Data in Part A

1983 Emissions, tons	Statewide	South Coast Air Basin
Stationary sources		
Solvents and minor industrial sources	99	13
Gasoline evaporation	4.7	2.3
Pesticides	65	14
Solid fuel production	1.1	0
Landfills	Unknown	(100[a])
Vehicular (from gasoline)	61	26
Atmospheric Half-Life, days		
(OH· attack, polluted atmosphere)	42	42
Ambient Concentration, ppt[b]		
Average (1983)	Unknown	between 19 & 110
Highest 24-hour[c]	Unknown	390

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[a] less reliable than other entries; emissions from this source may have decreased considerably since 1983

[b] parts per trillion; away from the immediate locales of major sources; data from four stations

[c] January 1983 to May 1984.

B. HEALTH EFFECTS AND RISK

In response to the ARB staff's request and according to HSC Section 39660, the Department of Health Services (DHS) evaluated the health effects of EDC and the risks from exposure to EDC. To ensure satisfaction of the requirement in HSC for the consideration of all pertinent information, we provided DHS with a bibliography of all literature concerning the health effects of EDC. The bibliography (included in Part C) was obtained from the MEDLARS II and DIALOG data bases. Also, we sent a letter (included in Part C) to all known users of EDC and other interested parties to request additional information. The information so obtained was forwarded to DHS.

The DHS' draft report (Part B) was released to the public for comment. The comments received are included in Part C. The revised Part B is presented to the Scientific Review Panel after consideration of those comments.

In meeting the requirements in Section 39660 for DHS' evaluation, the DHS addresses these issues in Part B: 1) Is EDC a carcinogen for animals? 2) Should EDC be considered a carcinogen in humans? 3) May health problems other than cancer occur from exposure to ambient concentrations? 4) Is there a "threshold" exposure below which EDC will not cause cancer? 5) What is the range of added risk of cancer during a lifetime of exposure to typical ambient concentrations of EDC? In response to these issues, the DHS concludes (in paraphrase of the conclusions in Part B) that:

A. EDC at documented ambient concentrations should not have health effects other than cancer.

B. EDC is a carcinogen in animals when ingested and may be carcinogenic when inhaled.

C. EDC should be regarded as a potential carcinogen in people.

D. No threshold of carcinogenic response should be assumed for EDC.

E. The best estimate of the range of added lifetime risk of cancer due to exposure to EDC in the air is 53 to 88 cases per million people per part per billion of lifetime average concentration. The actual risks are not likely to be above this range.

These conclusions were drawn from the following observations:

- Many non-carcinogenic toxic effects of EDC are documented for animals and people but only at exposures several orders of magnitude greater than those corresponding to known concentrations in the ambient air.
- EDC is absorbed and eliminated rapidly by rats after oral administration or inhalation.
- For selected tissues, DNA binding after administering ^{14}C-EDC is greater for oral exposure than for inhalation.
- Reproductive effects of EDC on rats have been reported at doses several orders of magnitude above those corresponding to exposure via the ambient air.
- Genotoxic activity by EDC has been reported *in vivo* for several organisms and *in vitro* for others, including human lymphocytes.
- Two major bioassays have been conducted for the carcinogencity of EDC. The NCI biossay of 1978 (gavage) showed in rats statistically significant increases in carcinomas of the forestomach, hemangiosarcomas of the circulatory system, fibromas of subcutaneous tissue, and adenocarcinomas of the mammary gland. In mice, the NCI bioassay showed statistically

significant increases in hepatocellular carcinomas and pulmonary adenomas in males and pulmonary adenomas, mammary carcinomas, and endometrial tumors in females. The Maltoni bioassay of 1980 (inhalation) did not show carcinogenicity in rats or mice.

- The doses in the Maltoni study were not large enough to induce tumors at a statistically significant rate if the carcinogenic potency of EDC is estimated from the NCI results.
- No evidence demonstrates a carcinogenic threshold for EDC.
- DHS applied five risk models to the NCI's results for male rats hemangiocarcinomas and male mouse hepatocelluar carcinomas. The results for a lifetime human exposure of 100 ppt are, in cases per million people:

	Rats		Mice	
	MLE*	95 UCL**	MLE*	95 UCL**
One-hit	3.8	6.9	2.8	38
Multistage	4.3	6.3	1.6	4.6
Time-corrected multistage	5.3	8.8	2.9	7.4
Probit	8.3	330	0.0	1.1
Gamma multi-hit	18,000	22,000	4.6	94

* maximum likelihood estimate
** 95 percent upper confidence limit

- DHS believes that the time-corrected multistage model has the best biological basis for extrapolating bioassay data to ambient concentrations.

To estimate the range of risks associated with the measured ambient concentrations in the South Coast Air Basin, we applied the 95 percent upper confidence limit recommended by the DHS, 88 cases per million people per ppb, to the upper bound of the mean annual concentration, .100 ppb; and we applied DHS' maximum likelihood risk estimate, 53 cases per million per ppb, to the lower bound for the mean, .019 ppb. The resulting range of risk is 1 to 10 cases of cancer per million people in 70 years, or about 10 to 100 total cases in 70 years.

IV ENVIRONMENTAL EFFECTS

The identification of EDC as a TAC will not in itself have any environmental effects. If the Board lists EDC as a TAC, it and the air pollution control districts will evaluate the need for, and appropriate degree of, controls for emission sources. After this evaluation, the Board and the districts may adopt emission control measures. Hence, the identification of EDC as a TAC may ultimately result in the benefit of reduced concentrations of EDC and in other environmental effects that cannot be predicted now. Any environmental effects associated with control measures will be identified when such control measures are considered pursuant to HSC Sections 39665 and 39666.

V. RECOMMENDATION

Because EDC is a known animal carcinogen and potential human carcinogen and it is known to be emitted in California, the ARB staff recommends its listing as a toxic air contaminant treated as a substance without a carcinogenic threshold.

State of California
AIR RESOURCES BOARD

Technical Support Document

Public Hearing to Consider the Adoption of a Regulatory Amendment Identifying Ethylene Dichloride as a Toxic Air Contaminant

Agenda Item No.: 85- -
Scheduled for Consideration: September 19, 1985
Release Date: June 19, 1985

(This report has been reviewed by the staff of the California Air Resources Board and approved for release. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.)

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PART A - A REVIEW OF ETHYLENE DICHLORIDE'S USES, EMISSIONS AND PUBLIC EXPOSURE

Prepared by the Staff of
The Air Resources Board

June 19,1985

SUMMARY

Part A of this report on EDC includes information on the sources and quantities of emissions of EDC in California, the atmospheric persistence of EDC, its concentrations in the ambient air, and exposure to EDC in media other than the air.

In 1983, about 231 tons of EDC were emitted statewide. About 57 percent of this was due to the evaporation of pesticides or to the evaporation or burning of gasoline. Both of these sources have since been or will be severely reduced by actions of the U.S. Environmental Protection Agency. EDC's use as a solvent and related industrial uses will then become the dominant sources of emissions.

EDC is persistent in the atmosphere, having a half-life of about 42 days. The annual average concentration in the ambient air of the South Coast Air Basin is estimated from air monitoring data to be between 19 and 110 parts per trillion (ppt). At the midpoint of that range, the ambient air would provide a greater public exposure to EDC than do water or food.

No recent ambient air monitoring data are available for areas other than the South Coast Air Basin. If EDC is listed as a toxic air contaminant, such data will be made available at the time any emission controls are considered.

REPORT ON ETHYLENE DICHLORIDE
TO THE SCIENTIFIC REVIEW PANEL

Part A - A Review of Ethylene Dichloride's (EDC) Uses, Emissions, and Public Exposure

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I. USAGE AND EMISSIONS OF EDC

A. PRODUCTION AND USAGE

Ethylene dichloride (EDC), or 1,2-dichloroethane, is synthetically produced by the direct chlorination or oxychlorination of ethylene. There are no known natural sources of EDC.[1,2]

The production of EDC in the U.S. increased steadily from approximately one million tons in 1963 to 5.9 million tons in 1979 due to the increased demand for vinyl chloride, for which EDC is a principal chemical intermediate. However, EDC production decreased to 3.8 million tons in 1982 (in response to economic recession) and then increased back to 5.6 million tons in 1983.[1,3]

No EDC has been produced in California since the closure in 1982 of the Stauffer Chemical plant in Carson. This plant had an annual EDC production capacity of 155,426 tons.[4]

In California, the dominant use of EDC is in leaded gasoline as a scavenger of lead in the combustion exhaust. Its purpose is to form chlorides of the lead, which otherwise would deposit in the engine cylinders. The ARB staff estimates that 2,238 tons of EDC were consumed in leaded gasoline in 1983.[5,6] The consumption will decrease as less leaded gasoline is burned and as the allowable lead content of gasoline is lowered to 0.1 gram per gallon by the U.S. Environmental Protection Agency (EPA) in 1986. (The controlling standard for lead in gasoline is now the state limit of 0.8 gram per gallon, effective September 1984.)

The other known significant uses of EDC in California are as a solvent or a constituent of chemical products, a reactant carrier in the production of solid fuel, and as a pesticide. The first use, called "solvent and minor industrial use," includes applications in the manufacture of paints, coatings, and adhesives; solvent bonding of polycarbonate products; solvent extraction of seeds, animal fats, and pharmaceutical materials; cleaning textiles and polyvinyl chloride manufacturing equipment; preparation of polysulfide compounds; leaching copper ore; and the manufacture of film.[1,7] Rogozen et al[8] estimated that 124 tons of EDC were used in California in 1980 in these activities, mostly at facilities using less than two tons per year.[4] The only known use of EDC as a reactant carrier is in Sacramento. We do not know the amount used.

As a pesticide, 65 tons of EDC were applied in 1983.[9] However, the EPA has cancelled or suspended the registrations under the Federal Insecticide, Fungicide, and Rodenticide Act of all food fumigants that contain EDC.[16] Recently, these fumigants have accounted for most of the pesticidal use of EDC. EPA's action resulted from the failure of registrants to respond to a "call for information" on the health effects of EDC. Should manufacturers respond with information establishing the safety of their fumigants, the registrations could be re-instated.

The dominant use of EDC nationwide, as a reactant in the production of vinyl chloride, perchloroethylene, trichloroethylene, and vinylidene chloride, does not occur in California.

B. CURRENT AND PROJECTED EMISSIONS

The estimated emissions discussed in this section are summarized in Table I-1 on page I-8.

1. Stationary Sources

EDC's use in minor industrial processes (used mainly as a solvent) is the largest source of EDC emissions in California.* Of the total amount of EDC

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* Except, possibly, for emissions from landfills. As discussed, later, emissions from landfills are poorly quantified.

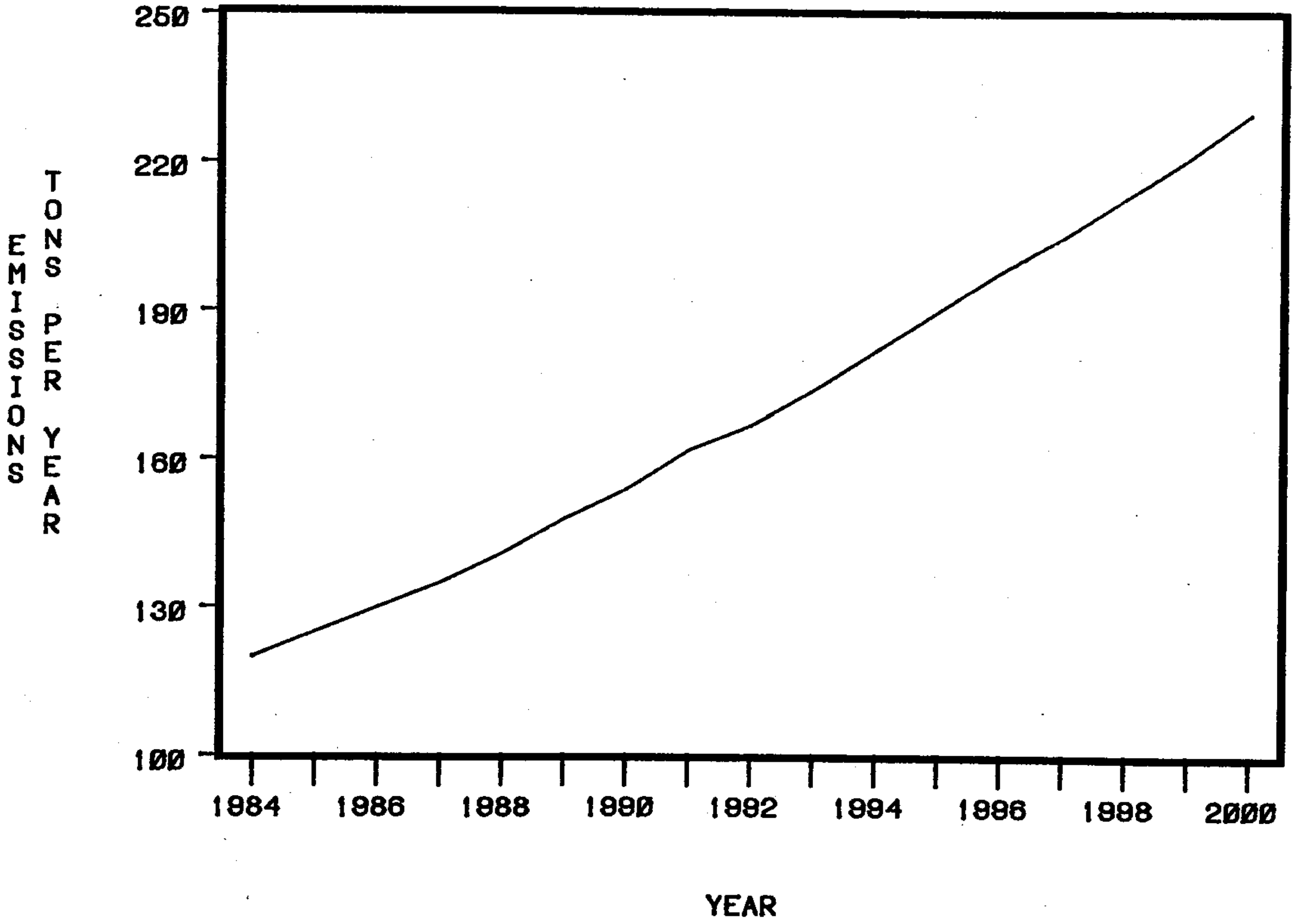
used in these processes, it is estimated that 20 percent is recycled and the remaining amount evaporates into the atmosphere. Statewide EDC emissions in this category were estimated as 99.2 tons in 1980,[5] of which 13.2 tons were emitted in the South Coast Air Basin (SCAB). At most, only three users in the SCAB emitted more than one ton of EDC in 1982.[4]

We can find no projections of the consumption of EDC as a solvent. However, the ARB staff has projected consumption of all solvents in the Chemical and Allied Product Industry (SIC 28XX) through the year 2000. This SIC code accounts for 75 percent of the solvent containing EDC in California. If the emissions of EDC from minor industrial uses follow this increased total use of solvents, the emissions will be as projected in Figure I-1. We contacted the three largest emitters of EDC in 1982 in the SCAB, accounting for 90 percent of the known emissions in the minor industrial use category. Of them, two had reduced their use of EDC by half or more in 1984 and one plans to install a carbon adsorption system to recover EDC.

Statewide EDC emissions from applying pesticides are estimated at 65 tons in 1983, of which 14 tons were emitted in the SCAB.[9] These estimates are based on the assumption that all the EDC applied as a pesticide eventually evaporates. EPA's cancellation of registrations for EDC-bearing fumigants will end, at least temporarily, almost all the emission from the recent uses of EDC as a pesticide.

EDC evaporates during the storage and transfer of leaded gasoline. Based on an emission ratio of 19×10^{-5} pounds of EDC per pound of evaporated gasoline (supported in Appendix C), 1983 emissions from gasoline marketing, storage and transfer were 2.9 tons and 1.4 tons in the entire state and the SCAB, respectively.[10]

FIGURE I-1. PROJECTED EDC EMISSIONS FROM SOLVENTS



EDC emissions from gasoline production are estimated at 1.8 tons statewide and 0.9 ton in the SCAB for 1983. This is based on 1983 estimates of EDB emissions from this source[11/] corrected for the two-to-one molar ratio of EDC to EDB in gasoline and their respective vapor pressures. Future EDC emissions from gasoline production, marketing, storage, and transfer are expected to decrease as the market for leaded gasoline is reduced.

Other potentially significant sources of EDC emissions include hazardous waste landfills and publicly owned treatment works (POTWs). Hazardous waste landfills emit EDC emissions during and after the burial of EDC-contaminated waste into the landfills. Emissions occur during the disposal and may continue for several years due to the evaporation of the buried volatile waste. Within California, landfills are estimated in 1982 to have collectively emitted to the atmosphere from 2800 to 5900 tons of non-methane volatile organic compounds, of which 1000 tons were emitted from the BKK landfill in the SCAB.[12/] Of the volatile organic compounds emitted from BKK, we estimate that 9 to 12 percent, or roughly 100 tons, were EDC. (Some of this EDC may be already "counted" in other categories of emissions such as pesticides and solvents.) The fraction of EDC in the total emitted gases was assumed to be that measured in the gas collection well manifolds during the "1982 Air Sampling Program" at BKK.

EDC emissions from hazardous waste landfills should decrease. Current and proposed bans for disposing certain wastes in landfills, closures of landfills, site cleanups, and the cessation of EDC waste-generation by Stauffer Chemical all reduce the amount of EDC placed in landfills and therefore lessen emissions. Also, new gas recovery systems reduce the emissions of already-buried EDC.

Large sewage treatment plants can emit significant amounts of EDC. EDC contained in the sewage can be released from aeration basins or other treatment operations where evaporation is promoted. A national study[13/] estimated potential EDC emissions as high as 861 tons per year from the largest plant evaluated. However, this estimate was qualified as preliminary and probably representative of the upper bound of actual emissions. The study suggested that emissions from most sewage treatment plants are one to two orders of magnitude lower than the estimate. Because relatively little EDC is used in California, its presence in sewage influent may be less than is typical nationally. Therefore, there are no data to allow an estimate of such emissions in California.

The Sacramento County Air Pollution Control District estimates 1.1 tons of EDC emitted annually during the manufacture of solid fuel at Aerojet General in Sacramento County. Aerojet's permit allows a maximum emission rate of 5.5 tons per year.

2. Mobile Sources

EDC is emitted with motor vehicle exhaust and with gasoline evaporating from vehicular fuel systems. EDC emissions in motor vehicle exhaust may vary with the size of the engine. Tsani-Bazaca and co-workers[14/] determined that the average EDC emissions from a 0.85-liter engine and a 3-liter engine were 1.67 and 3.56 lb EDC/lb EDB emitted, respectively. Based on these results, estimated EDC emissions in exhaust range from 13 to 28 tons per year statewide. This is based on 0.37 percent of EDB surviving in motor vehicle exhaust.[15/] However, since the results for EDC were obtained from the tests of only two cars and the cars were operated with gasoline containing a higher lead content than California's standard of 0.8 grams per gallon, the estimate for emissions of EDC from engine exhaust should be considered a rough approximation. Additional testing is needed to establish more reliable estimates.

EDC evaporative emissions from mobile sources are estimated at 41 tons per year. This estimate is based on an emission factor of 5.2×10^{-4} lb EDC/lb THC emitted, which was determined by using the vapor pressures of EDC and EDB, the two-to-one molar ratio of EDC to EDB in leaded gasoline, and the vehicular evaporative emission factor of 9.0×10^{-5} lb EDB/lb THC.[15]

Future EDC emissions from motor vehicles will decrease as less leaded gasoline is used. Also, EPA has enacted a sharp limitation of the lead content of gasoline. Projected EDC emissions from motor vehicles are shown in Figure I-2. It reflects the reduction of lead in leaded gasoline to 0.1 gram per gallon in 1986.

The combination of Figure I-1 (projected emissions from solvents) and Figure I-2 indicates a net increase of about 50 tons per year in total EDC emissions in the state through the year 2000. This could be offset by a decrease in the poorly quantified emissions of EDC from landfills. Emissions of EDC from landfills should decrease because of landfill gas recovery and the recent restrictions on burying EDC.

Table I-1. Estimated EDC Emissions

Source Category	Emissions (tons/year) Statewide	Emissions (tons/year) South Coast	Inventory Year	Reference
Pesticidal evaporation[f]	65	14	1983	9
Vehicular exhausts	20	10[a]	1983	12, c
Vehicular fuel evaporation	41	16.0	1983	8, c
Gasoline marketing	2.9	1.4[a]	1983	c
Gasoline production	1.8	0.9[a]	1983	c
Landfills	--	(100[d])	1982	c
Solid fuel production	1.1	0	1984	e
Solvent evaporation and minor industrial uses	99.2	13.2[b]	1980	4, 5
Total (ex. landfills)	231	55		

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[a] The fraction of statewide emissions attributed to the South Coast Air Basin was assumed equal to that area's fraction of total population.

[b] The inventory year is 1982.

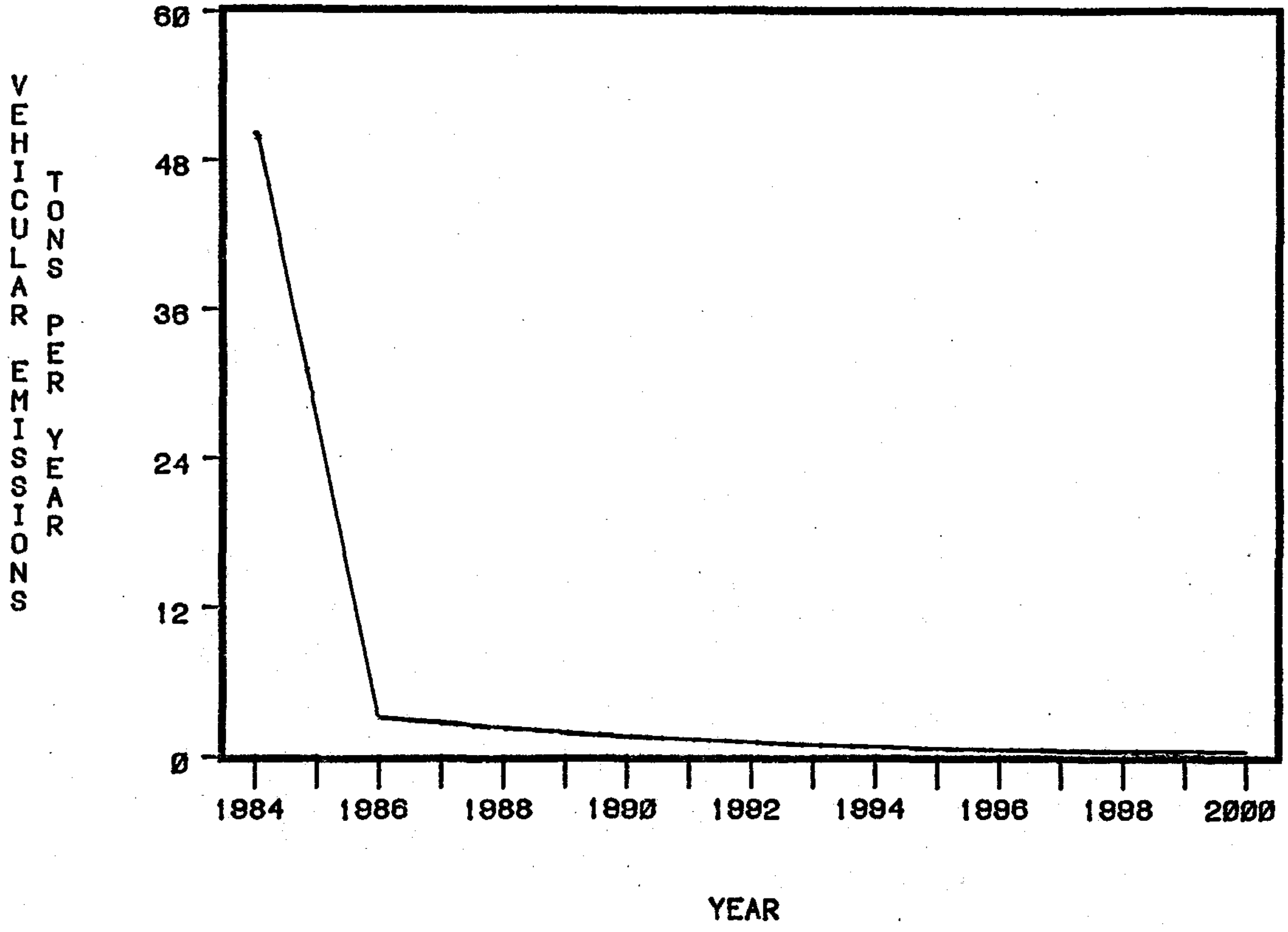
[c] estimate by ARB staff

[d] less reliable than other entries; emissions from this category may have decreased considerably

[e] Sacramento County APCD

[f] The EPA currently disallows EDC's dominant pesticidal use as a fungicide on food.

FIGURE I-2. PROJECTED EDC EMISSIONS FROM MOTOR VEHICLES



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II. PERSISTENCE IN THE ATMOSPHERE

A. PHYSICAL AND CHEMICAL PROPERTIES

EDC is a stable, non-polar compound with the structure denoted $ClH_2C\text{-}CH_2Cl$. It is soluble in ethanol, diethyl ether, and most other common laboratory solvents. It is moderately soluble in water. Various properties of EDC are shown in Table II-1.

Table II-1
Properties of EDC

Property	Value	Reference
Blood: air partition, 37°C	19.5	3
Boiling point, latm	183°F	1
Critical temperature	554°F	4
Density, liquid	1.25 g/cm^3	1
Dielectric constant, liquid	10.45	4
Explosive limits in air, 25°C	6.2 % to 15.6%	4
Heat capacity, 60°F	.297 cal/°C-gm	1
Heat of combustion	3.00 kcal/gm	4
Heat of formation, gas	-296 cal/gm	4
Heat of fusion	21.1 cal/gm	4
Heat of vaporization, 20°C	77.3 cal/gm	4
Index of refraction, 20°C, Na	1.45	4
Melting point	-31.5°F	1
Molecular weight	99.0	
Octanol: water partition ($\log_{10}$)	1.48	2
Solubility in water, 20°C	8.69 mg/cm^3	4
Vapor pressure, -45°C to 82°C	$\ln P$ (mmHg) $= -4178 \times 1/T(°K) + 18.39$	1
Vapor pressure at 20°C	62 mmHg	

B. FATE IN THE ATMOSPHERE

The principal chemical reaction of EDC in the atmosphere is attack by OH radicals (OH·). An estimate of the first order rate constant for this reaction at 23°C was published by Howard and Evensen,[5] who obtained the value $k = 22 \pm 5 \times 10^{-14}$ cm^3/molecule·sec. This value is consistent with analogous constants determined by those authors for other chlorinated ethanes.

Because 23°C is warmer than typical tropospheric (lower atmospheric) temperatures, the rate constant should be estimated at a lower temperature. An appropriate temperature is 15°C, the annual mean temperature at the inversion base in the SCAB.[7] For the range -8°C to 25°C, Altshuller[8] recommends a reaction rate-vs-temperature correlation equivalent to an activation energy of 2.67 kcal/g-mole. Applied to EDC, this yields the rate constant 19×10^{-14} cm^3/molecule·sec at 15°C.

Calvert[9] estimated the concentration of OH· in the morning in Los Angeles at 2.6×10^6 molecules/cm^3. This indicates a diurnal average of about 1×10^6 molecules/cm^3. This value combined with the above rate constant yields a half-life of 42 days* for EDC.

Free chlorine atoms can react with EDC[10]; however, Singh[11] found that free chlorine is too rare in the troposphere to make the reaction significant.

Culpitt[12] investigated physical processes as removal mechanisms for EDC in the atmosphere. He estimated the half-lives of EDC in rain wash-out, adsorption on aerosols, and dry deposition as 390 years, 13 years, and 25

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* $t_{1/2} = .693/k\ (OH\cdot)$

years, respectively. These removal mechanisms are thus clearly unimportant compared to attack by OH radicals. The half-life of EDC in the urban atmosphere is therefore estimated as 42 days. With such a long residence time, EDC is a persistent pollutant that can be transported throughout an air basin before it dissipates.

The sole reported product of the OH radical attack is chloroacetyl chloride ($ClCH_2COCl$),[13] which decomposes in water. It is an irritant at concentrations above 50 parts per billion.[6] However, it is rapidly removed from the atmosphere by rain and fog and thus cannot approach that concentration as a product of EDC at documented ambient concentrations. A possible second product of EDC is chloroacetaldehyde. There are no toxicological data available for this compound.

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III. EXPOSURE TO EDC

A. AMBIENT AIR DATA

The ARB's Haagen-Smit Laboratory (HSL) has monitored ambient EDC at four sites in the South Coast Air Basin (SCAB) since January 1983. These are in downtown Los Angeles (LA-North Main), Dominguez Hills, El Monte, and Riverside. All samples are collected over 24-hour periods, beginning at 9 a.m., in Tedlar bags at constant flow rates. Analysis of the samples is by gas chromatography. Details of the sampling and analytical procedures are in Appendix A. Samples are collected five days per week at the El Monte site and about once every six days in Los Angeles, Dominguez Hills, and Riverside.

Data are available from 566 samples collected between January, 1983, and August, 1984. Although the highest 24-hour EDC concentrations measured at each site ranged from 200 to 390 ppt, only 13 percent of all the analyses are above HSL's detection limit, 100 ppt(v). (Concentrations in the other samples were too low to measure with the techniques employed.)

By assuming that the unreportable analyses were all zero or all 100 ppt, one calculates an average result of 19 to 110 ppt, respectively, for all samples in 1983. This is taken as the range within which the annual average concentration falls in the SCAB. The rural background concentration (concentration not attributable to nearby sources) has been estimated independently at 40 to 50 ppt.1,2/ Appendix B provides greater detail.

As shown in graphs in Appendix B, the concentrations, for 1983 exceeded those for January to May, 1984 because of strong peaks during the winter of 1983 that were not repeated in 1984.

HSL's monitoring program provides the only long-term set of data on ambient concentrations of EDC. A few short-term programs by other people are summarized in Table III-1. The data taken between 1976 and 1980 are substantially higher than the data from HSL. However, the decrease by 1983 appears real because the data taken in February 1984 at Downey are consistent with HSL's data.

Table III-1

Short-Term Data on Ambient EDC

Site	Period	Sampling Time	No. Samples	ppt, mean
Dominguez	5/76	54 mins.	1	3660
Upland	8 to 9/76	48 hrs.	8	27
Los Angeles	4/79	24 hrs.	4	650
Oakland[a]	7/79	24 hrs.	9	84
Riverside	7/80	24 hrs.	11	350
Downey	2/84	12 to 24 hrs.	9	70[b]

[a] not in the SCAB

[b] This value is from reference 4; all others are from reference 3.

The higher ambient concentrations measured before 1983 may be explained in part by the then greater amount of EDC used in gasoline and the emissions from Stauffer Chemical Company's vinyl chloride plants in Long Beach and San

Pedro. These plants, which closed in 1982, emitted an estimated 28 tons of EDC per year.[5/] The decrease in ambient concentrations may also reflect unquantifiable but decreasing emissions of EDC from landfills.* EDC is quite volatile and has been detected in gaseous emissions from at least three landfills in the SCAB. However, the probable major inputs of EDC to landfills -- tank bottoms from leaded gasoline storage and vinyl chloride/EDC manufacturing wastes -- have declined since 1979, and many landfills have installed gas recovery systems. EDC emissions have therefore probably decreased in recent years.

A network of 15 monitoring stations has been set up in areas outside the SCAB. All will begin monitoring EDC concentrations in early 1985.

B. EXPOSURE THROUGH AMBIENT AIR

The measurements of ambient EDC at HSL's four monitoring sites could be extrapolated to other locales in the South Coast Air Basin if they could be shown to vary together in time (indicating uniformity across the region) or to follow some other variable that is measured widely over the region. The daily EDC data were tested for correlations between sites, for correlations with the concentrations of other pollutants, including carbon monoxide, and for correlations with aerometric (temperature and wind) data without success. Appendix B presents details.

The lack of a correlating variable leaves no means of extrapolating measured EDC concentrations to the rest of the basin or of estimating

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*However, no landfill known to emit EDC is located where it would strongly affect a particular monitor.

concentrations when the analyses were less than 100 ppt. Therefore, it can be stated only that the mean annual concentration among all four sampling sites lay in 1983 between 19 and 110 ppt.

The general ambient concentration may be augmented near discrete sources of EDC. The specifiable sources to which many people may be exposed include roadways, gasoline service stations, and landfills. Ambient monitoring data taken at landfills in the SCAB are summarized in Table III-2.

Table III-2

Ambient EDC Concentrations Near Landfills

Landfill	Sample Duration	No. Data	Period	Mean EDC, ppt
BKK[a]	24 hrs.	34	Jul.-Oct. 82	1,200
Ascon	--	5	Nov. 11, 80	22,000

[a] site A; other sites near BKK showed lower concentrations

There are no monitoring data for EDC near roadways or service stations, but dispersion modeling supplies rough estimates of upper bounds. Table III-3 presents modeling results. They indicate additions to the general ambient concentration of 3 ppt or less (annual average), except for additions of "less than 29 ppt" near service stations that do not use vapor recovery on the pumps. The table also shows 114 ppt calculated near a one ton per year point source of EDC at Aerojet General in Sacramento.

Thus, roadways and service stations apparently do not greatly elevate the local concentrations of EDC, but quite high concentrations have been measured near landfills. Also, a fairly large point source (Aerojet) can augment nearby concentrations by an amount equivalent to the estimated mean in the SCAB. Since the DHS has restricted the disposal of volatile halogenated solvents in landfills, and gas recovery systems have been installed, the data on concentrations near landfills may no longer apply.

Table III-3

Estimated EDC Concentrations

Situation Modelled	Model	Results[a]
Busy freeway under worst-case meteorology (ARB Technical Support Division)	CALINE 3 dispersion model; 20,000 vehicles/hr. 11% burn leaded fuel; 1.25 x 10^{-3} grams EDC/mile per leaded fuel vehicle; F stability and 1 m/s wind speed	One-hour EDC concentrations:[b] distance — ppt 0 m — 29 50 m — 11 100 m — 7.7 200 m — 2.2
Busy intersection, actual meteorology (ARB Technical Support Division)	ISCST model; Wilshire Blvd. @ Veterans Avenue, Los Angeles; 1.25 x 10^{-3} grams EDC/mile per leaded fuel vehicle	Annual average concentration at 25 to 40 meters from the road: .5 to 1.6 ppt
Gasoline service station, no vapor recovery (draft EPA document)	(not stated)	Maximum annual average concentration "in the vicinity": 29 ppt[c]
Aerojet, Sacramento[8]	ISCST model; 48 receptors zero to two miles from property line	Annual mean concentrations: highest -114 ppt; 2nd highest - 29 ppt

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[a] Concentrations are presented as increases to the general ambient concentration.

[b] Annual average concentrations would be at most 10% of these worst-hour values.

[c] The analogous value for stations with vapor recovery would be about 3 ppt.

C. EXPOSURE THROUGH OTHER MEDIA

Beside inhaling EDC with ambient air, many people could inhale it with polluted indoor air or ingest it with drinking water or fumigated grain products.

The EPA[6] found that cooked flour made from fumigated grain retains no detectable EDC.

The ARB staff knows of no data on EDC in indoor air. Because EDC has only minor industrial uses in California, exposures to EDC in work places are unknown.

There are far too few data on EDC in drinking water in California to characterize its concentration in the state's water supplies. However, in a review of data taken from around the United States, the EPA[7] found that less than five percent of water systems have detectable EDC and that detectable EDC concentrations are usually 1 ug/l or lower. A person drinking daily two liters of water with 1 ug of EDC per liter would ingest 730 ug of EDC per year. This weight of EDC would equal about one-third of the weight inspired annually if air contaminated with about 65 ppt of EDC (the midpoint of the range for the average in 1983 in the SCAB) were inspired constantly at the rate 20 cubic meters per day.

This analysis indicates that air is the major medium for exposure to EDC in the SCAB.

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APPENDIX A

SAMPLING AND ANALYSIS METHODS FOR ETHYLENE DICHLORIDE (EDC)

APPENDIX A

SAMPLING AND ANALYSIS METHODS FOR ETHYLENE DICHLORIDE (EDC)

1. Sites

1.1 Ambient toxic sampling for EDC by the ARB staff commenced at four locations in the South Coast Air Basin (SCAB) in January 1983. (See Figure 1 for locations).

1.2 The Downtown Los Angeles (DOLA) site is at the South Coast Air Quality Management District (SCAQMD) air monitoring station located in metropolitan Los Angeles.

1.3 The El Monte site is at the Haagen-Smit Laboratory of the Air Resources Board and is 15 kilometers east of DOLA.

1.4 Another site is located at the California State University, Dominguez Hills, in Carson, approximately 25 kilometers south of DOLA.

1.5 The fourth sampling site is located at the SCAQMD Riverside Station in Riverside, 125 kilometers east of DOLA.

2. Principle of the Method

2.1 Ambient air is pumped into a polyvinyl fluoride (Tedlar) sample bag at a constant rate for a 24-hour interval (9 a.m. to 9 a.m.) with an automatic sampler.

2.2 After sampling, the ambient air bag sample is returned to the laboratory and the contents are analyzed by gas chromatography (GC) using an electron capture detector.

3. Range and Quantitation Limit

3.1 The minimum measurable concentration of EDC ("quantitation limit") has been determined to be 100 parts per trillion (ppt) for 100 ml of sample concentrated with a freeze-out trap.

3.2 The analysis range of EDC is 100 ppt to 100 ppb. The upper limit may be expanded by diluting the sample.

4. Confirmation of Chemical Identity

4.1 Any organic compound present in the sample having a retention time similar to that of EDC under the operating conditions described in this method may interfere with the analysis. The chemical identity for EDC is confirmed in 10 percent of all samples using a second GC column (SP 1000 packed) followed by an electron capture detector.

5. Calibration, Precision and Accuracy

5.1 The calibration procedure employs the principles set forth in Volume I of the "Quality Assurance Handbook for Air Pollution Measurement Systems" (U.S. Environmental Protection Agency, 1976).

5.2 Standards are used in the linearity check at concentrations which bracket the anticipated range of pollutant concentrations. The calibration data are fitted to a straight line, $y=a + bx$, by the method of least squares. The calibration is acceptable if the f-ratio is less than the 95 percent rejection limit.

5.3 The 95 percent confidence intervals are obtained by multiplying the square root of variance by the appropriate value of 't' from a 't' table.

5.4 Estimate of Errors

5.4.1 Errors in EDC monitoring data occur through sampling errors (errors in obtaining an un-biased integrated 24-hour sample) and errors in analysis.

5.4.2 Errors in sampling occur through variations in flow rate and sampling time coupled with variations in the EDC concentration of the atmosphere. The error due to sampling is estimated to be about ±10 percent.

5.4.3 The sources of errors in analysis are the volumetric measurement of the GC sample aliquot, the preparation of the calibration standard, and fluctuations in the detector response. The analytical error is estimated to be ±10 percent when concentrations are above quantitation limit (100 ppt). The quantitation limit is defined as ten times the noise in the electron capture detectors output.

5.4.4 The overall estimate of error is ±20 percent for values above quantitation limits.

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6. Advantages and Disadvantages of the Sampling Method

6.1 The air sampling equipment is easily set up and involves no liquids.

6.2 A representative integrated sample is readily obtained because the equipment samples at a constant rate over a 24-hour period.

6.3 The accuracy of the analytical data is not dependent on the air volume collected by the sampling apparatus.

6.4 The minimum detection limit of the analysis may be lowered by freezing out a larger volume of the sample.

6.5 The maximum measurable limit of the analysis may also be increased by diluting the sample.

6.6 The polyvinyl fluoride (Tedlar) film sample bag is susceptible to leaks and permeation through the bag. However, the ambient concentration of EDC is stable for at least 72 hours in the Tedlar sampling bags when kept away from direct sunlight and not exposed to temperatures greater than 30 deg. C.

6.7 The sample is susceptible to contamination from the bag and the diaphragm pump.

7. Apparatus

7.1 The sampling system consists of a diaphragm pump, seven-day timer, flow indicator, pressure regulator, flow controller, flow by-pass system, and the sample bag (see Figure 2). The diaphragm pump (made of steel and Teflon or Viton) draws ambient air through the sample system at approximate 5 liters per minute. Thirty-five milliters per minute of this air stream are sampled, the remaining flow is by-passed and vented. The sample flows through a diaphragm pump, a solenoid valve, a pressure regulator (set for 2-3 psig to prevent any accidental bursting of over-filled sample bags), a flow control needle valve, a flowmeter and into the sample bag. A seven-day timer regulates the sampling period.

7.2 The Tedlar bags are equipped with stainless steel quick disconnect fittings. These bags have 2 mil wall thicknesses and 50 liter capacities.

7.3 Rigid opaque bag containers are used to protect the samples from sunlight and accidental puncture.

7.4 A gas chromatograph is used with a freeze-out system and electron capture detector.

7.5 The freeze-out system consists of a stainless steel loop, a liquid nitrogen Dewar and a hot water Dewar.

7.6 A glass column (6 ft x 1/4 inch), packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopack C, is used in the chromatograph.

7.7 An analog recorder is used with an integrator to quantitate peak areas.

7.8 A ground glass syringe is used to transfer air samples from the Tedlar bag to the GC sample inlet.

7.9 Assorted gas cylinder regulators, flow meters, thermometers and a barometer are used for flow control and measurement.

7.10 A 145 cubic foot (4160 liter) glass linked tank is used to prepared standard calibration mixtures.

8. Reagents

8.1 All chemicals used in the calibration are reagent grade: 1,2-dibromoethane (EDB), methyl chloride, methyl bromide, Freon-11, Freon-12, dichloroethane (ethylene dichloride or EDC), 1,2-dichloropropane, chloroform, 1,1,1,-trichloroethane (methyl chloroform), carbon tetrachloride, bromodichloromethane, trichloroethane (TCE), chlorodibromomethane, bromoform, Freon-113 and tetrachloroethane (PERC).

8.2 Helium, 99.995%.

8.3 Zero nitrogen, better than 99.9999% pure.

9. Procedure

9.1 Preparation of the bags

9.1.1. Bags are constructed from 2 mil Tedlar sheeting to form an envelope (27 inches x 27 inches).

9.1.2 The seams are heated sealed to form an envelope which contains about 50 liters.

9.1.3 Swagelock stainless steel quick disconnect fittings (Pt. No. SS-QC4-D-400VT) are attached with a stainless steel adapter having a Bunao-ring (Cajon Pt. No. SS-4-TA-OR-ST).

9.1.4 All newly fabricated bags are leak and contamination tested. This involves three pressurization and evacuation cycles using zero air. After a final pressurization to a drumhead tightness, the bags are stored for 24 hours to test for leakage. If the bags do not remain taut, they are repaired or discarded. If the bags remain taut, the contents of the bags are analyzed for EDC by GC. The contents of the bag must not exceed the EDC content of the zero air by more than 100 ppt. If these criteria are met, the bags are evacuated for field use. If the bags exceed the EDC level, the pressurization/evacuation and analysis cycle is repeated.

9.1.5 Due to extensive handling, most used bags are not suitable for recycling. Bags suitable for recycling are analyzed with a flame ionization detector, evacuated, refilled with zero air and evacuated for field use. The unsuitable bags are discarded after removing the fittings for reuse.

9.2 Preparation of sampling device for ambient sampling.

9.2.1 The sample bag is attached to the sampler via the stainless steel quick disconnect valve.

9.2.2 The sample pump is turned on and the flow adjusted with a metering valve to 35 ml/min as determined on the rotameter.

9.2.3 The timer is set to start the sampler from 7 to 9 A.M. of the scheduled sampling day and set for a 24 hour period.

9.2.4 Check the pressure regulator setting - (2 psig).

9. (Cont'd)

9.2.5 A label is attached to the sample bag, noting the bag number, sampling day, sampling time, starting sample flow and sampling location.

9.2.6 After sampling is completed, the sampler's operability is checked, and the final sample flow is noted on the bag label. The sampler is turned off and the sample bag is removed via the stainless steel quick disconnect fitting.

9.3 The sample bags are always kept in a rigid opaque container while being used (i.e. during sampling, transport, analysis and storage).

9.4 The bag samples received at the laboratory are logged in and analyzed within 24 hours.

9.5 Analysis of samples (freeze-out method)

9.5.1 Immerse the freeze-out loop in liquid nitrogen and allow the temperature to stablilize (approximately 5 minutes).

9.5.2 Flush the syringe with about 100 ml of sample, discharge the sample into a hood and withdraw exactly a 100 ml sample.

9.5.3 Transfer the sample into the precooled freeze-out loop through a Luerlock stopcock.

9.5.4 Back-fill the syringe with 100 ml of helium and transfer it into the loop; then further flush the loop with helium for 2 minutes.

9.5.5 Stop the helium flushing and remove the liquid nitrogen Dewar from the freeze-out loop.

9.5.6 Isolate the cryogenic loop with "isolation valve."

9. (Cont'd)

9.5 (Cont'd)

9.5.7 Replace the liquid nitrogen Dewar with a Dewar containing hot water at about 80 deg. C.

9.5.8 Allow the loop to come to equilibrium with the hot water.

9.5.9 Introduce the sample into the carrier gas stream with an "injection valve."

9.6 Measure the areas of each of the GC peaks with an electronic integrator.

9.7 GC conditions:

9.7.1 Helium gas flow: 25 ml/min

9.7.2 Make up gas: 10% methane in argon, 40 ml/min

9.7.3 Heating bath temperature: 80 deg. C

9.7.4 Column temperature: 6 to 160 deg. C at 8 deg. C/min

9.7.5 Detector temperature: 300 deg. C

9.7.6 Column backflush: 23 min after injection

10. Calibration and Standards

10.1 Standard Reference Material for ethylene dichloride is not available from the National Bureau of Standards. Since the same instrument is used to analyze various halogenated hydrocarbons, a standard calibration mixture is prepared within the Haagen-Smit Laboratory.

10.1.1 The standard calibration mixture is prepared for EDC and other compounds by diluting pure gases with zero air and vaporizing pure liquids into a large chamber of zero air.

10.1.2 The typical standard calibration mixture thus prepared has the following concentrations:

water	0.96%	
methanol	9400	ppb
methyl chloride	480	ppb
methyl bromide	220	ppb
dichloromethane	400	ppb
chloroform	11	ppb
trans-1,2-dichloroethene	57	ppb
1,2-dichloroethane (EDC)	54	ppb
1,1,1-trichloroethane	8.6	ppb
carbon tetrachloride	8.9	ppb
bromodichloromethane	10	ppb
1,2-dichloropropane	88	ppb
trichloroethene (TCE)	9.6	ppb
dibromochloromethane	10	ppb
bromoform	9.8	ppb
dibromoethane (EDB)	10	ppb
Freon-113	7.2	ppb
Freon-11	10	ppb
Freon-12	10	ppb
tetrachloroethene (PERC)	8.4	ppb

10.2 The typical standard is prepared according to the following procedure:

10.2.1 Clean the 145 cubic foot (4160 liters) glass-lined steel tank by evacuating the tank to 10-6 torr and then flushing it with zero air several times.

10.2.2 Pressurize the tank to 5 psia with zero air after the final evacuation.

10.2.3 Using zero air and glass gas bulbs introduce into the tank 100 ml of methyl chloride at 18.7 torr, 100 ml of methyl bromide at 8.7 torr, 100 ml of Freon-11 at 0.4 torr and 100 ml of Freon-12 at 0.4 torr.

10. (Cont'd)

10.2 (Cont'd)

10.2.4 Inject 100 microliters of the mixture of liquid standards into the tank through a heated injector (150 deg. C) with a He carrier flow of 100 ml/min. The mixture of liquid standards is prepared by mixing 3.0 ml of methylene chloride, 500 µl of trans-dichloroethene, 500 µl of 1,2-dichloroethane, 1 ml of 1,2-dichloropropane and 100 µl of each of the following: chloroform, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethene, chlorodibromomethane, bromoform, dibromoethane, Freon-113 and tetrachloroethene in 44 ml of methanol.

10.2.5 Humidify the contents of the tank by bubbling the zero air which is being used to fill the tank through 40 ml of water (heated to boiling) until all the water is vaporized.

10.2.6 Pressurize the tank to 20 psia with zero air.

10.2.7 Record the exact temperature and pressure.

10.2.8 Let the mixture stand for 24 hrs. (to be sure that an equilibrium between the wall surface and the gas is established).

10.2.9 Check the new standard mixture against the previous standard mixture and the EPA quality assurance cylinders to validate the concentrations before the new standard mixture is used for calibration.

10.3 Standards of lower concentrations are prepared by diluting the above mixture with zero nitrogen.

(Cont'd)

10.4 Calibration

10.4.1 Transfer various volumes (the volume used depends on the concentration of the sample, normally 10, 30, 70, or 100 ml) of the standard mixture from the 145 cubic foot tank into the GC and analyze according to the procedure in 9.5.

10.4.2 Fit the data to a straight line by the method of least squares. If the calibration is less than the 95% rejection limit, it is acceptable; otherwise, the calibration should be repeated.

10.4.3 A single calibration check is done by transferring 10 ml of the standard mixture from the tank into the GC and analyzing according to the procedure in 9.5.

11. Quality Assurance

11.1 Bag material tests are performed to determine the suitabilty of the Tedlar used to construct sample bags.

11.1.1 Bag contamination test: A bag is filled with zero nitrogen and the contents are analyzed. The EDC concentration should be below the quantitation level of 100 ppt.

11.1.2 Bag stability test: Six bags are filled with 10 ppb of EDC in zero nitrogen and contents are analyzed at various intervals. The EDC concentrations should remain stable for 72 hours.

11.1.3 Bag record: A log of each bag is kept to ensure that at no time has an ambient bag been used to sample high concentrations of (>100 ppb) any compound. The log contains dates of fabrication, leak testing, sampling, the sampling site/date, bag identification, and the bag destruction date.

11.2 Each sampler is tested for contamination before field use by pumping zero air into a sample bag. The contents of the bag are analyzed for EDC contamination. If the EDC concentration is found to be below the detection limit, the sampler system is then ready for field use. If the system fails this test, it is disassembled, decontaminated, reassembled and retested. This check is repeated every six months for each sampler system or more frequently if anomalies occur.

11.3 Analysis

11.3.1 Zero nitrogen is run every day to be sure the GC shows no signal for the blank: The instrument is cleaned out and the blank rerun until the GC passes the blank test.

11.3.2 A standard calibration is run before any samples are analyzed. This is to ensure the calibration factor of the instrument has not changed. If the calibration factor is changed by more than 5 percent, the GC is checked for any malfunction. If there is malfunction, it is repaired and the GC recalibrated. If there is no malfunction, two more calibration runs are performed during the day. If the calibration runs are within 10 per cent of each other, 11.3.2 (cont'd) the analyses for that day are calculated based on the average of the new calibration factors. If the calibration runs are not within 10 percent, the GC has to be examined for any malfunctions. When the instrument is repaired, the calibration is rerun.

11.3.3 Ten percent or more of the samples are reanalyzed to check precision.

11.4 Quality assurance audit: The standard mixture prepared in the Laboratory shall be checked annually with the EPA Quality Assurance Audit Cylinders. These QA cylinders are not available for all the compounds, but those that are available shall agree well (5-10%) with our standards.

12. Calculations

12.1 The EDC concentrations, in ppt, are calculated by a data system using the external standard method.

Concentration = Area x Calibration Factor

Area = Integrated EDC peak area

12.2 The calibration factor (CF) is calculated during calibration by the equation:

CF = Concentration/Peak Area

Replicate calibrations are averaged and the arithmetic mean is stored as the CF to be used in subsequent analyses.

12.3 Concentrations may be converted from ppt to ng/m^3 by means of the following formula:

$$\text{ng/m}^3 = \frac{(P)\,(MW)\,(ppt)\,(10^3)}{(82)\,(T)}$$

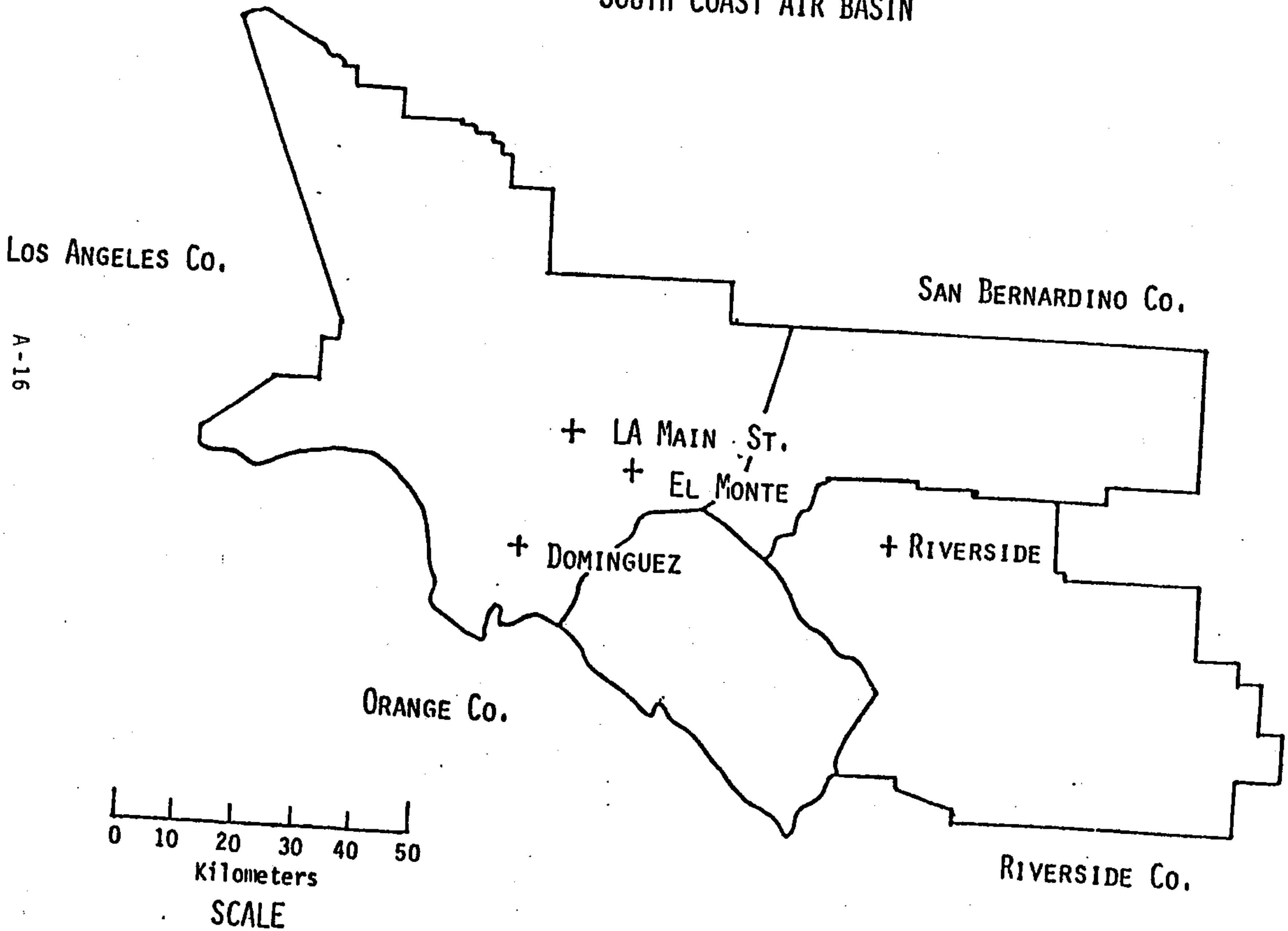
P = pressure in atmospheres

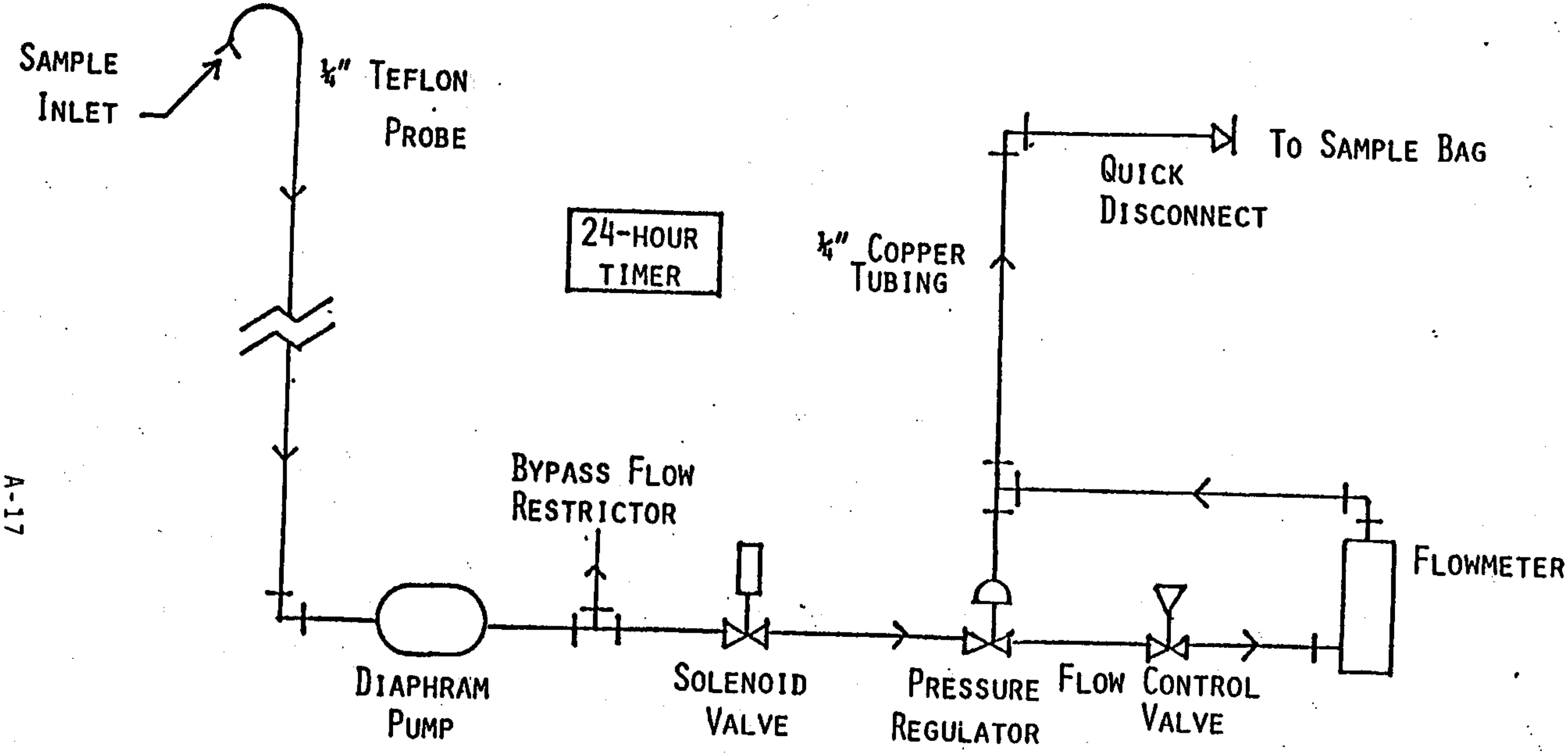
MW = molecular weight of 1,2-dichloroethane (EDC)

82 = gas constant in $(cm^3)(atm)/(deg.\ K)(mole)$

T = absolute temperature (deg. K)

EDC MONITORING SITES
SOUTH COAST AIR BASIN





Typical Bag Sampler Flow System

Figure 2

APPENDIX B

AMBIENT AIR MONITORING DATA AND ANALYSIS

APPENDIX B

AMBIENT AIR MONITORING DATA AND ANALYSIS

Ethylene dichloride (EDC) samples were collected at four locations in the South Coast Air Basin and analyzed by the Air Resources Board's Haagen-Smit Laboratory Division. EDC sampling began in January 1983 at the Dominguez Hills, El Monte, and Los Angeles-North Main sites; sampling at the Riverside-Magnolia site began in February 1983. Although sampling is continuing at the four sites, data are currently available only through August 1984. These 566 data are used in the following analyses.

Data were reported to a minimum value (detection limit) of 100 parts per trillion (ppt). The incidence of detectable concentrations at each sampling location is summarized in Table B-1. Thirteen percent of all EDC analyses were above the detection limit. Table B-2 shows the statistics for the reported (above detection limit) data among the stations.

The monthly trends of EDC measurements from 1983 and 1984 are shown in Figures B-1 through B-4. For these figures, monthly "average" have been computed using the value 50 for each undetectable concentration (i.e., less than 100 ppt). Although this treatment does not compute a true average concentration, it is useful for displaying trends in the data.

All four sites show maximum "average" EDC concentrations during January or February of 1983; in contrast, average concentrations at all sites during

January and February 1984 are much lower. Three sites, El Monte, Los Angeles-North Main, and Riverside-Magnolia, show secondary maximums during June of 1983; however, this secondary maximum is above the detection limit only at Riverside-Magnolia. Monthly averages during more than half of the sampling months are below the detection limit.

The four locations have different sampling schedules. Samples are collected at the El Monte site approximately five times each week. At the other three locations, samples are collected approximately once each week, but on different days. Consequently, on a given day, samples may be collected at two sites. These double sampling days usually comprise one sample at El Monte and a second sample at one of the other three locations.

Table B-3 shows the twenty-five highest twenty-four hour EDC concentrations measured at the four sites. This table also shows the same-day EDC concentration at any other site where a sample was collected. The comparison data are limited because many of the high concentrations occurred during January 1983 and no double samples were taken during this month. Of the high concentrations summarized in Table B-3, only ten have corresponding same-day comparisons. Of these ten, six pairs are both high while the other four are high at one site and low at the comparison site. The highest of the daily averages, 390 ppt, was measured on January 5, 1983 at El Monte; there is no corresponding measurement at another location. Because of the lack of consistency in comparisons and the large number of concentrations for which no comparison can be made, no conclusions about the relationship of EDC concentrations between sites are justified from these data.

In a second comparison, all same-day pairs of data between El Monte and each of the other sampling sites were tested for correlation. Should the other stations show a high correlation to El Monte, it would indicate that EDC emissions are uniform both spatially and temporally. Should they show little or no correlation, it would suggest that emissions are more localized and variable over the basin. The following number of data pairs were tested: El Monte/Dominguez Hills (57), El Monte/Los Angeles-North Main (69), El Monte/Riverside-Magnolia (68). Pearson correlation coefficients between El Monte and each other site range from +0.48 (Riverside-Magnolia) to +0.58 (Dominguez Hills). These values seem to indicate some degree of consistency between sites; however, because most measurements at each site were assigned the constant value 50 ppt, the correlation coefficients may be inflated. When data pairs containing measurements below the detection limit are eliminated from the analysis, the remaining data sets are too small to yield meaningful correlation results (El Monte/Dominguez Hills - 3 pairs; El Monte/Los Angeles-North Main - 4 pairs; El Monte/Riverside-Magnolia - 5 pairs). These results indicate that ethylene dichloride emissions are not uniform throughout the basin.

In addition to same day EDC correlations, we evaluated Pearson correlations for the twenty-four hour EDC concentrations and simultaneous concentrations of other halogenated compounds (measured as part of the toxic pollutants sampling program), criteria pollutants, and aerometric variables. Table B-4 is a list of variables to which we attempted to correlate EDC. Ethylene dichloride does not correlate to any of the variables; all correlation coefficients are below +0.25. However, the large proportion of measurements below the detection limit may make correlations difficult to spot. The apparent lack of correlation between all EDC and carbon monoxide data (correlation coefficient of +0.21) indicates that automobile exhaust is not a significant source of EDC emissions at the four sites. Correlations between EDC and carbon monoxide (CO) for each site individually yield comparable results (coefficients range from +0.15 to +0.46).

Ratios of peak daily EDC to mean annual concentrations (with undetectable concentration set at 50 ppt) during 1983 are summarized in Table B-5. Ratios range from 3.1 at Riverside-Magnolia to 5.7 at El Monte. The magnitude of the ratios and degree of similarity from site to site suggest that the samplers are most likely being influenced by emissions from sources located throughout the sampling areas rather than by isolated sources. Carbon monoxide peak to mean ratios (indicative of spatially homogeneous emission sources) for the same time period range from 2.7 at Riverside-Magnolia to 3.6 at Dominguez Hills. It is evident from these CO ratios, in comparison to the EDC ratios, that EDC emission sources are spread throughout the sampling areas; however, the overall distribution of sources is not as uniform around each sampling location as are CO emission sources.

Our analyses do not lead to any means whereby ethylene dichloride concentrations can be estimated at locations away from the four toxic sampling sites or for times when analyses were below the 100 ppt detection limit. Therefore, it can be stated only that the mean annual concentration among all four sampling sites lay between 19 and 110 ppt in 1983. These values are obtained by using zero or 100 ppt, respectively, for each undetectable concentration in 1983.

Table B-1

Incidence of EDC Concentrations Above the Detection Limit

Sampling Location	Total Number of Samples[a]	Percent of Samples Above Detection Limit
Dominguez Hills	78	10.3%
El Monte	327	13.5%
Los Angeles-North Main	82	12.2%
Riverside-Magnolia	79	19.0%

[a] January 1983 to August 1984 (to September 1984 at El Monte)

Table B-2

Summary of Detectable Concentrations from EDC Monitoring (ppt, mean)[a]

		Dom. Hills	Riverside	El Monte	La-No. Main
Jan-Dec, 1983	148	123	137	164	
Jan-Aug, 1984	-	128	103	-[b]	
All samples	148	125	135	164	

[a] average of data greater than 100 ppt

[b] data through September 1984

Table B-3

Twenty-five Highest 24-Hour EDC Concentrations With Same Day Concentrations at Other Stations (1983)

Highest Concentations					Same-Day Concentrations	
Rank	Month	Day	Site	Ppt	Site	(ppt)
1	1	5	El Monte	390	(None)	
2	1	6	LA-No. Main	280	(None)	
3	1	9	Dom. Hills	280	(None)	
4	2	6	El Monte	250	(None)	
5	1	19	LA-No. Main	240	(None)	
6	2	7	El Monte	230	LA-No. Main	50
7	2	15	Riverside	200	Dom. Hills El Monte	110 160
8	1	2	El Monte	190	(None)	
9	1	4	Dom. Hills	190	(None)	
10	1	16	LA-No. Main	180	(None)	
11	1	11	LA-No. Main	160	(None)	
12	1	13	El Monte	160	(None)	
13	2	15	El Monte	160	Dom. Hills Riverside	110 200
14	3	1	El Monte	150	LA-No. Main	110
15	3	30	Riverside	150	El Monte	50
16	6	13	El Monte	150	Dom. Hills	50
17	6	14	LA-No. Main	150	El Monte	150
18	6	14	El Monte	150	LA-No. Main	150
19	1	3	LA-No. Main	140	(None)	
20	1	26	El Monte	140	(None)	
21	2	13	LA-No. Main	140	(None)	
22	2	17	El Monte	140	LA-No. Main	120
23	2	21	El Monte	140	(None)	
24	5	25	El Monte	140	Riverside	50
25	11	7	El Monte	140	(None)	

TABLE B-4

Independent Regression Variables

Ambient Concentrations

Benzene
Carbon tetrachloride
Chloroform
Trans-1,2-dichloroethene
1,2-dichloropropane
Ethylene dibromide
Methyl chloroform
Methylene chloride
Perchloroethylene
Trichloroethylene

Carbon monoxide
Oxides of nitrogen

Aerometric Parameters

Minimum temperature
Maximum temperature
Daily temperature range
Resultant wind direction
Resultant wind speed
Average wind speed
850 mb temperature

TABLE B-5

Ratios of Peak Daily and Annual Average* EDC Concentrations (1983)

	Peak (ppt)	Mean (ppt)	Peak: Mean
Dominguez Hills	280	63.5	4.4
El Monte	390	68.8	5.7
Los Angeles-North Main	280	72.4	3.9
Riverside-Magnolia	200	65.5	3.1

*Computed using 50 ppt for each value less than 100 ppt; not necessarily the true mean ambient concentration.

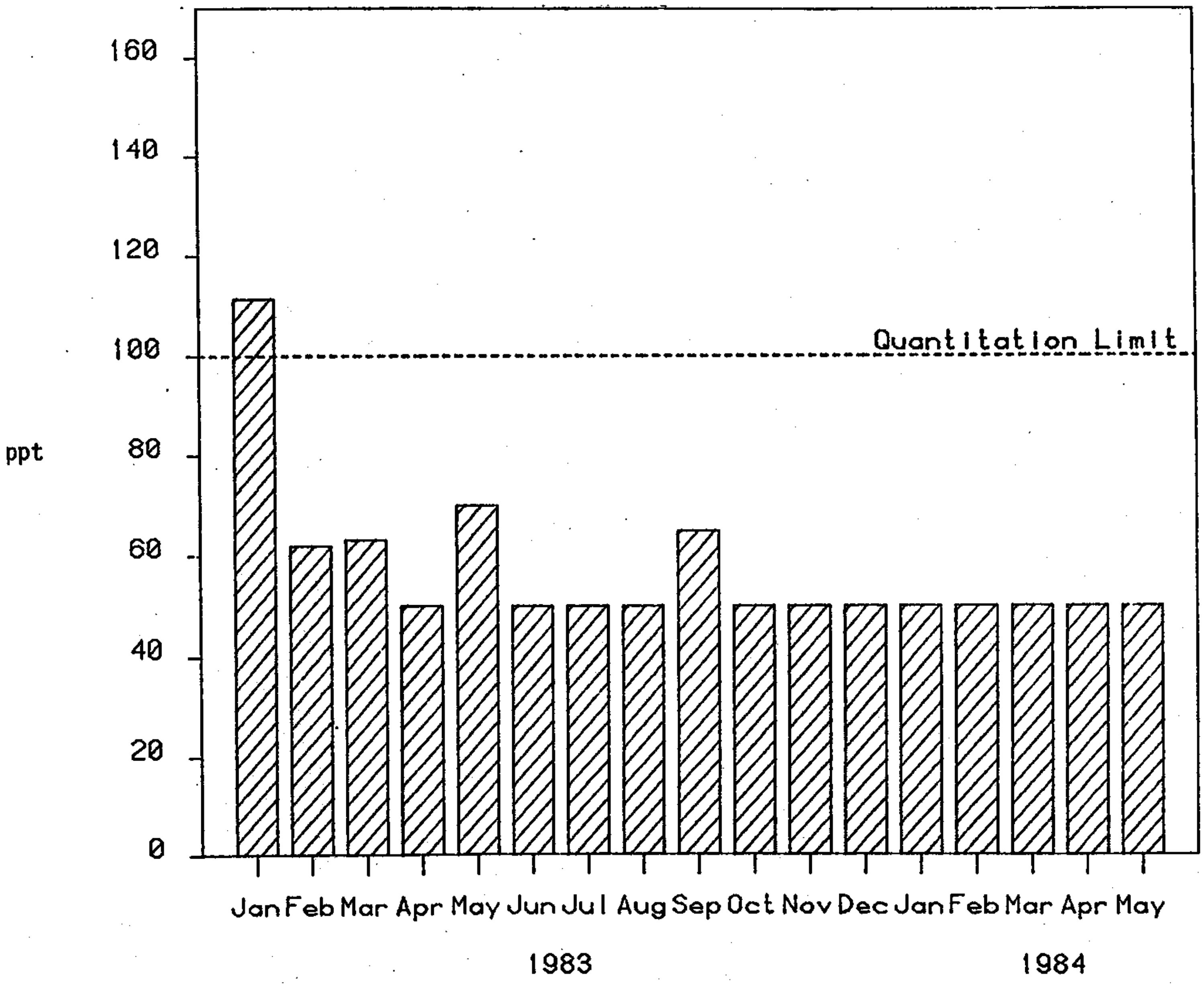


Figure B-1 Monthly Average EDC concentrations at Dominguez Hills

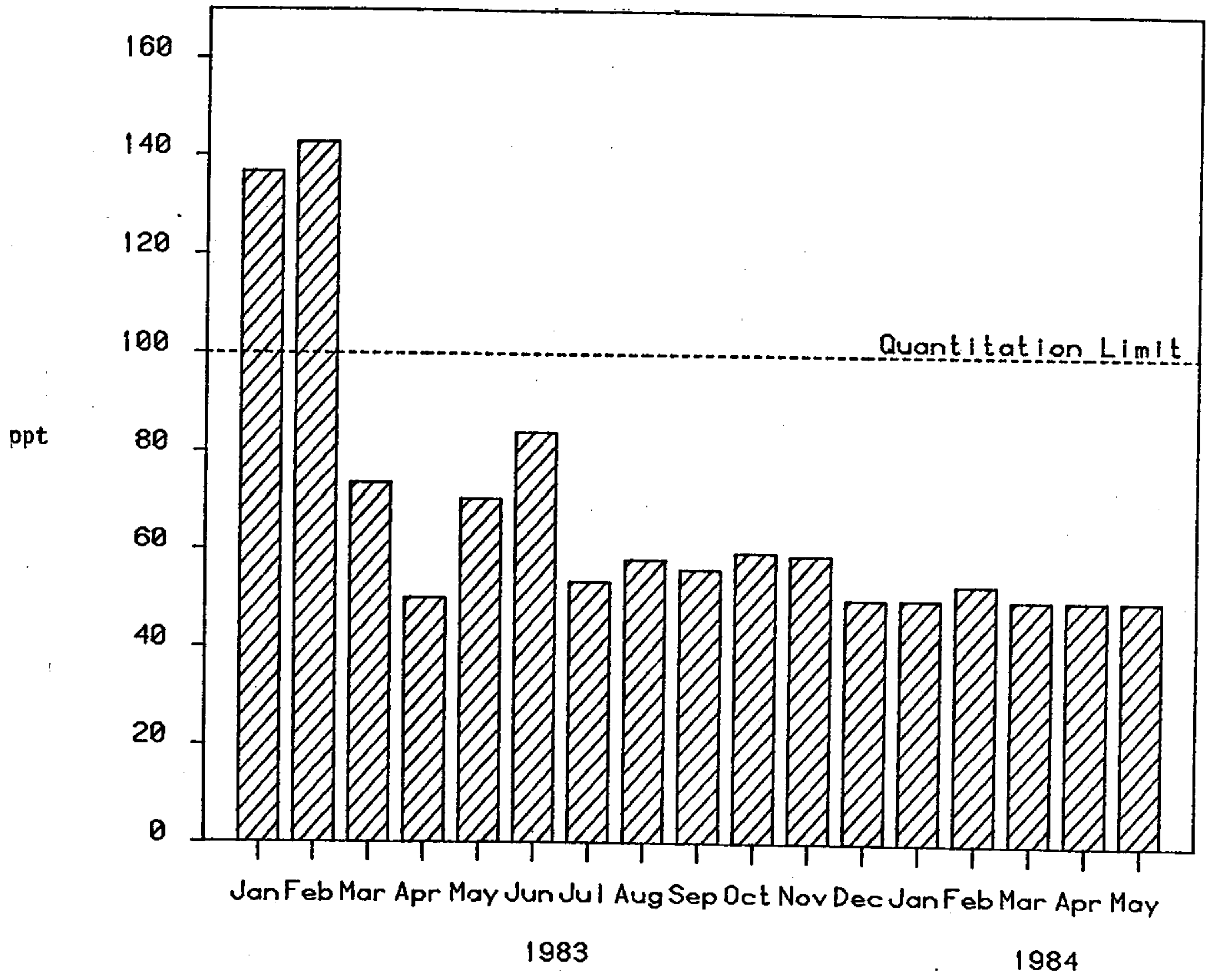


Figure B-2 Monthly Average EDC Concentrations at El Monte

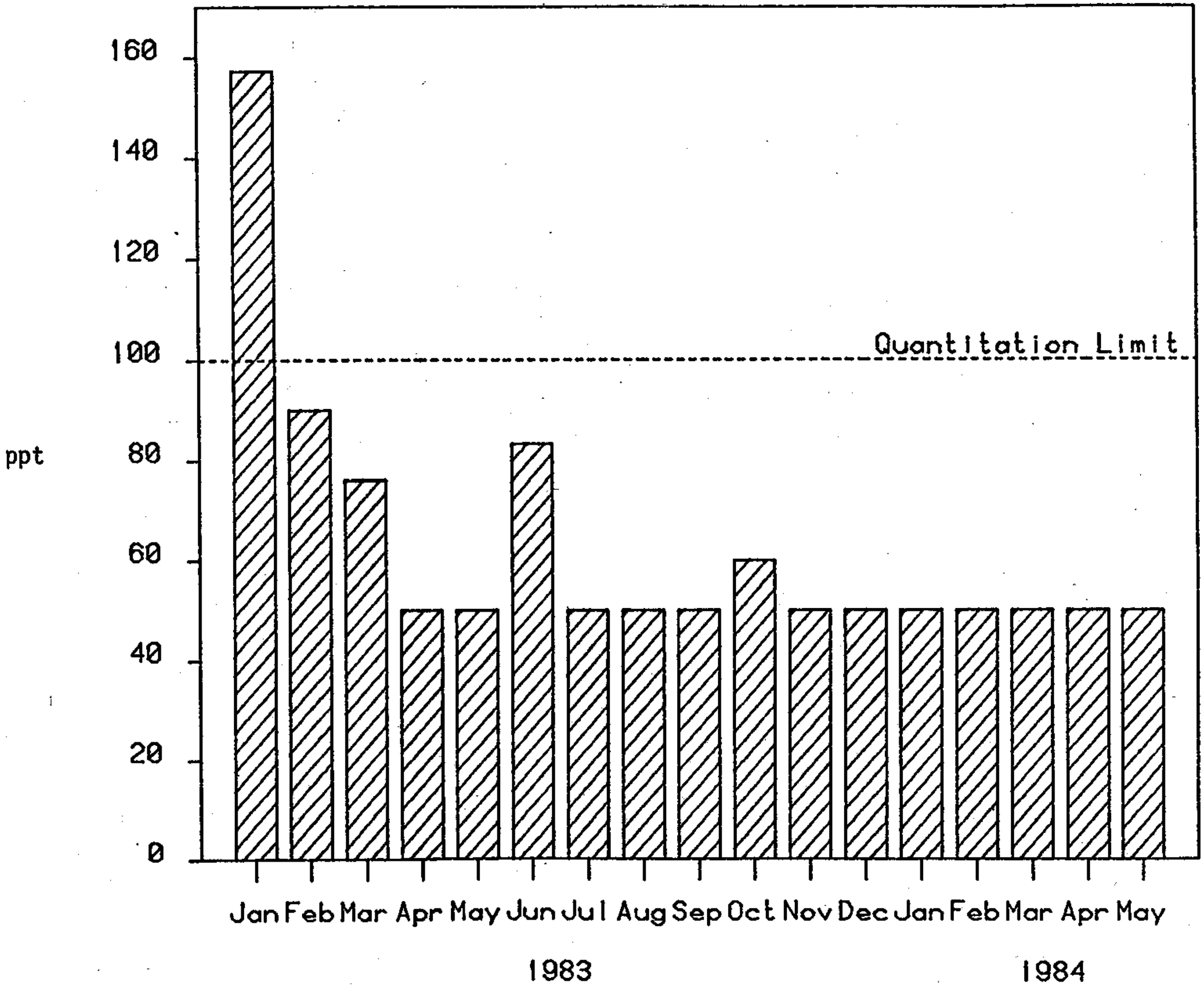


Figure B-3 Monthly Average EDC Concentrations at LA-North Main

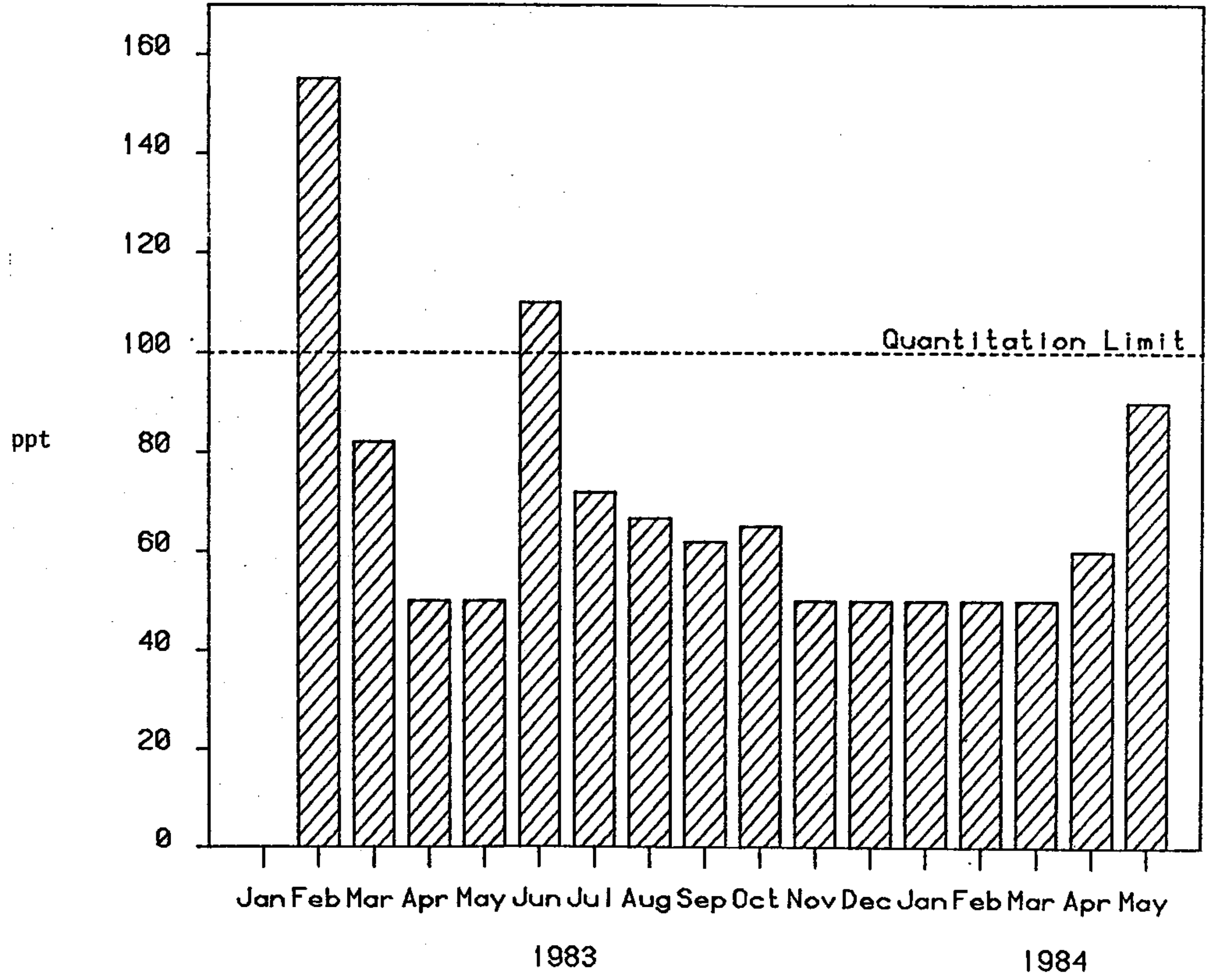


Figure B-4 Monthly Average EDC Concentrations at Riverside Magnolia

APPENDIX C

SUPPORTING INFORMATION ON EDC EMISSION ESTIMATES

APPENDIX C

CALCULATION OF EDC EVAPORATIVE EMISSION FACTOR

According to Raoult's law, the mole fraction of species in the vapor phase is

$$y_i = x_i P_i / P_t$$

where x_i and P_i are the mole fraction in the liquid phase and vapor pressure of the ith species, respectively, and P_t is the total pressure. Thus,

$$y_{EDC}/y_{EDB} = x_{EDC} \; P_{EDC}/x_{EDB} \; P_{EDB}$$

The vapor pressure of EDC (61 mm Hg) and EDB (11 mm Hg) at 20°C are known and the molar ratio of EDC to EDB in gasoline is estimated as 2:1.[1/] The molar ratio and the mole fraction ratio (x_{EDC}/x_{EDB}) are the same. Therefore, the evaporative emission factor of EDC can be approximated by the following:

$$y_{EDC}/y_{EDB} = \frac{2}{1} \times \frac{61}{11}$$

$$= 11 \text{ mole EDC/mole EDB}$$

CALCULATION OF VEHICULAR EVAPORATIVE EMISSIONS (VE Emissions)

VE Emission Factor = (11 mole EDC/mole EDB)(99/188)(9×10^{-5} lb EDB/lb THC)

= 5.2×10^{-4} lb EDC/lb THC

where the vehicular evaporative emission factor for EDB is 9×10^{-5} lb EDB/lb hydrocarbon[2/] and 99/188 is the ratio of molecular weights.

77,771 tons HC were emitted in 1983.[3/] Therefore,

VE Emissions = (77,771 tons HC/yr.)(5.2×10^{-4} lb. EDC/lb. THC

= 41 tons EDC year

CALCULATION OF GASOLINE MARKETING EMISSIONS

The weight ratio of tetraethyl lead to ethylene dichloride is 1.0:0.34 (Roberts, 1980, pg 3-82). The volume percent of EDC in leaded gasoline is therefore:

$$
\begin{aligned}
\text{Vol \% EDC} &= (0.304 \text{ g.EDC}/1.0 \text{ g.TEL})(323 \text{ g.TEL/mole})(207 \text{ g.Pb/mole})^{-1} \\
&\quad (1.1 \text{ g.Pb/gal. gasoline})(1.25 \text{ g.EDC/ml})^{-1} \\
&\quad (3785 \text{ ml/gal.})^{-1} (100\%) \\
&= 0.011\%
\end{aligned}
$$

In an EPA report, the mass fraction of EDC in saturated gasoline vapor for 0.030 Vol % EDC at 70°F is 5.2×10^{-4} (EPA, 1984, pg 2-7). Assuming EDC in saturated gasoline vapor is directly proportional to the volume percent of EDC in gasoline, an EDB emission factor for gasoline marketing based on these data is:

$$
\begin{aligned}
\text{EDC emfac} &= (5.2 \times 10^{-4} \text{ lb/EDC/lb.THC})\ (0.011\%/0.030\%) \\
&= 1.9 \times 10^{-4} \text{ lb.EDC/lb.THC}
\end{aligned}
$$

The TOG emissions from gasoline marketing, including emissions from point sources, are estimated as 36,800 tons in 1983. Assuming TOG emissions from leaded gasoline are proportional to the amount of leaded gasoline produced at the refineries, 41.2 percent of the estimated TOG emissions are from leaded gasoline (calculated by the percentage of leaded gasoline to total gasoline output from refineries - CEC, 1984, pg. 30,31).

For gasoline evaporation, a ton of TOG is equivalent to a ton of THC (CARB, 1983, pg H-17). The EDC emissions from gasoline marketing are thus:

$$\text{EDC Ems} = (36{,}800 \text{ tons TOG/yr}) (\text{THC/TOG}) (0.412) (1.9 \times 10^{-4} \text{ lb.EDC/lb.THC}) = 2.9 \text{ tons/year.}$$

CALCULATION OF GASOLINE PRODUCTION AND BLENDING EMISSIONS (PG & B Emissions)

The estimated THC release from gasoline mixing, transfer and storage operation at Douglas refinery in 1979 was 38 lb/hr (Roberts, 1980, pg 3-92).

Gasoline production capacity at Douglas refinery in 1979 was 8,500 bbl/day (Roberts, 1980, pg 3-84). Assuming production at 70% capacity, 5,950 bbl/day of gasoline would have been produced at the Douglas refinery. An emission factor for gasoline production calculated from these data is thus:

$$\text{EDC emfac} = (38 \text{ lb.THC/hr}) (1.9 \times 10^{-4} \text{ lb.EDC/lb.THC}) (24 \text{ hr./d}) (5950 \text{ bbl/day})^{-1} = 2.91 \times 10^{-5} \text{ lb.EDC/bbl gasoline}$$

The total leaded gasoline production in 1983 was 119,472,000 bbls (CEC, 1984, pg 31). Using these data, EDC emissions for gasoline production are estimated to be:

EDC Ems = (119,472,000 bbl/yr) (2.91 x 10^{-5} lb.EDC/bbl)
(ton/2,000lb)
= 1.8 tons/yr.

CALCULATION OF VEHICULAR EXHAUST EMISSIONS (V.Exh. Ems)

The survival rate of EDB (wt. in the exhaust/wt. in fuel) is 0.0037.[2] The relative weight fractions of EDC to EDB in the exhaust are:[7]

1.67 lb. EDC/lb. EDB (for 0.85-liter engine)
3.56 lb. EDC/lb. EBB (for 3.0-liter engine)

(These data were calculated for idle and constant speed conditions).

2112 tons of EDB were used in California leaded gasoline for motor vehicles in 1983.[8] Therefore,

V. Exh. Ems (for 0.85-liter engine) = (2112 tons EDB/yr)(0.0037)(1.67 EDC/EDB)
= 13 tons/yr., or
V. Exh. Ems (for 3.0-liter engine) = (2107 tons EDB/yr)(0.0037)(3.56 EDC/EDB)
= 28 tons/yr.

REFERENCES FOR APPENDIX C

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